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VALORIZATION OF BIO-ALCOHOLS INTO ADDED VALUE CHEMICALS

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*To my parents,
who have always supported me,
and to my sisters,
who have always inspired me.*

The research presented in this PhD thesis was carried out in the Department of Industrial Chemistry “Toso Montanari” of the Alma Mater Studiorum – Università di Bologna (Unibo) and in the “Instituto de Tecnología Química” (ITQ) of the “Universitat Politècnica de Valencia” (UPV) within the cotutelle agreement between University of Bologna in Italy and UPV in Spain

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KEY WORDS

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Zirconia

Sepiolite

Heterogeneous Catalyst

Gas-phase

Continuous-flow processes

ABSTRACT

Fossil fuels reserves are running out and their usage is known to be the main contributor to climate change and global warming. Therefore, the transition toward alternative sources of energy and chemicals products more sustainable and environment friendly is critically important. Biomass-derived ethanol (bio-ethanol) production is believed to grow worldwide in the near future and its conversion into added value derivatives is becoming more and more attractive. The present research work focused on the valorisation and upgrading of bio-ethanol over heterogeneous catalysts in a lab-scale continuous gas-flow system.

Firstly, in the laboratories of the Department of Industrial Chemistry of the University of Bologna (Unibo), the catalytic ethanol gas-phase conversion was studied over hydroxyapatite (HAP) based catalysts. Catalytic tests have been carried out in the temperature range 300-600°C by feeding an ethanol/He mixture into a quartz lab-scale fixed bed reactor of pelletized catalyst. The focus was placed on enhancing the formation of higher condensation products in order to obtain an organic mixture with application as bio-fuel. After choosing the reaction conditions, ion-exchanged hydroxyapatite with transition metals (i.e., Fe, Cu) and alkaline earth metal (i.e., Sr) have been synthesized and tested. While the transition metal-exchanged HAP acted essentially as acid catalysts, yielding mainly the dehydration product of ethanol, ethylene, the Sr-HAP catalyst led to the formation of a complex reaction mixture the composition of which need further optimization in order to fill the requisite to be used as fuel-blend.

Then, in the laboratories of the Institute of Chemical Technology (ITQ) of the Polytechnic University of Valencia (UPV), the study focused on two different catalytic materials, zirconium oxide and the natural clay sepiolite. Both the materials have been tested into the ethanol transformation carrying out the catalytic tests in the temperature range 300–450 °C by feeding an ethanol/N₂ mixture into a quartz lab-scale fixed bed reactor of pelletized catalyst.

Zirconium-oxide based catalysts have been prepared through two different methods, precipitation and hydrothermal, by varying some synthetic parameters (i.e., pH, the nature of the base) and by adding a transition metal as dopant agent (i.e., Ti and Y). The presence of a dopant into the zirconia structure favoured the stabilization of the tetragonal or cubic phase against the monoclinic one. All samples exhibited acidic behaviour. Interestingly, 5%mol Ti-doped zirconia exhibited a different catalytic behaviour yielding diethyl ether as major product at 300°C, while all the others samples produced mainly ethylene, both dehydration products of ethanol.

The effect of acid-base properties of sepiolite, using alkali metals (i.e., Na, K, Cs) with different metal loading (i.e., 2, 4, 5, 7, 14 wt%) as promoters, and of the redox properties of sepiolite-supported CuO or NiO, on the catalytic conversion of ethanol into *n*-butanol has been investigated. Thermal treated sepiolite samples mainly acted as acid catalyst, yielding preferentially the dehydration products of

ethanol (ethylene and diethyl ether). While the presence of a transition metal did not favour *n*-butanol production, the presence of an alkali metal into the catalytic system appeared to be crucial for *n*-butanol formation. Best results in terms of activity (ethanol conversion, 59%) and *n*-butanol selectivity (30%) were obtained at 400°C and a contact time, W/F, of 2 g/mL·s over the catalyst consisting of sepiolite calcined at 500°C modified with 7 wt% of cesium.

In order to understand the relationship between the catalytic performance and their physicochemical characteristics, all the tested catalysts have been deeply characterized by XRD, N₂ physisorption, CO₂ and NH₃-TPD, TGA, DR UV-Vis, SEM-EDX and RAMAN spectroscopy.

RESUMEN

Las reservas de combustibles fósiles se están acabando, y se sabe que su empleo es uno de los mayores responsables del cambio climático y al calentamiento global. Es por ello, que la transición hacia el empleo de fuentes de energía alternativas y la producción de productos químicos más adecuados y amigables con el ambiente posee una importancia crítica. Se espera que la producción mundial de etanol, derivado de la biomasa (bioetanol), se incremente en un futuro cercano, por lo que su transformación en productos químicos con un valor añadido se está convirtiendo cada vez en un proceso más atractivo. El presente trabajo de investigación está centrado en la valorización y la mejora del bioetanol, empleando catalizadores heterogéneos, en un reactor de flujo continuo a escala de laboratorio.

En primer lugar, en los laboratorios del Departamento de Química Industrial de la Universidad de Bolonia (Unibo), se ha estudiado la conversión catalítica del etanol en fase gaseosa sobre catalizadores basados en hidroxiapatitas (HAP). Los ensayos catalíticos se llevaron a cabo alimentando un reactor de lecho fijo a escala de laboratorio, empleando el catalizador en forma de pellets y una mezcla de etanol/He, en el rango de temperatura de 300-600 °C. El interés se focalizó en la formación de productos de alta condensación, con el fin de obtener una mezcla orgánica que pueda ser empleada como bio-combustible. Tras seleccionar las condiciones de reacción, se sintetizaron y probaron diferentes hidroxiapatitas con capacidad de intercambio iónico que poseen metales de transición (Fe, Cu) y metales alcalinotérreos (Sr) en su composición. Mientras que las HAP conteniendo metales de transición actúan esencialmente como catalizadores ácidos, produciendo principalmente el producto de la deshidratación del etanol, el etileno, el catalizador de Sr-HAP permite la formación de una mezcla de reacción compleja, la cual necesita de una mayor optimización para cumplir con los requisitos adecuados para su posterior empleo como biofuel.

A continuación, en los laboratorios del Instituto de Tecnología Química (ITQ) de la Universidad Politécnica de Valencia (UPV), el estudio se centró en dos materiales catalíticos diferentes, el óxido de zirconio y la sepiolita, una arcilla natural abundante en España. Ambos materiales se han probados para la transformación de etanol, en el rango de temperatura de 300-450 °C, empleando un reactor de lecho fijo a escala laboratorio, con el catalizador en forma de pellets, y usando una mezcla de etanol/N₂.

Los catalizadores con óxido de zirconio se prepararon mediante dos métodos diferentes, precipitación e hidrotermal, variando algunos de los parámetros de síntesis (pH, naturaleza de la base), y empleando algunos metales de transición como elementos dopantes (Ti, Y). La presencia de un elemento dopante en la estructura de la zirconia favorece la estabilización de las fases tetragonal y cúbica frente a fase monoclinica. Todas las muestras exhibieron un comportamiento ácido. Resulta interesante que la zirconia dopada con 5%mol de Ti exhibe un comportamiento

catalítico diferente, produciendo el dietiléter como principal producto a 300°C, mientras que los otros catalizadores producen principalmente etileno, ambos, productos de la deshidratación del etanol.

Por otra parte, se ha estudiado el efecto de las propiedades ácido-base de la sepiolita, modificada con metales alcalinos (Na, K, Cs) y cargas de metal variables (2, 4, 5, 7, 14 wt%), y de las propiedades redox de la sepiolita, como soporte de CuO o NiO, sobre la conversión catalítica de etanol a *n*-butanol. Las sepiolitas tratadas térmicamente actúan principalmente como catalizadores ácidos, produciendo preferentemente productos de deshidratación del etanol (etileno y dietiléter). Mientras que la presencia de un metal de transición no favorece la producción de *n*-butanol, la presencia de un metal alcalino en el sistema catalítico parece ser crucial para la formación de *n*-butanol. Los mejores resultados en términos de actividad (conversión de etanol, 59%) y selectividad (30%) de *n*-butanol se han obtenido a 400 °C y un tiempo de contacto, W/F, de 2 g/mL·s, con el catalizador basado en sepiolita calcinada a 500 °C, y modificada con 7 wt% de cesio, mediante impregnación en fase acuosa.

Para entender la relación entre el rendimiento catalítico y las características fisicoquímicas del catalizador, todos los catalizadores empleados fueron caracterizados mediante DRX, fisisorción de N₂, TPD de NH₃ o CO₂, ATG, DR UV-Vis, MEB-EDX y espectroscopia Raman.

RESUM

Les reserves de combustibles fòssils s'estan acabant, i se sap que el seu ús és un dels majors responsables del canvi climàtic i al calfament global. És per això, que la transició cap a l'ús de fonts d'energia alternatives i la producció de productes químics més adequats i amigables amb l'ambient posseeix una importància crítica. S'espera que la producció mundial d'etanol, derivat de la biomassa (bioetanol), s'incrementi en un futur pròxim, i la seua conversió en productes químics amb un valor afegit s'està convertint cada vegada en un procés més atractiu. El present treball de recerca està centrat en la valorització i la millora del bioetanol, emprant catalitzadors heterogenis, en un reactor de flux continu a escala de laboratori.

En primer lloc, en els laboratoris del Departament de Química Industrial de la Universitat de Bolonya (Unibo), s'ha estudiat la conversió catalítica de l'etanol en fase gasosa sobre catalitzadors basats en hidroxiapatitas (HAP). Els assajos catalítics es van dur a terme alimentant un reactor de llit fix, a escala de laboratori, contenint el catalitzador en forma de pèl·lets amb una mescla d'etanol/He, en el rang de temperatura de 300-600 °C. L'interès es va focalitzar en la formació de productes d'alta condensació, amb la finalitat d'obtenir una mescla orgànica que pugui ser emprada com a bio-combustible. Després de seleccionar les condicions de reacció, es van sintetitzar i van provar diferents hidroxiapatitas amb capacitat d'intercanvi iònic que posseeixen metalls de transició (Fe, Cu) i metalls alcalinotèrreos (Sr) en la seua composició. Mentre que les HAP contenint metalls de transició actuen essencialment com a catalitzadors àcids produint principalment el producte de la deshidratació de l'etanol, l'etilè, el catalitzador de Sr-HAP permet la formació d'una mescla de reacció complexa, la qual necessita d'una major optimització per a complir amb els requisits adequats per a la seua posterior ocupació com biofuel.

A continuació, en els laboratoris de l'Institut de Tecnologia Química (ITQ) de la Universitat Politècnica de València (UPV), l'estudi es va centrar en dos materials catalítics diferents, l'òxid de zirconi i sepiolita, una argila natural abundant a Espanya. Tots dos materials s'han provats per a la transformació d'etanol en el rang de temperatura de 300-450 °C, emprant un reactor de llit fix a escala laboratori, contenint el catalitzador en forma de pèl·lets, i usant una mescla d'etanol/N₂.

Els catalitzadors amb òxid de zirconi es van preparar mitjançant dos mètodes diferents, precipitació i hidrotermal, variant alguns dels paràmetres de síntesis (pH, naturalesa de la base), i emprant alguns metalls de transició com a elements dopants (Ti, Y). La presència d'un element dopant en l'estructura de la zircònia afavoreix l'estabilització de les fases tetragonal i cúbica enfront de fase monoclínic. Totes les mostres van exhibir un comportament àcid. Resulta interessant que la zircònia dopada amb 5%mol de Ti exhibisca un comportament catalític diferent, produint el dietilèter com a principal producte a 300 °C, mentre que les altres mostres produeixen principalment etilè, tots dos, productes de la deshidratació de l'etanol.

D'altra banda s'ha estudiat l'efecte de les propietats àcid-base de la sepiolita, modificada amb metalls alcalins (Na, K, Cs) i càrregues de metall variables (2, 4, 5, 7, 14 wt%), i de les propietats redox de la sepiolita, com a suport de CuO o NiO, sobre la conversió catalítica d'etanol a *n*-butanol. Les sepiolites tractades tèrmicament actuen principalment com a catalitzadors àcids, produint principalment productes de deshidratació de l'etanol (etilé i dietiléter). Mentre que la presència d'un metall de transició no afavoreix la producció de *n*-butanol, la presència d'un metall alcalí en el sistema catalític sembla ser crucial per a la formació del *n*-butanol. Els millors resultats en termes d'activitat (conversió d'etanol, 59%) i selectivitat (30%) de *n*-butanol s'han obtingut a 400°C i un temps de contacte, W/F, de 2 g/ml·s amb el catalitzador compost de sepiolita calcinada a 500 °C, i modificada amb 7 wt% de Cs.

Per a entendre la relació entre el rendiment catalític i les seues característiques fisicoquímiques del catalitzador, tots els catalitzadors emprats van ser caracteritzats en profunditat mitjançant DRX, fisisorció de N₂, TPD de NH₃ o CO₂, ATG, DR UV-Vis, MEB-EDX i espectroscopia Raman.

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NOMENCLATURE

AA = Acetaldehyde

BD = Butadiene

BuA = Butyraldehyde

BuOH = *n*-Butanol

CH₄ = Methane

CO₂ = Carbon Dioxide

DEE = Diethyl ether

EDX = Energy Dispersive X-Ray Spectrometry

EtOH = Ethanol

HAP = Hydroxyapatite

H₂ = Hydrogen

MP-AES= Microwave Plasma Atomic Emission Spectroscopy

MPV = Meerwein–Ponndorf–Verley reaction

N₂ = Nitrogen

NH₃ = Ammonia

SEM = Scanning Electron Microscopy

S = Selectivity

Sep = Natural Sepiolite

Sep@500 = Sepiolite calcined at 500°C

Sep@700 = Sepiolite calcined at 700°C

TGA = Thermogravimetric Analysis

TOS= Time on Stream

TPD = Temperature Programmed Desorption

Y = Yield

X = Conversion

XRD = X-Ray Diffraction

W/F = Weight/Flow, contact time

WHSV = Weight hourly space velocity

ZrO₂ = Zirconium oxide

1 INTRODUCTION

1.1 GREEN CHEMISTRY and BIOREFINERY

Fossil fuels (petroleum, natural gas, and coal) inevitable depletion and related adverse effects (e.g., the rising greenhouse gas concentrations in the atmosphere, global warming, ocean acidification and rising sea levels..) have meant that new approaches toward production of fuels and chemicals have been developed.¹ In the early 1990s in the USA it was introduced the concept of “Green Chemistry”, that has been defined as “the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.”² In practice, it focuses on production and employment of chemicals that have little or no pollution potentials or environmental risks, with process both economically and technologically feasible.³ Paul Anastas and John Warner in 1998, developed the following list of the “Twelve principle of Green Chemistry”, shaping a framework for making a greener chemical, process, or product:²

1. Waste prevention is better than treatment or clean-up
2. Chemical synthesis should maximize the incorporation of all starting materials
3. Chemical synthesis ideally should use and generate non-hazardous substances
4. Chemical products should be designed to be nontoxic
5. Catalysts are superior to reagents
6. The use of auxiliaries should be minimized
7. Energy demands in chemical syntheses should be minimized
8. Raw materials increasingly should be renewable
9. Derivations should be minimized
10. Chemical products should break down into innocuous products
11. Chemical processes require better control
12. Substances should have minimum potential for accidents

Together with the concept of green chemistry, the concept of sustainable chemistry has to be taken into account and it is based on “the maintenance and continuation of an ecological-sound development”.⁴ In 2015 the United Nations created a “universal call to action to end poverty, protect the planet, and ensure that all people enjoy peace and prosperity by 2030” that comprises 17 goals known as the Sustainable Development Goals (SDGs). This framework is being adopted by governments, industry, and many other organizations worldwide and both the concepts of green and sustainable chemistry have gained significant attention due to their potential to promote and

consolidate a transition towards more sustainable societies and to help achieve the SDGs and their targets.^{3,5}

In this regard, the use of renewable resources for the generation of energy and production of chemicals is considered a major imperative in the 21st century¹, especially considering the massive amount of advantages related with bio-based products. Indeed, exploiting bio resources has the potential to reduce greenhouse gas emissions (carbon-neutral nature)⁵, inherently allows to use renewable and expendable resources and to develop sustainable industrial production. The classical petroleum oil refinery from which chemicals have been mainly produced so far is related with the emission of carbon-based greenhouse gases.⁶ With the imperative of getting away from petrochemicals, the use of biomass as a chemical feedstock will become more and more important.

Biomass is the final product of the photosynthetic process in which nature stores solar energy converting it into a great variety of chemicals.⁷ It consists of a mixture of organic materials mainly composed of cellulose, hemicellulose, lignin and, in minor part, of lipids, proteins, simple sugars and starches.⁸ Biomass also contains inorganic constituents and a fraction of water. From an elemental point of view, the 90% of its dry weight is composed mainly by carbon (51 wt. %) and oxygen (42 wt. %). In addition, there are trace amounts of hydrogen (5 wt.%), nitrogen (0.9 wt.%) and chlorine (0.01–2wt.%).⁹ According to the Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009, the term “biomass” means “the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste”.¹⁰ Employing biomass as raw material could close the carbon cycle. For this reason the future chemical industries might increasingly rely on ‘biorefinery’,¹¹ a concept strictly connected to the one of “bio-economy” which “encompasses the production of renewable biological resources and the conversion of these resources and waste streams into value added products, such as food, feed, bio-based products and bioenergy”.¹²

Biorefinery is a sustainable means of generating multiple bioenergy products from various biomass feedstocks through the incorporation of relevant conversion technologies. With the increased attention of circular economy in the past half-decade with the emphasis globally addressing economic, environmental, and social aspects to the industrial-sector, biorefinery acts as a strategic mechanism for the realization of a circular bioeconomy.¹³ Ideally, biorefinery takes part of the integrated biomass zero-emission cycle (Figure 1.1).¹⁴ Indeed, it exploits biomass and the products CO₂ and ash that are recycled producing biofuels, heat, electricity and oxygenated organic chemicals such as alcohols, esters and carboxylic acids, from which bio-material can be produced.¹⁴

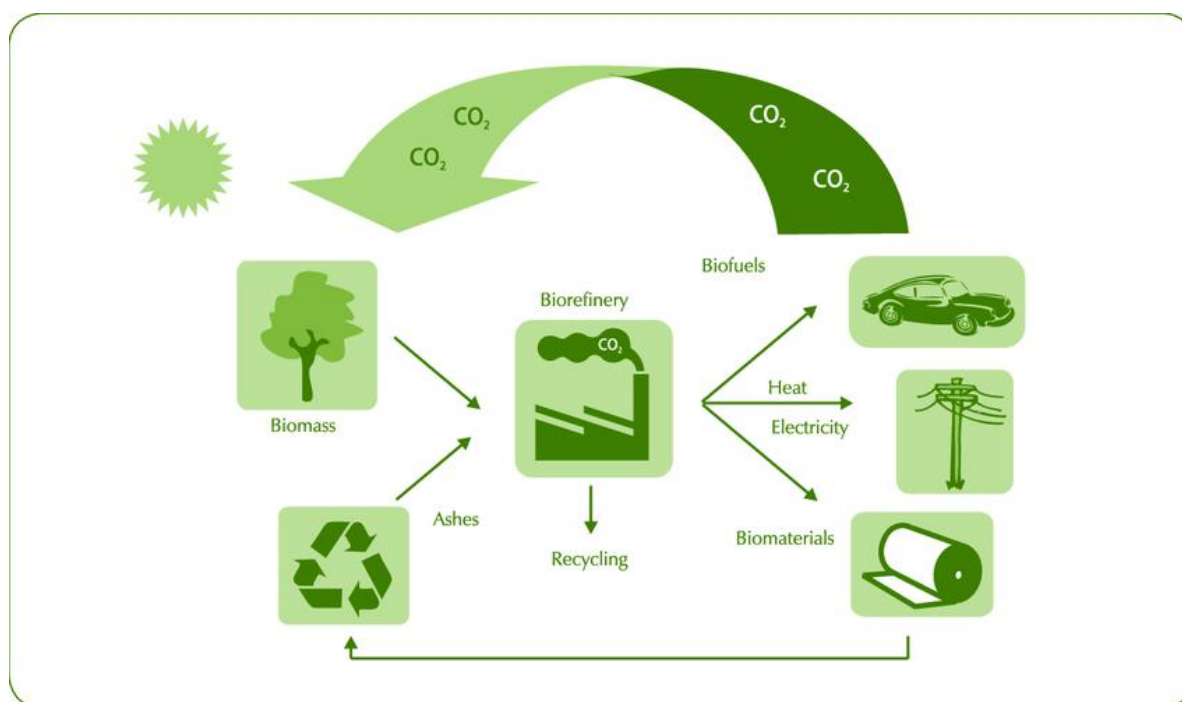


Figure 1.1 Complete integrated biomass-biofuel-biomaterial-bioenergy cycle. ¹⁵

Catalysis, together with biotechnologies and thermochemistry, enables designing a network of chemical transformations for upgrading biomass-derived compounds to a variety of chemicals, the so-called “biomass valorization”.¹⁶ Catalysis has been already a core technology in the fossil fuel based economy and more than the 90% of industrial chemical processes involve catalytic steps. In this optic, both heterogeneous and homogeneous catalysis technology will also have a key role in the transition to a biobased economy.^{16,17} In particular, catalytic processes find employment into the conversion of the so-called biomass derived “platform molecules” into added value products and/or intermediates within the biorefineries. These platform molecules, which correspond to the ‘commodities’ in a petro-based refinery, are obtained from biomass raw material previously treated. Those pre-processes encompass steps of fractionation, extraction and purification as well as deconstruction of the natural polymers. Then followed by bioprocessing to yield short molecules with most commonly less than 6 carbon atoms.¹⁶ Figure 1.2 outlines the possible routes of biomass valorisation.

gasification and pyrolysis is called “thermochemical conversions”, where raw materials are treated at high temperatures. Gasification of biomass occurs at high temperature, 600-1000°C or higher, in the presence of an oxidizing agent such as air, steam, or oxygen. Syngas, a mixture containing mainly CO, CO₂, H₂ and H₂O, is the product of the gasification of coal or biomass, allowing the utilization of a wider range of biomass types including low-cost organic wastes, without the need for specific fractionation.¹⁹ Then, the “biochemical processes” that are carried out in high water content conditions and ambient temperatures can yields hydrocarbon fuels.¹⁵ For example, fermentation converts sugars into alcohol that can be directly used as fuel, or in principle can be used as the raw material of a biorefinery plant for further upgrading. Triglycerides, derived from oil seeds, are used to be converted into biodiesel through transesterification processes.¹⁴

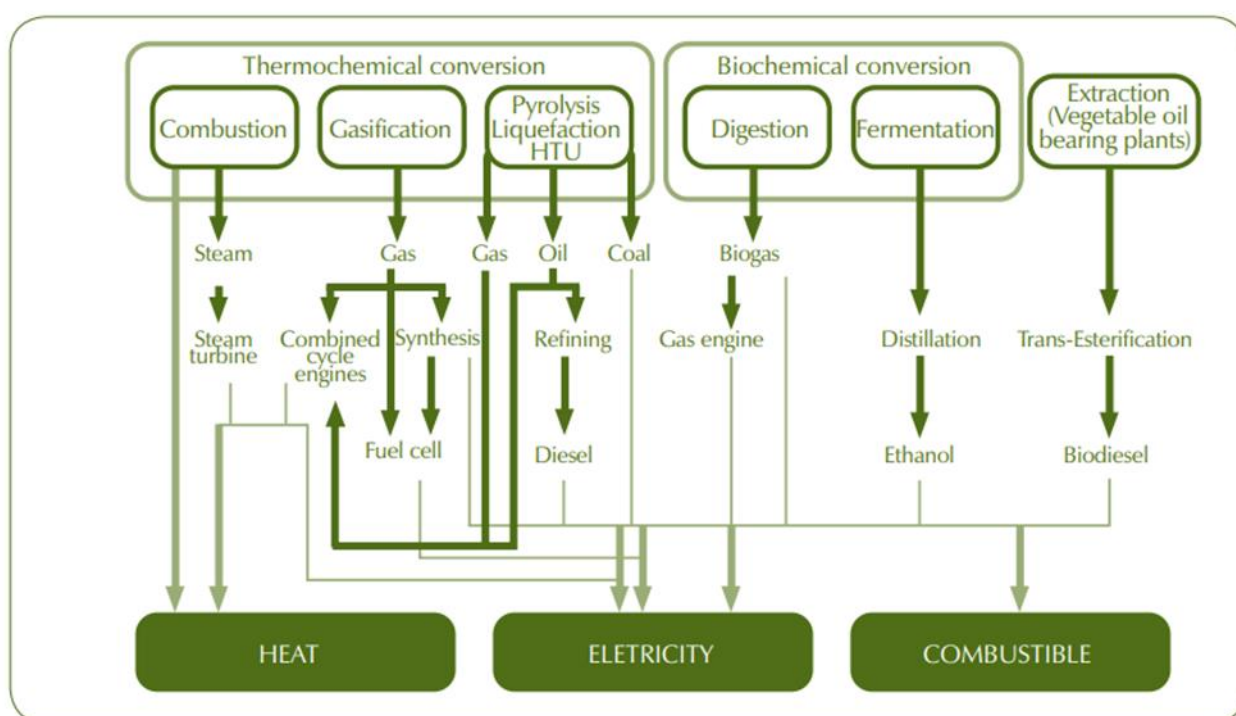


Figure 1.3 Technological routes for the production of bioenergy.¹⁵

Biofuels, i.e. cellulosic bioethanol, *n*-butanol and biodiesel, are therefore of considerable interest to researchers, industrial partners and governments. In particular, bioethanol is considered a promising drop-in fuel, which could provide an alternative to petrol in the transport sector.²⁰ It can be directly used as a transportation fuel or it can be blended with gasoline. Bio-ethanol can be mixed with gasoline (mainly in 10% ethanol concentration, known as E10) and burned in traditional combustion engines without any modifications needed. In Brazil, the world’s largest exporter of bio-ethanol, it is used pure or blended with gasoline in a mixture called gasohol (24% bio-ethanol and 76% gasoline).²¹ In addition, due to the increasing demand of heavy middle-distillate fuels, the exploitation of ethanol as renewable feedstock to produce hydrocarbon mixture has become more and more attractive.

1.2 BIO-ETHANOL and bio-alcohols

Among various biofuels, platform molecule and end-use products derived from biomass, bio-ethanol is the most important one.²² In recent years, the amount of ethanol produced has increased significantly, mostly due to the rising demand for bio renewable alternatives to petroleum-based fuels and chemicals.²³ It is estimated that up to 30% of the transportation fuels will be derived from biomass by the year of 2030 in order to limit CO₂ emissions, and cellulosic ethanol will be a leading player as it can be used not only as a renewable fuel itself but also as a starting material for producing other hydrocarbon fuels.²²

Ethanol is currently produced both as a petrochemical, through the hydration of ethylene and via biological processes. The main part of the production of bio-ethanol is still obtained by a 1st generation fermentation process, meaning from fermentation of carbohydrates such as starch and sugars.^{24,25} But, in order to be truly sustainable, its production should not compete with food production. Therefore, much researches focused on the development of more efficient technologies starting from low-cost and non-food biomass sources, such as from lignocellulosic feedstock (second generation bio-ethanol).^{7,26–31} For large scale production of bio-ethanol, first, sugars are obtained from enzymatic saccharification or hydrolysis of carbohydrates, such as cellulose and starch. Then, the following steps lead to ethanol production: microbial (yeast) fermentation of sugars, distillation, dehydration, and denaturation.³² In addition, promising results are reported for ethanol production from algal feedstock (third generation)^{7,16,26–31} and even by fermentation of syngas.^{33–38} Several papers describe the chemocatalytic conversion of syngas into ethanol and higher alcohols.^{39,40} Three different pathways from syngas to ethanol are reported: direct selective hydrogenation of CO over a solid catalyst, homologation of methanol which involves reductive carbonylation on a redox catalyst, or a classical methanol synthesis reaction followed by carbonylation to acetic acid and subsequent hydrogenation to ethanol.⁴¹ Noteworthy, the quality of the obtained bioethanol is completely the same as the one produced from petrochemical feedstock⁴² and, since it contains carbon recycled from the atmosphere by photosynthesis, it is classified as carbon neutral in the Kyoto Protocol adopted by the United Nations Framework Convention on Climate Change, COP3 (1997).^{43–45}

To date, bioethanol, has dominated the bio-gasoline market, used on its own or as a blend with conventional fuels. The addition of up to 10% ethanol is believed not to affect present gasoline-based vehicle engines, and 10% ethanol-containing gasoline (gasohol) is sold as E10 in the United States, while in Brazil 22-26% ethanol is already included in gasoline sold for general use. However, ethanol is characterized by a relatively low vapour pressure, has a lower energy density (70% that of gasoline), it readily absorbs water leading to separation and dilution problems in storage tanks, and it is corrosive to current engine technology and fuel infrastructure. Indeed, even the E10 fuel has the defeat of evaporative emissions and increased aldehyde emissions. Moreover, for gasoline

containing 85% ethanol (E85) and for 100% ethanol fuel, a specially designed car engine is necessary and the fuel efficiencies for hybrid cars using the E85 mixture are only 75% compared to the standard cars. Hence, using ethanol blended with gasoline presents several drawbacks that can be overcome by using higher alcohols with better fuel properties.⁴¹

Accordingly, *n*-butanol is essentially noncorrosive, immiscible with water, and its energetic value (29.2 MJ/L) is higher than the one of ethanol (19.6 MJ/L), and the 90% of that of gasoline.^{46,47} This improved performance has led to *n*-butanol being termed an “advanced biofuel”, and the commercial availability of this material as a green drop-in alternative to gasoline is gaining ground. Nevertheless, *n*-butanol is a valuable product with many applications as solvent, additive in many commercial products or as chemical intermediate, for instance is a crucial building block for acrylic acid and acrylic esters.^{47,48} Its petrochemical-based route of synthesis, the so-called Oxo process, involves several reaction steps, some of which use homogeneous catalysts and non-renewable resources such as propylene and CO.⁴⁷ Hence, alternative ways for the bulk synthesis of *n*-butanol from bio-sustainable feedstock have been taken into account recently. Bio-butanol can be obtained through the ABE (Acetone, Butanol and Ethanol) fermentation process, where this organic mixture is produced by the use of strains of the bacterium *Clostridium acetobutylicum*. However, it's a challenging fermentation process limited by the toxicity of *n*-butanol itself, with low conversion and modest selectivity.^{49,50} An attractive alternative approach to obtain bio-butanol is to catalytically convert or upgrade widely available bio-ethanol through the so-called “Guerbet reaction”, which enables C–C bond formation between alcohols.^{51,52} In addition, through the Guerbet route higher alcohols than *n*-butanol can be produced, both linear and branched (mainly 2-alkyl alcohols named “Guerbet alcohols”), that can be considered an added benefit since higher alcohols have an appropriate energy density to be combined with gasoline (e.g., the energy densities of 1-hexanol and 1-octanol are the 94% and 99% of that of gasoline, respectively)⁵³ or to be employed in fuel blends for diesel engines.⁵⁴ In particular, the branched Guerbet alcohols have a much lower melting point than their linear counterparts. They are used for the synthesis of functional liquids that have to remain fluid at very low temperatures, like some lubricants or hydraulic fluids for aircrafts, but also for its use as jet fuel precursors.⁵⁵ Then, they can have a wide range of applications in cosmetics and detergent formulations.⁵² However, large-scale production of such alcohols from renewable biomass is still a great challenge, but the Guerbet chemistry represents an interesting opportunity even due to the rapidly growing availability of renewable alcohols.⁵³

Overall, along with the fuels market, ethanol is used in the beverage market, in the formulation of industrial products (e.g., cosmetics, pharmaceuticals and inks).¹⁶ In chemistry, ethanol is widely used both as a solvent and as a platform molecule for the synthesis of other products. Therefore, ethanol is often regarded as the most important C₂ platform molecule because, even if being a very simple molecule, a prosperous chemistry can be derived from ethanol used as a platform molecule and it is

considered as a key compound in biorefineries^{16 14,16} In the next chapter, some of the main reactions starting from ethanol reported in the literature will be examined.

1.2.1 ETHANOL as building block

Being one of the largest bulk-biochemical, which can be used as additive blend with gasoline but also for synthesizing value-added chemicals and advanced fuels. In particular, ethanol can be converted into other important chemicals such as acetaldehyde, ethylene ethyl ether, 1,3-butadiene, *n*-butanol, ethyl acetate, acetone, propylene and isobutene. In addition, bio-ethanol can be upgraded to advanced fuels including hydrogen (by steam reforming) and higher hydrocarbons.⁵⁶ (Figure 1.4).

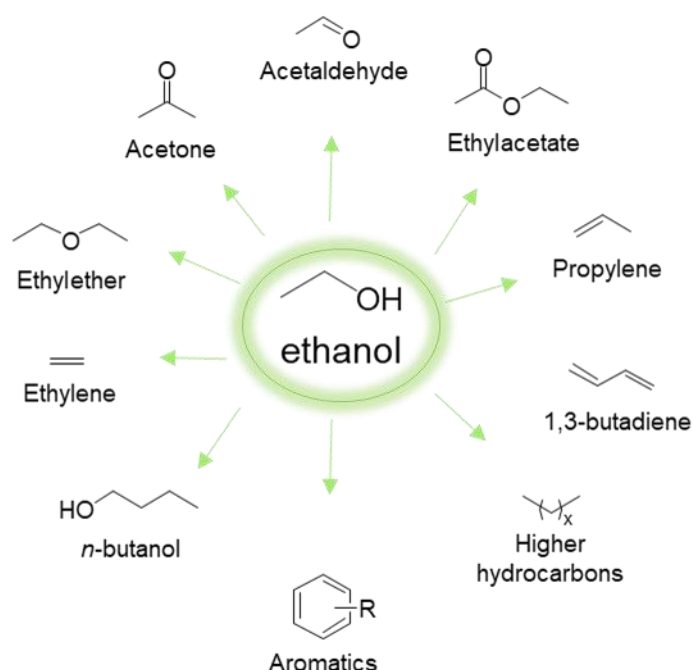


Figure 1.4 Ethanol as building block.

By varying the nature of the catalyst employed and the reaction conditions, many different products can be obtained. Regarding the heterogeneous conversion of ethanol, the general first surface molecular unit has been identified as the ethoxy group forming on the catalyst surface by ethanol dissociative adsorption.^{57,58,59} Then, depending on the nature of the catalyst, different products can be formed. Generally, ethylene or ethyl ether are formed on acidic catalysts. When acid sites are located near to basic sites, the ethoxy group can lose hydride species and producing acetaldehyde, from which aldol-like condensations can take place. The low selectivity frequently observed in ethanol conversion is mainly caused by its high versatility, especially when performed over complex multifunctional catalysts. In fact, complex catalytic materials have, together with the desired functionality, also undesired functionalities. Hence, an optimized catalyst design with well-balanced functionalities is crucial to selectively transform ethanol into the target product.

1.2.1.1 Ethanol to higher alcohols: the Guerbet reaction

Ethanol can undergo coupling reaction yielding *n*-butanol and higher alcohols through the so-called Guerbet route.⁶⁰ The main reaction mechanisms proposed for the Guerbet reaction are two: one based on the direct ethanol condensation (“direct route”) and one based on aldol condensation (“aldol-condensation route”). Figure 1.5 depicts the two routes to forming *n*-butanol starting from ethanol, the direct one (in red) and the aldol-condensation one (in green). The issue is still object of debate, especially when the ethanol upgrading reaction it is studied over heterogeneous basic catalysts, as shown by the presence of several alternative mechanisms proposed in the literature. This variety is related to the different reaction conditions performed over different catalytic systems characterized by diverse physicochemical properties, so it's difficult to reach a universal conclusion.

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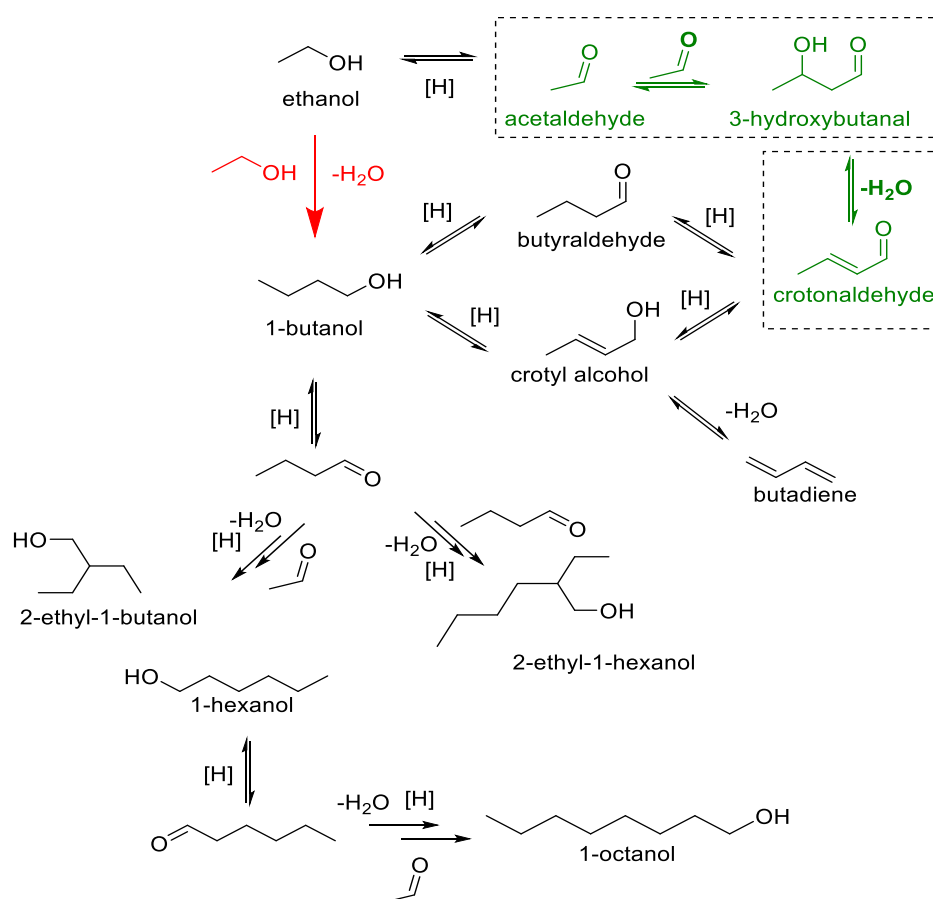


Figure 1.5 Generally accepted pathway for ethanol transformation through Guerbet routes to higher alcohols (in red is highlighted the direct route, in green is highlighted the aldol-condensation reaction from acetaldehyde).

Although different reaction mechanisms have been proposed, the most commonly accepted one is the aldol-condensation route (Figure 1.5). The mechanism starts with the dehydrogenation of ethanol over basic or redox active sites producing acetaldehyde, commonly reported as the key intermediate. Acetaldehyde can then undergo to the aldol condensation to yield 3-hydroxybutanal (acetaldol).

Then the reduction of the aldol can occur through the H-transfer mechanism from ethanol, the Meerwein–Ponndorf–Verley (MPV) reaction.⁶² Nonetheless, the in-situ formed hydrogen (from ethanol dehydrogenation) might also play a role as reducing agent. However, other mechanistic options have been reported: acetaldol may undergo reduction by ethanol to form 1,3-butanediol, the dehydration of which possibly leads to either crotyl alcohol or 3-butene-2-ol. Notably, both compounds can be further dehydrated into butadiene (Lebedev process on bifunctional acid-base catalysts).⁶³ The fact that it has been observed that at least one of both reacting alcohols requires an α -methylene group in order to undergo Guerbet condensation supports the aldol-type mechanism since it is a requisite for the formation of the aldol condensation product.⁶⁴

On the other hand, some studies performed over basic heterogeneous catalysts suggested the direct condensation route, which involves the condensation of two ethanol molecules with no intermediate gaseous compounds. The main direct pathway is suggested to occur by direct coupling of two ethanol molecules with dehydration occurring by the elimination of the hydroxyl of one molecule and the hydrogen attached to the α -carbon of the second one (Figure 1.6, A). Then, the direct condensation of an alcohol with its corresponding aldehyde and consecutive hydrogenation of the higher aldehyde so-formed (Figure 1.6, B) or condensation with its enol form (Figure 1.6, C) are reported as minor reaction pathways.^{46,48,48,65,66}

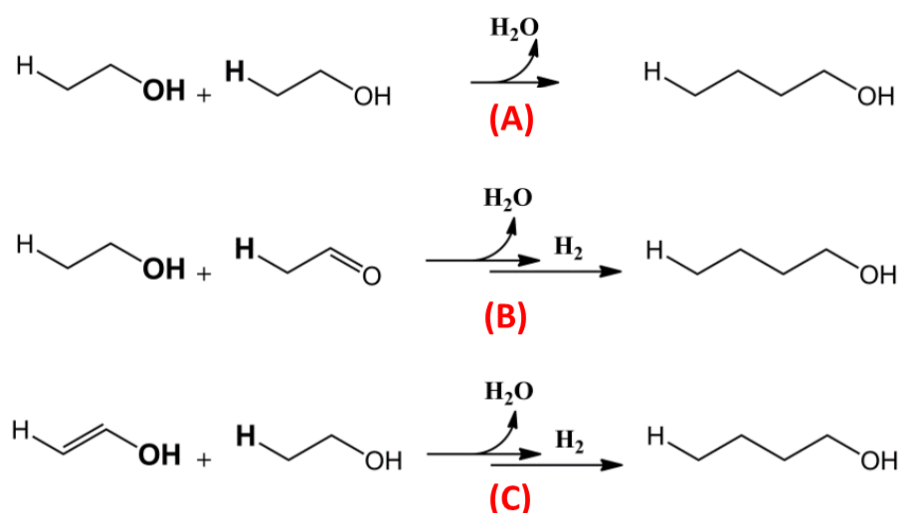


Figure 1.6 Schematic representation of the direct condensation mechanisms for ethanol. A) main mechanism; B) and C) minor mechanisms proposed for the direct condensation.⁶⁰

Similarly, to the mechanism A in Figure 1.6, Chiericato et al. proposed a direct mechanism in 2015. By conducting kinetic experiments in combination with in situ infrared spectroscopy (DRIFTS), MS and DFT calculations, they formulate a new mechanism for transformation of ethanol into *n*-butanol, explaining the formation of the Guerbet alcohols as kinetic primary product. Their mechanism is based on the formation of a carbanion species on the catalyst surface which directly attacks another ethanol molecule with elimination of water leading to the direct formation of *n*-butanol. In this way,

they discharged the key role of the intermediate products characterizing the aldol-route (i.e., acetaldol and crotonaldehyde).⁶³

Anyway, regardless the mechanism, one molecule of water is formed for every molecule of *n*-butanol produced. In general, through the Guerbet route, a higher alcohol containing the double number of carbon atoms of the reagent alcohols is produced; hence the Guerbet reaction product of ethanol is *n*-butanol. Similarly, a mixture of *n*-butanol and ethanol can react to form 2-ethylhexanol (by condensation of two molecules of *n*-butanol), *n*-butanol (by condensation of two molecules of ethanol), *n*-hexanol and 2-ethylbutanol (by condensation of a molecule of *n*-butanol with a molecule of ethanol). Therefore, if at least one of the two materials undergoing condensation contains an α -methylene group, a certain amount of condensation reactions can occur between the alcohols present in the reaction environment yielding a series of higher molecular weight alcohols.⁵¹

Considering the most-accepted pathway, which is the “aldol condensation route”, some general thermodynamic consideration can be made. Indeed, from a thermodynamic point of view, the intermediate reaction steps show different behaviours: dehydrogenation is endothermic, favoured at temperature above 300°C, while hydrogenation is exothermic and favoured at temperature lower than 300°C. The aldol condensation reaction (highlighted in green in the scheme reported in Figure 1.5) even if is slightly exothermic, is favoured in the temperature range 150-550°C, showing a negative ΔG value.⁶⁰ As a consequence, the reaction temperature should be chosen considering kinetic factors in order to optimize the yield of the Guerbet alcohols.

The aldol-condensation reaction step in generally is catalysed by basic, acidic or amphoteric catalysts and occur through the formation of an enol or an enolate. By being slightly exothermic, can be the rate determining step while performing the reaction at high temperature.⁵² Assuming that the subsequent hydrogenation step takes place with $H_2(g)$ as hydrogenation agent, the catalytic systems require a hydrogenation-dehydrogenation active site to facilitate it, such as transition metals, otherwise, higher reaction temperatures are needed due to the higher activation energy.⁶⁷ On catalytic systems that do not possess transition metals, the hydrogenation reaction is proposed to occur by transfer hydrogenation mechanism like the Meerwein–Ponndorf–Verley (MPV) reduction, in which the hydrogen is directly transferred to the unsaturated aldol from the reagent alcohol.⁶⁸ Since a plurality of reactions is involved, the process is particularly sensitive and unpredictable. Accordingly, it is imperative to develop a multifunctional catalytic system focusing on properly tuning both proportion and strength of the different active sites in order to maximize the production of the target alcohol. Indeed, the relatively complex Guerbet reaction requires the use of catalysts that exhibit simultaneously acidic (for the dehydration step), basic (for the aldol-condensation) and/or dehydrogenation/hydrogenation properties. Unfortunately, a lot of side reactions can take place, resulting in the formation of other compounds, such as esters, ketones and carboxylic acids. In this way, the process efficiency is lowered and the catalytic system can be poisoned. Indeed, it is known

that the Guerbet reaction generates numerous by-products, Figure 1.7 depicts some of the possible side reactions that can take place.^{66,69,70}

For instance, on acid sites the dehydration of the starting alcohols might occur leading to the olefin (ethylene, if starting from ethanol) and to ether (ethyl ether) formations.⁷¹ Dehydration reactions, are also required in a part of the Guerbet aldol-condensation route, where the enol is dehydrated leading to the formation of the α,β -unsaturated alcohol.^{72,73} In addition, the subsequent dehydration of the latter alcohol, can lead to the formation of conjugated olefins, and this route is frequently reported as the reaction mechanism for the formation of 1,3-butadiene (Lebedev, Figure 1.5).⁷⁴ Butadiene formation from ethanol will be better examined in section 1.2.1.4.

Over solid bases (e.g., alkaline earth oxides), the esterification of acetaldehyde or higher aldehydes can occur (Tischenko reaction), leading to the formation of ethyl acetate or higher esters.^{75,76} Indeed, esters can be formed via hydride shift, through the Tischenko reaction, and also through the Cannizzaro reaction. The latter includes the reduction of an alkanal species to the alkanol, the oxidation of another alkanal molecule to carboxylic acid, and their subsequent bimolecular reactions.^{77,78} Decomposition of esters⁷⁹ and coupling of carboxylates⁸⁰ are reported in the literature as possible ways to form ketones co-producing CO₂.^{81,82} The presence of CO₂ associated with ketones formation has been reported as detrimental for the Guerbet condensation.⁸³ Anyway, ketones can be formed even as isomer of the aldol intermediate product or its subsequent dehydration and hydrogenation.⁷⁷ Some aromatic compounds can be formed by cyclization reactions of conjugated C=C bonds. Indeed, alkyl-substituted aryl compounds are often observed as side products in Guerbet reaction.^{69,83} In general, many heavy products with different nature, mainly aldehydes, esters and ketones, can be formed as a results of further condensation reactions.

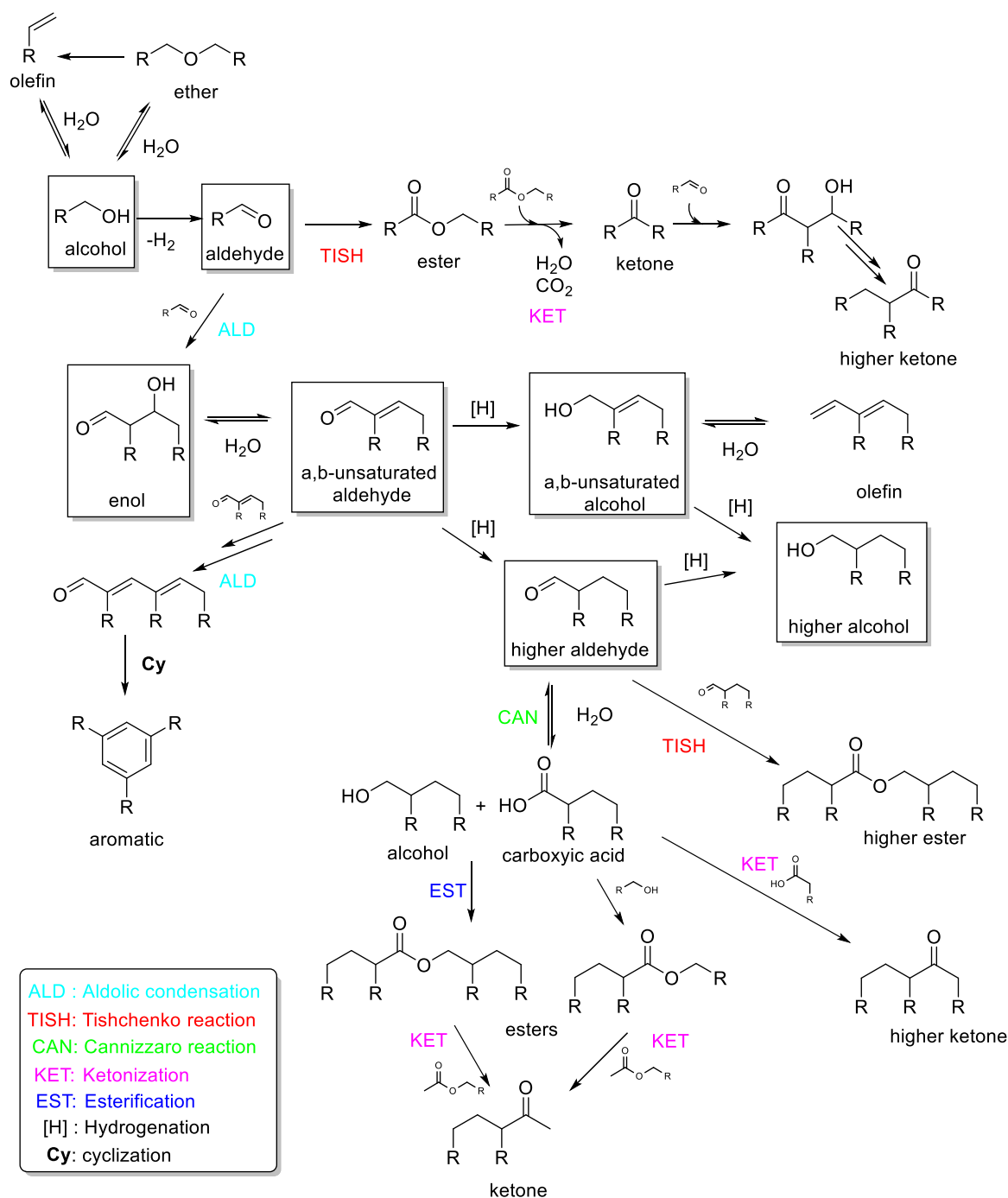


Figure 1.7 Scheme of the side reactions pathway. The Guerbet products are framed.

A variety of homogeneous, homogeneous/ heterogeneous, and heterogeneous catalyst systems have been studied for the Guerbet reaction. Most of the homogeneous systems employed use basic catalysts such as alkaline catalysts or systems modified by homogeneously or heterogeneously addition of a metal to accelerate the dehydrogenation and hydrogenation steps.⁸⁴ Many metal-organic complexes (Ir⁸⁵, Ru⁵³, Rh⁸⁶) have been used as catalytic system showing high performance toward Guerbet reactions, allowing to obtain *n*-butanol and Guerbet alcohols with high selectivity values (>80%).^{86,87} Overall, homogeneous catalysts generally offer the best performance in terms of selectivity, but they exhibit many drawbacks since they imposes thorough purification of the product

stream as well as recovery of the basic compound together with waste treatment. Also, these bases induce metal leaching, corrosion of reactor vessels and are often deactivated by the co-produced water resulting in incomplete conversions and by-products formation.⁸⁸ Homogeneous catalysts thus can be used as a model systems for the heterogeneous ones which provide many advantages in terms of separation and so production processes costs.⁸⁴ Indeed, completely heterogeneous catalytic systems are easily separated from the reaction mixture using filtration, therefore, the product contamination is reduced. Also, ideally they can be reused many times without comprehensive regeneration, they do not cause corrosion nor metal leaching.⁸⁹ They can be fixed in a catalyst bed, thus facilitating continuous operation e.g. in a simple plug flow reactor set-up. This allows for easier integration with subsequent post-treatment steps such as an extra hydrogenation step or purification by distillation.

The realization of the vapour-phase condensation flow system opens new routes for industrial production of *n*-butanol from bioethanol. Indeed, performing the reaction in vapour phase allows higher temperatures to be reached without pressure build-up, which generally imposes practical limitations to liquid phase systems such as autoclave. At high temperatures, typically 350-450°C, the basic catalyst also catalyses the dehydrogenation and hydrogenation reactions.⁶⁰ Therefore, there are many studies describing high temperature vapour phase reactions performed over catalysts devoid of transition metals as active phase. Indeed, the most studied heterogeneous catalyst by far is the basic magnesium oxide, which owing to its superior activity and selectivity has often been used as a reference catalyst for studying Guerbet mechanism.^{59,90-93} Tsuchida et al. proposed a dehydrogenation mechanism of ethanol over MgO surface, where $\text{Mg}^{2+}\text{-O}^-$ pairs are believed to be the active site for hydrogen abstraction (Figure 1.8): ethanol is dissociatively adsorbed to ethoxide on Mg (Lewis acid sites) and to proton-like hydrogen on ionically bound O (hard basic sites) near these acid sites. The acetaldehyde is formed by dissociation of the ethoxide releasing H_2 .⁵⁹

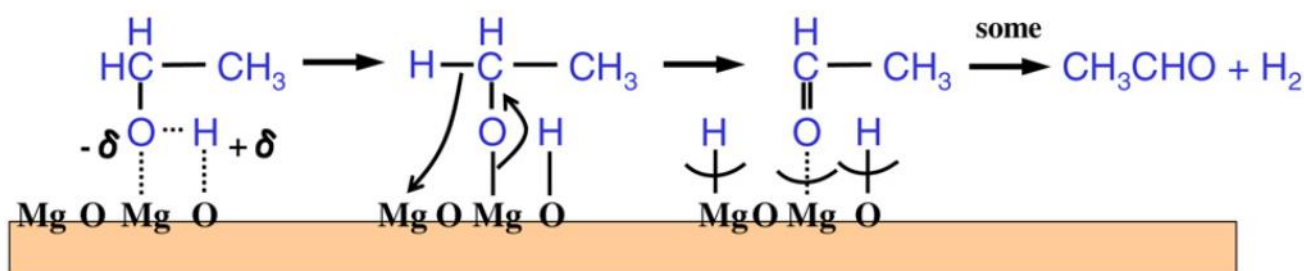


Figure 1.8 Dehydrogenation mechanism from ethanol on MgO catalyst.⁵⁹

Regardless, the Guerbet reaction has been studied over many different heterogeneous catalysts, including mixed metal oxides⁶⁶, hydrotalcite⁹⁴, cation exchanged zeolites⁴⁶ and supported metal catalysts. They have been studied both in gas and liquid phase, for example, via a one-pot liquid-phase reaction, different metals (Ru, Rh, Pd, Pt, Au, Ni, Ag) on alumina were reported to produce *n*-butanol from ethanol.⁹⁵

Furthermore, it has been carried out using hydroxyapatite (HAP) that has been shown to be the most active catalyst with high selectivity toward *n*-butanol.⁹⁶ In general, there is an inverse relation between *n*-butanol selectivity and ethanol conversion yield, indeed, the highest selectivity of 82% was obtained over Sr-P hydroxyapatite⁹⁷ with an ethanol conversion of 4%, while working at 300°C. Earley et al. managed to obtain a better compromise between *n*-butanol selectivity (45%) and ethanol conversion (67%) over Cu/CeO₂ catalyst in a continuous flow supercritical CO₂ reactor, but the process has the drawback of being less cost effective.⁹⁸

Both the studies over the Mg/Al mixed oxide and HAP based catalysts led to some analogous conclusion about the relation between basic and acidic catalytic sites. By varying the Mg/Al-ratios, hence changing the acid-base properties, the selectivity can be optimized towards dehydrogenation, aldolization and hydride-shifts. Strong acid sites are to be avoided for its dehydration property, yet a moderate amount of acidity facilitates coupling of the intermediates. Indeed, while basic sites are required to generate carbanion species by abstraction of hydrogen, the acid sites are needed for acetaldehyde adsorption that then produces the acetaldol by reaction with the carbanion species.⁶⁶ Similarly, Tsuchida et al. found that by varying the Ca/P ratio in HAP its acid-base properties can be optimized toward *n*-butanol selectivity.⁵⁹

In general, a fine-tuning of both the strength (weak acid sites are preferred)⁹³ and the amount of acid-base sites (the selectivity to *n*-butanol is favoured by high number of strong basic sites)⁹⁹ is crucial to obtain high *n*-butanol yield. Hence, both acid and basic sites are needed, in particular adjacent acid and medium basic sites are needed in order to generate the intermediate compounds in ethanol conversion through Guerbet route.⁹⁹ Many authors reported the necessity of a specific superficial atomic arrangement in order to adsorb two molecules of acetaldehyde, remove a proton from one of these aldehydes, and promote the nucleophilic attack. Hence, to promote aldol condensation, the catalyst surface should consist of one basic site adjacent to two acids sites.^{59,66,100}

1.2.1.2 Ethanol to hydrocarbon fuels

The dependence on fossil fuels for the production of energy is particularly drastic concerning the transportation sector, which relies almost entirely (95%) on petroleum-derived liquid hydrocarbon fuels (gasoline, diesel and jet fuels).¹⁰¹ Gasoline is a volatile (boiling points between 30 and 220 °C) and inflammable complex mixture of olefinic, paraffinic, naphthenic, and aromatic hydrocarbons in the C₄-C₁₂ range. It incorporates low contents of oxygenates and traces of sulfur, nitrogen, and metals, which introduce instability to the final mixture. Its variable compositions determine its physicochemical properties and relative engine performance.¹⁰² For example, gasoline produced by catalytic reforming (with high content of aromatic hydrocarbons and isoparaffins) and by catalytic cracking (with high olefins content) are characterized by low self-ignition point and consequently high

octane values. Improved combustion characteristics can be achieved by addition of oxygen-containing additives (alcohol and tertiary ethers) instead of aromatic hydrocarbons. Methyl tertiary butyl ether (MTBE) and ethanol are most widely used oxygen-containing compounds for octane rating improvement. MTBE dominates markets in Europe and USA, but its application is decreasing due to its solubility with water and toxicity of its dissociation products.¹⁰³

Gasoline is the world's major automotive fuel and influences each country's economy and energy strategy. Nevertheless, the demand for gasoline is also projected to decrease over the next few decades, while the worldwide demand for heavier C₈–C₂₂ distillate fuels such as jet fuel and diesel is projected to increase.¹⁰⁴ In 2016 the International Civil Aviation Organization (ICAO) reported that 2% of global CO₂ emissions can be attributed to the aviation sector and with increasing demand, the aviation industry could become a significant fossil-based CO₂ emitter by 2050.¹⁰⁵ Table 1.1 resumes the main properties featuring petroleum derived fuels and ethanol.

Table 1.1 Fuels properties, from Ref. ¹⁰⁶

<i>Fuel</i>	<i>Density [g/mL]</i>	<i>Net heating value [MJ/L]</i>	<i>Carbon range</i>	<i>Freezing point [°C]</i>	<i>Boiling point [°C]</i>	<i>Flash point [°C]</i>	<i>Max aromatic content [vol%]</i>	<i>Cetane</i>
Gasoline	0.735	31.8	4–12	–	40–215	–45	35	–
Jet (A-1)	0.808	34.1	8–16	<–47	140–300	>38	25	–
Diesel	0.85	36.2	10–22	–17	170–370	>52	35	>40
EtOH	0.789	21.1	2	–114	78	13	–	8

The most common jet fuel (Jet A-1) is a complex mixture of hydrocarbons in the C₉–C₁₆ range, composed by linear alkanes (providing energy density); slightly branched alkanes or isoalkanes (lowering freezing point); cycloalkanes/naphthenes; and aromatics ($\leq 25\%$)¹⁰⁷. (Figure 1.9). The carbon length and relative amount of each families of hydrocarbons have to be controlled in order to provide to jet fuel the desired properties.^{108,109} It must have high flash points (to reduce fire hazard on board), low freeze points (to ensure good cold flow properties at high altitudes and long international flights), high energy density (to minimize fuel storage room), and good sealing properties (to avoid fuel leakage on board).¹⁰⁷ A certain amount of aromatics is mandatory to promote the swelling of elastomeric valves in fuel systems, thereby ensuring proper sealing.¹¹⁰ Above this amount (exactly 25%)¹¹¹, aromatics do not provide beneficial effects to the jet fuel, negatively affecting the combustion performance of the fuel. In addition it have been observed that aromatics contribute considerably to non-volatile particulate matter emissions (i.e. soot).¹¹² A fuel must have a flash point of at least 38 °C to be classified as Jet A-1, and aviation fuels have a higher volumetric energy density (net heating value = 34.1 MJ L^{–1}) than does gasoline (31.8 MJ L^{–1}). In

general, jet fuel specifications are stricter than those of gasoline or diesel, which are typically more regionally determined.

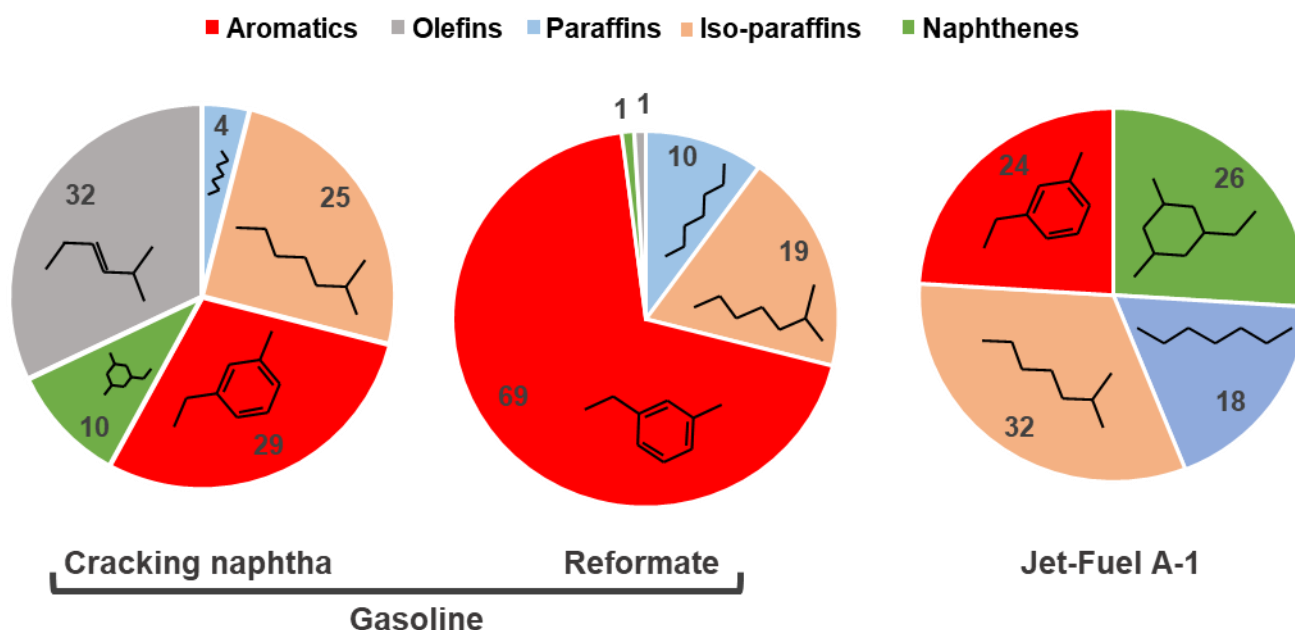


Figure 1.9 Average chemical composition of gasoline (from cracking of naphtha and reforming) ¹⁰³ and jet fuel Jet A-1. ¹⁰¹

Given the fact that hydrocarbon fuels are mainly produced from crude oil and considering the issues related to its usage (e.g., diminishing petroleum reserves, energy security concerns, release of CO₂ in the atmosphere as primary cause of global warming), the shift from fossil-based to renewable-based fuels is needed.^{101,113} The existing liquid biofuels most widely used are the crop-based bioethanol and biodiesel, produced by fermentation and transesterification technologies respectively.¹¹⁴ However, their implementation has inherently issues related to their nature, requiring proper engines and infrastructure. Hydrocarbon biofuels that are “drop-in replacements” for conventional petroleum-derived transportation fuels, since chemically identical, are expected to gradually supplant ethanol and biodiesel.^{113,113} Considering the lignocellulosic biomass, it can be converted to syngas through gasification which can then be converted to fuel hydrocarbons by Fischer–Tropsch conversion. Otherwise, the alcohols derived by fermentation of sugars and ethanol in particular, can be upgraded to hydrocarbon fuels (C₃₊ hydrocarbons) undergoing several chemical transformations.^{69,115,116} The valorisation of ethanol into longer chain hydrocarbons mixtures (resembling the gasoline composition) has gained importance in both industry and academic researches. Technologies for converting alcohols and other oxygenates to jet fuel are being developed by several companies, still at laboratory and pilot level, and most of them by partnering bio-alcohol producers and companies able to perform the upgrading.^{101,107} For instance, Vertimass is currently commercializing a process for making bioderived jet fuel and BTEX (benzene, toluene,

ethylbenzene, and toluene) from ethanol.¹¹⁷ While Gevo and BioChemtes¹¹⁸ cooperated to convert bioalcohols into jet fuels in the C₁₂–C₁₆ range.

The main strategies to transform ethanol into hydrocarbon mixtures and can be gathered into two different approaches.¹¹⁹ The first one, the most studied, involves acid-catalysed ethanol dehydration to ethylene followed by olefin oligomerization over solid acids, mainly zeolites. Then through hydrogenation it is possible to obtain a mixture suitable to be used as gasoline or jet fuel. However, one of the challenges of this process is to tailor the catalyst composition in order to control the product distribution. Ethylene oligomerization is slow and requires operative temperature above 300 °C where undesirable side-reactions including cracking, hydrogen transfer, and aromatization can take place, lowering the overall selectivity.^{120,121} As a result, such processes are limited to producing mainly C₃–C₈ paraffins and C₆–C₁₂ aromatics, species suitable for use in gasoline or in the chemical industry (e.g. BTEX).¹²² This first approach is a process similar to much more studied technology named methanol-to-gasoline (MTG) developed by Mobil Corp. (now Exxon Mobil Corp.)¹²³ on HZSM-5 zeolite. Hence this approach has been frequently named the ethanol-to-gasoline process (ETG) and is based on the so-called “hydrocarbon pool” mechanism.^{42,124,125} According to this model, the overall process is catalysed not only by the zeolite itself, but also by the organic compounds retained within the voids, that constitute the “hydrocarbon pool” mainly composed by alkyl substituted aromatics compounds, that participate to the reactions as co-catalysts.¹⁰⁶ In this case the main factors affecting the product distribution are the Si/Al ratio of the zeolites, which affects the surface acidity of the catalyst and consequently the reaction temperature required. The main obstacles encountered with this approach are related to the catalysts deactivation due to the extensive coke formation and the competition between cracking and oligomerization reactions, limiting the yield in longer chain hydrocarbons. The control of heavier products formation has been reported to be easily obtained through a two-step oligomerization. Pacific Northwest National Laboratory (PNNL) has developed a two-step oligomerization process that converted ethanol into isobutene/propene-rich gas mixture over Zn₁Zr_{2.5}O₂ catalyst, followed by oligomerization over solid acid resin (Amberlyst-36), obtaining a gasoline-range hydrocarbon mixture. They managed to obtain a jet-range hydrocarbons by separating the light gases (i.e., H₂, CO₂, etc.) from olefins before performing the oligomerization step.¹²⁶

The other approach to convert ethanol into middle distillate hydrocarbons is based on ethanol dehydrogenation followed by aldolization. In this context, when heterogeneous bifunctional acid/base catalyst is used, such as a hydroxyapatite, the ethanol could be converted into higher hydrocarbons, namely longer chains alcohols, through a completely different synthetic mechanism generally based on the Guerbet condensation reaction, the mechanism of which has been deepened in the previous section (1.2.1.1). In particular, this approach has been applied by Ueda et al. over hydroxyapatite based catalysts, this topic is further detailed in section 1.3.1. In general, the main challenge with using Guerbet coupling to form C-C bonds and produce distillate-range molecules is

reaching high conversions while maintaining high selectivities for the alcohol products. Nevertheless, *n*-butanol and higher alcohols produced can be directly used as fuels or can be subsequently dehydrated to mixed olefins, which can be used to make jet range fuel via oligomerization reactions.

23,69

1.2.1.3 Ethanol dehydration

The dehydration products of ethanol are diethyl ether (DEE) and ethylene, and the reaction is catalysed by various solid acid catalysts such as silica-alumina and zeolites. Ethylene and diethyl ether are important products for the chemical and petroleum industries.^{127,128} Ethylene is one of the most demanded intermediate chemicals, widely used in the industrial synthesis of polymers and a variety of other valuable products of organic chemistry, due to its high reactivity. When derived by fossil fuels, its production is based on steam cracking of petroleum liquids and natural gases. However, this process is endothermic and requires high reaction temperatures (780–1200°C) and the use of steam as a heat transfer agent at a ratio of 1: 1. The overall process releases great amounts of carbon dioxide into the atmosphere.^{129,130} Catalytic dehydration of ethanol is an alternative ecological route for production of ethylene, which reduces the greenhouse gas emissions and dependency on limited fossil fuels.^{72,73,131} Diethyl ether is a valuable chemical and an attractive motor vehicle fuel alternative¹³² since it has excellent transportation fuel properties (cetane number > 125).^{133,134} Good burning properties of DEE make it a promising alternative fuel or fuel additive for diesel fuel¹³². Also, blending of DEE with ethanol was reported to improve the cold start problem of ethanol fueled cars.

When ethanol reacts on solid acid catalysts, the products generally found are ethylene, water and diethylether. There is no general agreement in the literature on the reaction pathway, that has been observed to depend to some extent on the catalyst used, but it can be resumed as reported in Figure 1.10. Where ethylene could be formed by a consecutive intramolecular dehydration reaction where DEE acts as intermediated obtained by interdehydration of two molecules of ethanol; ethylene and ethyl ether are products of parallel reactions or both parallel and consecutive reactions take place.

135

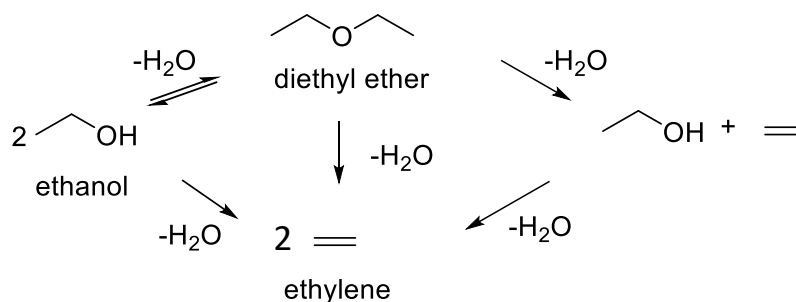


Figure 1.10 Ethanol dehydration pathways. ¹³⁵

Reaction temperature plays an important role in the product distribution since the two reactions have an opposite thermodynamic behaviour. The production of ethylene is endothermic and the highest selectivity towards ethylene is obtained at 300–500 °C. Higher temperatures shift the reaction towards acetaldehyde production, while the slightly exothermic production of diethyl ether (DEE) is only favoured below at lower temperatures.^{72,73,131,136} For these reasons, the potential to achieve of DEE with high yields is quite low in a conventional flow reactor.¹³⁶ From the catalytic point of view, the activity and respective selectivity between DEE and ethylene has been correlated with both the amount and strength of the acidic centres of the catalysts employed.¹³⁷ It has been observed that generally, ethanol is adsorbed on the catalysts surface as ethoxy group, that then can crack over acidic catalyst-producing ethylene by an elimination reaction or can react as a nucleophile, which attacks un-dissociated ethanol producing diethyl ether.¹³⁶ In addition, the mechanism of the dehydration of ethanol reaction suggested that two separate types of sites are responsible for the ethylene and DEE formation. Generally, it has been observed that low-temperatures and medium strength of acid sites favour DEE production.^{138,139}

1.2.1.4 Ethanol to butadiene

Butadiene is one of the most important bulk chemicals produced in the petrochemical industry, widely used in the production of polymers and polymer intermediates.¹⁴⁰ It is mainly produced as a by-product of ethylene steam cracking of naphtha or by the catalytic or oxidative dehydrogenation of *n*-butane and *n*-butene respectively.¹⁴¹

Butadiene production from ethanol has gained interests in recent years and is often considered as product of a parallel reaction to the Guerbet reaction pathway.^{74,142} The most encountered processes that lead to butadiene production starting from ethanol are made up by one or two steps. The two-step process which is called “Ostromislensky process” and is based on a first dehydrogenation step of ethanol yielding acetaldehyde and a second one where acetaldehyde and ethanol react over a tantalum promoted silica catalyst to yield butadiene.³² Then, the one-step process, the so-called “Lebedev process” which requires a bifunctional catalyst, exhibiting both dehydrating and dehydrogenating activity.¹⁴³ Lebedev first proposed a radical mechanism but in recent years all the

reaction mechanism for both processes proposed consider acetaldehyde as the key intermediate and its conversion toward crotonaldehyde.⁷⁴ Indeed, Toussaint and et al. proposed a mechanisms based on the aldol condensation between two acetaldehyde molecules formed upon ethanol dehydrogenation. The overall mechanism includes the formation of acetaldol via the aldol condensation of two acetaldehyde molecules, followed by dehydration of the aldol to crotonaldehyde, in accordance with the reaction mechanism showed in Figure 1.11.¹⁴⁴ Then crotonaldehyde is reduced via Meerwein–Pondorf–Verley (MPV) mechanism to crotyl alcohol, where ethanol (or any other alcohol present in the system) served as a hydrogen donor, requiring the participation of acid and basic sites.^{32,145} Finally, the dehydration of crotyl alcohol yield butadiene. However, there are different perspectives and mechanism proposed, even concerning the rate controlling stage of the reaction.¹⁴³

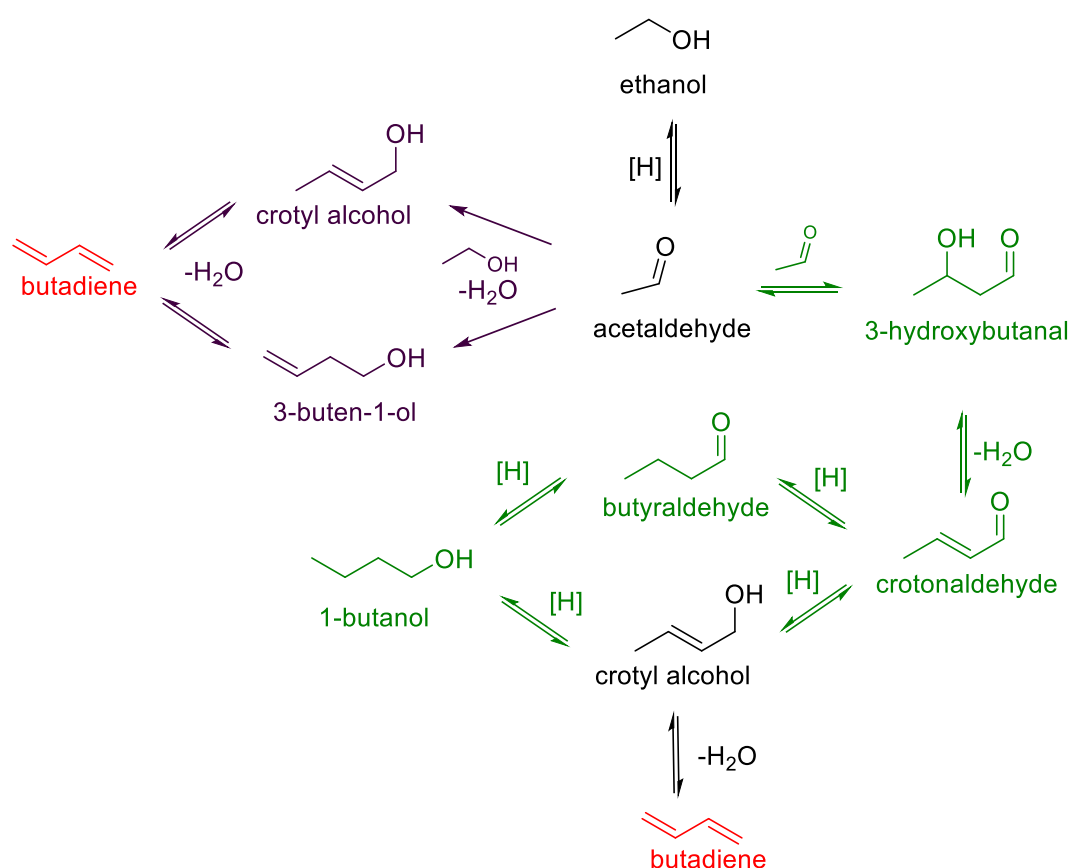


Figure 1.11 Mechanism formation of butadiene from ethanol. In purple the alkenols route, in green the aldol-condensation route.

Recently, Chieragato et al., by studying the ethanol conversion over MgO, proposed the direct route of *n*-butanol formation. Accordingly, they proposed a different reaction mechanism for butadiene production as well, suggesting that it is formed by condensation between ethanol and acetaldehyde, leading to alkenols (mainly crotyl alcohol) which are then dehydrated into butadiene.⁶³

Similarly to the Guerbet reaction, a multifunctional catalyst with balanced basic, acid and redox properties is required for the reactions of condensation, dehydration and hydrogenation. Over the

years, butadiene formation from ethanol has been studied over many catalytic systems (e.g., $\text{ZrO}_2\text{-Fe}_2\text{O}_3$, doped Al_2O_3 , metal oxide-promoted MgO-SiO_2 (e.g., CuO , NiO , ZnO), metal modified sepiolite, Zn-containing talc and zeolite-based catalysts).^{146–149} For instance, Angelici et al. managed to obtain butadiene with 53% of selectivity while performing the reaction at 425°C over a $\text{CuO/SiO}_2\text{-MgO}$ catalyst. They stated that the addition of CuO as a promoter on the physical mixture of $\text{SiO}_2\text{-MgO}$ systems improved butadiene yield and that the nature of the CuO played a crucial role in butadiene formation (i.e., cluster-like species of CuO), that is strictly related to the synthesis method applied. Nevertheless, the main issues generally encountered were the formation of the many side products, lowering the overall yield and the negative effect of water produced on the surface of the catalyst.¹⁴⁸

1.3 CATALYSTS

1.3.1 Hydroxyapatite

Calcium hydroxyapatite (Ca-HAP , $\text{Ca}_{10-x}(\text{PO}_4)_{6-x}(\text{HPO}_4)_x(\text{OH})_{2-x}$), with $0 < x \leq 1$) is the basic mineral constituent of human bone and tooth enamel.¹⁵⁰ Naturally, it can be extracted from mineral rocks, biogenic products (e.g., eggshells, mussel shells) and bio-wastes (e.g., fish bones, mammal bones). Otherwise, it can be synthesized by wet chemical methods (i.e., precipitation, sol-gel technique, hydrolysis, hydrothermal, emulsion method) starting from its inorganic precursors (e.g., calcium hydroxide, calcium nitrate, phosphoric acid, ammonium phosphate).¹⁵¹

The stoichiometric HAP contains calcium (Ca) and phosphorus (P) at a molar ratio of 1.67 (Ca/P) and a H_2O content of 1.79 wt%. However, HAP in human bones is usually nonstoichiometric due to Ca deficiency with Ca/P ratios varying from 1.5 to 1.67, which affects the biological and mechanical properties of HAP.¹⁵⁰ Indeed, it is easy to find HAP in its non-stoichiometric composition caused by the relationship in size between its Ca^{2+} and P^{5+} ions, which allows HAP structure to tolerate a certain degree of substitution of ions during crystal formation, for this reason HAP is classified as a distorted apatite.^{23,69} Its structure (Figure 1.12) comprises three-dimensional networks of hexagonally packed tetrahedral PO_4^{3-} ions. These ions make a first channel around Ca^{2+} ions [type 1 Ca, “Ca1”] with a diameter of 2.5 Å, Ca1 is coordinated to 9 oxygen atoms.⁶¹ A second channel with a diameter of 3.5 Å, bordered by triangular Ca^{2+} ions [type 2 Ca, “Ca2”], hosts the OH^- species along the c-axis, C2 is coordinated to 7 oxygen atoms.^{61,152} “Non-stoichiometric hydroxyapatite” is represented by the formula $\text{Ca}_{10-z}(\text{HPO}_4)_z(\text{PO}_4)_{6-z}(\text{OH})_{2-z} \cdot n\text{H}_2\text{O}$; $0 < z \leq 1$, $n = 0\text{-}2.5$, with OH^- sites that can be partially substituted with H_2O . It is characterized by the presence of a vacancy defect in cationic site and OH. In addition, the non-stoichiometry affects the crystallinity, that is lower the further hydroxyapatite is

from stoichiometry and simultaneously, its solubility increases.¹⁵³ Thus, hydroxyapatite surface exposes different functional groups, acting as acid and basic sites and conferring a peculiar amphoteric character, which can be more or less pronounced depending on the HAP composition, in particular on the Ca/P ratio.¹⁵⁴ In addition, it has the intrinsic capability to exchange the Ca^{2+} ions and to distribute some other metal ions analogously to zeolites allows one to obtain interesting functionalized materials with modulated number and strength of acid and basic sites.^{152,23,69} Both cationic and anionic substitutions can take place. Several cations can substitute calcium ions in either type1 and type 2 Ca positions or in both positions simultaneously, for instance, Ca (II) can be exchanged with Mg(II), Sr(II), Ba(II), Co(II), Cd(II), Cu(II), Fe (III), Ce(III), Eu (III).^{155–158} Similarly, several anions can replace either OH^- or PO_4^{3-} ions or both, for example the trivalent anion PO_4^{3-} can be exchanged with VO_4^{3-} , CO_3^{2-} or SO_3^{2-} .^{152,153,159,160}

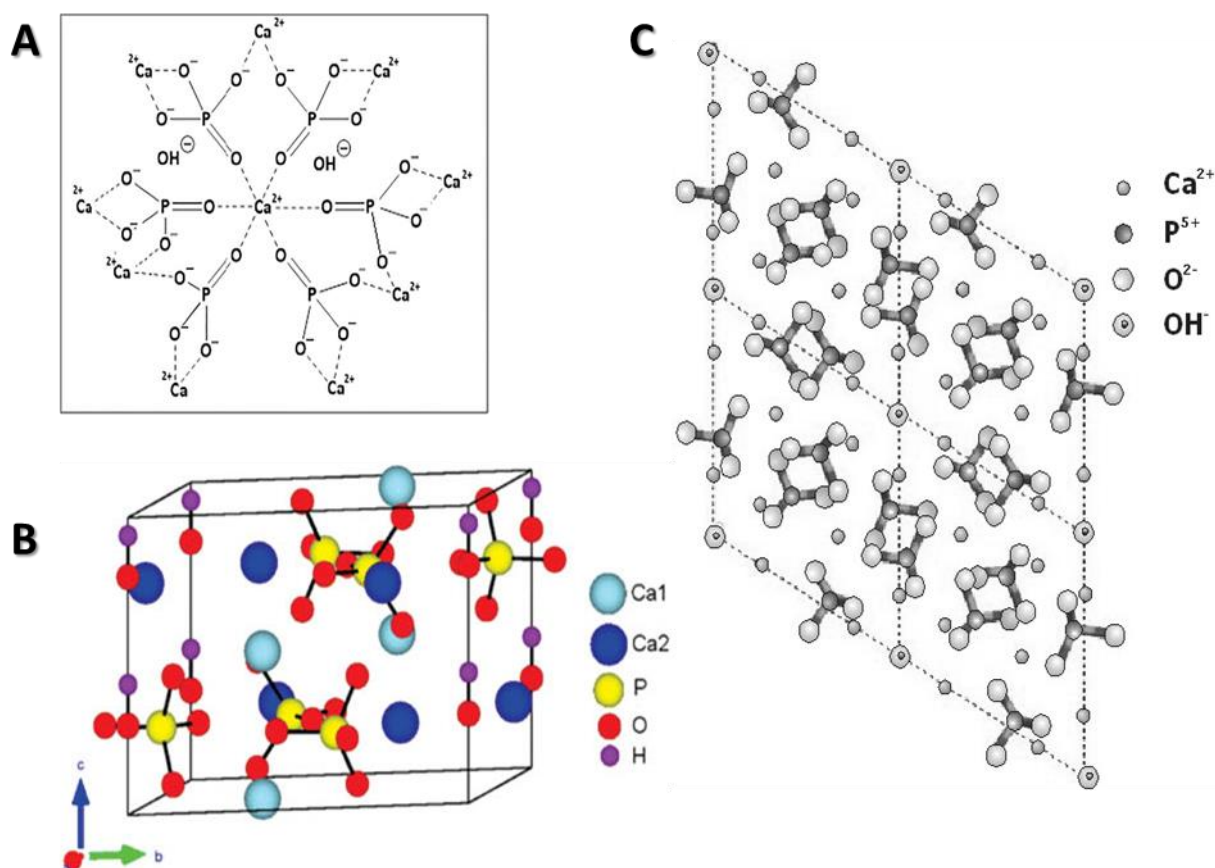


Figure 1.12 A) Structure of hydroxyapatite,¹⁶¹ B) Hexagonal unit cell of SHAp,¹⁵⁰ C) Crystal structure of hydroxyapatite.¹⁵⁰

Besides its ion-exchange ability, HAP has a remarkable thermal stability, allowing to be processed at high temperature (up to 800°C) without undergoing physical modifications, letting it be really suitable to be used as heterogeneous catalyst to perform gas-phase reaction. In addition, its functionalization with metal species could lead to multifunctional catalysts that would benefit from the combination of the electron transfer capacity and Lewis acidity associated with the metal centres and of the amphoteric surface properties of HAP.¹⁶²

Me-HAP based catalysts have been used for environmental protection reactions, such as the abatement of volatile organic compounds and denitrifications (i.e., de-VOCs and de-NO_x).¹⁶² Then, it has been observed quite effective for the C-C coupling reactions. In particular, it incorporates the ideal multifunctionality to be used as multifunctional catalyst for the ethanol Guerbet condensation. In this regard, it has been extensively employed by several authors and it has been shown to be the most active catalyst with high selectivity toward *n*-butanol.^{96,58,59,163} The highest selectivity obtained up to now has been 82% over a Sr-substituted HAP, at 300°C and atmospheric pressure, nevertheless, it was related to a low value of EtOH conversion of 4%.⁹⁷ In addition, Silvester et al. managed to obtain an overall alcohols selectivity of 76.4% with 13% of ethanol conversion over a 100 mol% Sr substituted apatite, by working at 350°C and GHSV = 5000 mL·h⁻¹·g⁻¹.⁶¹ The same research group in a former study, obtained a total alcohols selectivity of 83% over a carbonate containing apatite (Hap-CO₃).¹⁶⁴

Ho et al. studied the mechanism of *n*-butanol formation starting from ethanol over HAP catalyst. They stated that ethanol is adsorbed by dissociative adsorption on the Ca-O sites forming ethoxide and hydroxyl species on the surface that lead to the formation of acetaldehyde which migrates to the neighbouring sites CaO/PO₄³⁻ undergoing aldol-condensation and yielding crotonaldehyde. The two hydrogenation steps that yield *n*-butanol take place by hydrogen transfer from ethanol via Meerwein-Ponndorf-Verley (MPV) reduction. The mechanism is depicted in Figure 1.13. Nevertheless, the acid-base cooperation was found to accelerate the aldol condensation rates.⁵⁸

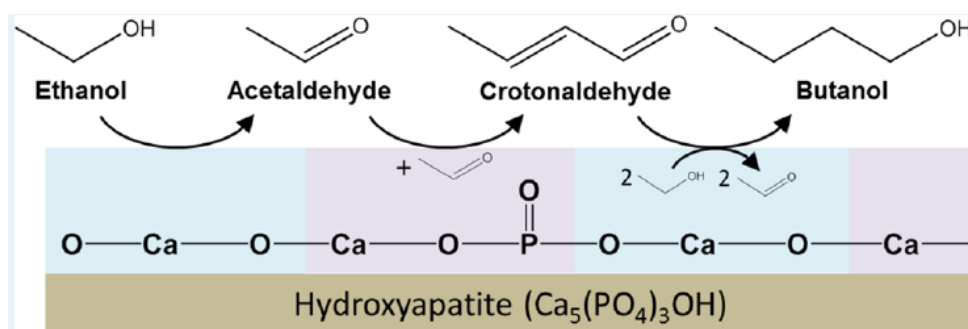


Figure 1.13 Ethanol Guerbet conversion over hydroxyapatite catalyst.⁵⁸

Ogo et al. and Silverster et al. investigated the effects of ion-substitution on the catalytic activity of ion-exchanged HAP. The substitution with VO₄³⁻ anions increases its selectivity for acetaldehyde dimerization to crotonaldehyde, while by exchanging CO₃²⁻ anions and Sr²⁺ in the HAP structure, it was highlighted the importance of balancing acid and base sites in order to enhance the selectivity for the Guerbet coupling of ethanol.^{61,164} In particular, it was found an optimal ratio of 4 between acid and basic sites over a series of Sr-substituted hydroxyapatite⁶¹, while HAP with predominantly acid sites functions as a dehydration catalyst.⁶³ Nevertheless, the extent of ethanol conversion has been strictly related to the surface area of the catalyst.⁶¹

Due to the well-known good performance of HAP in the ethanol Guerbet coupling reaction, it has been recently used as “Guerbet catalyst” in a patented process. In detail, Sakuma et al., patented a two-step approach for producing a mixture of hydrocarbon of C₄-C₁₂ resembling gasoline starting from ethanol. They fed ethanol from the top of a two fixed bed reactor consisting of “Guerbet catalyst” such as HAP (the first bed) producing a longer chain compounds mixture and a hydrogenation catalyst (the second bed) to reduce it. They used hydrogen as carrier gas or they fed hydrogen only in the second step and they even studied the reaction by using only the hydrogen generated in the first step as hydrogenation agent for the second step using helium as carrier gas in this case. They conducted the first step at 1-200 atm, 100-600°C and using a contact time of 0.1-600 seconds whereas the second step was conducted at 1-200 atm, 0-400°C.¹⁶⁵

In the context of pushing the Guerbet reaction toward the production of higher alcohols and condensed products, Tsuchida et al. studied the ethanol gas phase conversion over HAP and by working at 500°C they obtained a product mixtures from C₂ to around C₁₂ hydrocarbons.^{23,69} The obtained liquid contained oxygenates such as alcohols, aldehydes, and ketones, which are not found in commercial gasoline, and at the same time, aromatics such as benzene, toluene, and xylene, in smaller quantities than in commercial gasoline. They suggested a new mechanism for the synthesis of biogasoline from ethanol consisting of two consecutive reactions: the propagation of ethanol (to produce Guerbet alcohols) followed by dehydration/dehydrogenation of the generated alcohols (i.e., 2-ethyl-1-butanol; n-hexanol; 2-ethyl-1-hexanol; n-octanol; two kinds of branched C₁₀ alcohols and n-decanol). They observed that with high Ca/P ratios, close to stoichiometry, the good acidic/basic sites ratio can promote the dehydrogenation properties of the catalyst (i.e., lower Ca/P led to higher acidity). Indeed, using nonstoichiometric HAP as catalysts for the conversion of ethanol brought to hydrocarbon fuels (up to C₁₂) containing, in addition to non-oxygenated hydrocarbons, a fraction of oxygenated hydrocarbons (alcohols, aldehydes).⁶⁹ Conducting ethanol conversion over HAP with a Ca/P ratio of 1.64 at a contact time of 1.78 s and a reaction temperature of 300°C resulted in a *n*-butanol selectivity as high as 76%.²³ In 2008, Tsuchida et al. managed to synthesize biogasoline from ethanol in one step over a highly active nonstoichiometric HAP catalyst.⁶⁹ The biogasoline produced has a research octane number of 99 and contains dienes and oxygenates almost entirely absent from the product of MTG or ETG over a zeolite catalyst. They found that the ratio of oxygenates in the biogasoline could be adjusted by changing the reaction conditions (mainly reaction temperature).

In 2017, Quintana et al. prepared a carbonate hydroxyapatite by precipitation (i.e., B-type CHAP [Ca_{10-x/2}(PO₄)_{6-x}(CO₃)_x(OH)₂]) and tested for ethanol conversion.¹⁶⁶ They managed to obtain a hydrocarbon fuel mixture with carbon chain lengths in the range C₄-C₁₈₊ with high yield (97%). The carbon chain lengths obtained was quite higher than those reported in the literature (e.g., C₄-C₁₀₊) on HZSM-5¹⁶⁷ and nonstoichiometric HAP catalysts⁶⁹, suggesting that carbonate ions may play an

important role in the formation and breakage of C-C, C-H and C-O bonds, favouring the production of large hydrocarbon molecules.

1.3.2 Zirconia

Several studies have been performed on the structures and properties of oxides surfaces, in order to understand the roles that oxides play in the catalytic processes. Among various metal oxides, zirconia (ZrO_2) is of particular interest and has received widespread attention thanks to its ideal mechanical and chemical stability. Moreover, zirconia also possesses excellent properties of high melting point, high electrical resistivity, high refractive index and low thermal expansion coefficient, and therefore is considered as one of the most important ceramic materials.¹⁶⁸ In nature, zirconium oxide occurs as the mineral baddeleyite. The normal procedure used to prepare zirconia consists of calcination of the zirconium hydroxide (hydroxylated gel) which is prepared by hydrolysis of zirconium salts. This gel presents two different kinds of OH⁻ group, terminal and bridged, the ratio of which depends mainly on the precursor used to form the gel. The polymorphic nature of ZrO_2 is well known and has been subject of many studies.¹⁶⁹ Zirconia has three polymorphs: monoclinic ($T < 1000^\circ\text{C}$), tetragonal ($T > 1170^\circ\text{C}$) and cubic phases ($T > 2370^\circ\text{C}$). In addition, it can even exist as an amorphous solid. The final crystal structure of ZrO_2 is strictly affected by the preparation method.¹⁷⁰ Nevertheless, the monoclinic phase is thermodynamically stable at room temperature, while the tetragonal and cubic phases are metastable.¹⁷¹ The transition from the monoclinic phase to the tetragonal phase starts around 1050°C , completing around 1170°C . During this transformation, the volume decreases of 3–5%. A metastable tetragonal phase can be obtained by quenching to room temperature.¹⁷² The crystal structures related to these phases are shown in Figure 1.14

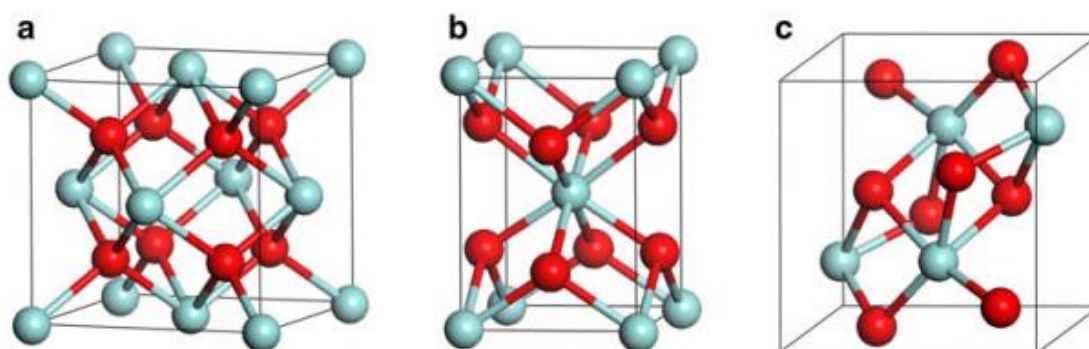


Figure 1.14 Crystal structures of ZrO_2 : a) cubic; b) tetragonal and c) monoclinic. Red and blue spheres correspond to oxygen and zirconium atoms respectively.¹⁶⁸

The cubic ZrO_2 has an ideal fluorite structure (Fig. 1.14a). The Zr cations are situated at the corners of the cubic elementary cell as well as at the halves of the [110] directions, in a face-centred cubic (fcc) lattice. The oxygen anions lie at the quarters of [111] directions, which are the tetrahedral

interstitial sites associated with this fcc lattice. In this structure, each Zr cation is coordinated to eight equivalent nearest-neighbour oxygen anions at the corners of a cube, and each O anions is tetrahedrally coordinated to four Zr cations.¹⁷³ Consequently, zirconium and oxygen are octahedrally and tetrahedrally coordinated, respectively. The unit cell contains one zirconium and two oxygen atoms with Zr–O distances of ≈ 2.2 Å.¹⁷⁴ The tetragonal ZrO_2 possesses a distorted cubic structure (Fig. 1.14b), obtained by displacing opposite pairs of oxygen atoms alternatively up and down along the [001] direction. In the tetragonal ZrO_2 , each Zr cation is still surrounded by eight oxygen anions, with four oxygen neighbours arranged in a flattened tetrahedron at a short Zr–O distance, 2.065 Å, and the rest in an elongated tetrahedron rotated 90° at 2.455 Å from Zr. Each oxygen anion is bonded to two Zr cations at 2.065 Å, and two more Zr cations are 2.455 Å away.¹⁷⁵ Finally, monoclinic zirconia has a lower symmetry and a more complex geometric structure. The primitive cell contains four ZrO_2 , so 12 atoms (Fig. 1.14c). Each Zr cation is in sevenfold coordination to oxygen anions, and there are two non-equivalent oxygen sites: threefold O_I and fourfold O_II .¹⁷⁶ There is a large dispersion of interatomic Zr–O distances, with average values of 2.07 Å and 2.21 Å for Zr– O_I and Zr– O_II , respectively. Zirconia also has a high-pressure (10 GPa) orthorhombic structure which can be stabilized at atmospheric pressure by addition of >12 mol% of niobia or tantala or a mixture of them.¹⁷⁷ Stable lower oxides of zirconium are not known, although oxygen dissolved in the zirconium metal lattice has led to the identification of some superstructures as $\text{ZrO}_{0.3}$.¹⁷⁸ While stabilized zirconias are insulators at room temperature, at elevated temperatures the vacancies in the anion lattice allow oxygen ions to diffuse and the zirconia becomes a solid electrolyte with applications in oxygen sensors and high-temperature fuel cells.¹⁷² Zirconium monoxide, ZrO , has been observed in mass spectrographic measurements.¹⁷⁹

Zirconia has both acidic and basic properties, that depend greatly on both the synthetic procedure and the calcination temperature.¹⁸⁰ Moreover, it is possible to control the acid–base properties of zirconium oxide by modifying the phase composition because it was shown that various crystalline modifications of zirconia differ in acid–base characteristics. In particular, it was found that tetragonal ZrO_2 is characterized by higher basicity than the stable monoclinic phase.¹⁸¹ The various crystal forms of ZrO_2 reflect how the hydroxide was prepared and treated. In this sense, a gel with a high proportion of bridged OH groups gives the tetragonal form, while if terminal OH groups are predominant in the gel, the monoclinic form is formed.¹⁸² In the literature there are many hypotheses and theories about the factors that can stabilize the metastable phases, tetragonal (*t*) and/or cubic (*c*) form versus the monoclinic (*m*) one.¹⁸³ For instance, the tetragonal phase may be stabilized by using additives. Lanthanum or yttrium oxides as well as sulphate ions are frequently used for this purpose.¹⁸⁴ The cubic phase of zirconia can be stabilized down to room temperature by the addition of magnesium, calcium, yttrium, or rare earth oxides, whose presence creates vacancies in the zirconium anion lattice. These stabilized zirconium oxides contain from 3% yttria to 8% calcium oxide.¹⁷²

The flexible amphoteric character, the high thermal stability, the versatility to modifications, the non-toxicity and its relative low cost are all promising characteristics for zirconia to be used as catalytic material.^{182,185} Indeed, it has been widely used also in heterogeneous catalysis. In particular, it has been used in many catalytic reactions as catalysts itself or as catalyst support, as well as an additive to improve the catalytic performances of other catalysts.¹⁶⁸ For example, the addition of zirconia to ceria (CeO_2) can greatly increase the “oxygen storage” property of ceria.¹⁸⁶ At the same time, ceria has been added as stabilizer for the tetragonal ZrO_2 . The ZrO_2 – CeO_2 mixed oxide catalyst containing 10 wt% of ceria showed enhanced basicity and promoted the Guerbet route favouring the *n*-butanol formation.¹⁸⁷ In this context, bare zirconia has been showed to act as acid catalyst and its Lewis surface acidity directs the ethanol preferentially toward its dehydration into ethylene.⁹² By contrast, when its tetragonal phase is stabilized by yttrium addition, zirconia showed great activity toward *n*-butanol formation, obtaining a 16.8 % yield at 300°C.¹⁸¹

Generally, zirconia can be used to catalyze a wide variety of reactions including the alkene isomerization¹⁸⁸, the Meerwein-Ponndorf-Verley reduction reactions with an alcohol as H-donor^{189,190}, aldol condensation¹⁹¹, alcohol dehydration and alcohol dehydrogenation^{192–194} and hydrocarbon hydrogenation, dehydrogenation, cracking, hydrodesulfurization¹⁹⁵. As previously mentioned, ZrO_2 has also been used as a support in several catalytic reactions. For example CO oxidation^{196–198}, low-temperature water–gas-shift (WGS) reactions^{199,200} and selective hydrogenation of unsaturated organic compounds²⁰¹.

1.3.3 Sepiolite

Sepiolite is a typical fibrous Mg-rich silicate mineral belonging to the clay family, with the fiber length up to several micrometres.²⁰² In nature, sepiolite usually precipitates from water bodies undergoing evaporation but it can precipitate also from interstitial fluids sediments. It occurs in two forms and is designated as α -sepiolite, derived by hydrothermal process, and β -sepiolite from precipitation.²⁰³ Besides the formation processes, sepiolite can originate from magnesium–silicate substrates or pre-existing minerals during diagenesis. The widely accepted mechanism for sepiolite formation is the direct precipitation from solutions containing dissolved ionic species (silica and magnesium).^{204,205} The reserve of sepiolite in the world is estimated to be 8000 million tons, and the largest mine of sepiolite is located in Spain, with the total reserve over 3800 million tons.²⁰³ The most well-known Spanish sepiolite deposit is that of Vallecas-Vicálvaro on the outskirts of Madrid, where the sepiolite was formed mainly by neoformation in a continental environment of Miocene age.²⁰⁶ In general, clay minerals may be one-dimensional, such as sepiolite, and two-dimensional. They have special crystal structures with a variety of physicochemical properties, such as expansion of the interlayer space, cation exchange, small particle size, high surface area, and so forth. They are naturally occurring,

cheap, eco-friendly, nontoxic and abundantly available.²⁰⁷ Thus, considering the “Green and Sustainable Development” concept, sepiolite gained both industrial and academic attention.²⁰³

Sepiolite is a hydrated magnesium silicate having an internal structure of channels which can accommodate zeolitic water and other molecules structure (Figure 1.15), its structure was firstly described in 1995 by Nagy and Bradley.^{202,208} Its molecular formula is $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$, with stoichiometric variations in the number of protons, surface hydroxyl groups and crystallization water molecules, depending on the origin and taking into account the peculiar properties thereof.²⁰⁹

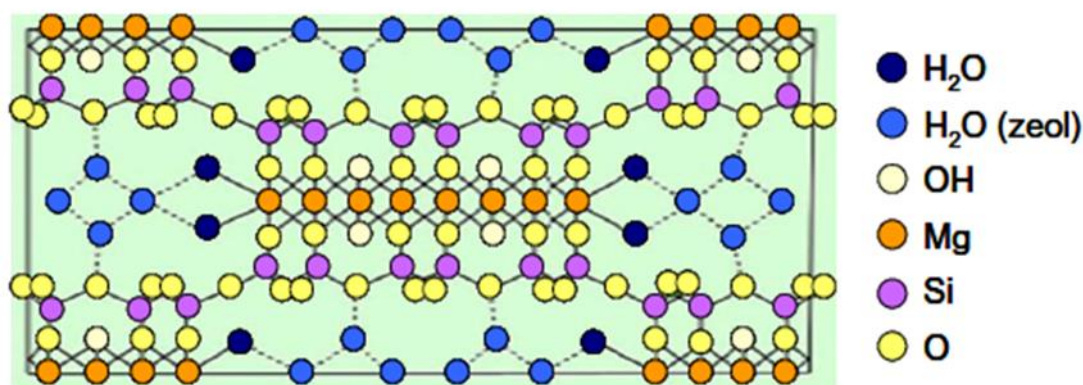


Figure 1.15 Structure of sepiolite.²¹⁰

Sepiolite exhibits microfibrillar morphology, showing an alternation of blocks and tunnels that grow up in the fibre direction. Each structural block is composed of two tetrahedral silica sheets linked by means of oxygen atoms to a central sheet of magnesium oxide-hydroxide, so that the tetrahedral sheet is continuous, but with the directions of the apical end of the silica tetrahedrons of the adjacent ribbons inverted. Along the fibre axis, each ribbon alternates with channels (or “zeolitic tunnels”) that are filled with weakly bound zeolitic water and exchangeable cations (Figure 1.16). Theoretically, every octahedral site of the ideal sepiolite is occupied by $\text{Mg}(\text{II})$ cations. The magnesium ion in sepiolite crystal is exchangeable with various transition metal ions.²¹¹ In the formation process of sepiolite, octahedral $\text{Mg}(\text{II})$ cations are easily substituted by $\text{Al}(\text{III})$ and/or $\text{Fe}(\text{III})$, which may cause the generation of negative charges and formation of structural defects. Moreover, the substitution of tetrahedral $\text{Si}(\text{IV})$ cations by $\text{Al}(\text{III})$ is also possible. It is for these reasons that a considerable number of exchangeable cations exist in the channels to compensate for the structural negative charges.²¹² There are three types of water in sepiolite structure: in addition to zeolitic water molecules present in the channels, crystal water is bonded by hydrogen bonds at the external surface and the coordination of octahedral cations is completed by coordination H_2O molecules (Figure 1.16B).²¹³ At the edges of the tunnels opened to the external surface of the sepiolite particles, several silanol groups ($\text{Si}-\text{OH}$) are present, which, together with structural H_2O molecules, are the active hydrogen-bonding sides of sepiolite. This special crystal structure makes sepiolite having large specific areas and high surface activity.²⁰³ In principle, these clay minerals can accommodate larger molecules

between their layers than rigid framework silicates (zeolites) could do.²¹⁴ Those characteristics together with its fibrous crystal morphology and active silanol groups, give sepiolite excellent adsorption, reinforcing, and supporter functions. Therefore, sepiolite has been applied widely in many areas, e.g. adsorption, catalysis, polymer composites.^{203,215,216}

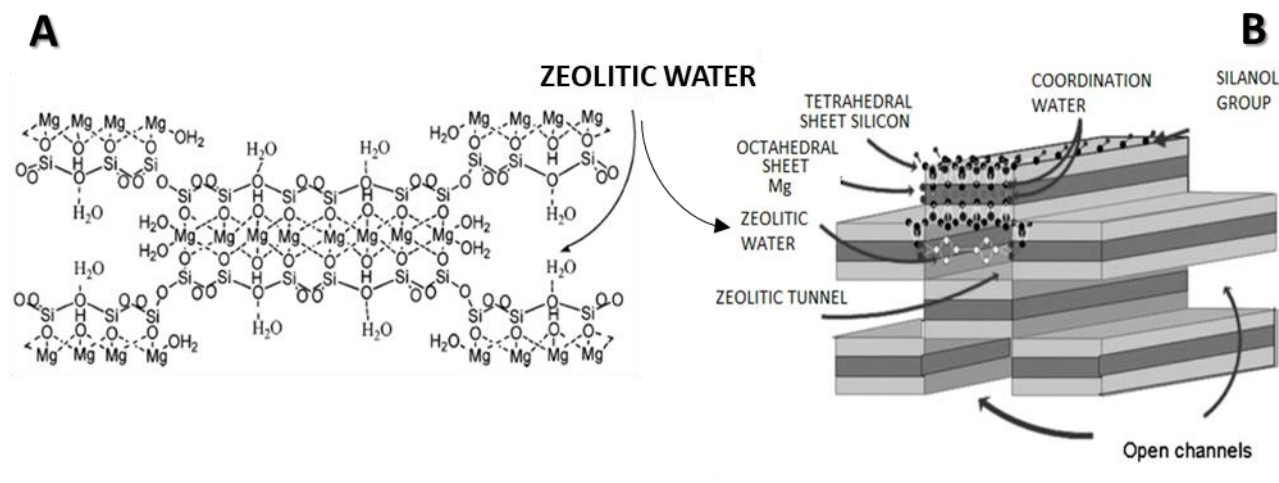


Figure 1.16 (A) Structure of sepiolite, zeolitic water.²¹³ (B) Crystalline structure and fiber structure of sepiolite.²¹⁷

Sepiolite structure can be modified and regulated through different methods including thermal activation, acid activation, cationic exchange, and organic modification.²⁰³ When sepiolite is heated in air at temperatures greater than 200°C, micropores are destroyed, and the surface area is decreased.²¹⁸ In particular, the water molecules contained into its structure can be released after thermal treatment at different temperatures, and thus the structure, specific surface area, pore size, and surface activity of sepiolite will be changed.^{203,210,219} There are several studies about the calcination temperature effect over the sepiolite structure.^{219,220} Some temperature intervals of sepiolite thermal treatment have been individuated: i) the first one at 25–250 °C for dehydration of the zeolitic or channel water, ii) 250–400 °C and iii) 400–600 °C for the respective first²¹⁹ and second dehydration stages of the crystalline water, iv) 600–700 °C for the chemical removal of the structural hydroxyls, and v) 800–900 °C for collapse of the crystal.²²⁰ During the first stage in the temperature range 250–400°C, the sepiolite structure is maintained but adsorbed water and water bonded to exchangeable cations in the raw material are removed and a new phase of "sepiolite dihydrate" ($\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4 \cdot (\text{H}_2\text{O})_2$) is formed (Figure 1.17A, eq2).²²⁰ Then "sepiolite anhydride" ($\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4$) is formed in the second dehydration stage by heating the sepiolite up to 550°C (Figure 1.17A, eq.3). After heating of the sample up to 850°C the formation of enstatite (MgSiO_3) and silica by the degradation of sepiolite anhydride consisting of its dehydroxylation (Figure 1.17A, eq.4) takes place.

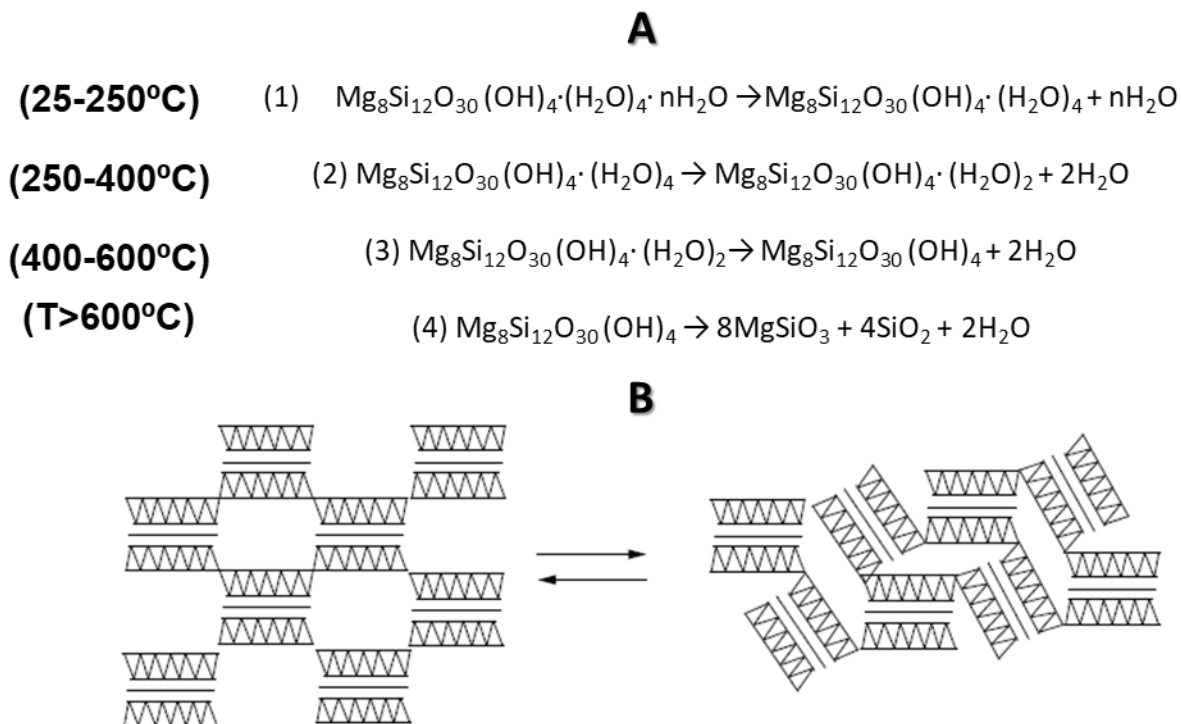


Figure 1.17 Thermal treatment of sepiolite. A) Phase changes with thermal treatment. B) Structure folding after thermal treatment. ²²¹

Sepiolite structure can be “activated” by acid treatment with HCl, H₂SO₄, and HNO₃ which can lead to an alteration of its surface area and activity, dissolving soluble impurities and changing the Lewis and Brønsted surface acid centers. ²²² M. Myriam et al. found that the mild acid attack results in a progressive dissolution of the octahedral cations, such as Al(III), Mg(II), Fe(III), and Fe(II), accompanied by an obvious increase of the micro- and meso-porosities and specific surface area of sepiolite. ²²³ Modification of sepiolite with metal salts can be achieved by a cationic exchange process, where the metal ions (M) can substitute the tetrahedral and/or octahedral cations (i.e., Si[IV], Al[III] and Mg[II]), leading to the formation of a series of M⁺-sepiolite materials with active acidic or alkali sites. In general, acidic or alkali strength of the obtained ion-exchanged sepiolite is influenced by nature of different metals ions. ²⁰³ J. Perez Pariente et al. prepared modified sepiolites, with aluminium, chromium or protons substituting octahedral magnesium. By measuring the surface acidity with pyridine adsorption, they noticed that has been created Brønsted acidity and also hydrothermal stability increased. ²²⁴ Some alkali treatment have been patented^{209,225} and in general, alkali exchanged sepiolite has been used as basic catalyst. ^{226–228} From those studies emerged that the ion-exchange capability of sepiolite can be enhanced by treating it with base. Previous reports in the literature have demonstrated that the basic strength of the alkali-exchanged sepiolites increases in the order Na⁺ < K⁺ < Cs⁺. ²²⁶ Corma et al. prepared a sodium-sepiolite based catalyst. By using the obtained system as support for impregnating palladium phase, they found that upon

magnesium to sodium exchange, the sepiolite increased its basic strength and that the resulting PdCl₂/NaSep sample exhibited a notable activity for the Heck reaction.²²⁷

Sepiolite has the ideal properties to be used as catalyst support such as its fibrous crystal morphology, large specific surface area, and good surface reactivity. Indeed, it has been utilized as catalyst support for various catalytic reaction systems including methanation of CO₂ with H₂, synthesis of light olefins from CO₂ hydrogenation, purification of ammonia synthesis feed gas by methanation method and for oxidation reactions.²²⁹ In recent years, a variety of catalysts have been prepared by loading active components such as metals (i.e., Zn, Cu, Mo, Ag, Ti) and their alloys, metal oxides, solid acids, and other metal compounds onto sepiolite.²²¹ Degirmenbasi et al. used its K-impregnated form to catalyse the transesterification of oil to biodiesel, finding the catalyst quite stable upon five reaction cycles. They explained such stability by the special structure of sepiolite, less prone to leaching.²²⁹

Among its catalysis applications, when sepiolite has been employed as heterogeneous catalyst for ethanol conversion the formation of 1,3-butadiene has been observed quite often. For example, A. J. Dandy and M. S. Nadiye-Tabbiruka studied the catalytic activity of natural sepiolite for the dehydration and dehydrogenation of ethanol at 150 - 300°C using a flow reactor (before reaction the catalyst was treated under hydrogen flow at 150°C for 3h). Sepiolite acted as bifunctional catalyst; indeed they observed the formation of water, carbon dioxide, ethene, acetaldehyde, diethyl ether, butadiene and crotonaldehyde with the proportions changing with temperature.²⁰⁸ In 1981, Kitayama Y. and Michishita A. studied the catalytic conversion of ethanol over Manganese supported on sepiolite. They got a butadiene maximum yield of 33.4% with complete conversion of ethanol with the manganese contents of Mn-sepiolite(II) of 79 mol% for the reaction performed at 300°C for 7 h.²³⁰ Kitayama, Y. et al. studied the catalytic conversion of ethanol over a ZnO supported over sepiolite, synthesized by ion-exchange. They found that, while only acidic sites existed on sepiolite, both acidic and basic sites were produced by supporting ZnO on sepiolite. This bifunctional characteristic has been claimed as crucial for the production of 1,3 butadiene.²¹¹ Gruver et al. prepared an ammonium-exchanged aluminated sepiolite and a silver-exchanged aluminated sepiolite (6wt%) and they tested them in the ethanol conversion in a gas flow reaction system. Over the Al-sepiolite, diethyl ether and ethylene were the main products. Also, they observed a significant selectivity toward acetaldehyde, which they related to the presence of Lewis acid sites over the catalyst surface that could even catalyse the dehydrogenation reaction. Interestingly, they found that the modification of the previous catalyst with the dispersion of Ag led to the formation of a bifunctional catalytic system that brought to the formation of butadiene.²³¹ They connected the formation of butadiene to two possible routes: the aldol condensation reaction followed by hydrogenation and the Prins routes, an acid or Lewis acid catalysed reaction of addition aldehydes or ketones to alkenes via an oxonium ion, between acetaldehyde and ethylene.²³²

A. Corma et al. showed that when Al^{3+} is introduced in the octahedral sheet by exchanging Mg^{2+} ions, sepiolite develops medium and strong acidity and becomes quite an active catalyst for the dehydration of ethanol, with a reaction pathway and kinetics characteristic of a strong acid catalyst. They tested in a gas-flow system a Al-exchanged sepiolite with an Al content of 2.60 wt% in a temperature range of 300-400°C, obtaining mainly ethyl ether and ethylene.¹³⁵ Chen et al. prepared by co-precipitation synthesis a sepiolite supported cobalt-cerium catalyst, where the Ce was added to strengthen catalytic performance. By testing the multicomponent Co-xCe/SEP catalysts in the ethanol steam reforming they found that the Ce amount influenced the catalyst performance in terms of activity and stability and the Co-0.3Ce/SEP has been optimized to reach 90.8% carbon conversion and over 69.1% H_2 yield at S/C=3, T=600 °C and WHSV=21.5 h^{-1} .²³³

2 AIMS OF THE WORK

The aim of the work presented and discussed in this thesis was to exploit the versatile nature of bio-ethanol in being converted into various added-value chemical compounds and hydrocarbon mixtures by studying its valorisation over heterogeneous catalysts of a different nature. In particular, it was intentional to investigate the catalytic gas-phase conversion of bio-ethanol into added value derivatives. The objectives can be divided by means of the nature of heterogeneous catalyst employed:

1. To investigate the gas-phase catalytic conversion of bio-ethanol into hydrocarbon fuels via the Guerbet condensation route. To do so, a commercial hydroxyapatite sample has been used as catalyst and modified by ion-exchange method, varying its acidic/basic and redox properties. (Experimental work at Unibo).
2. To investigate the influence of the synthetic strategies on zirconia oxide formation and the resulted effects of its surface properties on the catalytic ethanol gas-phase conversion. (Experimental work at ITQ-UPV).
3. To investigate the gas-phase catalytic conversion of bio-ethanol through the Guerbet route over the natural clay Sepiolite catalyst. In order to modulate the acid-base surface characteristics of the clay, a crucial catalyst's feature that has to be optimized for the complex Guerbet reaction mechanism, sepiolite has been modified by impregnation with different alkali-metals salts. (Experimental work at ITQ-UPV).

3 MATERIALS AND METHODS

The herein presented PhD thesis resumes the work carried out as a joint PhD programme (“Cotutelle”) between two institutions, the laboratories of the Department of Industrial Chemistry “Toso Montanari” in the University of Bologna and the laboratories of the “Instituto de Tecnología Química” (ITQ) of the “Universitat Politècnica de Valencia” (UPV). Accordingly, this chapter will be divided in two parts, describing the different facilities and procedures used at the two institutions.

3.1 Upgrading of ethanol to bio-fuel mixtures at UNIBO

3.1.1 Materials used

Table 3.1 Summary of the materials utilized to perform the experiments.

<i>Compound</i>	<i>MW (g/mol)</i>	<i>Supplier</i>
Ca ₁₀ (OH) ₂ (PO ₄) ₆ , 34-40% Ca	1004.67	Alfa Aesar
Cu (NO ₃) ₂ ·3H ₂ O	241.60	Carlo Erba
Sr(NO ₃) ₂ anhydrous	211.63	Alfa Aesar
Fe(NO ₃) ₃ ·9H ₂ O	404.00	VWR chemicals
Cu(NO ₃) ₂ · 2,5H ₂ O	232.59	Aldrich
HNO ₃	63.01	Aldrich
Absolute ethanol	46.07	Aldrich
<i>n</i> -butanol	74.12	Aldrich
Crotyl alcohol	72.11	Aldrich
2-Ethyl-1-butanol	102.10	Aldrich
Hexanol	102.18	Aldrich
2-Ethyl-1-hexanol	130.23	Aldrich
Octanol	130.23	Aldrich
Decanol	158.28	Aldrich
Acetaldehyde	44.05	Aldrich
Ethyl Ether	74.12	Aldrich

Acetone	58.08	Aldrich
Butyraldehyde	72.10	Aldrich
Ethyl Acetate	88.10	Aldrich
Butyl-benzene	134.22	Aldrich
1,2,4 Trimethyl benzene	120.19	Aldrich
o-Xylene	106.16	Aldrich
Ethyl benzene	106.167	Aldrich
Toluene	92.14	Aldrich
Hexanal	100.16	Aldrich
Decanal	156.2	Aldrich

3.1.2 Catalytic tests: general procedure

3.1.2.1 Reaction system

The catalytic activity was studied in a gas phase continuous-flow quartz reactor working at atmospheric pressure. The amount of catalyst, loaded as pellet (20-40 mesh), was kept constant at 0,6 g for the most of the catalytic tests; however, in some reactions the quantity of the catalyst was varied in order to study the effect of the contact time, calculated as volume of catalyst (mL) divided for the total feed flow (mL/s). The activity of the catalysts was investigated in respect to the time on stream. The inlet gas feed composition was maintained at 5 mol% EtOH in He (95 mol %) unless otherwise stated. These tests were conducted via vaporization of the liquid ethanol that was fed by means of a syringe pump (KPS 100 Syringe Pump) into a stainless steel heated line to obtain an instant vaporization. That heated line has an inlet with the carrier gas (He) and is connected with a tubular quartz reactor (length 600 mm, inner diameter 11 mm) containing the catalyst. The reactor was placed inside a furnace and its inlet and outlet were covered with heating tapes equipped with an electrical resistance to regulate the inlet (230°C) and outlet (230°C) temperature, the same treatments was used for the connecting line between the reactor outlet and the on-line GC inlet valves (both at 260°C). Indeed, the outlet gas stream was analyzed with an on-line Agilent 6890A gas-chromatograph. The latter was equipped with two TCD detectors and the products were separated using a PLOT-Q (30 m x 0.32 mm x 20 µm) column and a DB-1701 (30 m x 0.53 mm x 1 µm) column. Figure 3.1 represents the scheme of the reaction plant.

The main products that might derive from the reaction were calibrated. Some samples of the reaction products were analyzed by means of a gas chromatograph coupled with a mass spectrometer (GC-MS), in order to identify unknown by-products.

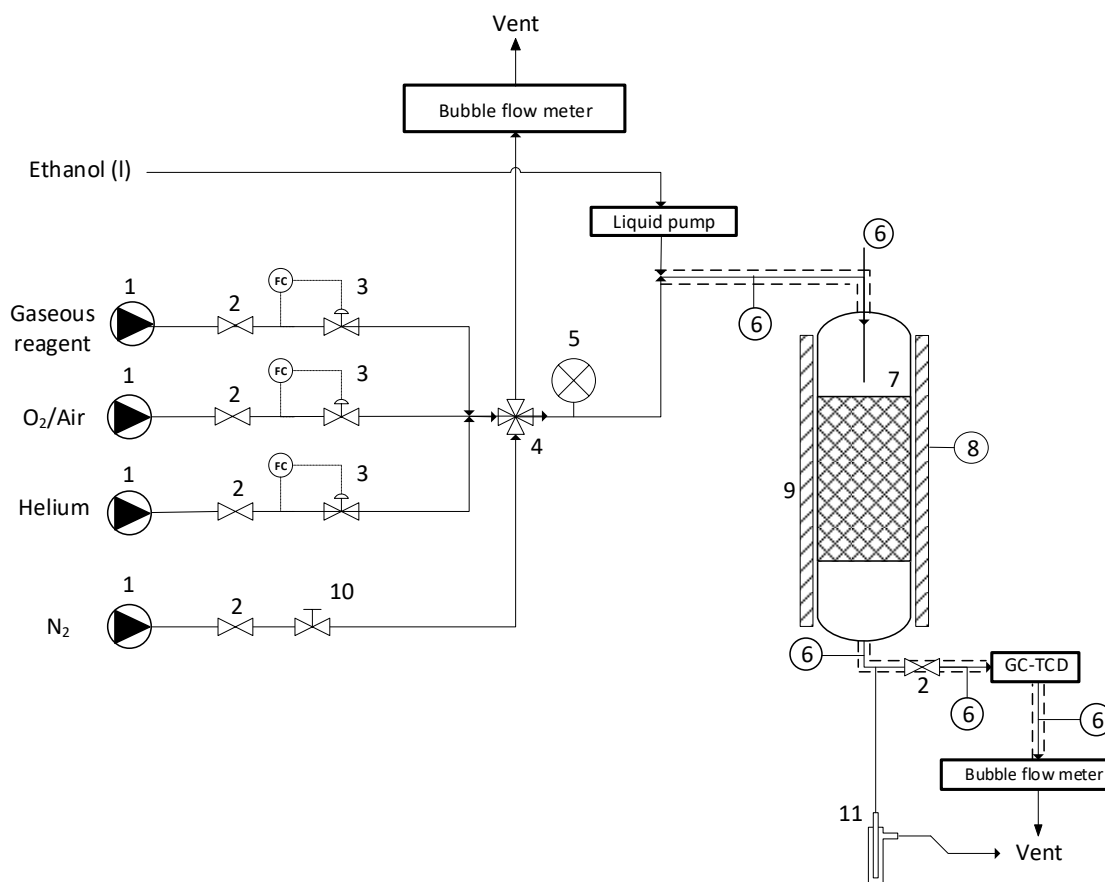


Figure 3.1 Plant scheme. 1: Gases; 2: On/off valve; 3: Mass flow meters; 4: Four ways valve; 5: Manometer; 6: Thermocouple; 7: Reactor; 8: Temperature control; 9: Reactor oven; 10: Needle valve; 11: Gas bubbler; -- : heated line.

The conversion (X%), yield (Y%), selectivity (S%) and the product carbon balance (%) were calculated as follow:

$$\chi\% = \frac{mol_{EtOH}^{in} - mol_{EtOH}^{out}}{mol_{EtOH}^{in}} \times 100$$

$$Y_p\% = \frac{C_{atom}^p \cdot mol_p^{out}}{C_{atom}^{EtOH} \cdot mol_{EtOH}^{in}} \times 100$$

$$S_p\% = \frac{Y_p}{\chi} \times 100$$

$$Carbon\ balance = \frac{\sum_i Y_{p_i}}{\chi} \times 100$$

The contact time τ (s) was calculated as the ratio between the volume of the catalyst loaded in the reactor (V_{CAT} , mL) and the total volumetric gas flow ($\dot{V}$, mL/min) at the related reaction temperature:

$$\tau = \frac{V_{catalyst}}{\dot{V}_{total}} \times 60$$

3.1.3 Compounds analysis and quantification

3.1.3.1 Qualitative analysis - GC-MS

Qualitative analyses were performed by manual injection of sample into the GC-MS system. This gas-chromatograph (Agilent 6890N coupled with mass spectrometer Agilent Technologies 5973 Inert) was equipped with an HP-5ms (30m x 250 μ m x 0.25 μ m) capillary column and the injection was made with a split ratio of 50:1 using He as carrier with a flow of 1 mL/min. The following temperature ramp was employed: hold at 45 °C for 7 minutes, ramp to 250°C at 5°C/min then held for 5 minutes.

3.1.3.2 Quantitative analysis

In order to analyse the composition of the outlet stream gas, the reaction system was equipped with an on-line gas chromatograph. The instrument was supplied with two different columns, both connected with a dedicated TCD detector. In particular the lighter products such as CO₂, ethylene, butadiene, 1-butene, 2-butene, CH₄ and ethane were analysed using a PLOT-Q (30 m x 0.32 mm x 20 μ m) column; while the heavier products (namely alcohols, aldehydes, esters and aromatics) were quantified using a DB-1701 (30 m x 0.53 mm x 1 μ m) column. The analytical method was optimized with the aim of separate the components that could be produced in the reaction taking into account the total time needed for the analysis. With helium as carrier, the flow in the column was 1.4 mL/min in the HP-PLOT Q and 1.6 mL/min in the DB-1701 column. The temperature program of the method is depicted in Figure 3.2; in this way the total method lasted for 38.8 min.

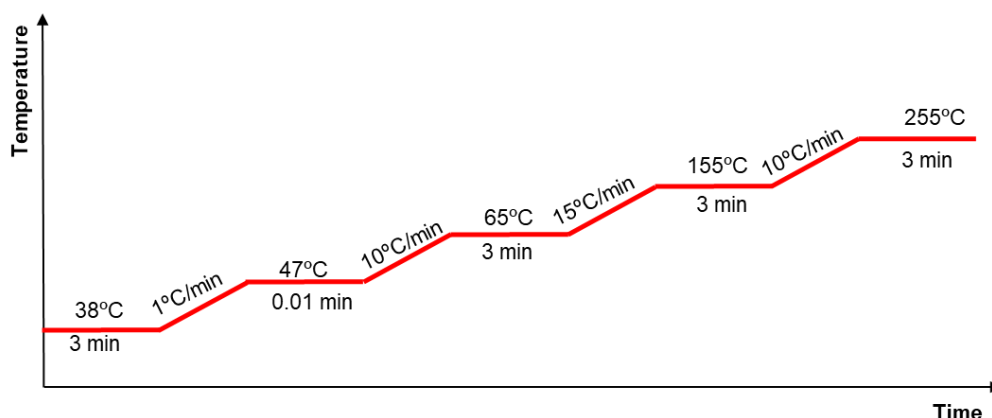


Figure 3.2 Temperature ramp of the on-line GC analysis.

After performing some catalytic tests, the calibration of the chemical compounds was expanded to some aromatic compounds and to higher aldehydes. Specifically, butyl-benzene, 1,2,4 trimethyl benzene, o-xylene, ethyl benzene, toluene, hexanal and decanal standards were used to perform the calibration, realized by feeding every liquid mixture of the standard compounds with the syringe pump into the empty reactor heated at 300°C. In this way, the vaporized compounds were analysed directly through the on-line gas chromatograph, simulating the reaction conditions.

After that, the quantification of the so-called "other products" was revised and calculated as follows: the products were gathered into three groups named "Light others", "Mid others" and "Heavy others" considering the retention times of the peaks obtained during the on-line analysis, specifically (Figure 3.3):

- Light others, C₄-C₆, (alkenes, alkenols, benzene, light ethers, ketones): from 0 to 15.6 minutes;
- Mid others, C₆-C₁₀ (alkenes, alkenols, xylenes, styrene, methylated phenols, ketones; alkylated aromatics compounds): from 15.6 to 25,6 minutes;
- Heavy others, C₁₀-C₁₆, (alkenes, alkenols, alkylated aromatics compounds, alkylated phenols) from 25.7 till the end of the analysis.

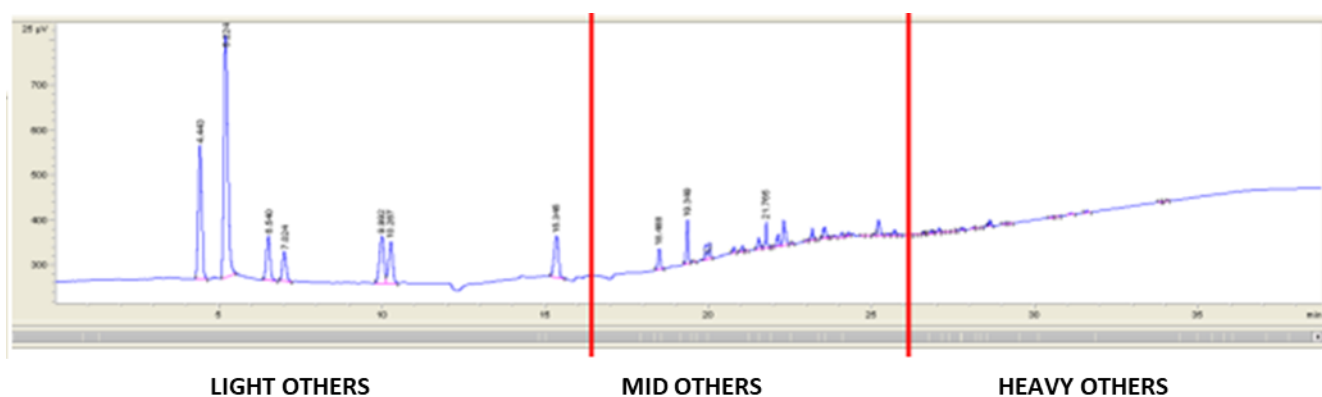


Figure 3.3 Example of a chromatogram obtained with the GC on-line while performing a reaction that brought to the production of a wide distribution of products.

The response factor of each groups was obtained by the arithmetic average of the ones known related to the calibrated compounds that are retained into the relative period, regardless the functional group of the molecules. The stoichiometric coefficient considered for each group was extrapolated from the ones known and detected through the GC-MS analysis. In this way the yields of the three groups of other products was calculated as follows:

$$Y_{LIGHT\ OTHERS}\% = \frac{6 \cdot mol_p^{out}}{C_{atom}^{EtOH} \cdot mol_{EtOH}^{in}} \times 100$$

$$Y_{MID\ OTHERS}\% = \frac{9 \cdot mol_p^{out}}{C_{atom}^{EtOH} \cdot mol_{EtOH}^{in}} \times 100$$

$$Y_{HEAVY\ OTHERS}\% = \frac{14 \cdot mol_p^{out}}{C_{atom}^{EtOH} \cdot mol_{EtOH}^{in}} \times 100$$

3.1.4 Catalyst Synthesis

3.1.4.1 Hydroxyapatite (HAP)

A commercial Ca Hydroxyapatite (provided by Alfa Aesar, Calcium phosphate tribasic, 34-40% Ca) was selected for the preliminary catalytic investigations. The powder was calcined at 600°C in a muffle furnace under static air (10°C/min ramp until 600°C, and then kept for 2 hours). The calcined powder was pressurized with a manual hydraulic press and then crushed to a particle size of 20 to 40 mesh (841-400 μm) in order to be used in the quartz reactor of an inner diameter of 11 mm.

3.1.4.1.1 Ion-exchanged Ca-HAP

Calcium hydroxyapatite (Ca-HAP, $\text{Ca}_{10-x}(\text{PO}_4)_6-x(\text{HPO}_4)_x(\text{OH})_{2-x}$, with $0 < x \leq 1$) crystallizes in the hexagonal system, space group P63/m, its structure comprises three-dimensional networks of hexagonally packed tetrahedral PO_4^{3-} ions. These ions make a first channel around Ca^{2+} ions [type 1 Ca] with a diameter of 2.5 Å. A second channel with a diameter of 3.5 Å, bordered by triangular Ca^{2+} ions [type 2 Ca], hosts the OH^- species along the c-axis.¹⁵² This structure is flexible to both cationic and anionic substitutions, several cations can substitute calcium ions in either type1 and type 2 Ca positions or in both positions simultaneously. Similarly, several anions can replace either OH^- or PO_4^{3-} ions or both.^{152,159} This intrinsic capability to exchange the Ca^{2+} ions and to allocate some other metal ions analogously to zeolites, allow to obtaining interesting functionalized materials with modulated number and strength of acid and basic sites.¹⁵²

A commercial Ca Hydroxyapatite (Ca-HAP) (provided by Alfa Aesar, Calcium phosphate tribasic, 34-40% Ca) was modified by means of ion-exchange method.²³⁴ By means of this post-synthetic method, it possible to introduce new ions into the HAP structure modifying its surface composition without alteration of the bulk properties.²³⁵ In this way, the acid/base properties or dehydrogenation properties of the HAP surface can be modified.¹⁶⁰ In particular, samples of Fe, Cu and Sr-HAP were prepared following a synthesis method found in literature²³⁶, after that they were characterized with different techniques and then tested in the gas-phase reaction system for the conversion of ethanol to higher analogues. All the exchanged hydroxyapatite catalysts are symbolized as Me-HAP samples.

3.1.4.1.1.1 *Cu-HAP and Sr-HAP – Ion exchange*

Both copper and strontium-modified HAP were prepared by conventional ion exchange (I.E.) procedure.²³⁷ Regarding the Cu-HAP, its synthesis was performed as follows: 6 g of HAP powder was dried at 120°C overnight and then added to 250 mL of 0.02 M Cu(II) nitrate solution ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99,5%, Carlo Erba) under vigorous magnetic stirring at 40°C for 20h. After filtration, thorough washing with 2L of hot water (40 °C) and drying at 120 °C for 16 h, a light-blue-green coloured sample was recovered. This sample was calcined at 600°C in a muffle furnace under static air (10°C/min ramp until 600°C, and then kept for 2 hours), obtaining a green-brown powder. The calcined powder was pressurized with a manual hydraulic press and then crushed to a particle size of 20 to 40 mesh (841-400 µm) in order to be used in the quartz reactor of an inner diameter of 11 mm.

The Sr-HAP was prepared by following the same procedure, using strontium (II) nitrate ($\text{Sr}(\text{NO}_3)_2$ anhydrous, Alfa Aesar) as metal precursor. In this case, both fresh and calcined samples consisted in white powders.

3.1.4.1.1.2 *Fe-HAP – Flash Ion Exchange*

The iron-loaded samples were prepared by a modified ion exchange procedure ²³⁷, in which very short contact time of HAP in the Fe-solution took place, in order to prevent morphological and structural damages to HAP. In a typical preparation, 250 mL of 0.02 M iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, VWR chemicals) solution was heated to 40 °C, then the pH was adjusted to ~3 by HNO_3 addition for preventing the precipitation of iron (III) hydroxide. HAP powder (~6 g, previously dried at 120 °C, overnight) was added to the iron solution and the suspension was maintained under stirring at 40 °C for 15 min. The sample was then filtered, thoroughly washed with 2 L of hot water (40°C) , dried at 120 °C overnight, obtaining a yellow powder. After that, the sample was finally calcined at 600 °C for 2 h in static air, becoming an orange-brown powder that was then pressurized with a manual hydraulic press and crushed to a particle size of 20 to 40 mesh (841-400 μm).

3.1.5 Catalyst characterization

The catalysts were characterized by means of powder X-ray diffraction (XRD) in order to check the crystallinity of the material. Some MP-AES analysis of the filtration waters were made in order to check the amount of metals exchanged during the catalyst synthesis; those analysis results were used to compute the amount of metal loading of the synthesized catalysts. Their specific surface area was determined by nitrogen physisorption using the BET equation. Moreover, the characterization of acid and basic sites of the catalytic surface was performed with TPD analysis using NH_3 and CO_2 as probe molecules for the determination of acid and basic sites respectively.

3.1.5.1 X-ray diffraction (XRD)

X ray diffraction (XRD) is one of the main techniques used to study the bulk properties of solid samples.

The most important features that can be determined with this technique are:

- ▶ Crystallinity of the solid;
- ▶ Crystallites dimensions;
- ▶ Phases;
- ▶ Atoms present in the structure and cell parameters.

A beam of X rays is directed to the solid sample, the incident radiation is diffracted in some specific direction which depends on the solid characteristics, in particular on the Bragg's law:

$$N\lambda = 2d\sin\theta$$

Where:

- ▶ n is a whole number,
- ▶ λ is the wavelength of the incident X rays,
- ▶ d is the interplanar distance within the crystal,
- ▶ θ is the angle of incidence.

The diffracted ray's intensity is plotted versus the diffraction angle.

The Bragg's law shows that each diffraction peak corresponds to a specific interplanar distance d ; analysing this parameter is possible to identify the corresponding phase, comparing the obtained diffractogram with the JCPDS databank.

It is possible to calculate the average crystallites size (D , nm) of each phase with the following equation (Scherrer equation)²³⁸.

$$D = \frac{B\lambda}{\beta(1/2) \cos \theta}$$

Where:

- ▶ $B = 0.9$ (Scherrer constant);
- ▶ $\beta_{1/2}$ = full width at half maximum (FWHM) in radians;
- ▶ θ is peak position, radians;
- ▶ λ is the wavelength of the incident X ray (nm); $\lambda(\text{CuK}\alpha) = 0.154\text{nm}$.

The Scherrer equation relates the width of a powder diffraction peak to the average (by volume) dimensions of crystallites in a polycrystalline powder.

It is possible to correlate the crystallinity of a mineral with the related XRS pattern obtained. For the purpose of application, the crystallinity of a mineral could be simply represented by the crystallite size or equivalent to the FWHM of a typical reflection of XRD pattern concerned. In general, the bigger the crystal is, the better the crystallinity, and the sharper and more isolated the XRD reflections are. In recent years, many researchers have demonstrated this consideration of crystallinity in their publications—for example, broad XRD peak means low crystallinity²³⁹, narrower XRD peak indicates an increase in the crystallinity²⁴⁰, the appearances of narrow and different XRD peaks mark more crystalline²⁴¹, and the lower XRD peak indicated a lower degree of crystallinity²⁴².

The X-ray diffraction (XRD) analysis of the sample was carried out using a PANalytical X'Pert diffractometer equipped with a copper anode ($\lambda_{\text{mean}} = 0.15418\text{ nm}$) and a fast X'Celerator detector. Wide-angle diffractogram was collected over 2θ range from 5 to 80° with a step size of 0.05° and counting time 15s.

3.1.5.2 *N₂ Adsorption/desorption*

The catalyst's surface area is the ratio between the exposed surface and its mass; it is commonly expressed in m^2/g .

Surface area is one of the most important parameters used to characterize a material from the catalytic point of view.

The surface area value is obtained measuring the quantity of physisorbed gas at a known temperature. The most common gas for this purpose is N_2 ; for that, physisorption is usually carried out at 77 K, which is the nitrogen boiling point. This process has several advantages:

- ▶ It occurs spontaneously;
- ▶ It has a low specificity, letting the gas occupy all the sample's surface without preferential sites;
- ▶ It is fast;
- ▶ It is reversible.

First of all, physisorbed products on the solid's surface are eliminated by increasing the temperature and place the sample under vacuum, after that the sample is submerged in a liquid nitrogen dewar to decrease the temperature to 77K. A nitrogen flow is provided by the instrument, starting its adsorption. The instrument measures the thermal conductivity difference between the initial gas and the one after the adsorption. Since nitrogen is adsorbed by the solid's surface, the final conductivity will decrease. At the end of the analysis, the instrument plots the adsorbed amount versus the relative pressure, giving an adsorption isotherm.

This technique is based on the BET model (due to Brunauer, Emmett, and Teller), an extension of the Langmuir method, the Langmuir assumptions are:

- ▶ The adsorption process has a kinetic behaviour;
- ▶ The adsorption rate is equal to the desorption rate;
- ▶ The heat of adsorption is constant and does not depend on the degree of coverage;
- ▶ Gas molecules behave ideally;
- ▶ Only a monolayer is formed;
- ▶ All surface sites are equivalent;
- ▶ There is no interaction between the adsorbate's molecules, and they can't move.

The BET model assumptions are:

- ▶ The surface is homogeneous;
- ▶ There are no lateral interactions between molecules;
- ▶ All the surface sites have the same adsorption energy for the adsorbate;

- ▶ Multilayers can be formed, and their adsorption energy is the same;
- ▶ The theory can be applied to all the layers.

The BET equation is:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{P(C - 1)}{V_m C P_0}$$

Where:

- ▶ V=Total adsorbate volume
- ▶ V_m=Monolayer volume
- ▶ P=adsorbant pressure
- ▶ P₀=adsorbant vapor pressure
- ▶ C= BET constant

This linear equation can be used to calculate the monolayer volume (V_m) by which is possible to calculate the sample specific surface area (S_{BET}):

$$S_{BET} = \frac{\frac{V_m}{V_0} * N_A * A_{N_2}}{g}$$

- ▶ V₀= Adsorbant molar volume
- ▶ N_A= Avogadro number
- ▶ A_{N₂}= N₂ molecular cross-sectional area
- ▶ g= Mass of the sample

The specific surface area of the catalysts was determined by N₂ absorption–desorption at liquid N₂ temperature using a Sorpty 1750 Fison instrument. Around 0.2 g of the sample was typically used for the measurement, and the sample was outgassed at 150°C before N₂ absorption.

3.1.5.3 Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) technique allows one to study the interaction of reaction gases with solid surfaces, thereby being a powerful tool for both the evaluation of active sites on catalyst surfaces and the understanding of the mechanisms of catalytic reactions including adsorption, surface reaction and desorption. When ammonia and carbon oxide are used as probe molecules, the acidity and the basicity respectively of the materials are investigated.

The experiments were performed in an Autochem II (Micrometrics) instrument with catalyst in pellets (calcined) for the analysis of the acid/base properties of catalyst. The sample was placed in a quartz tubular reactor and pre-treated under 30 mL/min He flow to the calcination temperature (600°C) for

60 min, in order to remove adsorbed H₂O and CO₂ from the catalyst surface prior to adsorption. Then the catalyst was cooled down to 40°C and 100°C for CO₂-TPD and the NH₃-TPD analysis, respectively. NH₃ was adsorbed at 100°C to eliminate the contribution of very weak acid sites and improve the spectrum resolution. In this way, the catalyst surface was saturated with the probe molecule for 1 h (flow rate of 30 mL/min of 10 vol. % of CO₂ or NH₃ in He). Both physisorbed CO₂ and NH₃ were removed by flowing He (30 mL/min) for 60 min. Then, the sample was heated at 10°C/min up to 600°C and the desorbed probe molecules were monitored and recorded using TCD detector and an online mass spectrometer (Cirrus 2, MKS instruments) which was calibrated by manual injections of pure CO₂ (m/z= 44) and NH₃ (m/z=17) pulses.

3.1.5.4 Thermogravimetric analysis (TGA)

Using a SDT Q 600 instrument, TG/DT analyses were performed over fresh and spent catalysts in order to identify the amount of heavy compounds absorbed on the catalyst surface. 20mg of the sample was typically used for the measurement and the temperature increased from room temperature up to 1000°C, with a heating rate of 10°C/min in air flow (100 mL/min).

3.1.5.5 MP-AES analysis

In order to evaluate the obtained metal loading of the hydroxyapatite-based catalyst prepared via ion exchange, the filtrate solution was analysed with MP-AES technique. In this way the amount of Fe²⁺, Cu²⁺ or Sr²⁺ detected in the solution (measuring the absorbance at 325 nm, 372 nm and 431 nm, respectively) was used to calculate the actual metal loading obtained for the prepared catalyst. The analyses were made using a MP-AES instrument (Agilent 4210 MP-AES). After calibration with standard solutions, the concentration of the determined metal-ion of the filtrate waters was evaluated and then related to the amount of the metal deposited over the HAP support.

3.2 Catalytic gas-phase ethanol valorisation at ITQ- UPV

During the research period spent in the laboratory of “Instituto de Tecnología Química” (ITQ) of the “Universitat Politècnica de Valencia” (UPV), the work focused on two main topics that can be gathered for the nature of the catalysts: i) zirconia based catalysts; and ii) natural sepiolite based catalysts. All the catalytic systems have been characterized by means of different techniques and tested in a lab-scale fixed bed gas-flow reactor to evaluate their activity in the gas-phase ethanol

conversion. In the following section the characterization techniques and instruments used as well as the reactor and analysis systems used will be widely explained.

3.2.1 Materials used

Table 3.2 Summary of the materials utilized to perform the experiments.

Compound	MW (g/mol)	Supplier
ZrO(NO ₃) ₂ · xH ₂ O	231.22	Aldrich
(NH ₄) ₂ Ce(NO ₃) ₆ · 6H ₂ O	348.23	Aldrich
Y(NO ₃) ₃ · 6H ₂ O	383.01	Aldrich
TiOSO ₄ hydrate	159.93	Riedel-de Haen
Cu(NO ₃) ₂ · 2,5H ₂ O	232.59	Aldrich
NaOH pellets	39.99	Merck
NH ₄ OH	25%wt in H ₂ O	Aldrich
Urea	60.06	Aldrich
Absolute ethanol	46.07	Scharlab
Natural Sepiolite	-	Tolsa, S.A.
Na ₂ CO ₃ (99.8%)	105.99	Aldrich
K ₂ CO ₃ (99%)	138.21	Aldrich
CS ₂ CO ₃ (99%)	325.82	Aldrich
Ni(NO ₃) ₂ · 6H ₂ O	290.79	Aldrich

3.2.2 Catalytic tests: general procedure

3.2.2.1 Reaction system

The catalytic tests were performed in gas phase continuous-flow quartz reactor, with a 330mm length and an internal and external diameter of 10 and 12 mm respectively, working at atmospheric pressure.

The inlet gas feed composition was maintained at 5 mol% EtOH in N₂ (95 mol %). The tests were conducted via vaporization of the liquid ethanol that was fed by means of a syringe pump into a

stainless steel heated line to obtain an instant vaporization. That heated line had an inlet with the carrier gas (N_2) and was connected to the tubular quartz reactor containing the catalyst (with a particle dimension of 0.25-0.6 mm). The reactor was placed inside an oven and its inlet and outlet were covered with heating tapes equipped with an electrical resistance to regulate the inlet (160°C) and outlet (180°C) temperature, the same arrangements were used for the connecting line between the reactor outlet and the on-line GC inlet valves (both at 180°C). Indeed, the outlet gas stream was analysed with an on-line Agilent 7890A gas-chromatograph. The latter was equipped with two columns a Rt-U-Bond (30 m x 530 μm x 20 μm) column and a HP-FFAP Polyethylene glycol (50 m x 320 μm x 0,5 μm) connected with two detectors, a TCD and a FID, respectively. Figure 3.4 represents the scheme of the reaction plant.

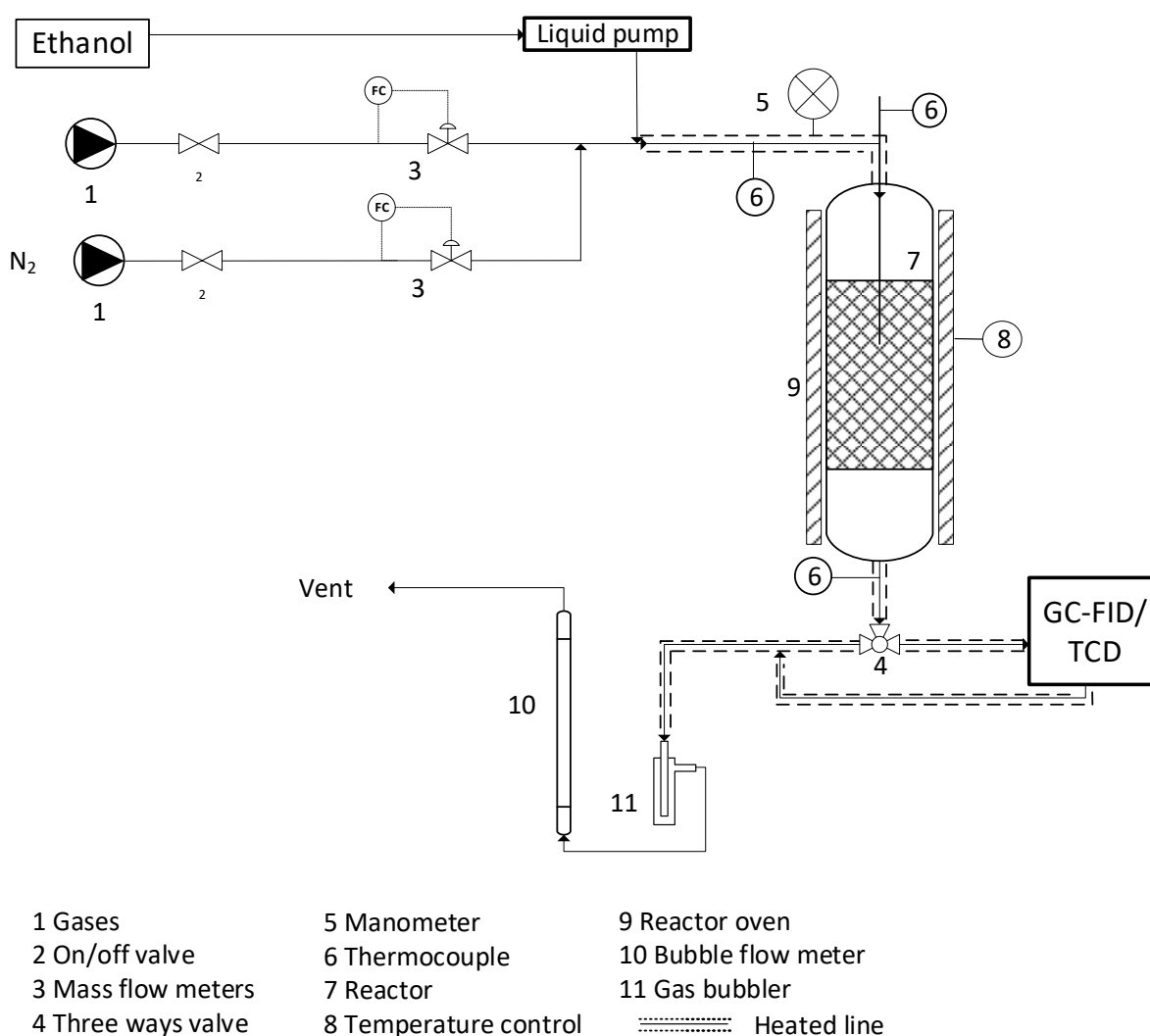


Figure 3.4 Plant scheme.

The main products that might derive from the reaction were calibrated. Some samples of the reaction products were analysed by means of a gas chromatograph coupled with a mass spectrometer (GC-MS), in order to identify unknown by-products.

3.2.3 Compounds analysis and quantification

In this section the analytical method used to identify and quantify the reaction products is described. The most common performance indicators (conversion, X; yields, Y and selectivity, S) have been calculated. The gaseous outflowing stream was analysed with an on-line GC system, while to identify some unknown outcoming products, an aliquot of condensated products of the exit gaseous stream was manually sampled with a gas-syringe and injected to a GC-MS system.

3.2.3.1 Quantitative analysis

The utilised gas-chromatograph is an Agilent 7890A GC System, equipped with two different columns, connected to a Thermal Conductivity Detector (TCD) and using He as carrier gas:

- i) An Agilent 19091F-115, HP-FFAP Polyethylene glycol (50 m x 320 μm x 0,5 μm) column connected to a Flame Ionization Detector (FID) was used to quantify the volatile hydrocarbons and the oxygenated compounds such as acetaldehyde, ethyl ether, acetone, ethyl acetate, *n*-butanol, 2-pentanone, butyraldehyde and the higher alcohols, namely 2-ethyl butanol, hexanol, 2-ethylhexanol and 1-octanol.
- ii) For the separation and quantification of the light products (ethylene, ethane, CO₂, butadiene) an Agilent 19750 column, Rt-U-Bond (30 m x 530 μm x 20 μm), was used.

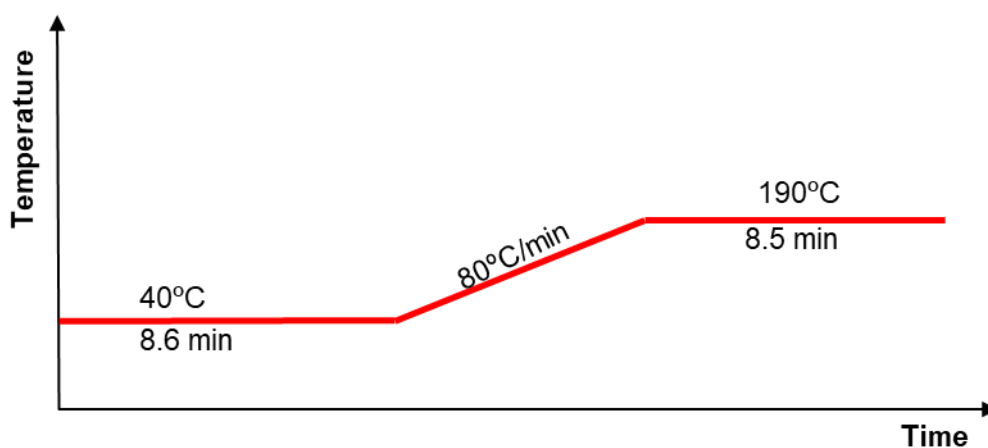


Figure 3.5 Temperature ramp of the on-line GC analysis.

The oven temperature was kept at 40 °C for 8,6 min, then the temperature was increased with an 80°C/min rate to 190°C and kept at this temperature for 8.5 min, reaching a total runtime of 18,975 min (Figure 3.5). FID was kept at 300°C with 450 mL/min air flow and 40 mL/min H₂ flow. TCD was kept at 250°C with a reference flow of 22 mL/min and a He flow of 4.5 mL/min. FID works burning the molecules exiting from the column in a hydrogen/oxidant flame, the formed ions are collected and analysed giving a signal proportional to the analyte's quantity. TCD evaluates the thermal

conductivity of the flow, since most of the compounds have a smaller thermal conductivity than the carrier gases (He or H). This difference will increase the temperature of a resistor, causing a change in resistance of that filament and a consequent change in voltage due to a Wheatstone bridge. That change in voltage is proportional to the analyte's concentration in the gas flow. This detector was used to quantify the same products of the FID, and the products that cannot be detected with FID such as N₂, CO, CO₂, ethylene and ethane.

In order to quantify ethanol conversion and the principal products yields and selectivity, the reagent and the obtained products have been calibrated by using standard compounds. Each product was calibrated measuring the area of the peak and plotting it versus its volumetric concentration. In this way, response factors of each component have been calculated. For each product, a response factor relative to ethanol was calculated by dividing the product's response factor by the ethanol one. In the following table, the quantified products, their relative response factors (F_{ij}), and their retention time are indicated, specifying the detector utilised for the calibration.

Table 3.3 Analytic parameters utilized in the reaction products quantification into the GC-online system.

	Detector	Retention time [min]	Relative Response Factor to EtOH
EtOH	TCD	11,8	1,00
Acetaldehyde	FID	5,6	1,33
Ethyl ether	FID	5,1	1,33
Acetone	FID	6,8	3,33
Ethyl acetate	FID	8,7	6,67
n-Butanol	FID	14,0	6,67
Butadiene	TCD	11,3	1,13
Ethylene	TCD	2,9	1,00
CO₂	TCD	2,9	1,00
2-Pentanone	FID	10,75	6,67
Butyraldehyde	FID	8,75	3,33
2-ethyl butanol	FID	15,6	13,33
1-hexanol	FID	15.9	10,00
2-ethyl hexanol	FID	16.7	16,67
1-octanol	FID	17.3	16,67

The following formulas have been utilized for the main performance indicators calculation, such as conversion (X, %) of ethanol (j) and selectivity (S, %) of the main products (i).

➤ i= calibrated compound; j= EtOH;

➤ $C_i = x_i \left(\frac{mol_i}{mol_{TOR}} \times 100 \right);$

➤ $F_i = \frac{A_i}{C_i}; F_{ij} = \frac{F_i}{F_j};$

➤ $X_{EtOH} = \frac{\sum \left(\frac{A_i}{F_{ij}} \times \frac{w_i}{w_j} \right)}{\sum \left(\frac{A_i}{F_{ij}} \times \frac{w_i}{w_j} \right) + A_{EtOH}} \times 100;$

➤ $S_i = \frac{\frac{A_i}{F_{ij}}}{\sum \left(\frac{A_i}{F_{ij}} \times \frac{w_i}{w_j} \right)} \times 100;$

➤ w_i, w_j = stoichiometric coefficients.

Not all the reaction products have been identified and calibrated, the unidentified products, named “NID others” have been quantified by means of an artificial response factor calculated through mathematical average of the ones obtained from standards calibration. Considering their retention

times into the obtained on-line chromatogram, an average stoichiometric coefficients of 4 has been considered. Given that these are approximate values it is possible that within experimental tests, they will be underestimated or overestimated but since they were generally secondary products, the intrinsic error was considered acceptable.

The contact time, W/F (in $\text{g}_{\text{CAT}}/\text{mL}\cdot\text{s}^{-1}$), and the weight hourly space velocity, $WHSV$ (in $\text{g}/(\text{g}_{\text{CAT}}\cdot\text{h})$), that are defined as the ratio between the mass of the catalyst loaded in the reactor (g_{CAT}) and the total volumetric gas flow ($\dot{V}$, mL/min) and as the mass flow rate of ethanol ($\dot{m}$, g/h) divided by the weight of catalyst (g_{CAT}) respectively, were calculated with the following formulas:

$$W/F = \frac{w_{\text{catalyst}}}{\dot{V}_{\text{total}}} \times 60$$

$$WHSV = \frac{\dot{m}}{w_{\text{catalyst}}}$$

3.2.3.2 Qualitative analysis - GC-MS

Since several peaks have been detected during the GC analysis of the reaction mixture in all the reaction tests, a qualitative analysis of the outlet flow was planned. By the help of a gas-syringe, a sample of the gaseous products flow was taken from a rubber septum placed after the reaction zone and injected to a GC-MS for the analysis. GC-MS analysis couples two different techniques: gas chromatography (GC) firstly separates the compounds present in the mixture, subsequently, mass spectrometry (MS) ionizes and breaks the compounds, detecting them depending on the mass-to-charge ratio. The coupling of these two techniques allows to identify the molecules that have a similar retention time in gas chromatography and molecules with similar pattern at the mass spectrometry.

The utilized instrument was an Agilent 6890N GC System connected to a Mass Selective Detector 5973 Network. The GC was equipped with an Agilent 19091S-433 column, HP-5MS (5%Phenyl Methyl Siloxane) (30 m x 250 μm x 0,25 μm); the inlet was a Split-Splitless kept at 250°C, the carrier gas was He. During the elution time, the temperature was initially kept for 5 min at 50°C, then raised with a 3°C/min rate until reaching 80°C, 1 min of isotherm at this temperature completes the elution.

3.2.4 Catalysts Synthesis and Characterization

3.2.4.1 Zirconia catalysts synthesis

In order to evaluate the effect of the synthesis techniques on the catalyst properties, several zirconium oxide catalysts have been prepared with three different methods: hydrothermal²⁴³, precipitation²⁴⁴ and urea-precipitation. Several synthetic parameters have been studied:

- Synthetic method;
- Precipitating agent;
- pH of the synthesis;
- Dopant addition.

Y, Ti, and Ce have been selected as possible dopants for the zirconia catalyst. A certain amount of one of these elements has been added to the zirconyl nitrate water solution by using respectively: $\text{Y}(\text{NO}_3)_3$, TiOSO_4 , and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. The metal precursors solution has been prepared in order to have a Zr:Dopant molar ratio of 95:5. Before performing the reaction, all the calcined samples have been shaped into 0.25-0.6 mm pellets.

3.2.4.1.1 Hydrothermal method

The hydrothermal method synthesis was performed as found in literature and was performed as follows. 20 mL of a 0.5M water solution of zirconyl nitrate hydrate, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, has been prepared and hydrolysed with a basic solution. Two different precipitating agents have been used: 25% aqueous ammonia solution NH_4OH and 5M NaOH water solution. The precipitating agent has been added until reaching a certain pH value in the range between 7 and 13, measured with a SevenMulti™ Mettler Toledo pH-meter. The obtained mixture has been placed into an ultrasonicator for 30 minutes, after that, 8 mL of absolute ethanol were added. The mixture has been placed into a Teflon-lined autoclave for the hydrothermal treatment in an oven at 175°C for 24 h. After, the mixture has been filtered under vacuum and abundantly washed with water and/or absolute ethanol. Finally, the obtained solid has been dried overnight at 100°C and calcined at 500°C for 3 h (2°C/min) in air.

3.2.4.1.2 . Precipitation method

The synthesis method through precipitation was performed by modifying the one found in literature.

²⁴⁴ A 0.5 M water solution of zirconyl nitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) has been prepared and hydrolysed with a basic solution. Two different precipitating agents have been used: 25% aqueous

ammonia solution NH_4OH and 5M NaOH water solution. The precipitating agent has been added under stirring at room temperature until reaching a certain pH value between 7 and 13, measured with a SevenMulti™ Mettler Toledo pH-meter, maintaining the pH value constant for 1 h. Finally, the obtained mixture was filtered under vacuum and abundantly washed with water and/or absolute ethanol, the solid has been dried overnight at 100°C and calcined at 500°C for 3 h (2°C/min) in air.

3.2.4.1.3 Urea precipitation method

The samples have been prepared weighting 5g of zirconyl nitrate dihydrate and a 12,2g of urea to reach a $n_{\text{UREA}}/n_{\text{METALS}} = 10$. These components have been dissolved in 80 mL of milliq water. This solution have been heated in reflux condition (around 100°C) for 16 h or 88 h. After cooling at room temperature, the solution pH have been measured with a SevenMulti™ Mettler Toledo pH-meter, the mixture have been filtered under vacuum and abundantly washed with water. The obtained solid have been dried overnight at 100°C and calcined at 500°C for 3h (2°C/min) in air. Since the synthesis pH is given by the urea thermal hydrolisis, to obtain different pH values from the one obtained by temperature increasing, the pH has been raised before thermal hydrolisis using a 3 M NaOH water solution.

3.2.4.2 MgO synthesis

Magnesium oxide was synthesized by precipitation method ²⁴⁵. The precipitation has been conducted at pH 5 with a NH_4OH 1.3 M solution, of a magnesium acetate $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solution with an oxalic acid $\text{C}_2\text{O}_4\text{H}_2 \cdot 2\text{H}_2\text{O}$ solution, the magnesium oxalate $\beta\text{-MgC}_2\text{O}_4$ precipitate immediately. The solid obtained was filtered, washed, and dried at 80°C overnight. Then, the obtained solid has been calcined at 700°C for 3 h with a 2°C/min ramp, obtaining the magnesium oxide MgO. The obtained MgO have been shaped into 0.25-0.6 mm pellets before testing into the reaction system.

3.2.4.3 Sepiolite catalysts preparation

Sepiolite catalysts were prepared starting from a sample of sepiolite natural (Sepiolite 11AS-13) provided by Tolsa, S.A.

The samples of sepiolite based catalysts were prepared using different synthetic methods: the ion-exchange capability of sepiolite was exploited in order to modify the sepiolite support, as well as active phase was added by incipient wetness impregnation or by wet impregnation.

All the sepiolite catalysts samples have been calcined at different temperature (500°C or 700°). In general, the heating treatment have been performed by keeping the temperature for 3h with a heating ramp of 2°C/min. Before performing the reaction, all the calcined samples have been shaped into 0.25-0.6 mm pellets.

3.2.4.3.1 Incipient wetness impregnation

The sepiolite supported catalysts were prepared by an impregnation procedure using an appropriate amount of aqueous metal hydroxide/carbonate solutions (incipient wetness method) after a previous measure of the mud point of the support. The required weight of the alkali-metal precursor was dissolved in the minimum amount of water to wet the dry sepiolite supports before a slurry is obtained. The aqueous solution was added to the support dropwise and the powdery solid was manually mixed in order to accomplish the maximum homogeneity. (Figure 3.6)

Then, the solids were dried at 100°C (16 h) and calcined in air at 500°C for 3h with a heating ramp of 2°C/min. The catalysts were pelletized and sieved into 0.25-0.6 mm pellets before testing into the reaction system.

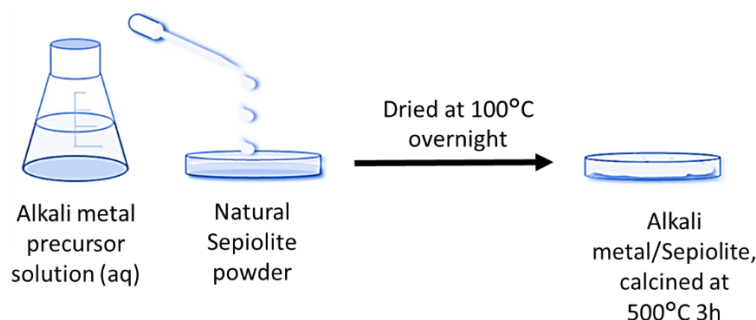


Figure 3.6 Incipient wetness impregnation catalyst synthesis.

In particular, the following catalysts have been synthesized:

- 2Na/Sep@500, 5Na/Sep@500, 2Na/Sep@700, 5Na/Sep@700, 0.5Na/5CuO/Sep@500;
- 2K/Sep@500, 5K/Sep@500,
- 2Cs/Sep@500, 4Cs/Sep@500, 7Cs/Sep@500, 14Cs/Sep@500.

The general symbols for the catalysts used was XMe/Sep@Y, where X was the number related to the metal amount expressed as weight percent (wt %), Me the alkali metal concerned and Y the calcination temperature of the sepiolite support.

3.2.4.3.2 Wet impregnation

Copper or nickel were deposited over the sepiolite supports by wet impregnation. Copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ or nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ have been used as metal precursor for the preparation of the metal solution. The support was added to the metal solution and stirred for 2 hours in a rotavapor at 60°C without vacuum. After 2h the vacuum was added in order to remove the excess of water and then the sample was recovered and dried overnight at 100°C in furnace. The catalyst was calcined at 500°C for 5 h with a $2^\circ\text{C}/\text{min}$ heating ramp. The resulting catalysts were all pelletized and sieved into 0.25-0.6 mm pellets before testing into the reaction system.

In particular, the following catalysts have been synthesized:

- CuO/MgO 5wt%, $\text{CuO}/\text{Sep@500}$ 5 wt%, $\text{CuO}/\text{Sep@700}$ 5 wt%, $\text{CuO}/\text{Sep@700}$ 5 wt% $\text{CuO}/\text{Sep@500}$ 10 wt%, $\text{CuO}/2\text{Na}/\text{Sep@500}$ 5 wt%, $\text{CuO}/2\text{Na}/\text{Sep@500}$ 10 wt%,
- $\text{NiO}/2\text{Na}/\text{Sep@500}$ 5 wt%.

3.2.4.4 Powder X-ray diffraction (XRD)

XRD analysis has been carried out at room temperature with a PANalytical X'Pert PRO equipped with a Cu K α radiation and an X'Celerator detector in Bragg-Brentano operating at 40 keV and 30 mA.

In order to compare the phases obtained in the different zirconia samples synthesized, this characterization technique has been used to evaluate their tetragonal fraction (%t). It was calculated according to the so-called “Garvie Nicholson” method, used to estimate the monoclinic ($m\text{-ZrO}_2$) and the tetragonal ($t\text{-ZrO}_2$) phases content in a zirconia sample.^{169,244,246} This technique uses the relation between the reflections intensities in the diffraction patterns of the $(\bar{1}11)$ plane of $m\text{-ZrO}_2$ and the (101) plane of $t\text{-ZrO}_2$. Accordingly, the tetragonal fraction has been calculated applying the following equation²⁴⁴:

$$\%t = \frac{I_{t(101)}}{I_{t(101)} + 1.6 I_{m(\bar{1}11)}} \times 100$$

Samples Preparation:

XRD samples have been prepared grinding the solid to analyse in an agate mortar. The grinded solid has been placed into a steel sample holder and introduced into the diffractometer, which was equipped with an auto-sampler.

3.2.4.5 Raman spectroscopy

The Raman effect is one of the possible results of the interaction between light and matter. If the photon energy is not sufficiently high to give an electronic transition of the target molecule, it can be scattered in three different ways:

- ▶ Elastic scattering
- ▶ Inelastic scattering

In the first case, the photon energy after the interaction does not decrease, leading to a Rayleigh scattering. When inelastic scattering occurs, the photon can remove or increase the target molecule's energy. These types of inelastic interactions lead respectively to Stokes scattering and Anti-Stokes scattering. The energy gain in Stokes scattering is vibrational energy, when it is lost gives Anti-Stokes scattering.²⁴⁷ The change in the radiation's energy is characteristic of the target molecule and independent on the incident radiation's energy. Raman spectroscopy is a non-destructive technique, which studies the inelastic scattering of the monochromatic radiation by the use of laser with a wavelength within visible, near IR or near UV regions. In particular, the molecular vibrations variation of the specimen's bonds is investigated to get structural information about the sample²⁴⁸.

The Raman spectroscopy is composed of:

- ▶ A sample holder;
- ▶ A laser light source;
- ▶ A collection optic for the scattered photons;
- ▶ A monochromator;
- ▶ A detector for the measurement of the Raman signals relative intensities, at different wavelengths;
- ▶ A computer.

The most interesting band section to analyse for the zirconium oxide is the one between 100-900 cm^{-1} . Since the XRD cannot let us distinguish the tetragonal from the cubic phase of zirconia, Raman spectroscopy has been used as a complementary technique. Raman spectra were obtained with a Renishaw 1000 In Via spectroscopy, equipped with an Olympus microscope. The light source was a 20W Ar laser with a wavelength of 512 nm.

Sample Preparation:

The analysis has been carried out on grinded calcined catalyst samples.

3.2.4.6 Scanning Electron Microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDS or EDX) is a standard method for identifying and quantifying elemental compositions in a very small sample of material (even a few cubic micrometers).²⁴⁹ EDX spectroscopy, as well as the previously discussed X-Rays Diffraction, is a characterization technique which studies the X-Rays radiations obtained after the interaction between an electron beam with a specimen.^{250,251} When the beams hits the sample, it can remove a core electron creating an electron hole. An electron of a higher level can fill the hole emitting a radiation in the X-Ray region, with a wavelength which depends on the energy difference between the higher and lower level of this electronic transition. Since each element of the periodic table presents a unique atomic structure, the obtained spectrum will be unique for each element. In Figure 3.7, a scheme of the used instrument is presented. The output of this kind of analysis is a graph in which on the x axis the energies of the emitted X-Rays are indicated, on the y axis the intensity revealed by the detector. Each peak formed can be attributed to a specific element, allowing to know the sample's composition. This procedure is called energy dispersive X-ray spectroscopy (EDS) and is useful for analysing the composition of the surface of a specimen.

Scanning electron microscopy (SEM) micrographs were collected in a JEOL 6300 microscope operating at 20 kV. The quantitative EDX analysis was performed using an Oxford LINK ISIS System with the SEMQUANT program. In this work, Energy Dispersive Spectroscopy was used to perform a semi-quantitative analysis of the elements.

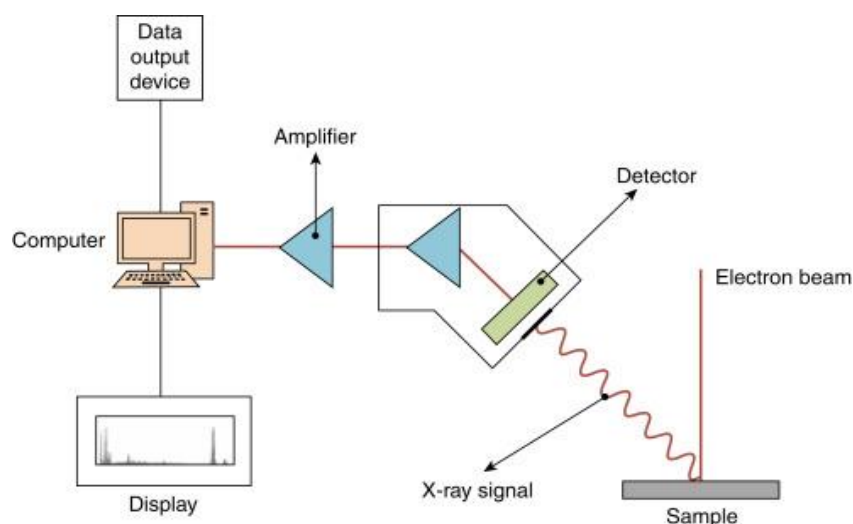


Figure 3.7 EDX Spectroscopy scheme. ²⁵¹

3.2.4.7 *N₂ Adsorption/desorption*

Surface areas were obtained from N₂ adsorption isotherms using the BET method; a Micromeritics ASAP 2000 instrument was used. Samples were degassed in situ under vacuum at a 250 °C temperature. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and pore volumes were obtained by the Barrett–Joyner–Halenda (BJH) method.

3.2.4.8 *Temperature Programmed Desorption (TPD)*

The temperature-programmed desorption of ammonia (TPD-NH₃) experiments have been carried out as follows:

- ▶ Sample Pre-treatment;
- ▶ Ammonia pulse-adsorption;
- ▶ Physisorbed ammonia desorption;
- ▶ Chemisorbed ammonia desorption following a temperature profile.

The instrument used was a TPD/2900 apparatus from Micromeritics. 0,30 g of sample were pre-treated in an Ar stream at 350 °C for 1 h. Ammonia was chemisorbed by pulses at 100 °C until equilibrium was reached. Then, the sample was fluxed with a He stream for 15 min, prior to increasing the temperature up to 500 °C in a helium stream of 100 mL min⁻¹ and using a heating rate of 10 °C min⁻¹. The NH₃ desorption was monitored with a thermal conductivity detector (TCD) and a mass-spectrometer following the characteristic mass of ammonia at 15 a.m.u.

Temperature programmed desorption of CO₂ (TPD-CO₂) experiments were performed in an Autochem II (Micromeritics) instrument with catalyst in pellets (calcined) for the analysis of the base properties of catalyst. The sample was placed in a quartz tubular reactor and pre-treated under 30 mL/min He flow to the calcination temperature (500°C) for 60 min, in order to remove adsorbed H₂O and CO₂ from the catalyst surface prior to adsorption. Then the catalyst was cooled down to 40°C and the catalyst surface was saturated with the probe molecule for 1 h (flow rate of 30 mL/min of 10 v/v % of CO₂ He). Physisorbed CO₂ was removed by flowing He (30 mL/min) for 60 min. Then, the sample was heated at 10°C/min up to 500°C and the desorbed probe molecules were monitored and recorded using TCD detector.

3.2.4.9 *Thermogravimetric analysis (TGA)*

TGA allows to measure the weight losses that occurs during a pre-set thermic profile in a controlled atmosphere. This parameter can be extremely useful to choose the right calcination conditions. TGA

is usually coupled with DSC (Differential Scanning Calorimetry), which measures the heat flow during the thermal profile. The sample is usually loaded in an inert pot which is placed in a balance, another identical empty inert pot is placed in another balance as a reference. During the analysis, the instrument keeps the sample's temperature equal to the reference one. When a phase transition occurs, that can be exothermic or endothermic, the sample requires respectively a heat removal or a heat addition to keep the same temperature as the reference. DSC measures the energy needed to keep the sample and the reference at the same temperature. Combining the TGA and DSC results it is possible to predict which phase transformation occurred at a specific temperature value. The instrument used for the analysis was a NETZSCH STA 449 F3 Jupiter® that permits the simultaneous measurement of weight changes and thermal effects. The samples have been analysed with the same program. They have been heated up to 800°C starting from room temperature, with a 10 °C/min ramp. For both the catalyst spent and the solid precursors, the selected atmosphere were air.

Sample Preparation

TGA/DTA samples do not need a complex preparation, the powder of the precursor's or the spent catalyst pellets have been analysed without any previous treatment.

The thermogravimetric (TG) and differential thermal analysis (DTA) curves for the samples were simultaneously recorded in air at a heating rate 10 K min⁻¹ using a Setaram (Labsys SETSYS-1780) instrument.

3.2.4.10 Diffuse reflectance UV-visible spectroscopy (DRS-UV-vis)

UV–vis spectroscopic characterization of solid catalysts can provide information on the catalyst's oxidation state and coordination in metals and metal oxides, band gap in semiconductors, particle size and shape and surface adsorption in metal nanoparticles via surface plasmon resonance, among others.²⁵² Analysis made via diffuse reflectance (DRS-UV-vis), which is a surface analytical technique, are particularly convenient because they do not require sample preparation.²⁵² Hence, it uses photons as a probing medium (i.e. light, varying in wavelength from the near-UV through the visible to the IR region) that interact with strongly absorbing materials (e.g., metals, alloys, semiconductors, etc.) in the first 10–20 nm of the sample surface.²⁵³ If the material has electronic energy levels that are separated by an energy in the visible region, then it may absorb some of light energy to move electrons from the filled energy level (valence band) into this empty level (conduction band). The information obtained by DR spectroscopy is related to the energies which valence (or conduction) electrons absorb from interaction with photon. The relative optical spectra result from electron transitions between broad, outer electron bands, resulting in peaks broader than the ones that can be obtained from other techniques such as X-ray Fluorescence (XRF).²⁵³ This technique can be used to study the local environment and oxidation state of transition metals.²⁵⁴ Diffuse

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reflectance spectra in the UV-visible region were collected with a Shimadzu UV-2010 PC spectrophotometer equipped with a reflectance attachment.

4 RESULTS AND DISCUSSION

4.1 The continuous-flow upgrading of ethanol to bio-fuel mixtures- UNIBO

The first part of my PhD period has been accomplished into the laboratories of the Department of Industrial Chemistry “Toso Montanari”, of the University of Bologna. The topic of the whole research has been the valorisation of ethanol through its gas-phase conversion over heterogeneous catalysts into added value products. The heterogeneous catalysts object of this first part of the thesis have been hydroxyapatite-based materials.

As extensively discussed in the introduction sections (Chapter 1.2.1.1) the conversion of EtOH to *n*-butanol is better known as Guerbet reaction. The reaction pathway through which it takes place is still a matter of debate and different results have been obtained over materials of different nature. Nevertheless, the most accepted mechanism rely on the aldol condensation of the dehydrogenation product of the alcohol reagent and subsequent hydrogenation of the condensed products. Accordingly, the resulting higher alcohol can undergo the same mechanism and yield longer chains alcohols, both linear and branched. As a result, by optimizing the reaction conditions it could be possible to obtain a longer chain organic compounds mixture that, after undergoing the appropriate treatments, has comparable characteristics with the ones of gasoline (C₄-C₁₀)²⁵⁵ or even jet-fuel (C₉-C₁₆)²⁵⁶. In order to catalyse this complex reaction mechanism, the presence of both acid/basic and redox sites on the surface of the catalyst is mandatory. Among the multifunctional materials studied, hydroxyapatite has been widely used due to its good performances obtained by several authors.

59,69,257,258

In this work, a commercial CaHAP has been employed and then modified by ion-exchange (as explained in Section 3.1.4.1.1) to study the ethanol gas-phase conversion through the Guerbet route while trying to favouring consecutive condensation reactions and obtaining longer carbon chain hydrocarbons.

4.1.1 Catalysts characterization

4.1.1.1 Thermogravimetric analyses (TGA)

The results of the TGA analysis performed over the pellets of calcium hydroxyapatite are depicted in Figure 4.1. The two weight losses that can be noticed in the analysis carried out over the fresh sample (Figure 4.1A) are related to the dehydration of the hydroxyapatite, which is a gradual process. Indeed, as found in literature^{259,260}, hydroxyapatite has two types of water in its structure:

adsorbed and lattice water. Adsorbed water is lost in a reversible manner from 25 to 200°C. Lattice water is irreversibly lost at the temperature from 200°C to 400°C, which causes a contraction in a-lattice dimension during heating. At higher temperature (~800°C) the hydroxyapatite gradually dehydrates losing OH⁻ ions and then, around 1000-1360°C transforms to OHAP (oxyhydroxyapatite, where a bivalent oxygen ion and a vacancy substitute two monovalent OH⁻, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{O}_x\Box_x$, where $\Box$ stands for the vacancy).

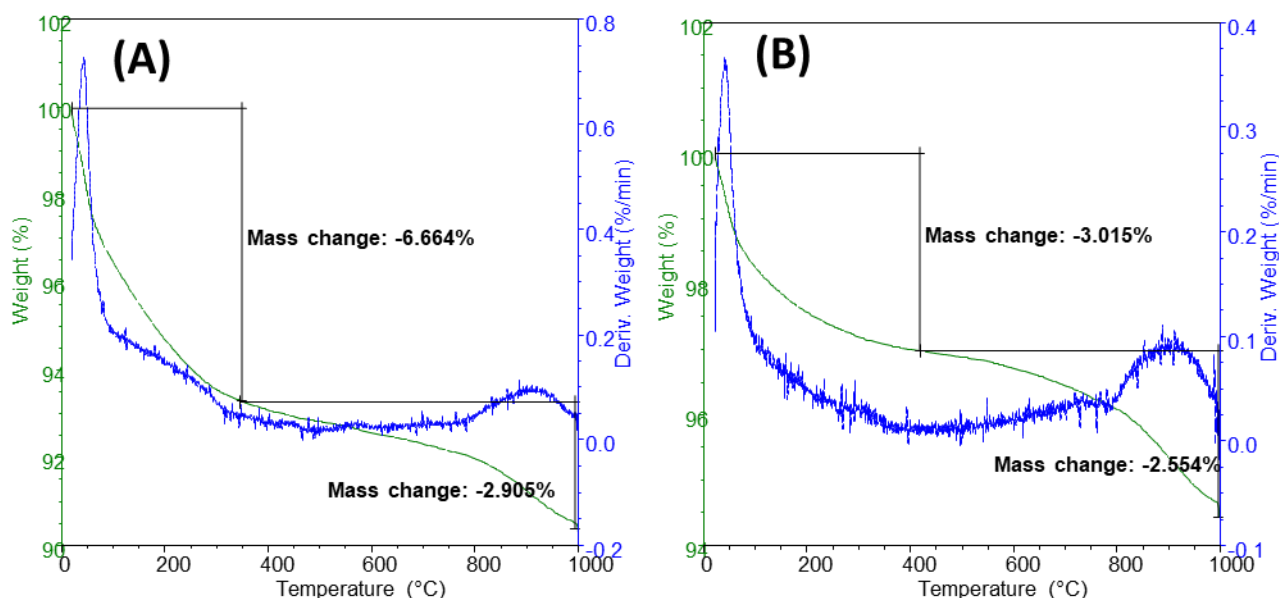


Figure 4.1 TGA results heating commercial Ca hydroxyapatite from room temperature until 1000°C. A) Fresh Ca-HAP B) Ca-HAP calcined at 600°C.

Figure 4.1B shows the TGA results obtained heating the calcined Ca HAP pellets. Since this sample has been already treated with heat at 600°C for 2 hours, the first weight lost (3.015%) is smaller than the one obtained treating the fresh one (6.664%), because even if it should have lost all the adsorbed water, a bit of it has been re-adsorbed during storage. This suggests that calcined samples should be stored in desiccator.

4.1.1.2 X-ray diffraction analysis (XRD)

4.1.1.2.1 Ca-HAP

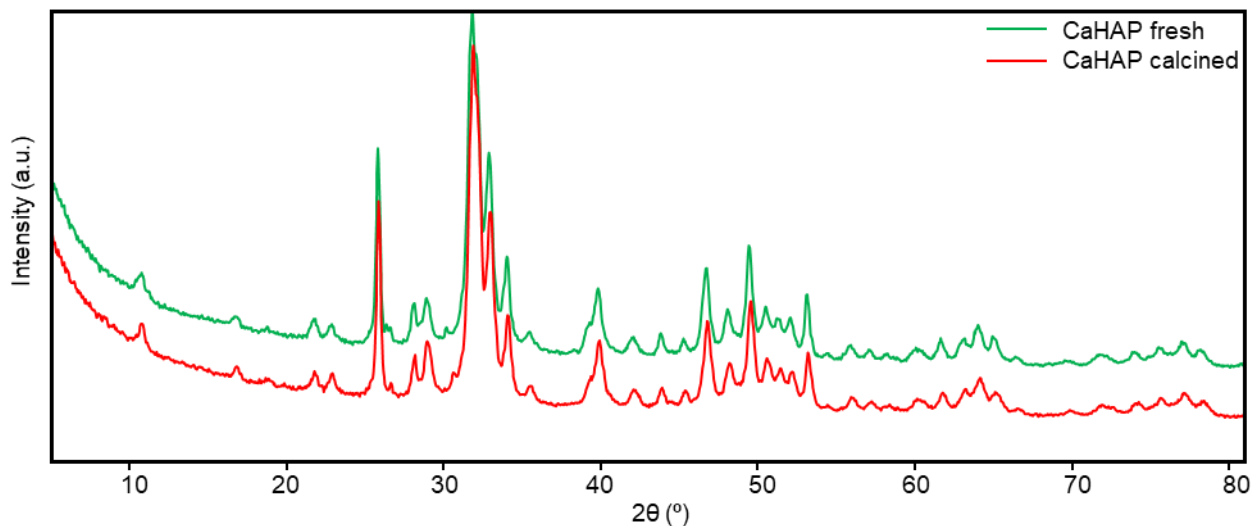


Figure 4.2 XRD patterns of Ca HAP fresh and calcined.

Figure 4.2 shows the powder diffraction pattern for Ca HAP fresh (green) and calcined at 600°C for 2 hours (red). The diffraction peaks of the samples of Ca HAP match with the XRD standard reference of the synthetic hydroxyapatite – HAP, ICDD#24-0033. This confirms that calcination did not alter the crystalline structure of the HAP sample.

4.1.1.2.2 Ion-exchanged HAP

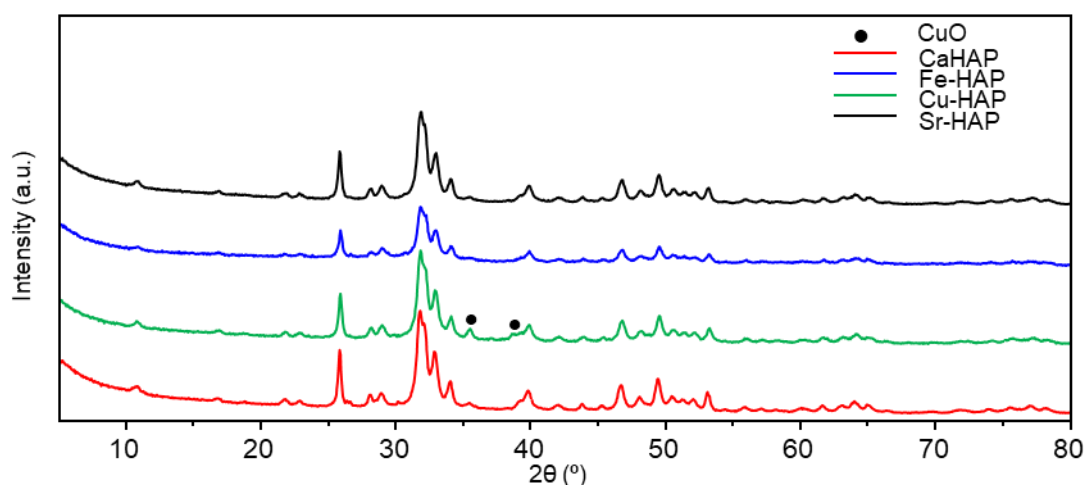


Figure 4.3 XRD patterns of ion-exchanged HAP samples.

Figure 4.3 depicts the XRD patterns of the Me-HAP exchanged samples, prepared as explained in Section 3.1.4. All Me-HAP exchanged samples, excepting for the Cu-HAP, showed XRD patterns

analogous to the structure of the commercial Ca-HAP without any additional peaks that could be related to the presence of other, segregated, phases. These results lead to the considerations that the metal ions substituted the calcium ones in the exchange positions of HAP (type 1 and type 2 Ca ions)²³⁶. The iron-exchanged hydroxyapatite (blue line) showed a slight decrease of crystallinity with smaller diffraction peaks.

Regarding the diffraction patterns of Cu-HAP, some additional peaks related to the formation of CuO aggregates were detected, so in this case not all the copper, calculated by means of MP-AES, is present in the HAP structure by ion-exchange but also segregated as oxide on the external surface of the material.

4.1.1.3 Textural characterization

In Table 4.1 are summarized the results obtained with the BET area measurements. No changes in surface area after calcination nor pelletisation were detected in the Ca-HAP.

In addition, after the ion-exchange process both Cu-HAP and Sr-HAP resulted with a lower specific superficial area, compared to the pristine Ca-HAP, while the Fe-HAP sample showed a slightly higher area. This increase of specific area can be related to dissolution-precipitation of HAP due to the pH of the solution during catalyst preparation.²⁶¹ This is in accordance with XRD results showing a decrease of crystallinity of the hydroxyapatite after ion-exchanging with iron.

Table 4.1 BET area measurement results.

	<i>A_{sup} [m²/g]</i>
Ca HAP commercial, calcined	63
Ca-HAP (20-40), calcined	65
Ca HAP pellets (20-40), calcined	63
Fe-HAP 4 wt% (20-40), calcined	73
Cu-HAP 5 wt% (20-40), calcined	45
Sr-HAP 1.6 wt% (20-40), calcined	40

4.1.1.4 Temperature-programmed desorption (TPD)

Temperature programmed desorption of ammonia (TPD-NH₃) and carbon dioxide (TPD-CO₂) experiments were performed to explore the surface acidity and basicity of the samples, respectively (Fig. 4.4 and Table 4.2). The NH₃-TPD profiles and amount of NH₃ desorbed from the catalysts can be considered as the acid strength distribution and the number of acid sites on the catalyst, including both the Brønsted and Lewis acid sites, respectively.²⁶² Generally, according to the acidic strength determined using the temperature of NH₃ desorption, the solid acid sites can be classified into three types: weak (150–300 °C), moderate (300–450 °C) and strong (450–650 °C) acid sites.¹³⁷ Similarly, the weak strength basic sites are related to curves that shows a maximum at temperature lower than

170°C, the ones between 170 and 270°C are assigned to medium strength basic sites, and finally, the ones above 270°C are strong basic sites.⁹⁹ Recorded spectra may be further deconvoluted by a Gaussian peak fitting method into separate peaks to be then attributed to different strength acid sites.

It is well known the bi-functionality of hydroxyapatite having both acid and basic sites in a single-crystal lattice (with the ability to promote dehydration and dehydrogenation reactions of ethanol in this specific case).²⁶³ According to E. G. Rodrigues et al. stoichiometric hydroxyapatite presents 2 types of basic sites and one of acidic site.²⁶⁴ With the temperature programmed desorption (TPD) of carbon dioxide CO₂ (red line, Figure 4.4A) it was possible to detect a higher concentration of weak basic sites for the Ca-HAP, corresponding to the desorption at 180°C and a second smaller peak at 260°C of medium strength basic sites. It can be noted a third small desorption peak at higher temperature (around 500°C) that can be attributed to lattice OH⁻ groups in the apatite structure, indeed the CO₂ evolved at higher temperatures can predominantly be linked to the reaction of CO₂ with basic OH⁻ groups ($\text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$).^{264,265} In the NH₃ desorption profile (red line, Figure 4.4B) only a single peak centred at 200°C can be noted related to the presence of well-defined Lewis acid sites according to E. G. Rodrigues et al.²⁶⁴

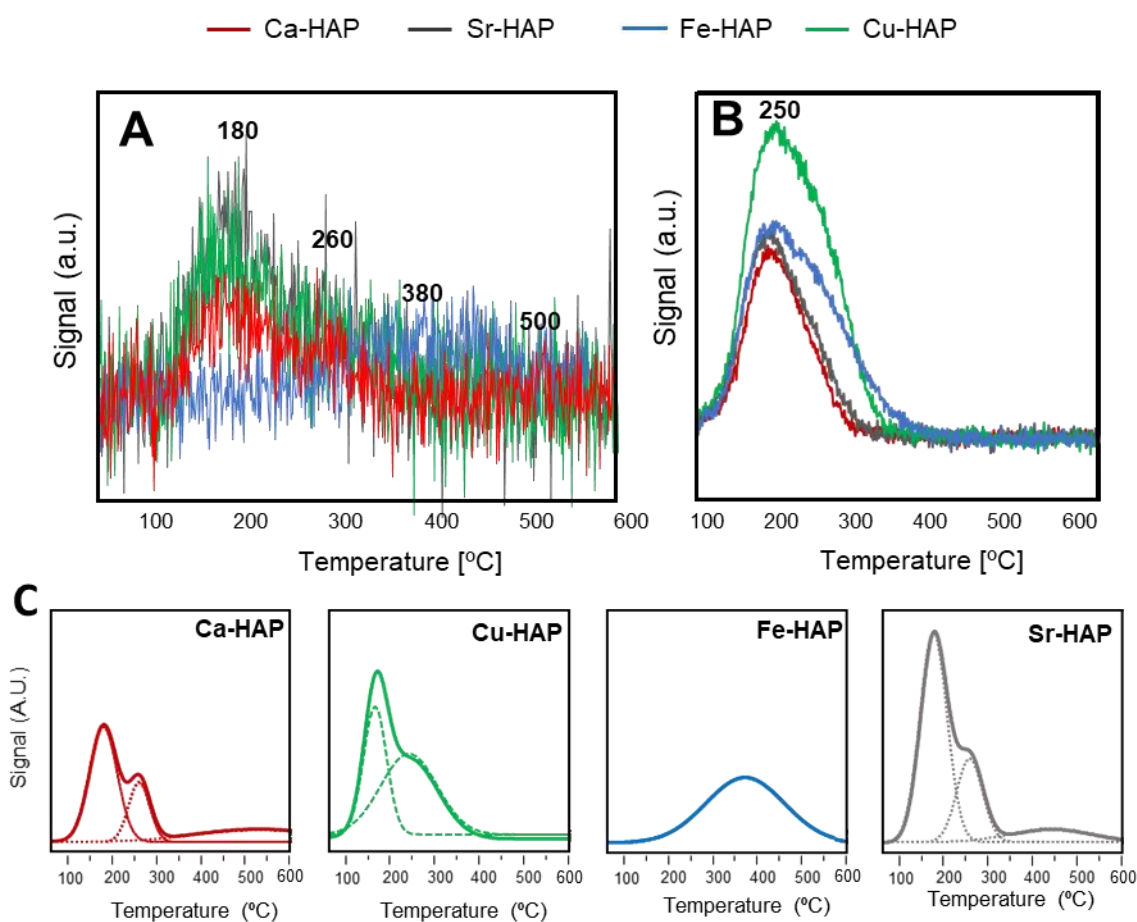


Figure 4.4 TPD profiles of the hydroxyapatite catalysts. Profile of the signals expressed as [$\mu\text{mol}_{\text{PROBEMOLECULE}}/\text{m}^2$]. (A): TPD-CO₂; (B): TPD-NH₃; (C): TPD-CO₂ deconvoluted.

The ion exchange modification of Ca-HAP led to some modifications of its acidic and basic characteristics. Table 4.2 summarizes the results obtained from the temperature programmed desorption analysis in terms of the amount of ammonia or carbon dioxide adsorbed ($\mu\text{mol NH}_3/\text{g cat}$ or $\mu\text{mol CO}_2/\text{g cat}$). In general, the exchange of Ca ions with the Fe or Cu ones led to the formation of new acid sites leading to a higher adsorption of the probe molecule NH_3 , those results are in accordance with literature²³⁷. According to Silvester et al., the exchange between Ca^{2+} ions with the strontium ones led to a decrease of acidity, but from the analysis performed over the Sr-HAP sample, a slight increase of the acidity even in this case has been observed.²⁶⁵

On the other hand, the TPD- CO_2 analyses showed that the exchange of Ca ions with other ions didn't lead to remarkable effects on the overall basicity of the material, in general quite low, as it can be observed in Table 4.2. The only exception that can be noticed is related to the Fe-exchanged HAP where a slight decrease of the adsorbed CO_2 from 17 to 11 $\mu\text{mol}/\text{g}_{\text{CAT}}$ has been observed together with a desorption peak at higher temperature (380°C), showing the formation of a small amount of stronger basic sites (Figure 4.4A, and deconvoluted Figure 4.4C). Overall, considering the changes in the acidic and basic properties of the materials, the exchange with a transition metals (i.e. Fe or Cu) led to a general increase of the acidity/basicity ratio of the catalyst surface. In contrast, the Sr-HAP sample presented a lower value of that ratio (i.e., 9.4 instead of 13.7), showing an indirect growth of the basic properties of the material over the acidic ones, in accordance with literature.²⁶⁵

Table 4.2 TPD- NH_3 and TPD- CO_2 results.

	S_{BET}	Acidity		Basicity		Acidity/Basicity ratio
	$[\text{m}^2/\text{g}]$	$[\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{CAT}}]$	$[\mu\text{mol}_{\text{NH}_3}/\text{m}^2]$	$[\mu\text{mol}_{\text{CO}_2}/\text{g}_{\text{CAT}}]$	$[\mu\text{mol}_{\text{CO}_2}/\text{m}^2]$	(A/B ratio)
Ca HAP	63	262	4.1	17	0.3	13.7
Fe HAP 4 wt%	73	483	6.6	11	0.2	33.0
Cu HAP 5 wt%	45	371	8.3	22	0.5	16.6
Sr HAP 1.6 wt%	40	189	4.7	22	0.5	9.4

4.1.1.5 MP – AES analysis

Cu, Fe and Sr loading was checked by measuring the relative absorbance of the filtrate waters to compute the residual metal concentration. In this way it has been possible to relate those data with the effective metal loading of the catalyst: Cu HAP ca. 5 wt%, Fe HAP ca. 4wt% and Sr HAP ca. 1.6 wt%.

4.1.2 Catalytic tests

The commercial Ca HAP was used as benchmark catalyst for the preliminary catalytic investigations. At the beginning, the effect of the reaction temperature was studied in condition of constant feed flow. To do so, many reaction parameters like the catalyst volume, the feed flow, the pressure and the reactants composition were kept constant. By keeping the feed flow constant using the same amount of catalyst, the contact time (calculated as $V_{\text{CAT}}/F_{\text{TOT}}$, mL/(mL/s)) varied in the reactions made at different reaction temperature between 0.35 and 0.23 seconds; while the so-called pseudo contact time (pseudo τ , W/F), calculated as the weight of catalyst divided by the total volumetric flow of the gaseous mixture at room temperature, was kept constant. For this reason, at a later time also the effect of the contact time was studied at 450°C by keeping all the other parameters (EtOH concentration, temperature and pressure) unvaried.

A typical catalytic test was performed as follows: the reactor charged with the catalyst was pre-heated at 100°C, at this temperature the vaporized ethanol was fed and analysed with the on-line GC in order to evaluate the exact starting concentration of the reagent. After that, the temperature of the furnace was set to the desired temperature and when was reached, the catalytic test started. For each test, fresh new catalyst sample was loaded inside the reactor.

Several blank tests were performed by feeding ethanol into the reactor, in the absence of the catalytic bed, in the range of the desired temperatures (300 - 600 °C). Ethanol conversion was negligible until 600°C, at this temperature ethanol conversion was around 10% with the concomitant formation of acetaldehyde.

4.1.2.1 Ca-HAP – Reaction temperature effect

The study of the temperature effect was performed maintaining the W/F around 0.5 g/mL·s⁻¹ by feeding the 5 %v/v EtOH/He gaseous mixture at a constant flow of around 60 ml/min throughout the reactor charged with 0.5 g of fresh catalyst. In this way the contact time was altered by the effect of the reaction temperature ranging from 0.35 s for the lowest T of 300°C to 0.23 s at 600°C.

4.1.2.1.1 Effect of reaction temperature over selectivity of products as function of the time on stream (TOS)

The effect of the reaction temperature was investigated in the range 300-600°C. The obtained results are summarised from Figure 4.5 to Figure 4.12. In particular, ethanol conversion, the product carbon balance (reported as the sum of the yields of quantified products divided for the ethanol conversion, $\Sigma Y/X$) and the selectivity of the main products are reported referred to the time on stream (TOS, h). In order to better summarize the results, the selectivity of the products were gathered as follows: C₄

(olefins): butadiene, 1-butene, 2-butene-cis and 2-butene-trans; C₂-C₃: ethylene, ethane, propylene and propane; C₁: methane and carbon dioxide; C₄ aldehydes: butyraldehyde and crotonaldehyde; Guerbet alcohols: hexanol, 2-ethyl-butanol, octanol, 2-ethyl-hexanol, decanol. On the other hand, the selectivity of both *n*-butanol and acetaldehyde have been directly reported on the graphs. As the reaction temperature increased, the same did the complexity of the composition of the out stream mixture in terms of amount of formed reaction products. These products were identified through GC-MS qualitative analysis, observing the formation of aldehydes (C₄-C₉), ketones (C₄-C₉), alkyl substituted aromatic compounds (C₇-C₁₀) and some alkenes. Those compounds were quantified using an artificial response factor evaluated from the available commercial samples and are gathered in the graphs as "others". Figure 4.5 depicts the catalytic results obtained at 300°C.

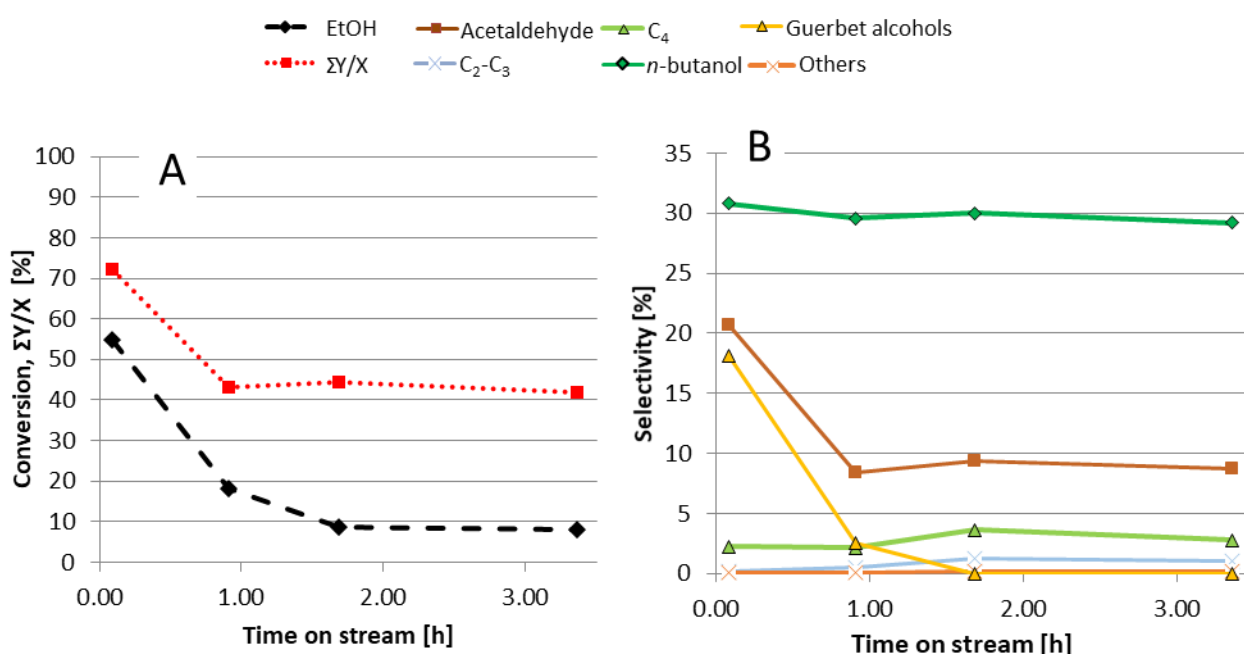


Figure 4.5 Catalytic results obtained in the Ethanol conversion over Ca HAP. Reaction conditions: EtOH 5% v/v in He, $T = 300^\circ\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.35 \text{ s}$. A) Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. B) Products selectivity as a function of the time on stream.

At 300°C, after an initial value of around 55%, since 90 minutes of reaction the conversion decreased to 10% remaining stable with the time on stream. The main products obtained in those conditions are related to ethanol dehydrogenation (acetaldehyde) and to the Guerbet reaction namely *n*-butanol and higher alcohols (hexanol, 2-ethyl-butanol, octanol, 2-ethyl-hexanol, decanol), grouped in the graphs as "Guerbet alcohols". In particular, the selectivity of *n*-butanol is predominant. Indeed, its selectivity at 300°C was around 30% and constant for all the time on stream investigated while the product carbon balance decreased to a low steady value of around 40% with the time on stream. This deficit in product carbon balance needs further investigation since couldn't be explained with carbonaceous deposition investigated with TGA analysis (see section 4.1.1.1).

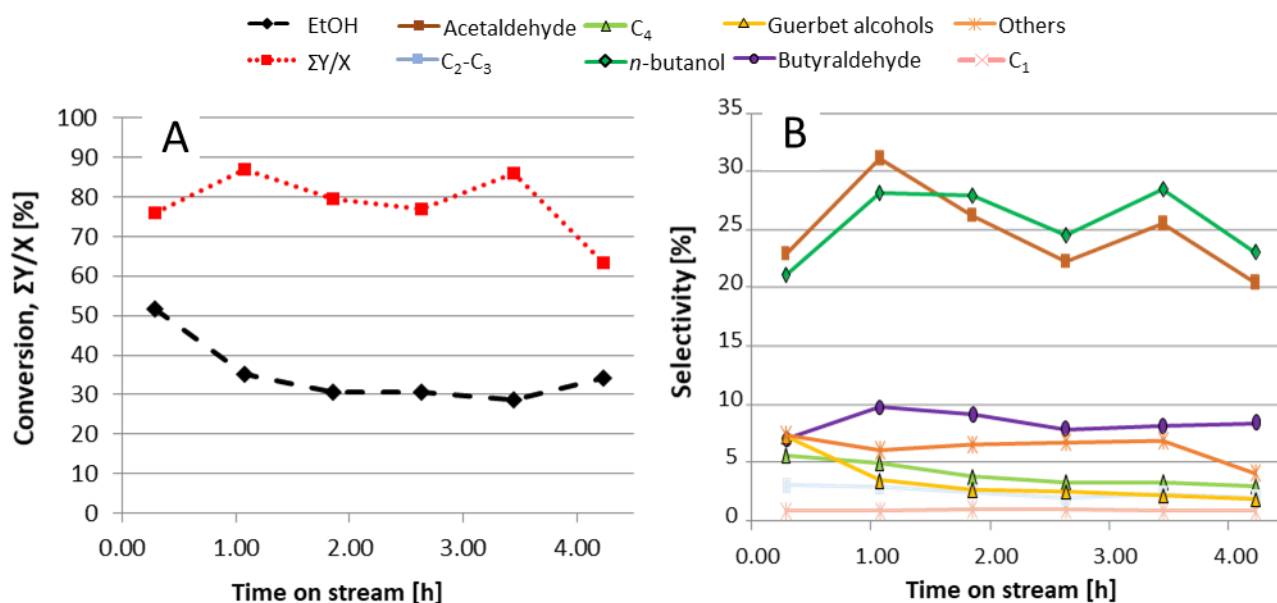


Figure 4.6 Catalytic results obtained in the Ethanol conversion over Ca HAP. Reaction conditions: EtOH 5% v/v in He, $T = 400^\circ\text{C}$, $P = 1\text{ atm}$, $\tau = 0.30\text{ s}$. **A)** Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. **B)** Products selectivity as a function of the time on stream.

At 400°C (Figure 4.6) ethanol conversion reach the stationary state at around 30% after 1 hour of time of stream. Interestingly, both the conversion and the product carbon balance seemed to reach a steady value of 30% and 80%, respectively. Even in this case, the main products were still acetaldehyde and n -butanol, of which the selectivity profiles showed a similar trend over the time on stream, fluctuating around a value of 25%. Even butyraldehyde and crotonaldehyde were produced in a considerable amount (around 7%). In this condition some higher Guerbet alcohols were formed in small quantity even if their selectivity decreased with the time of stream. Moreover, also the formation of “others” products started to be detectable, mainly at the beginning of the reaction. Indeed, the overall selectivity of those products reached an initial value of 7% decreasing with the time on stream. The changing observed in the products distribution with the time on stream are probably due to a partial deactivation of the catalyst caused by heavier carbonaceous compounds depositions on the catalyst surface.

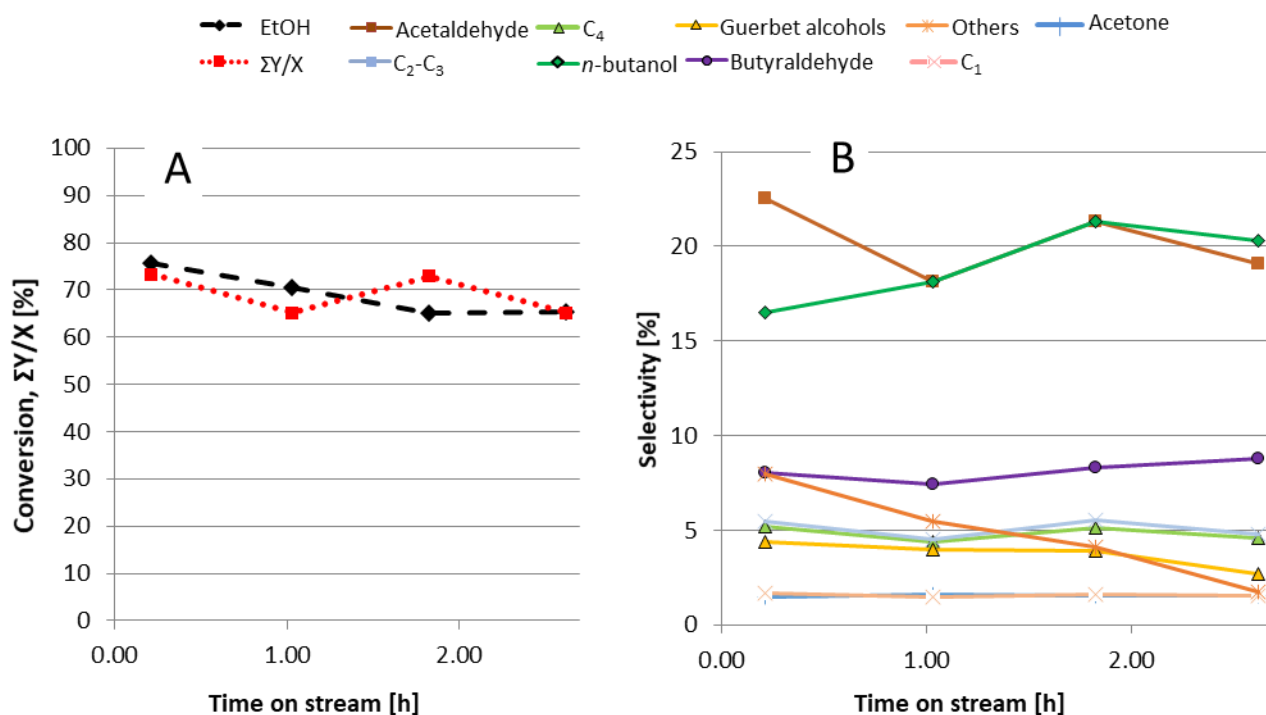
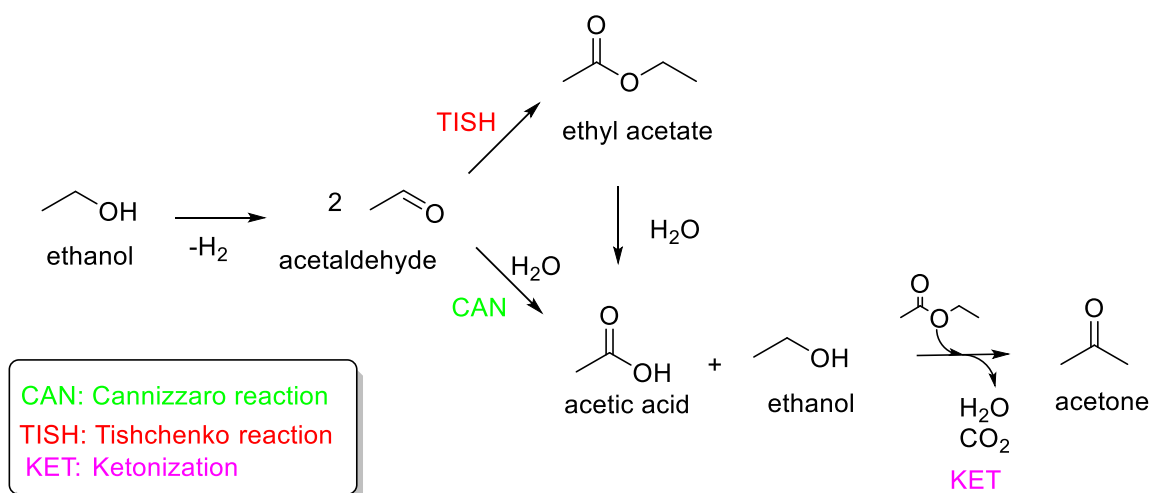


Figure 4.7 Catalytic results obtained in the Ethanol conversion over Ca HAP. Reaction conditions: EtOH 5% v/v in He, $T = 450^\circ\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.28 \text{ s}$. A) Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. B) Products selectivity as a function of the time on stream.

Figure 4.7 reports the results obtained at 450°C , where similar trends to the one obtained at 400°C can be noticed. As expected, the kinetic is favoured at higher temperature; as a result, the conversion of ethanol reached a greater value of around 65%. Interestingly, the products distribution does not seem to be strongly affected by the increase of reaction temperature compared to 400°C ; however, both the higher conversion and the improved product carbon balance allowed to increase the yields into the target Guerbet products. Nevertheless, a slight decrease of EtOH conversion with the time on stream can be noticed, namely from 75% to around 65% after 2.5 hours. Although the distribution of the main products have not been considerably affected from the time on stream, a slight increase of the C_4 aldehydes and a concomitant decrease of the “other” products can be observed. This could again suggest a partial deactivation of the catalyst with the time on stream, where consecutive side-reactions which start from butyraldehyde and/or crotonaldehyde are progressively suppressed. At 450°C acetone has been detected, its formation could be related to a two consecutive reactions starting from acetaldehyde. The dehydrogenation step of ethanol yielding the corresponding aldehyde, acetaldehyde, has been found as necessary first step for the “alcohols ketonization” reaction to happen.⁸¹ Indeed, the reaction mechanism that is likely to take place to from acetone is the following: firstly, acetaldehyde underwent Cannizzaro or Tishchenko-like disproportionation reactions, producing the related acid, alcohols or ester, respectively. The same ester can undergo hydrolysis yielding the corresponding acid.⁸² Then, the acids underwent decarboxylative condensation (i.e. ketonization) reaction, producing non-symmetric or symmetric ketones with the evolution of carbon dioxide as co-product (Scheme 1).



Scheme 1. Reaction mechanism of ethanol toward acetone. Adapted from Ref. ⁸¹

Thanks to the manual injection into the GC-MS of gaseous samples collected during reactions, it was possible to identify most of the compounds constituting the group named “others” and it was found that is made up of different classes of compounds. Figure 4.8 shows the complex chromatograph obtained by a manual injection into the GC-MS obtained after 75 minutes of time on stream during reaction performed at 450°C. In Figure 4.9 some of the compounds detected and gathered in the group named “others” are shown. Higher aldehydes (as 2-ethylbutanal, hexanal) were detected, which were formed through the consecutive Guerbet reaction pathway. Furthermore, higher dienes as hexadiene and 1,3-butadiene-2-ethyl were recognized, probably formed through the Lebedev mechanism.¹⁴⁶ Some ketones were noticed (pentanone, hexanone, heptanone, nonanone), the formation of which can be related to the mechanism showed in Scheme 1. Otherwise, ketone formation could be related to another two-step reaction¹⁶⁶: first the carbonylation of olefins that forms carboxylic acid and then two carboxylic acids react obtaining the ketones by ketonization reaction. A significant amount of alkyl substituted cyclic and aromatics compounds (i.e., xylene, ethyl-benzene, benzene-1,2-diethyl, butylbenzene and ciclohexane-4-methyl) was noticed. The formation of aromatic compounds probably started from ethylene that underwent aromatization that requires acid sites in the catalyst surface.²⁶⁶

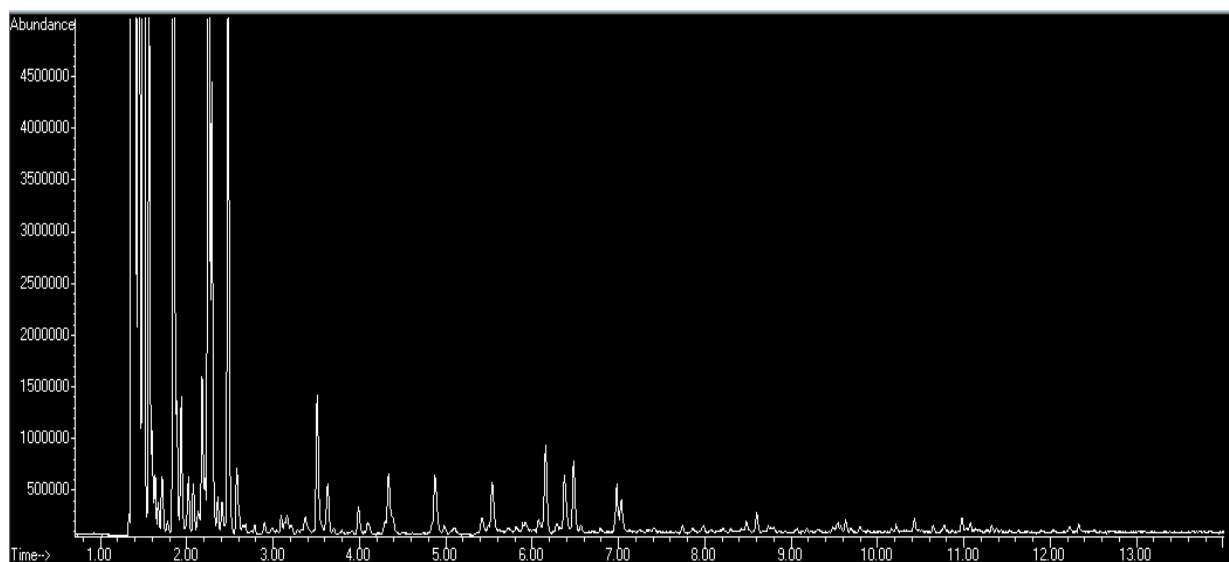


Figure 4.8 Chromatogram obtained after injection of a sample of the outlet gas stream of the reactor during reaction at 450°C.

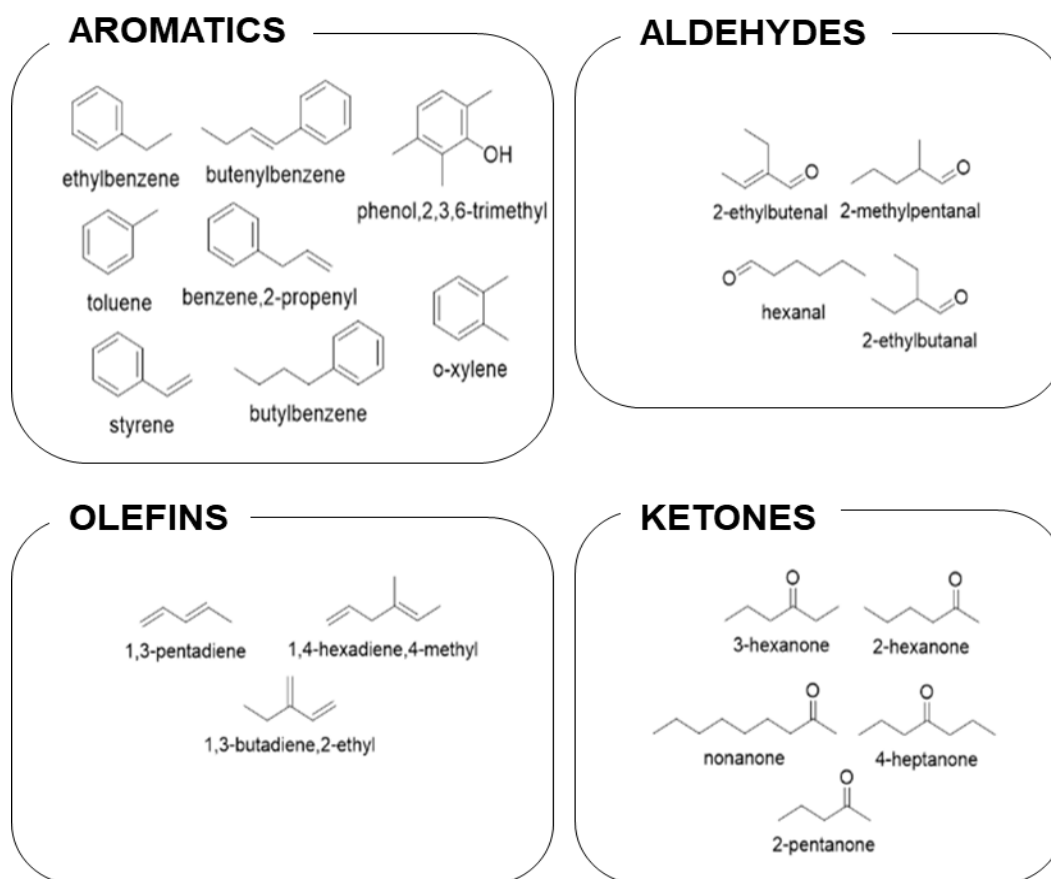


Figure 4.9 Some of the compounds detected through the manual injection into the GC-MS.

Finally, at 500°C the conversion of ethanol was completed (100%) from the beginning and endured over the time of stream with the product carbon balance slightly constant around 65% (Figure 4.10). The increase of reaction temperature favoured the production of other products but even the

formation of C₃ and C₄ unsaturated compounds, as well as of CO₂, that is the co-product of the formation of acetone (and probably higher ketones) from ketonization reactions.

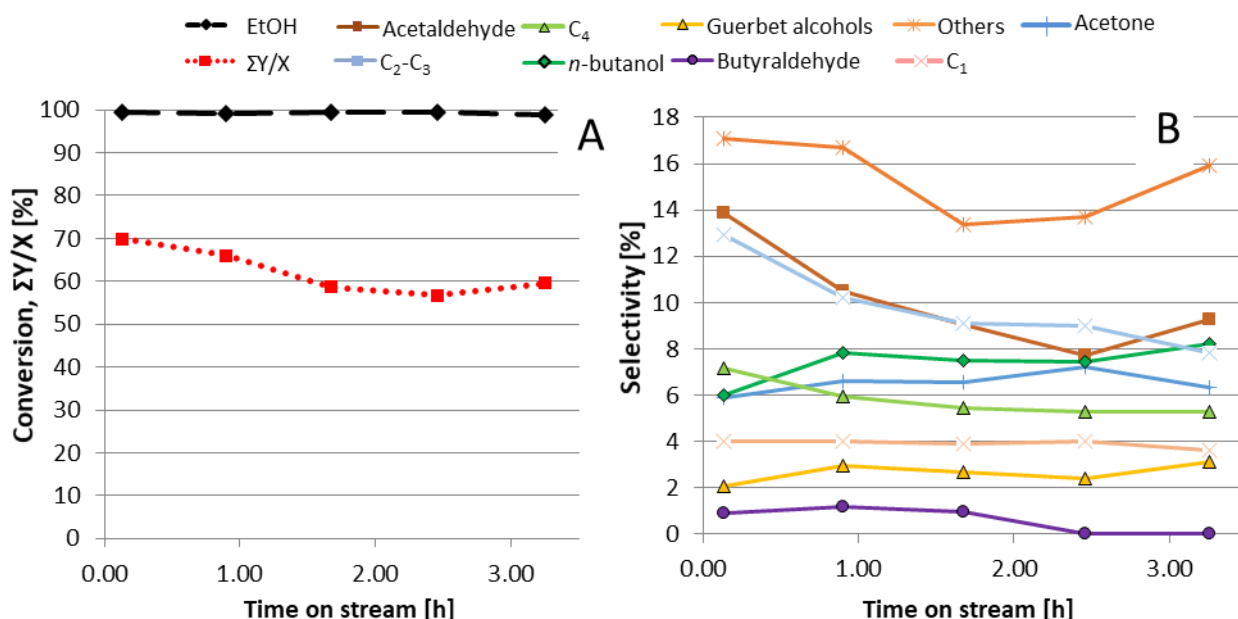


Figure 4.10 Catalytic results obtained in the Ethanol conversion over Ca HAP. Reaction conditions: EtOH 5% v/v in He, $T = 500^\circ\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.27 \text{ s}$. A) Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. B) Products selectivity as a function of the time on stream.

Figure 4.11 reports the catalytic results obtained at 550°C. After 190 minutes of time on stream, the conversion of ethanol, initially completed, decreased to 96% while the product carbon balance fluctuated around 70%. In this case, the product distribution is similar to the one obtained at 500°C even if when the conversion decreased so did the selectivity of the “others” products while the ones of acetaldehyde, *n*-butanol and butyraldehyde increased, all factors that indicated a partial deactivation of the catalyst with the time on stream.

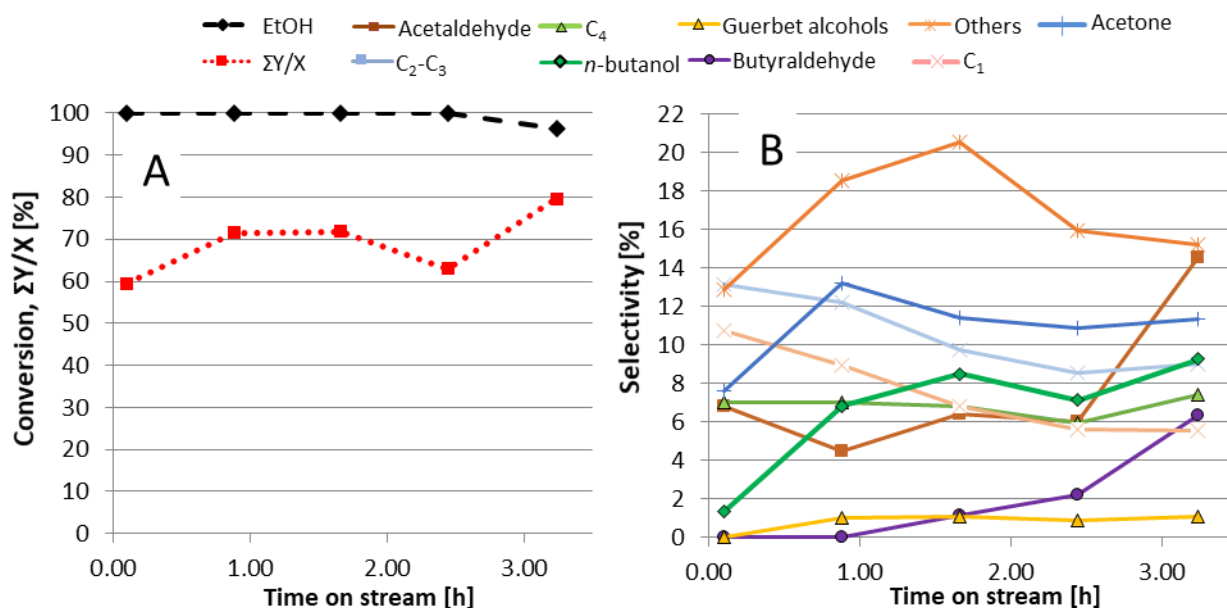


Figure 4.11 Catalytic results obtained in the Ethanol conversion over Ca HAP. Reaction conditions: EtOH 5% v/v in He, $T = 550^\circ\text{C}$, $P = 1\text{ atm}$, $\tau = 0.25\text{ s}$. A) Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. B) Products selectivity as a function of the time on stream.

Interestingly, at 600°C , the ethanol conversion rapidly drop from 100% to 25% over the time of stream, probably due to a quick deactivation of the catalyst as a result of hydrocarbon decomposition to hydrogen-poor compounds, i.e. coke (Figure 4.12). Indeed, the spent catalyst was completely black after reaction. On the other hand, the product carbon balance increased during the reaction from 42% to 93% after 160 minutes. At this temperature, n -butanol was not formed while the main reaction products were acetaldehyde (reaching a value of selectivity of 70%) and ethylene (with a selectivity of $\sim 20\%$). They are both products of endothermic reactions, i.e. dehydrogenation and dehydration. Accordingly, their production could be favoured at higher temperature. The catalytic results suggest that heavier products have been rapidly produced from ethylene and acetaldehyde as intermediates resulting in the deactivation of the catalyst for coke deposition on its surface.

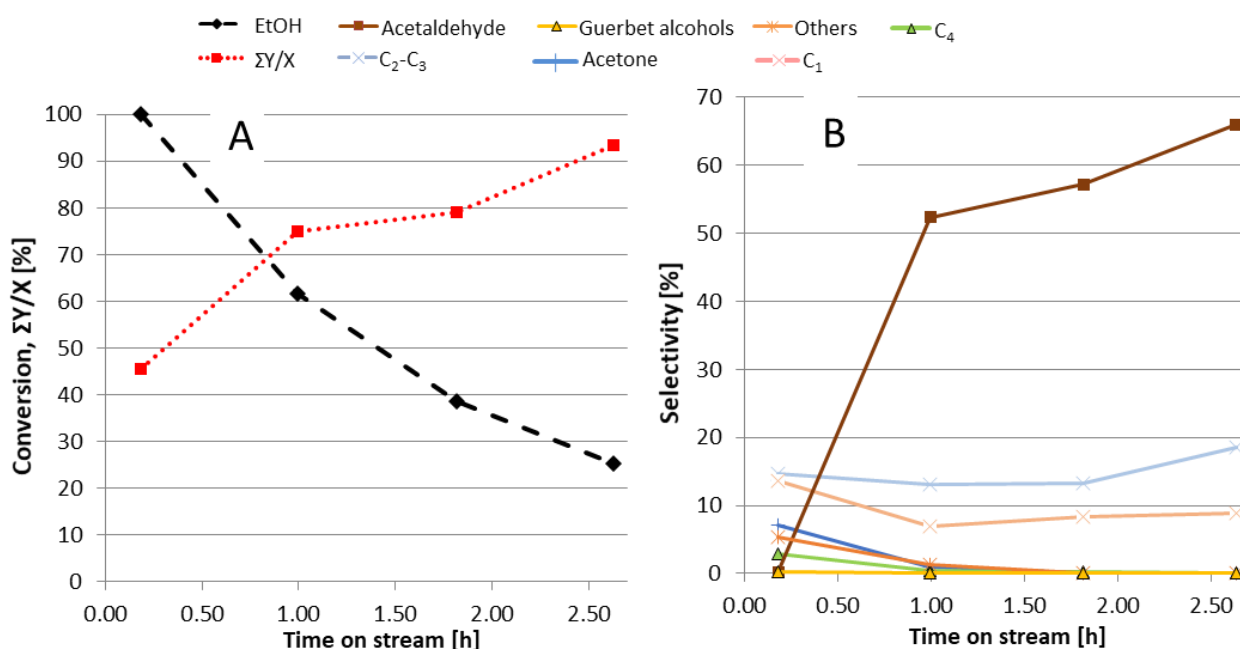


Figure 4.12 Catalytic results obtained in the Ethanol conversion over Ca HAP. Reaction conditions: EtOH 5% v/v in He, $T = 600^\circ\text{C}$, $P = 1\text{ atm}$, $\tau = 0.23\text{ s}$. A) Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. B) Products selectivity as a function of the time on stream.

4.1.2.1.2 The effect of the reaction temperature: overview

In Figure 4.13 are depicted the trends of the conversion of EtOH, the product carbon balance and the selectivity of the quantified products as function of the reaction temperature. In this case, the showed data are an arithmetic average of all the results obtained at each temperature avoiding the first point of reactivity in order to show what happened in the stationary state.

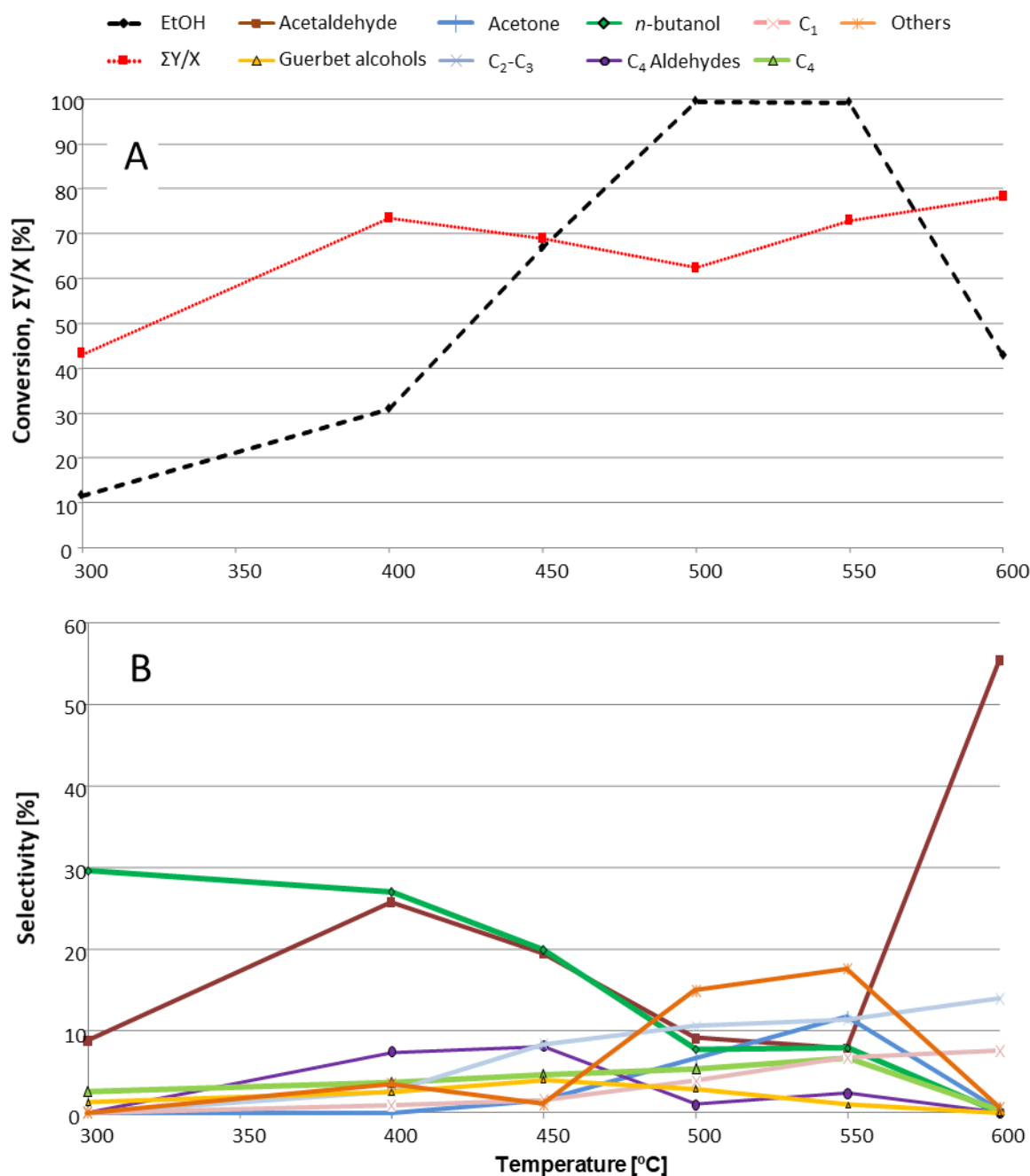


Figure 4.13 Average catalytic results in terms of conversion of EtOH, product carbon balance and selectivity of products as a function of reaction temperature, for the ethanol gas-phase conversion over Ca-HAP catalyst. Reaction conditions: $p = 1$ atm, EtOH 5% v/v in He, $F_{TOT} = 60$ ml/min, $m_{CAT} = 0.5$ g A) Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the reaction temperature [°C]. B) Products selectivity as a function of the reaction temperature [°C].

With increasing temperature, the conversion of EtOH increased from 11 % at 300°C to complete conversion (100%) at 500°C, as expected from a kinetic point of view. Surprisingly, at 600°C the conversion decreased to 42 %. These results are in accordance with J.J Lovón-Quintana et al. who obtained a decreasing conversion of EtOH over a modified hydroxyapatite after increasing temperature from 550°C to 600°C.²⁶³ Anyway, the reason of this drop in ethanol conversion at 600°C could be related to a quick deactivation of the catalyst due to coke deposition.

The product carbon balance showed an upward trend with increasing reaction temperature, indeed at 300°C it was about 40% and then it fluctuated around 70%. In general, in those reaction conditions, the main reaction products were *n*-butanol and acetaldehyde. The *n*-butanol selectivity showed a decreasing trend over the reaction temperature, with a maximum value of 30% at the lower temperature studied (300°C) that decreased to 0% at 600°C. Acetaldehyde selectivity varied with reaction temperature and the main difference to the one of *n*-butanol is noticeable at 600°C where it was the main product with a value of 55%. Since acetaldehyde is the dehydrogenation product of ethanol, which is an endothermic reaction favoured at higher temperature, this result is in accordance with the thermodynamics. In the temperature range 300-450°C the selectivity toward Guerbet reaction products was remarkable while an increase of reaction temperature seems to favour the production of side products that were identified as mainly aromatic compounds. It is worth to notice that with increasing reaction temperature the production of ethylene (grouped in C2-C3) linearly increased, so did the one of C1 compounds, mainly methane.

Since it has been observed a general progressive deactivation with the time on stream, the same results of the effects of the reaction temperature have been computed by plotting the first point of reactivity, that is the one in which can be noticed the activity of the fresh catalyst before deactivation. In those conditions, the effect of the reaction temperature is better pointed out, as can be observed in Figure 4.14. The effect of the reaction temperature on the selectivity of *n*-butanol is revealed, which decreased from 30% to 0% with increasing temperature from 300 to 600°C.

By considering the results obtained over the fresh catalyst, the trends of Guerbet alcohols is noted, with a decreasing trend from 17% at 300°C to 0 % at 600%. The trend of selectivity of acetaldehyde differs from the average one showed in the previous Fig. 4.13, in particular considering the lowest and the highest temperature studied. Indeed, at 300°C the starting value is higher (20%) than the one obtained after the partial deactivation of the catalyst (10%). In contrast, at higher temperature (i.e., 600°C) the selectivity of acetaldehyde was initially very low (i.e., almost 0%) while after the deactivation of the catalyst it became the main reaction product, reaching a selectivity value of 55%. Generally, at medium reaction temperature (400-550°C), as the reactivity reached a stable value over the time on stream very quickly, the results reported with the average values calculated and with the first point of reactivity were very similar. On the contrary, at lower (300°C) and higher temperatures (600°C), the deactivation had a greater effect on the products distribution, the two kind of results reported were rather different; such as the selectivity of both acetaldehyde and Guerbet alcohols.

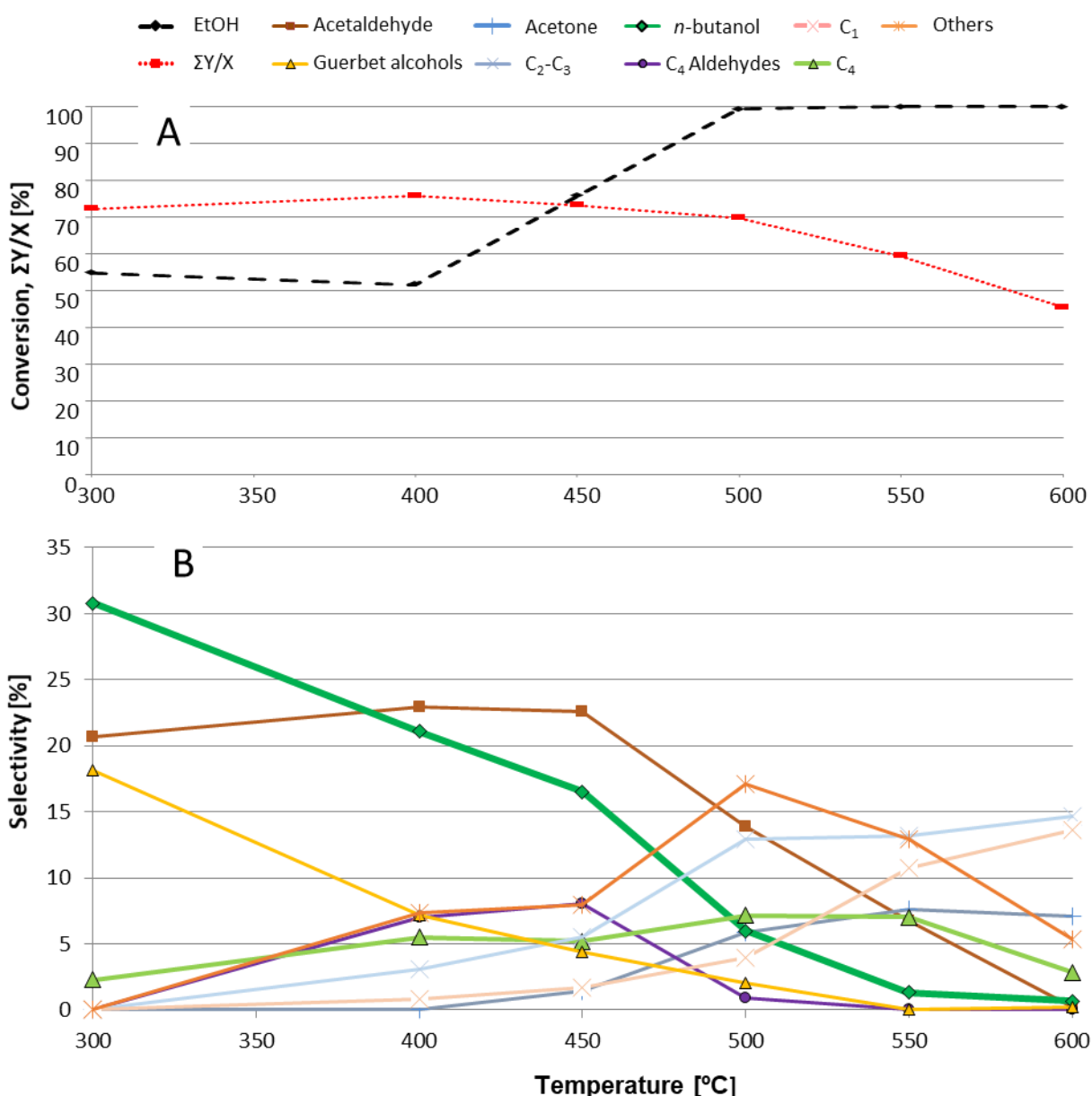


Figure 4.14 Results obtained over the fresh catalyst, in terms of conversion of EtOH, product carbon balance and selectivity of the quantified products as a function of reaction temperature. Reaction conditions: $p = 1$ atm, EtOH 5% v/v in He, $F_{TOT} = 60$ ml/min, $m_{CAT} = 0.5$ g. A) Ethanol conversion and carbon balance $\Sigma Y/X$ as a function of the reaction temperature [°C]. B) Products selectivity as a function of the reaction temperature [°C].

To deepen the possible causes of catalyst deactivation, some Thermogravimetric analysis (TGA) under an air flow of 100 ml/min (10°C/min of ramp until 100°C followed of an isothermal for 1 h) were performed over the spent catalysts after reaction. Figure 4.15 shows a representative thermogram obtained with the catalyst spent after the reaction performed at 550°. This Ca HAP sample exhibits three different stages of mass loss, the first around 200°C can be related to the dehydration of adsorbed water. The last mass loss that started around 800°C is the same observed with the fresh catalyst (See Section 4.1.1.1). The middle stage of mass loss from 200°C to 600°C can be related to the loss of carbonaceous residues adsorbed over the surface of the catalyst.

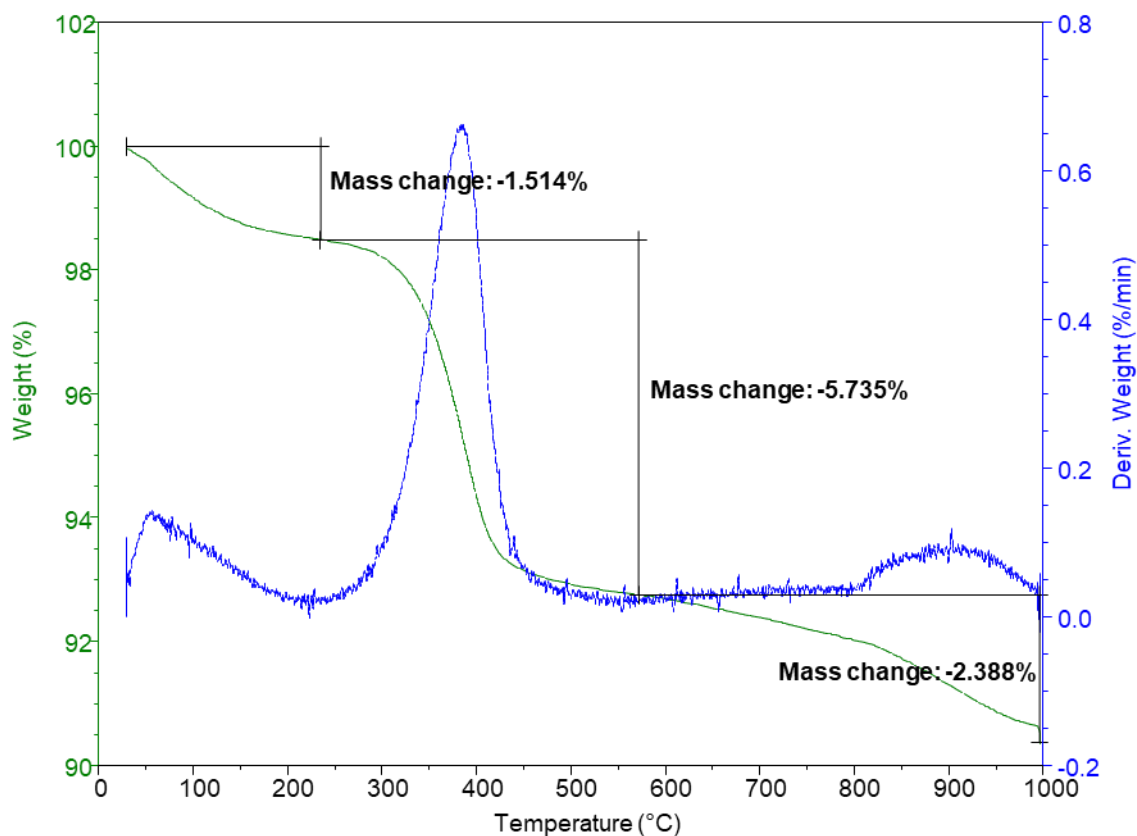


Figure 4.15 TGA results with Ca HAP spent catalyst after the reaction performed at the reaction temperature of 550°C.

Table 4.3 summarized the results obtained from the TGA analysis of all the spent catalysts after the reactions performed at different temperatures and the weight loss tabulated is the one attributed to the carbonaceous residues (i.e. coke). The increase of this weight loss with rising reaction temperature can be related to a general higher coke formation at higher reaction temperature. This trend resembles the one observed for product carbon balance, which decreased with reaction temperature, as can be noticed in Figure 4.14 The highest coke content was observed over the spent catalyst used in the reaction performed at 600°C, this result is in line with the catalytic results (Figure 4.12), where a high rate of deactivation with the time on stream can be noticed.

Table 4.3 Thermogravimetric analysis (TGA) of the spent catalysts performed under flow of air.

<i>Reaction temperature [°C]</i>	<i>Overall time on stream [min]</i>	<i>Weight loss [%]</i>	<i>Temperature of desorption [°C]</i>	<i>Mass of heavy compounds deposited per minutes[g/min]</i>
300	202	2.4	377	5.87E-05
400	254	1.9	368	3.74E-05
450	157	1.6	372	5.10E-05
500	196	2.1	383	2.79E-05
550	194	5.7	384	1.46E-04
600	158	6.8	386	2.15E-04

The weight loss obtained from the TGA analysis can be referred to the deposition of heavy organic compounds over the catalytic surface during the reaction. In this way, it is possible to quantify the total mass of the deposited organic compounds over the catalyst during the time on stream. However, these values alone does not explain completely the deficit in the product carbon balance.

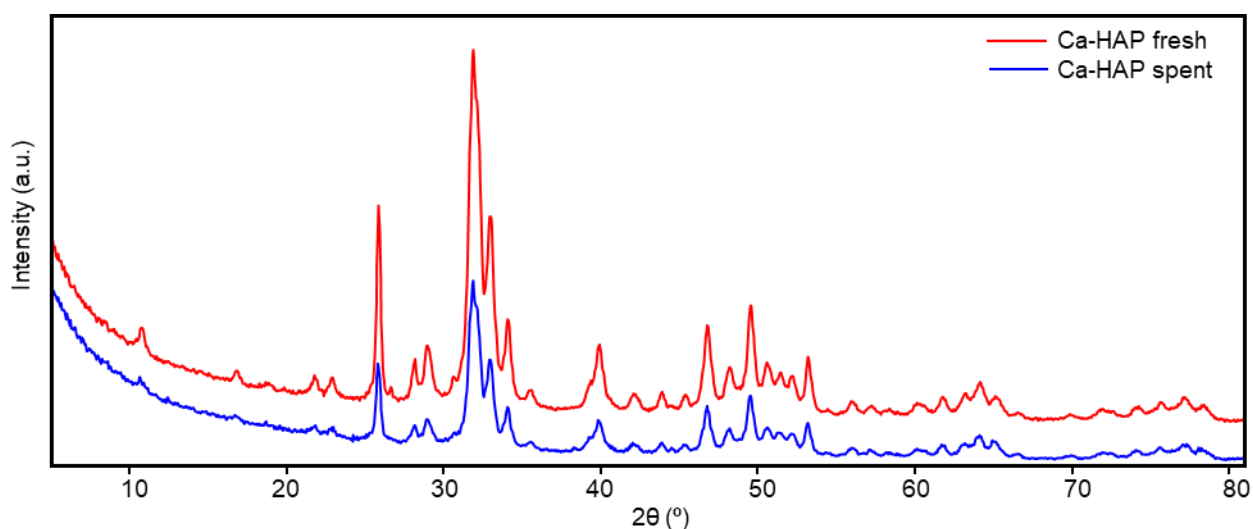
**Figure 4.16** XRD patterns of Ca-HAP fresh and spent.

Figure 4.16 shows the powder diffraction pattern for Ca-HAP catalyst before reaction (Ca-HAP fresh, red line) and after the reaction performed at 600°C (Ca-HAP spent, blue). The XRD analysis made over the spent catalyst after the reaction performed at 600°C showed a decrease in the crystallinity of the material without any significant change in the crystal phase or segregation of any components.

4.1.2.2 Ca-HAP – Contact time effect

From the previous tests, the best catalytic result, in terms of catalyst activity and relative product carbon balance, has been achieved at 450°C. Indeed, at 450°C and EtOH conversion of 70% with a

product carbon balance of 70% have been obtained, with reasonable selectivity of Guerbet products. Indeed, in those conditions, the main products were Guerbet alcohols (or related aldehydes) with medium length chain. For all these reasons, 450°C was chosen as suitable reaction temperature for the investigation of the effect of contact time on the product distributions. In fact, by increasing contact time it could be possible to promote the consecutive condensation reactions of higher aldehydes, finally favouring the formation of products characterised by a longer carbon chain. Specifically, the contact time employed have been $\tau = 0.28, 0.56, 0.94$ s.

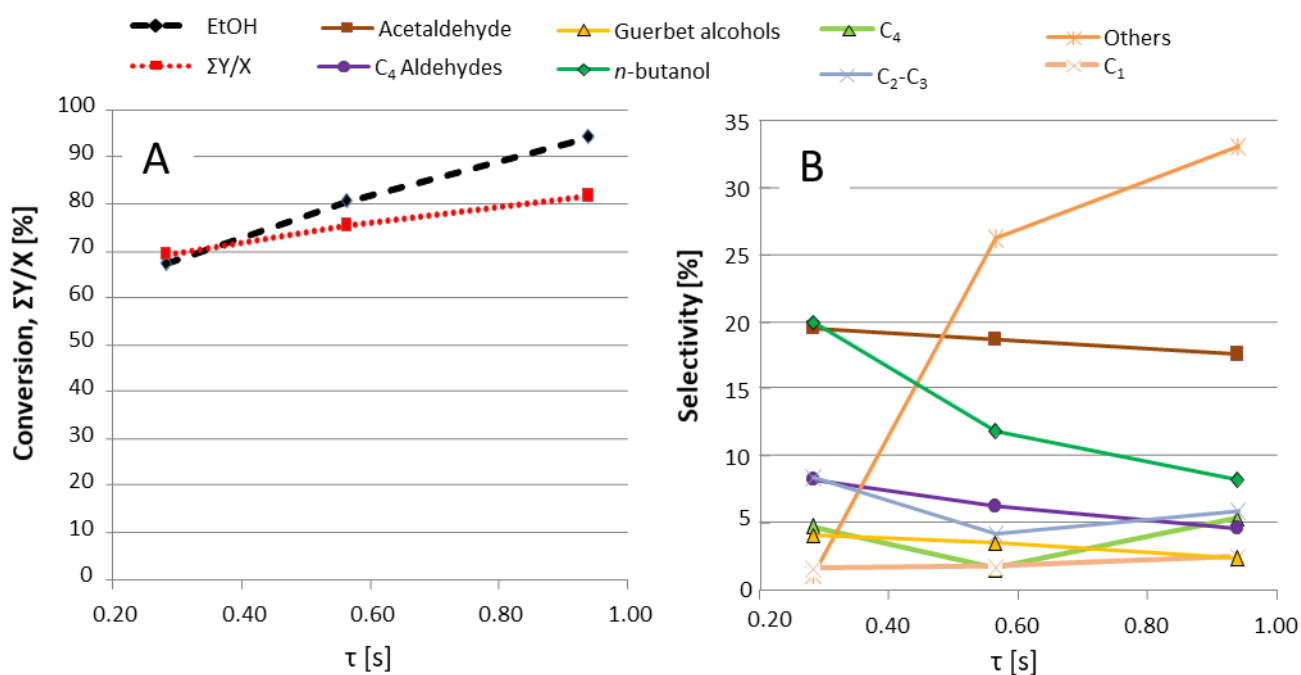


Figure 4.17 Catalytic results obtained in the Ethanol conversion over Ca HAP. Reaction conditions: EtOH 5% v/v in He; $T = 450^\circ\text{C}$; $P = 1$ atm; $\tau = 0.28, 0.56$ or 0.94 s. **A)** Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the contact time [s]. **B)** Selectivity to reaction products as a function of the contact time [s].

The results reported in Figure 4.17 represents an arithmetic average of all the results obtained at each τ avoiding the very first hour of reaction (time in which, generally, is reached the steady state, as observed in previous tests). As expected, the increase of the contact time led to a slight increase of ethanol conversion values (from 68% to 92 %). However, also an impressive increase in the selectivity of other products (mainly aromatic compounds) with a concomitant drop in both n -butanol and C_4 aldehydes selectivity was observed. On the other hand, the selectivity toward acetaldehyde was almost unaffected by the contact time. These results are probably suggesting that consecutive reaction on n -butanol and C_4 aldehydes can occur for longer contact time leading to the formation to unsaturated compounds that can undergo radical oligomerisation or Diels Alder reaction toward the formation of aromatic compounds (mainly ethyl benzene, toluene and xylenes).

Figure 4.18 depicts the results obtained at the highest contact time studied (0.94 s) as a function of the time on stream. Even in this case ethanol conversion (initially 95%) decreased a bit with the time

on stream but after 1 hour it reached a stable value of 80% and the product carbon balance remained almost stable to 75-80% for all time on stream studied. In general, after 1 hour of time of stream the reaction mixture was composed by almost a 25% of the “others” products, 20% of acetaldehyde, 12% of *n*-butanol, 7% of C₄ aldehyde, 5% of Guerbet alcohols and the lighter products were produced in a very low quantity. Anyway, the slight decrease of the other products selectivity could be related to the use of an average response factor that could underestimate some products.

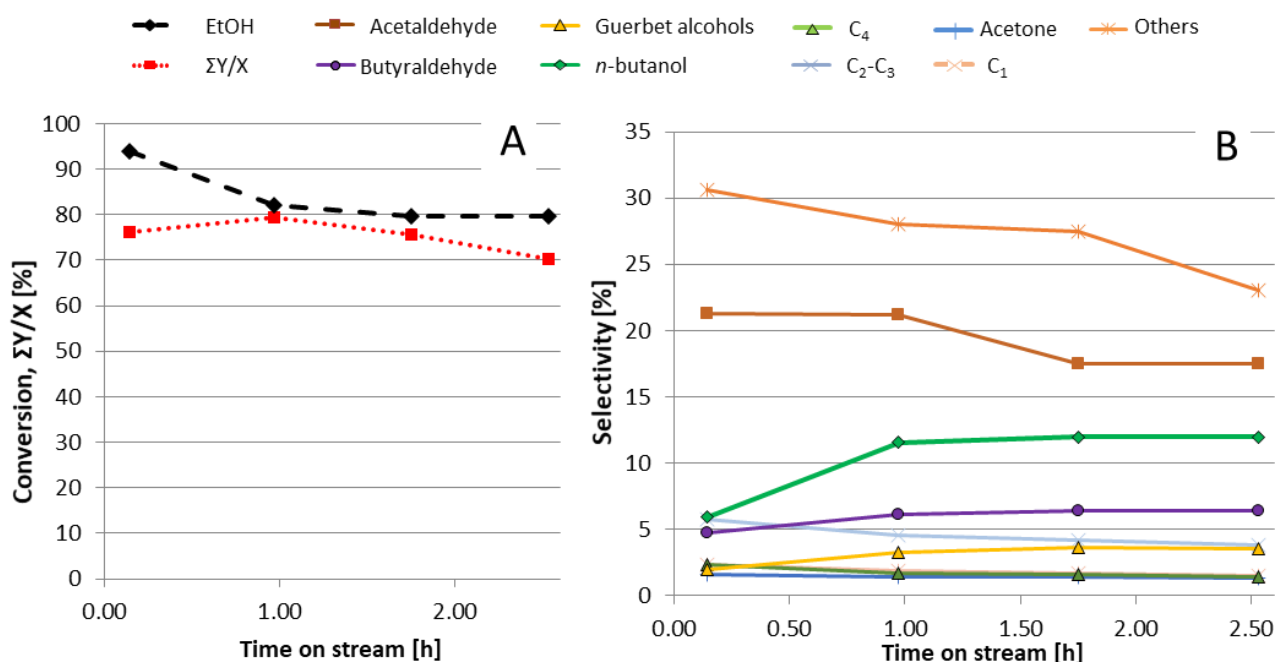


Figure 4.18 Catalytic results obtained in the Ethanol conversion over Ca HAP. Reaction conditions: EtOH 5% v/v in He, $T = 450^{\circ}\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.94 \text{ s}$. **A)** Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. **B)** Selectivity to main reaction products as a function of the time on stream.

4.1.2.2.1 Ca-HAP results resume

In summary, as expected ethanol conversion increased with increasing temperature reaching the value of 100% at 500°C . The conversion drop observed at 600°C has been related to a rapid deactivation of the catalyst due to the formation of heavy carbonaceous compounds over the surface. In addition, a partial deactivation of the Ca-HAP over the time on stream has been generally observed in all the reaction condition tested.

Generally, as can be observed in Figure 4.13 and Figure 4.14, the products distribution depends significantly on the reaction temperature. With increasing temperature, the production of other products, mainly aromatic compounds, became relevant. In addition, the production of ethanol dehydration product, ethylene, increased with increasing temperature. It is well known that the latter reaction requires acid catalyst. Furthermore, ethylene is the key intermediate for the formation of aromatic hydrocarbons as it happens in the Ethanol to Gasoline (ETG) process, which consists in feeding ethanol over an acid heterogeneous catalysts, namely zeolite with the structure of HZSM-

5.²⁶⁷ The just mentioned process comprises ethanol dehydration to ethylene and ethylene oligomerization to higher hydrocarbon. The aromatization of ethylene involves a complex network of reactions consisting in ethylene oligomerization and cracking of the formed higher olefins, followed by dehydrogenation and cyclisation over Brønsted acid sites.²⁶⁶ The fact that aromatic compound formation was favoured at higher temperature observed while performing the catalytic tests is in accordance with literature.²⁶⁶

At 450°C both the ethanol conversion and the product carbon balance reached a value of around 70%. In addition, at this temperature the main products were *n*-butanol, acetaldehyde, and other Guerbet alcohols such as hexanol, 2-ethyl-butanol, octanol and 2-ethyl-hexanol as well as butyraldehyde. By studying the effect of the contact time at this reaction temperature, it was noticed that as the contact time increased so did the production of other products. Even if some of the other products detected through injection into the GC-MS were higher aldehydes and ketones, the nature of most of them was aromatic. However, Ca-HAP presented partial deactivation over the time on stream in all the reaction conditions tested with the concomitant formation of a considerable amount of aromatic compounds while trying to push the reaction to the production higher molecules.

Accordingly, the following reaction conditions have been chosen to study the catalytic activity of the ion-exchanged hydroxyapatite synthesized: 450°C, 0.6 s of contact time and continuously feeding ethanol in a helium stream (EtOH 5 mol%).

4.1.2.3 Ion-Exchanged HAP

4.1.2.3.1 Fe-HAP and Cu-HAP

The first ion-exchanged hydroxyapatite that was tested for the target reaction was Fe-HAP 4 wt%. Figure 4.19 reports the results obtained in terms of ethanol conversion, product carbon balance (reported as the sum of the yields of quantified products divided for the ethanol conversion, $\Sigma Y/X$) and the selectivity of the main products as a function of the time on stream [h]. In this case, the insertion of a transition metal with redox properties in the catalytic system led only to a slight increase in the formation of the dehydrogenation product of ethanol, acetaldehyde. Nonetheless, the main products obtained was ethylene with yields around 50%. This is typically an acid catalysed reaction and the results are in accordance with the one obtained by TPD-NH₃ analysis that showed an increased acidity of the catalyst surface after ion-exchange reaction between Ca²⁺ and Fe³⁺ ions. Interestingly, it is possible to notice that the selectivity of C₄ (butadiene and unsaturated butenes) increased with the time on stream reaching the value of 10% after 2.5h. Anyway, in these conditions, Fe-HAP was very active allowing a stable, complete conversion of ethanol for more than 2.5 hours.

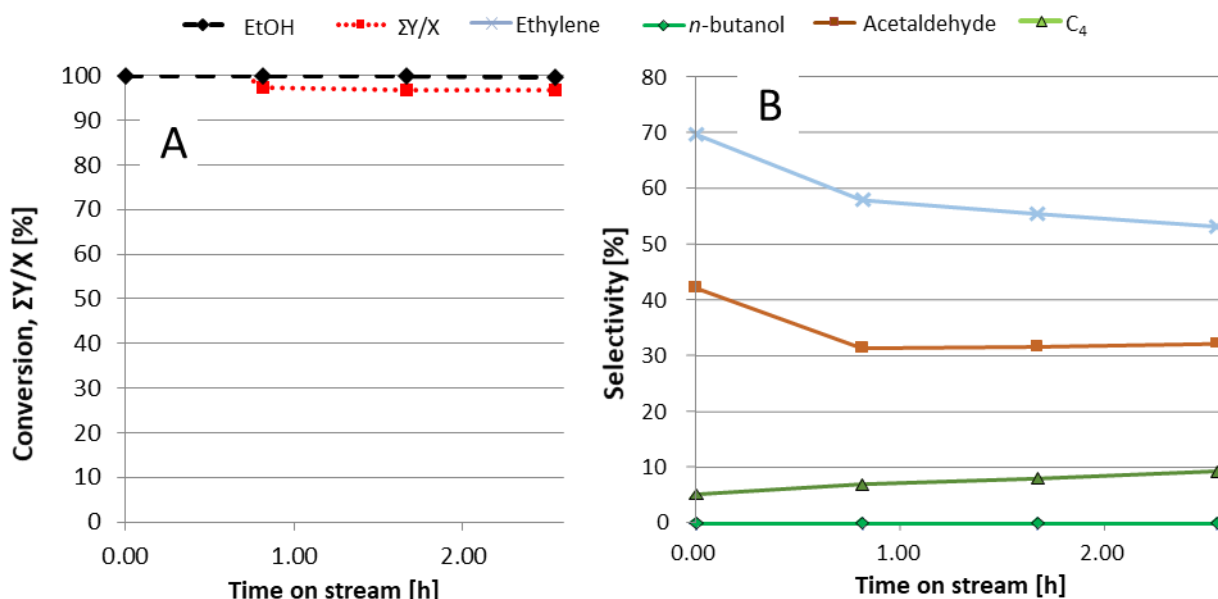


Figure 4.19 Catalytic results obtained in the Ethanol conversion over Fe-HAP. Reaction conditions: EtOH 5% v/v in He; $T = 450^\circ\text{C}$; $P = 1\text{ atm}$; $\tau = 0.6\text{ s}$. “C4”: butadiene, 1-butene, 2-butene-cis and 2-butene-trans. **A)** Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. **B)** Selectivity to main reaction products as a function of the time on stream.

Figure 4.20 depicts the catalytic results obtained over the Cu-HAP 5wt% catalyst. As it is possible to notice from the figure, the effect of the addition of copper into the catalytic system is similar to the one of iron: even in this case the two main products were acetaldehyde and ethylene (with yield above 60%) with complete conversion of ethanol. The selectivity of the products obtained over the transition metal-exchanged hydroxyapatite did not seem to be influenced by the nature of the metal, indeed they were obtained with similar values when testing, in the same reaction conditions, both catalysts. Nevertheless, since the main activity was acidic in nature, and no consecutive condensation reactions have been catalysed, no further experiments have been performed over those materials.

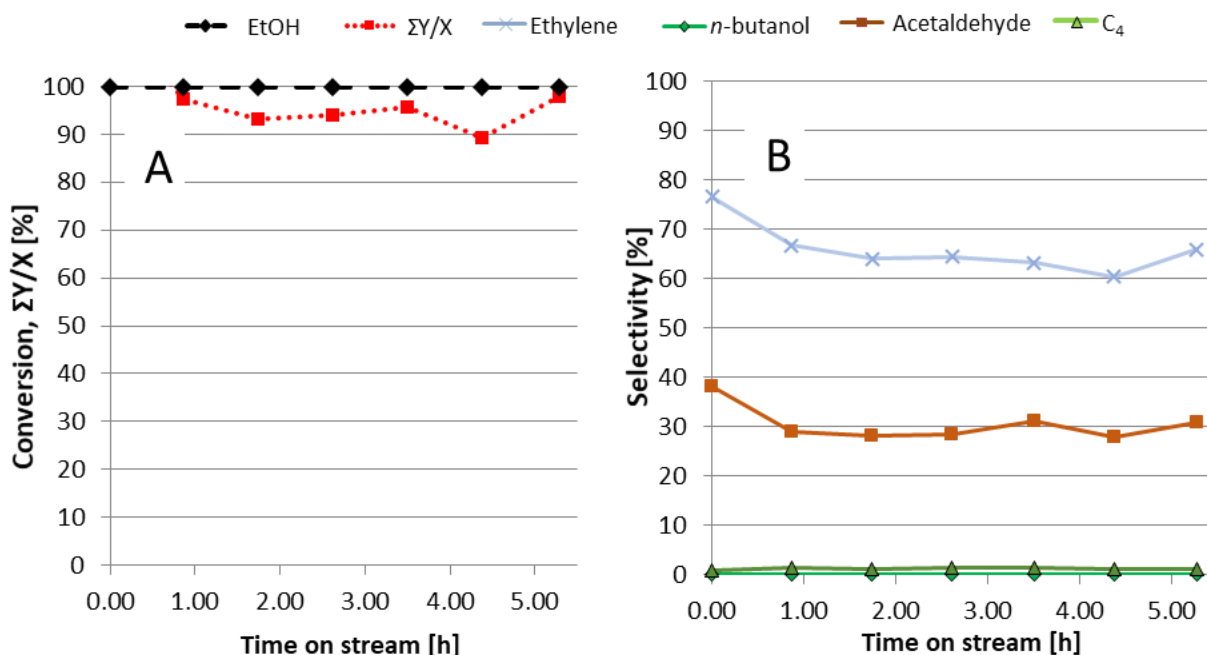


Figure 4.20 Catalytic results obtained in the Ethanol conversion over Cu-HAP. Reaction conditions: EtOH 5% v/v in He, $T = 450^\circ\text{C}$, $P = 1\text{ atm}$, $\tau = 0.6\text{ s}$. “C4”: butadiene, 1-butene, 2-butene-cis and 2-butene-trans. **A)** Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. **B)** Selectivity to main reaction products as a function of the time on stream.

4.1.2.3.2 Sr-HAP

The Sr-HAP 1.6 wt% catalyst was tested in the same conditions explained before and the results obtained are shown in Figure 4.21. The reaction mixture obtained in this case was pretty complex. In order to better summarize the results, the selectivity of the products were gathered as follows: “C4”: butadiene, 1-butene, 2-butene-cis and 2-butene-trans; “C1”: carbon dioxide; “C4 aldehydes”: butyraldehyde and crotonaldehyde; “Guerbet alcohols”: hexanol, 2-ethyl-butanol, octanol, 2-ethyl-hexanol, decanol. In addition, new compounds groups have been used to quantify the reaction products after optimizing the analytical method by calibrations of new standards, as explained in Section 3.1.3. Therefore, the group name “Aromatics” corresponds mainly to toluene, *o*-xylene, ethyl-benzene, butyl benzene and the one named “Higher aldehydes” is the summed contribution of both hexanal and decanal. In addition, the quantification of other unknown products has been improved in order to better understand the results of the catalytic tests. More specifically, the unknown compounds have been gathered in “Light” (i.e., C_4 - C_6), “Mid” (i.e., C_6 - C_{10}) and “Heavy Others” (C_{10} - C_{16}), accordingly to their retention times in the chromatogram.

Interestingly, the Sr-exchanged hydroxyapatite was pretty active, with an ethanol conversion of around 90% and a product carbon balance of 70%. From Figure 4.21, it can be noticed a complex reaction mixture. *n*-Butanol and C_4 aldehydes selectivity slightly increased with the time on stream, probably due to a partial deactivation of the catalyst. Indeed, at the same time, there was a

concomitant decrease of the formation of heavy compounds (mainly aromatics, as it will be discussed later in this section). These results are probably suggesting that even in this case, consecutive reactions on *n*-butanol and C₄ aldehydes can occur leading to the formation to unsaturated compound that can undergo to radical oligomerization or Diels Alder reactions toward the formation of aromatic compounds (mainly benzene, ethyl benzene, toluene and xylene).

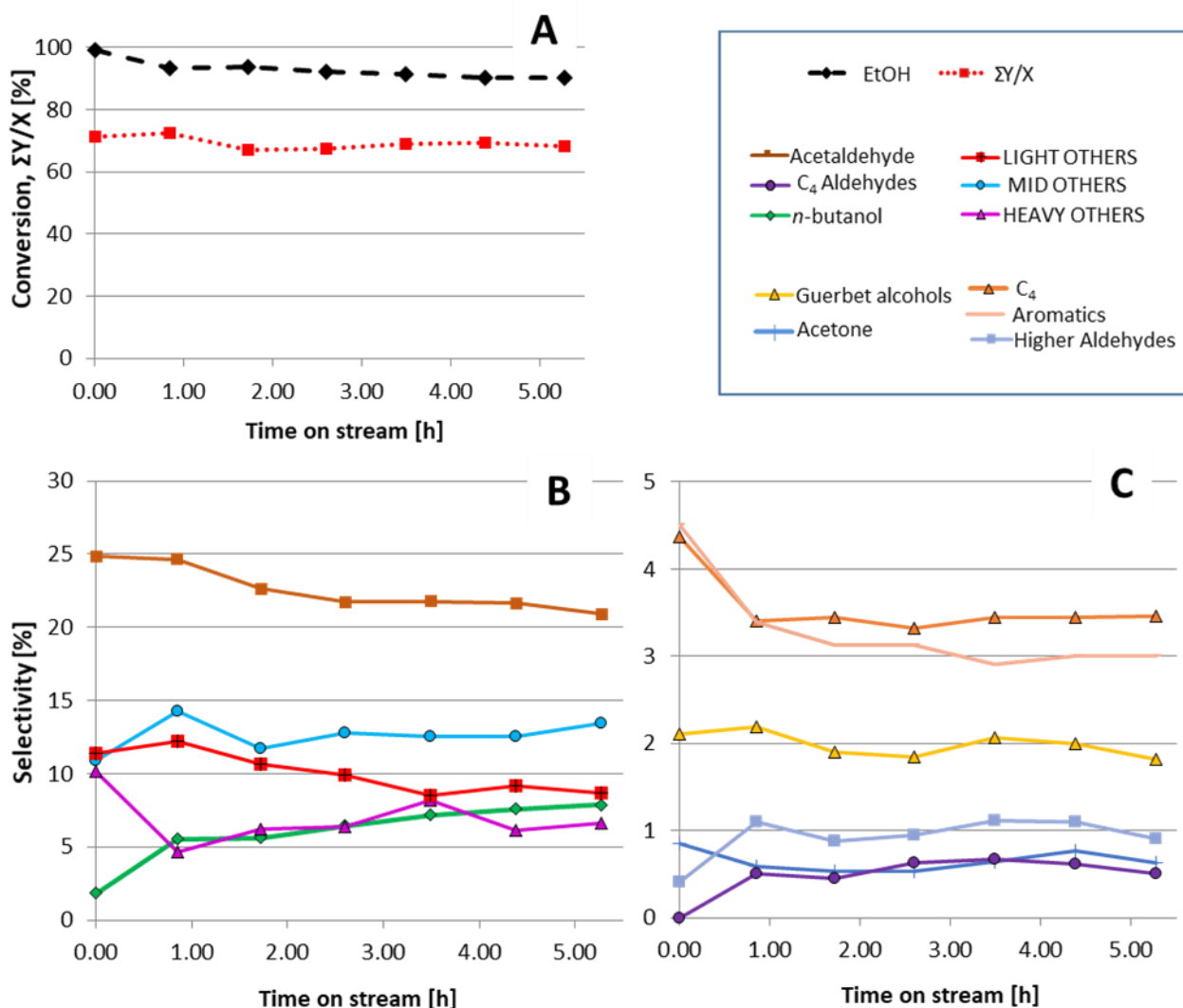
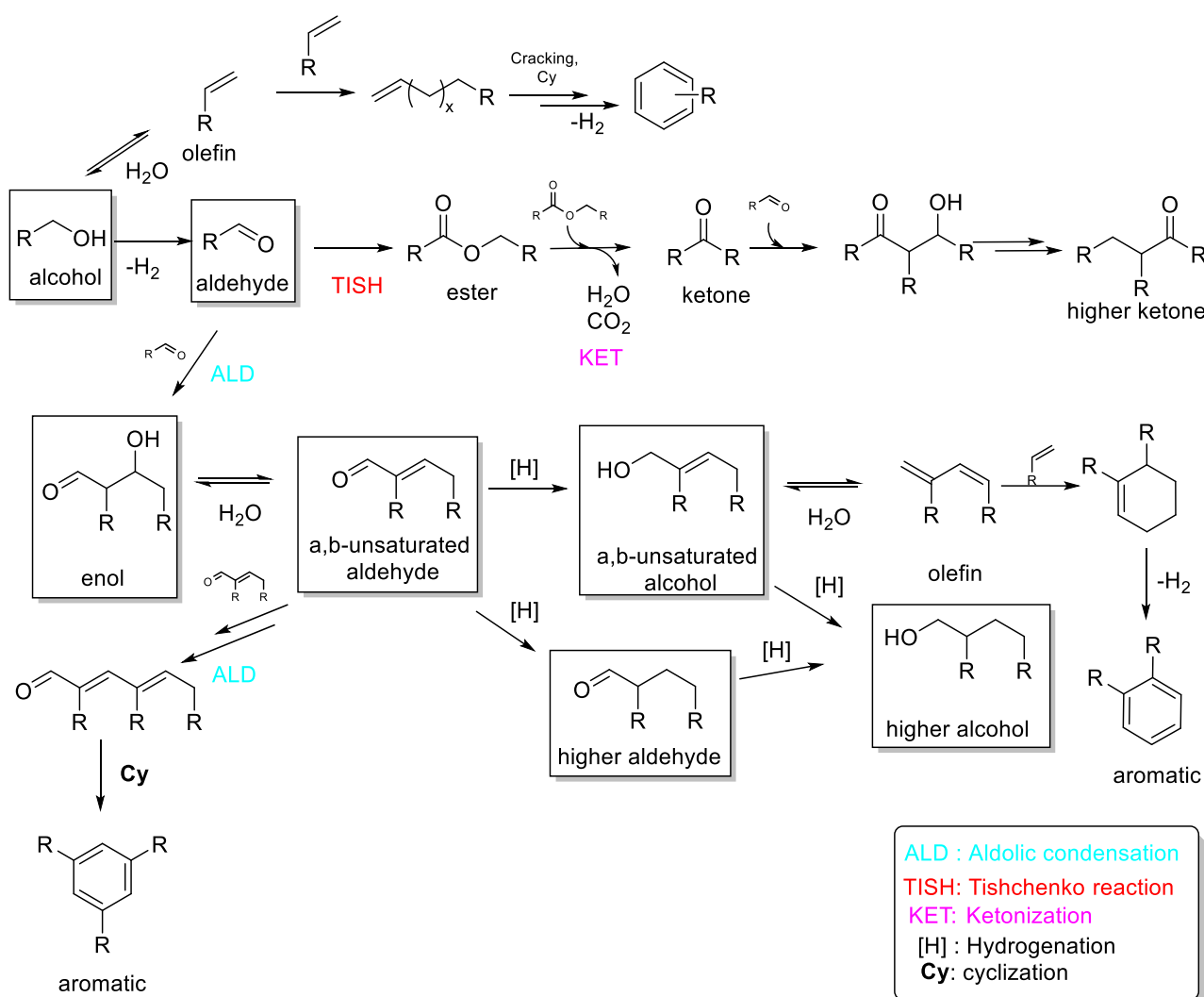


Figure 4.21 Catalytic results obtained in the Ethanol conversion over Sr-HAP. Reaction conditions: EtOH 5% v/v in He, $T = 450^\circ\text{C}$, $P = 1\text{ atm}$, $\tau = 0.6\text{ s}$. "C4": butadiene, 1-butene, 2-butene-cis and 2-butene-trans; "C1": methane and carbon dioxide; "C4 aldehydes": butyraldehyde and crotonaldehyde; "Guerbet alcohols": hexanol, 2-ethyl-butanol, octanol, 2-ethyl-hexanol, decanol. Higher aldehydes: hexanal, decanal; Aromatics: toluene, o-xylene; "Light, Mid and Heavy Others": other unknown products gathered by retention times in the chromatogram. **A)** Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. **B)** Selectivity to main reaction products as a function of the time on stream. **C)** Minor products selectivity as a function of the time on stream.

Thank to offline sampling and injection into the GC-MS system, some of the other products were identified (Figure 4.22-4.23). Higher aldehydes (as 2-ethylbutanal, hexanal, decanal) were detected, which were formed through the consecutive Guerbet reaction pathway. Furthermore, higher dienes as hexadiene and 2,4-octadiene were recognized, probably formed through a Lebedev-type

mechanism.²⁶⁸ Some ketones were noticed (pentanone, heptanone), the formation of which can be related to a sequential reactions²⁶³, as showed in Scheme1. A significant amount of alkyl substituted aromatics and cyclic compounds (such as xylene, ethyl-benzene, benzene-1,2-diethyl, butyl benzene and ciclohexane-4-methyl) was noticed. The formation of aromatic compounds can arise from three different pathways: i) ethylene aromatization;²⁶⁶ ii) radical or Diels-Alder type reactions between conjugated dienes compounds (such as butadiene) and a dienophile (such as ethylene) and subsequent dehydrogenation of the cyclic compounds;²⁶⁹ iii) the cyclization reactions of conjugated C=C bonds of higher aldehydes.⁵⁹

Scheme 2 depicts the possible reactions pathways that can happen over the Ca-HAP and Sr-HAP catalysts leading to the formation of the complex reaction mixture observed.



Scheme 2. Reaction pathway for the formation of the main products detected into the reaction mixture. The Guerbet-derived products are framed.

From off-line GC-MS analysis, it was possible to extrapolate the percentage composition of the gaseous reaction mixture, sampled at around 4.5 h of time on stream. Figure 4.22 and Figure 4.23

show the compounds present in the highest amount detected by analysing the gaseous out-flowing reaction mixture using both Ca-HAP and Sr-HAP as heterogeneous catalysts. Although the latter catalytic system seemed promising for the production of higher molecules (such as decanal), the production of aromatic compounds seemed to be predominant, around the 33%.

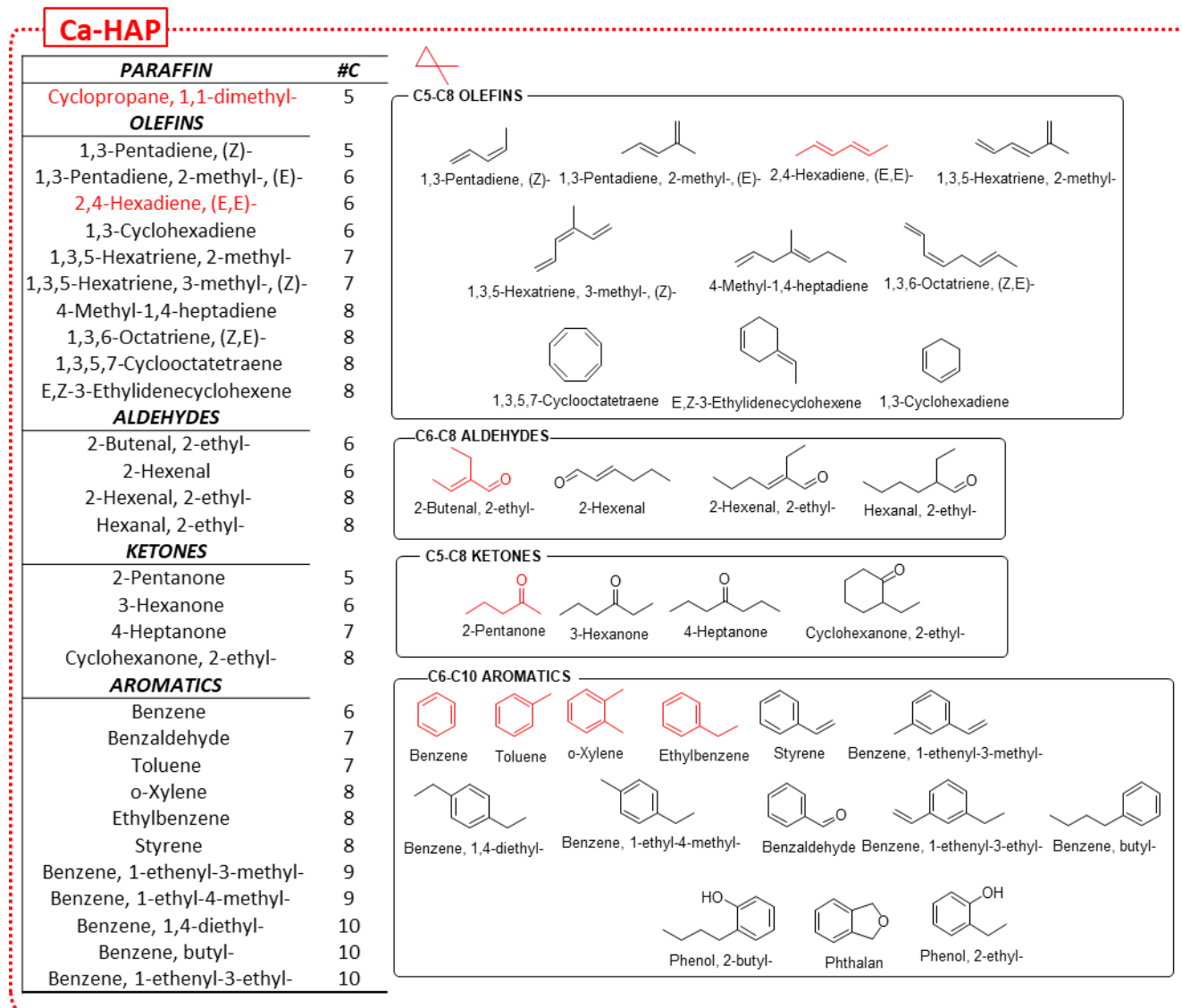


Figure 4.22 Compounds detected by manual injection into the GC-MS analysis system of a reaction-mixture sample obtained for the ethanol gas-phase conversion over Ca-HAP catalyst (in red are highlighted the prevalent ones).

Sr-HAP

PARAFFIN	#C
Cyclopropane, 1,1-dimethyl-	5
OLEFINS	
1,3-Pentadiene, (Z)-	5
2,4-Hexadiene, (E,E)-	6
1,3-Cyclopentadiene, 1-methyl-	6
1,3-Cyclohexadiene	6
1,3,5-Heptatriene, (E,E)-	7
1,3-Cycloheptadiene	7
1,3,6-Heptatriene, 5-methyl-, (E)-	8
E,Z-3-Ethylidenecyclohexene	8
1,3,6-Octatriene, (Z,E)-	8
1,3,5,7-Cyclooctatetraene	8
ALDEHYDES	
2-Butenal, 2-ethyl-	6
Butanal, 2-ethyl-	6
2-Hexenal	6
2-Hexenal, 2-ethyl-	8
Hexanal, 2-ethyl-	8
Decanal	10
2-Octenal, 2-butyl-	12
KETONES	
2-Pentanone	5
3-Hexanone	6
4-Heptanone	7
Cyclohexanone, 2-ethyl-	8
4-Nonanone	9
AROMATICS	
Benzene	6
Toluene	7
o-Xylene	8
Ethylbenzene	8
Styrene	8
Phenol, 2-ethyl-	8
Benzaldehyde, 2-methyl-	8
Benzene, 1-ethenyl-3-methyl-	9
Benzene, butyl-	10
Benzene, (2-methyl-1-propenyl)-	10
Phenol, 2-methyl-5-(1-methylethyl)	10
Benzene, 1,4-diethyl-	10

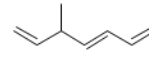
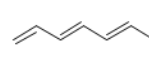
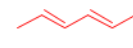
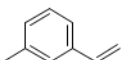
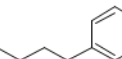
**C5-C8 OLEFINS****C6-C12 OLEFINS****C5-C9 KETONES****C6-C10 AROMATICS**

Figure 4.23 Compounds detected by manual injection into the GC-MS analysis system of a reaction mixture sample obtained for the ethanol gas-phase reaction over Sr-HAP catalyst (in red are highlighted the prevalent ones).

4.1.2.3.2.1 *Effect of ethanol feeding concentration*

The presence of longer chain compounds, such as decanal, into the reaction mixture while performing the ethanol gas-phase conversion over the Sr-HAP catalyst at 450°C and 0.6 s of contact time has been noticed. Therefore, attempts have been made in enhancing the formation of higher products by consecutive reactions by studying the effect of reaction parameters such as the contact time and the starting concentration of ethanol.

The first strategy adopted was based on increasing the ethanol feeding concentration in order to try to enhance the production of the heavy other products, i.e. by increasing the density of ethanol and/or acetaldehyde over the catalyst surface thus promoting the condensations reactions. The effect of the ethanol feeding concentration was studied in the range of 5, 10 and 20% v/v in He over the Sr-HAP catalyst. The obtained results are summarised from Figure 4.24 until Figure 4.31.

By feeding a 10% v/v ethanol in helium mixture at 450°C and 0.6 s of contact time, both conversion of ethanol and the product carbon balance fluctuated around 85% (Figure 4.24). Even in this case the main product obtained was the ethanol dehydrogenation product, acetaldehyde, with a selectivity value of around 25%. It can be noticed an increasing trend of the selectivity of the mid and heavy “other” compounds with the time on stream. Since they gather many different compounds, it is not easy to relate this trend to a specific product but it is likely that they encompassed intermediate products that initially were converted to consecutive products. With the time on stream the catalyst partially deactivated and the selectivity of those intermediate other products increased.

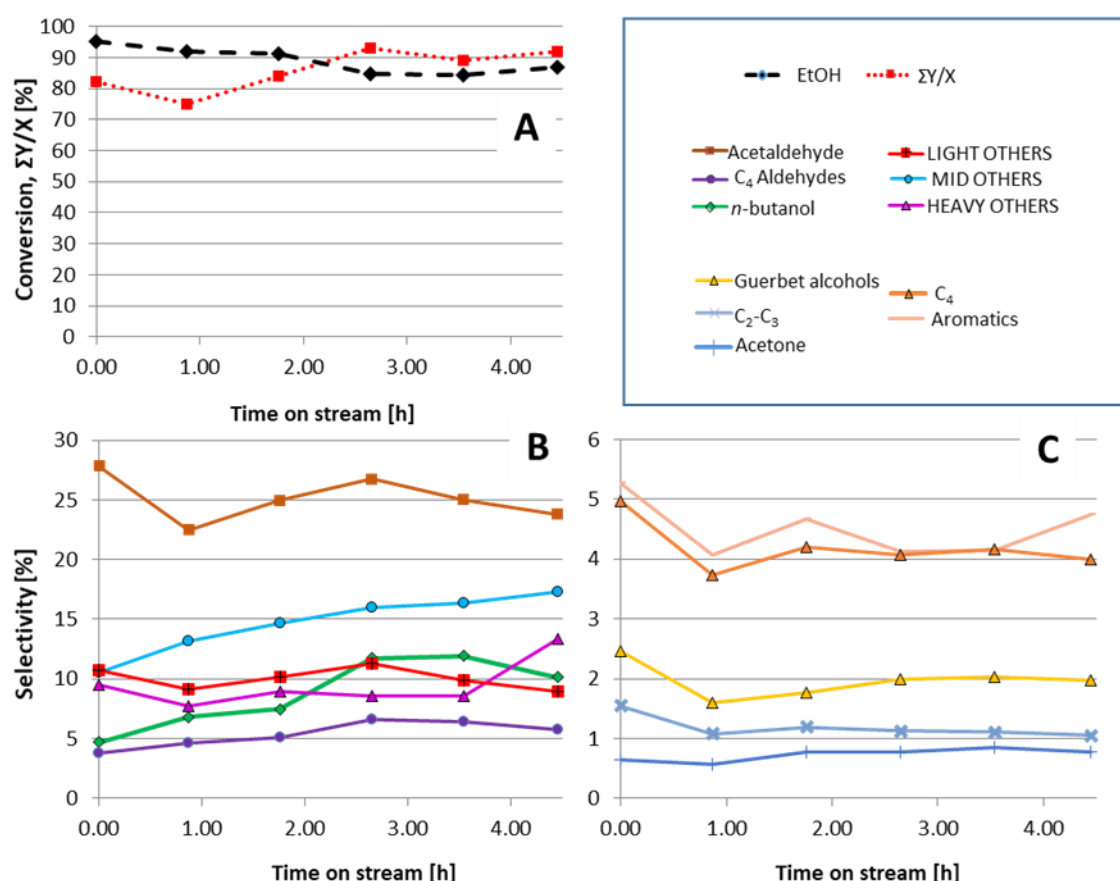


Figure 4.24 Catalytic results obtained in the Ethanol conversion over Sr-HAP. Reaction conditions: EtOH 10% v/v in He, $T = 450^\circ\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.6 \text{ s}$. "C4": butadiene, 1-butene, 2-butene-cis and 2-butene-trans; "C1": carbon dioxide; "C4 aldehydes": butyraldehyde and crotonaldehyde; "Guerbet alcohols": hexanol, 2-ethyl-butanol, octanol, 2-ethyl-hexanol, decanol; "Aromatics": toluene, o-xylene, ethyl-benzene, butyl benzene; "Light, Mid and Heavy Others": other unknown products gathered by retention times in the chromatogram. **A)** Ethanol conversion and product carbon balance $\Sigma Y/X$ as a function of the time on stream. **B)** Main products selectivity as a function of the time on stream. **C)** Minor products selectivity as a function of the time on stream.

Figure 4.25 shows the results obtained while feeding a 20% v/v ethanol in helium mixture. Both the conversion and the product carbon balance seemed to reach a steady value of about 80%. Even in this case, the main product was still acetaldehyde of which the selectivity profiles showed a similar trend over the time on stream, fluctuating around a value of 25%. Both the selectivity of light and mid others reached almost the 8% while the one of the heavy products was near the 5%. In this case, even the so-called C4 alcohols, that are unsaturated alcohols intermediate products, were detectable probably due to the higher starting concentration of the reagent.

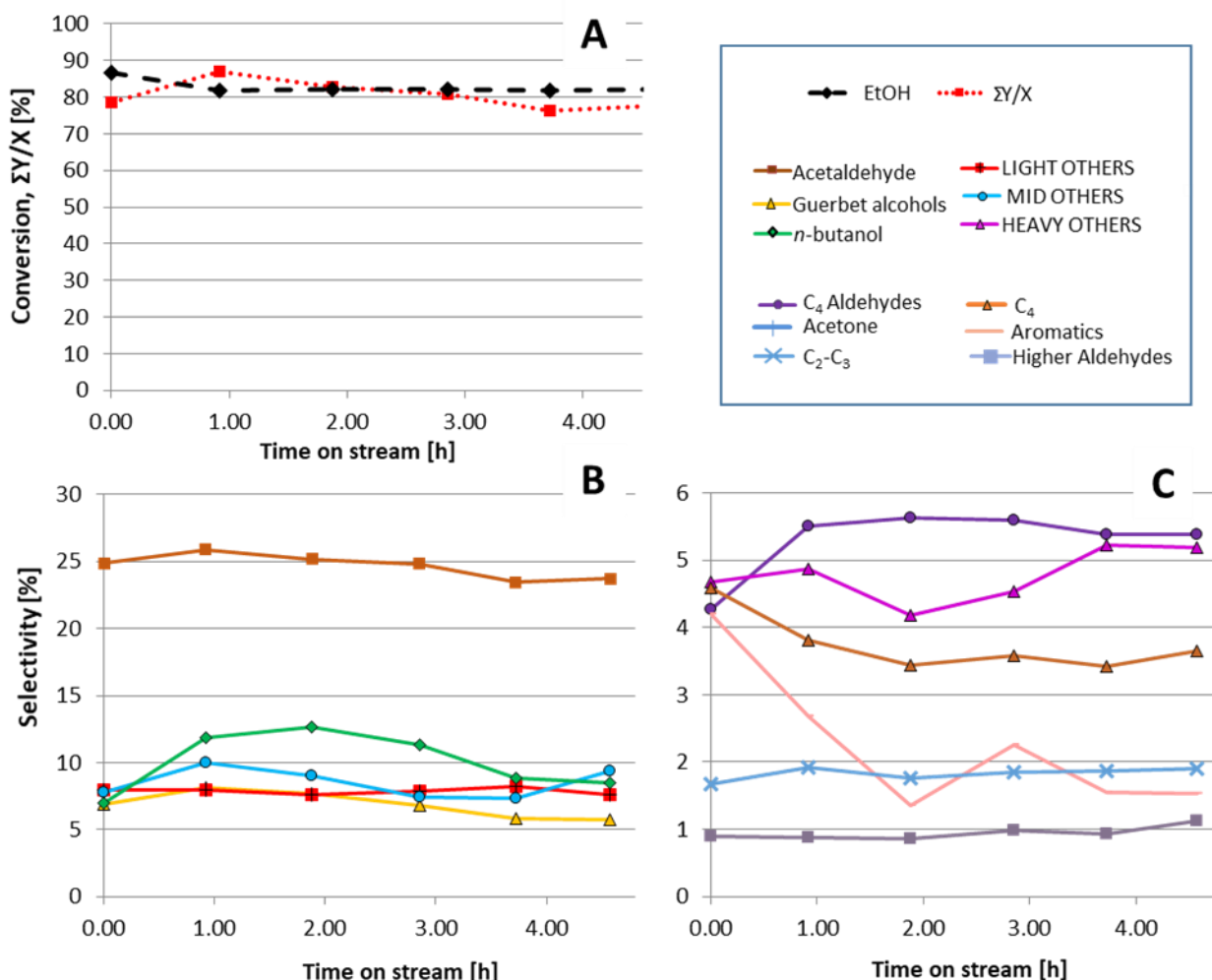


Figure 4.25 Catalytic results obtained in the Ethanol conversion over Sr-HAP. Reaction conditions: EtOH 20% v/v in He, $T = 450^\circ\text{C}$, $P = 1\text{ atm}$, $\tau = 0.6\text{ s}$. "C4": butadiene, 1-butene, 2-butene-cis and 2-butene-trans; "C1": carbon dioxide; "C4 aldehydes": butyraldehyde and crotonaldehyde; "Guerbet alcohols": hexanol, 2-ethyl-butanol, octanol, 2-ethyl-hexanol; "Higher aldehydes": hexanal, decanal; "Aromatics": toluene, o-xylene, ethyl-benzene, butyl benzene; "C4 alcohols": crotyl alcohol, 3-buten-1-ol; "Light, Mid and Heavy Others": other unknown products gathered by retention times in the chromatogram.

Figure 4.26 and Figure 4.27 depict the trends of the conversion of ethanol, product carbon balance and the selectivity of the other products as a function of the feeding concentration of ethanol. The results showed correspond to the average value obtained after reaching the steady state, after around 1,5 h. With increasing feeding concentration of ethanol, its conversion decreased as expected, while the product carbon balance presented a maximum with a feeding mixture of 10% ethanol in helium. Since the product carbon balance was calculated considering even the yields of the "others" products, that are quantified with an average response factor, it is possible that this difference depends on a defective quantification. Anyway, by feeding ethanol with a concentration of 10% v/v in He, the highest value of the selectivity of medium (C_6-C_{10}) and heavy ($C_{10}-C_{16}$) other products was reached: 16%, and 8.5%, respectively. Figure 4.27 highlights the results obtained with an EtOH concentration of 10 % v/v by grouping the "Mid" and "Heavy" other products, their

cumulative selectivity in those conditions reached the 25%. Indeed, higher molecules were detected through offline injections into the GC-MS system. Nevertheless, the nature of the compounds detected was mainly aromatic.

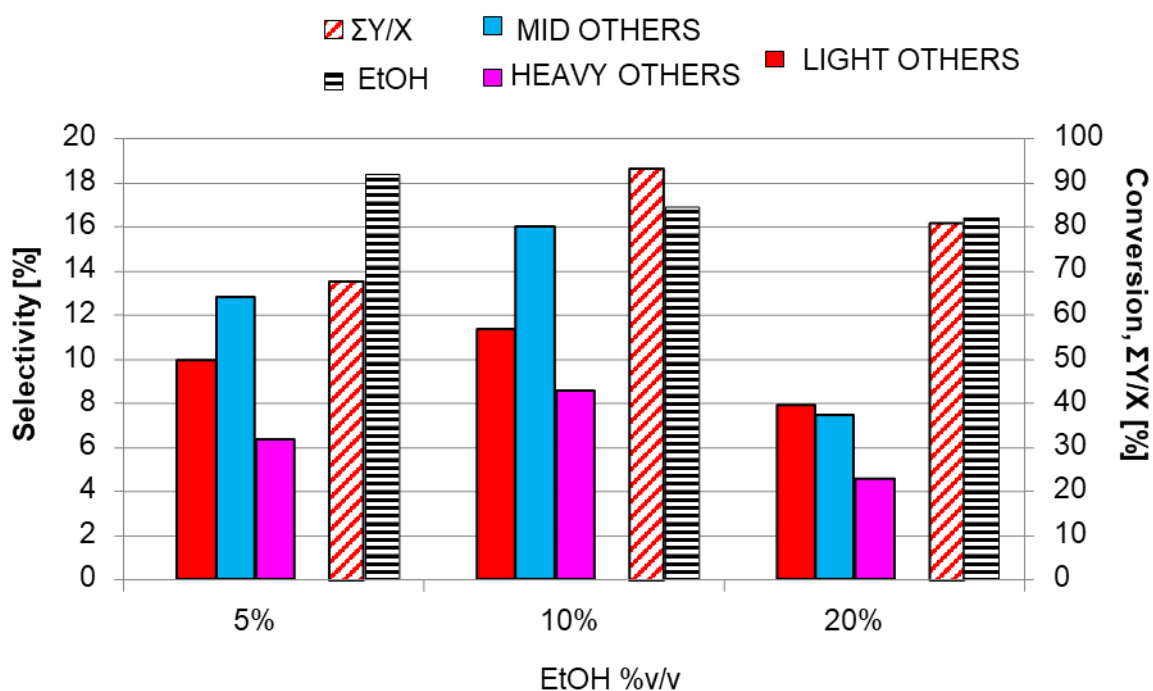


Figure 4.26 Effect of the ethanol feeding concentration over the ethanol conversion and the product carbon balance, expressed as the sum of the products yields divided by the ethanol conversion. Catalytic results obtained in the Ethanol conversion over Sr HAP. Reaction conditions: EtOH 5-10-20 % v/v in He, $T = 450^\circ\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.6 \text{ s}$.

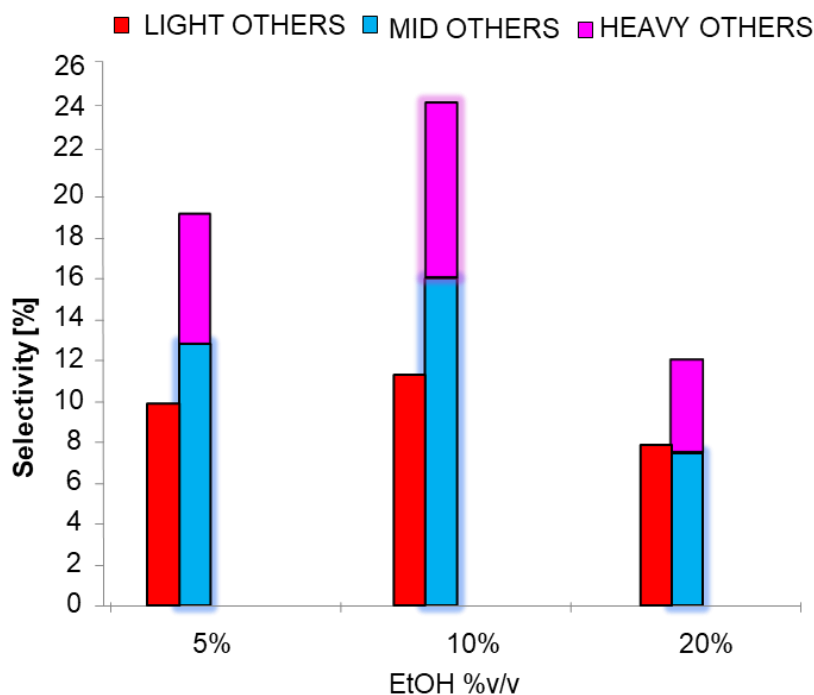


Figure 4.27 Effect of the ethanol feeding concentration over the selectivity of the so-called others products. Catalytic results obtained in the Ethanol conversion over Sr-HAP. Reaction conditions: EtOH 5-10-20 % v/v in He, $T = 450^{\circ}\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.6 \text{ s}$.

4.1.2.3.2.2 Effect of the contact time

Another way to favour the formation of consecutive reactions, thus fostering the production of heavier compounds, could be represented by the increase of the contact time of the reactants over the catalyst. Indeed, by increasing the contact time it could be possible to promote the condensation reactions of even the higher aldehydes produced from ethanol, finally favouring the formation of products characterised by a longer carbon chain.

In order to study the effect of the contact time (τ), the feeding flows of both ethanol and helium were adjusted so that the 5% v/v of ethanol was maintained and the quantity of the catalyst charged was modified obtaining a contact time doubled compared to the previous tests (new τ : 1.2 s). Figure 4.28 depicts the results obtained in those last conditions.

Complete conversion of ethanol was reached, so rising the contact time led to an increase of the ethanol conversion, as expected (a comparison of the results obtained by varying the contact time is showed in Figure 4.29). The product carbon balance value was around 65% and wasn't affected by the higher contact time. Regarding the products distribution, again the main product was acetaldehyde, even if in this case its selectivity was lower than in the other cases: it fluctuated around 20% while in the previous cases it fluctuated around 25%. In those conditions the performances seemed almost stable with the time on stream, except for the selectivity of the medium others that

increased from 4% to 8.5% after 1.6 h of time on stream. This trend can be related to the artificial response factor that could underestimate some products and overestimate other products.

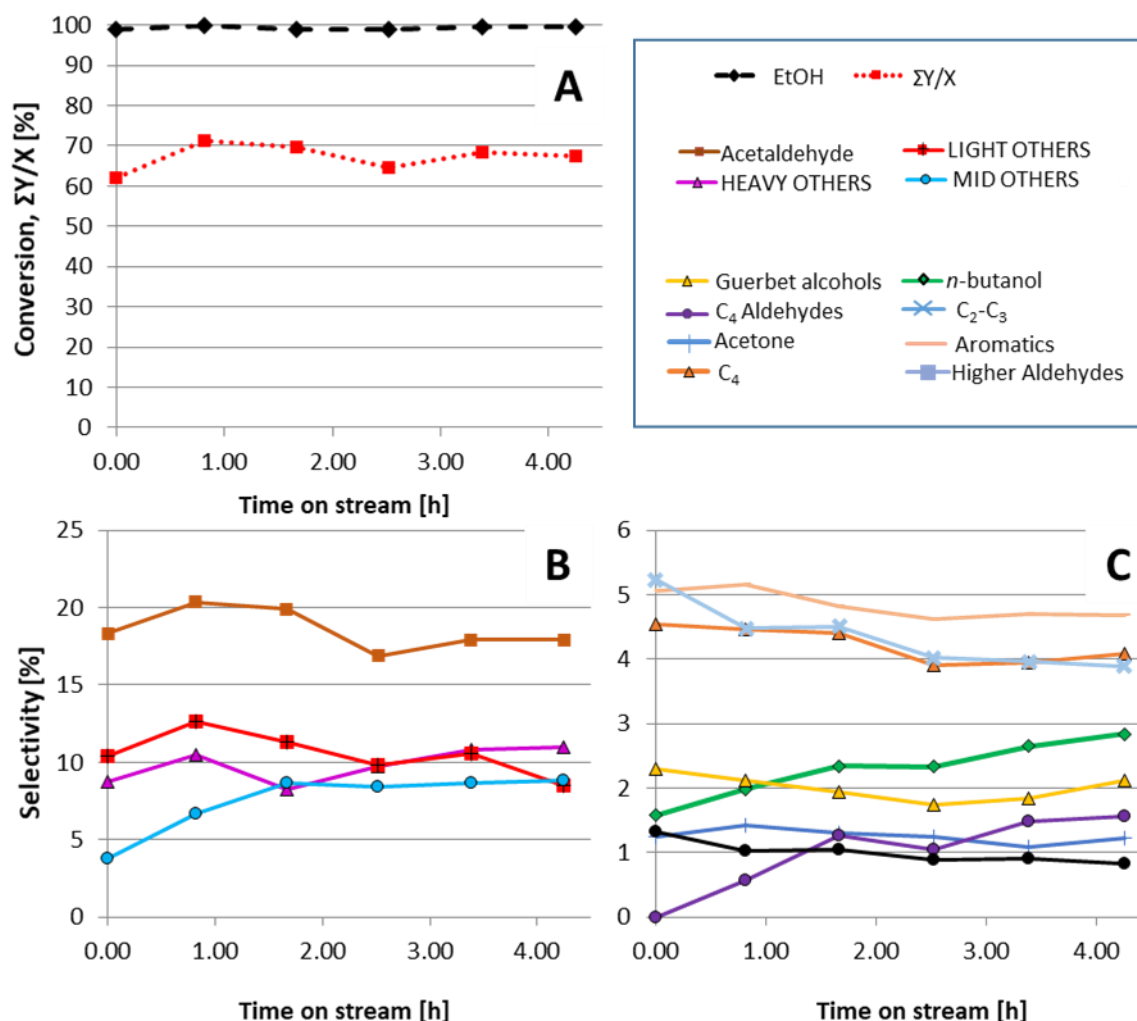


Figure 4.28 Catalytic results obtained in the Ethanol conversion over Sr-HAP. Reaction conditions: EtOH 5% v/v in He, $T = 450^\circ\text{C}$, $P = 1\text{ atm}$, $\tau = 1.2\text{ s}$. "C4": butadiene, 1-butene, 2-butene-cis and 2-butene-trans; "C4 aldehydes": butyraldehyde and crotonaldehyde; "Guertbet alcohols": hexanol, 2-ethyl-butanol, octanol, 2-ethyl-hexanol,, decanol; "Aromatics": toluene, o-xylene; "Light, Mid and Heavy Others": other unknown products gathered by retention times in the chromatogram.

The effect of the contact time over the selectivity in the other products can be easily noticed in Figure 4.29: by doubling the contact time the selectivity of the "heavy" products increased from 6 to almost 10%; probably due to the conversion of intermediate products gathered in the "medium others" group the selectivity of which decreased from almost 12% to 8.5% with increasing contact time.

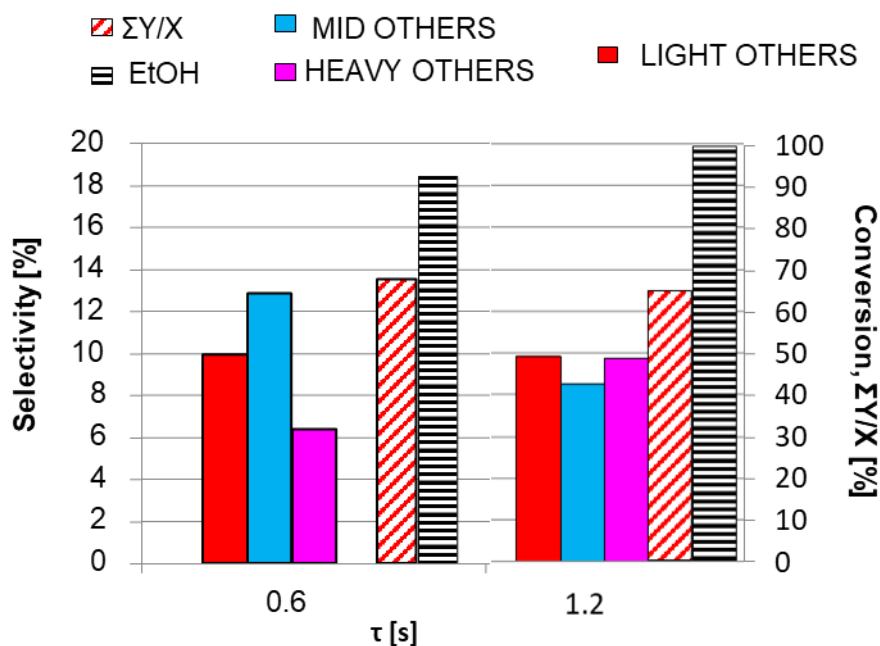


Figure 4.29 Effect of the contact time over the ethanol conversion, the product carbon balance ($\Sigma Y/X$) and the selectivity of the other reaction products. Catalytic results obtained in the Ethanol conversion over Sr-HAP. Reaction conditions: EtOH 5 % v/v in He, $T = 450^\circ\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.6 - 1.2 \text{ s}$.

It has been observed that by feeding EtOH with a concentration of 10 v/v% and by working with a contact time of 1.2 s, the formation of heavy products is favoured. Accordingly, a catalytic test combining those conditions has been performed, i.e., by feeding ethanol, 10 %v/v in He, over Sr-HAP at 450°C and with 1.2 s as contact time. The catalytic results are depicted in Figure 4.30 and Figure 4.31.

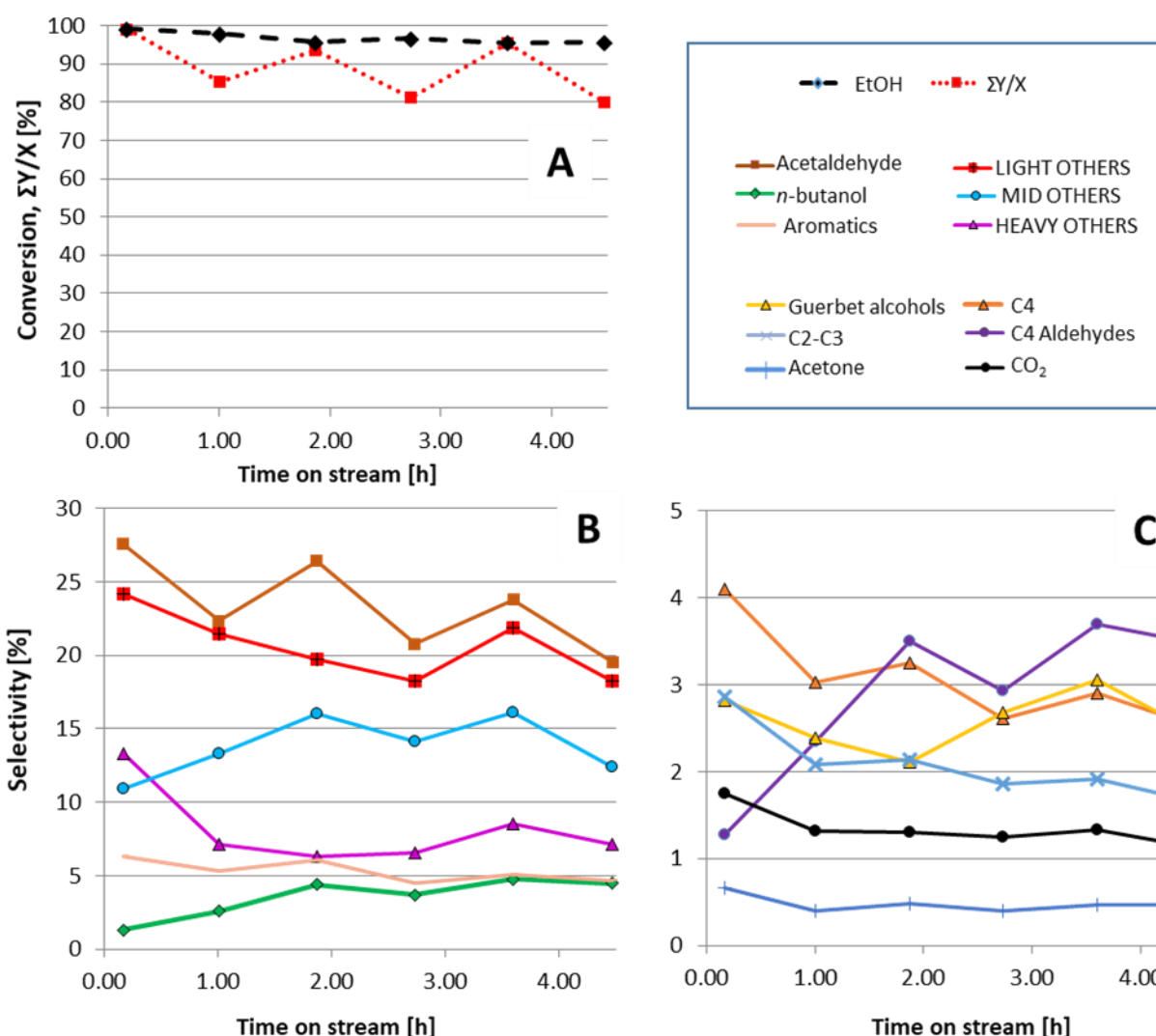


Figure 4.30 Catalytic results obtained in the Ethanol conversion over Sr-HAP. Reaction conditions: EtOH 10% v/v in He, $T = 450^\circ\text{C}$, $P = 1\text{ atm}$, $\tau = 1.2\text{ s}$. "C2-C3": ethylene, ethane, propylene; "C4": butadiene, 1-butene, 2-butene-cis and 2-butene-trans; "C4 aldehydes": butyraldehyde and crotonaldehyde; "Guerbet alcohols": hexanol, 2-ethyl-butanol, octanol, 2-ethyl-hexanol, decanol; "Aromatics": toluene, o-xylene; "Light, Mid and Heavy Others": other unknown products gathered by retention times in the chromatogram.

Unexpected results have been obtained while performing the reaction with the reaction conditions just described. Indeed, instead of favouring the formation of heavier products by increasing the contact time and the ethanol feeding concentration, those mentioned conditions led to an increase of the lighter part of the other unknown products, of which the selectivity raised from 11 to 19% by doubling the contact time (Figure 4.31). At the same time, the average formation of the heaviest part of them seemed decreased by rising the contact time. Nevertheless, the trends of the products selectivity with the time on stream could suggest a rapid partial deactivation of the catalyst. For instance, an abrupt decrease from 13 to 7% in the first hour of time on stream of the "heavy other" products selectivity can be noticed, the formation of which could be related to the "medium" ones as intermediate since their selectivity simultaneously increased. (Figure 4.30).

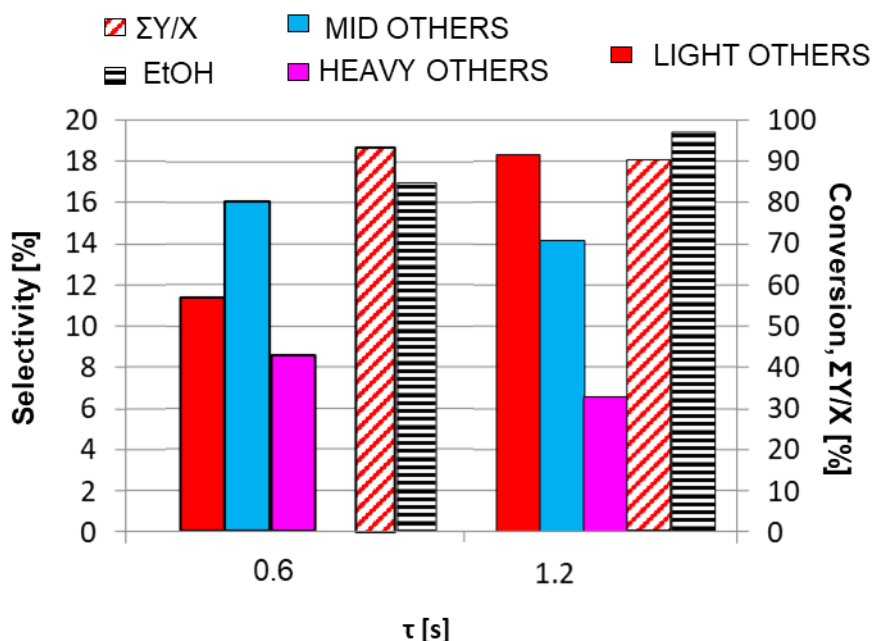


Figure 4.31 Effect of the contact time over the ethanol conversion, the product carbon balance ($\Sigma Y/X$) and the selectivity of the other products. Catalytic results obtained in the Ethanol conversion over Sr-HAP. Reaction conditions: EtOH 10 % v/v in He, $T = 450^\circ\text{C}$, $P = 1 \text{ atm}$, $\tau = 0.6 - 1.2 \text{ s}$.

Furthermore, a general decreasing trend of the product carbon balance with the time on stream can be noticed. It could be possible that part of the products could have been condensed into the lines connecting the reactor with the analytic system, affecting the overall catalytic quantification results. Since the heaviest products should be characterized by higher boiling point, an optimization of the reaction system has been performed, in order to better collect and analyse the heaviest part of the product mixture. Indeed, by adding a condenser into the line connecting the bottom of the down-flow reactor, before the on-line GC system, it could be possible to collect by condensation the heaviest part of the reaction products. Figure 4.32 depicts the reaction system modification, the condenser has been highlighted. In addition, for speeding up the condensation, the possibility of putting the condenser in an ice-bath has been considered.

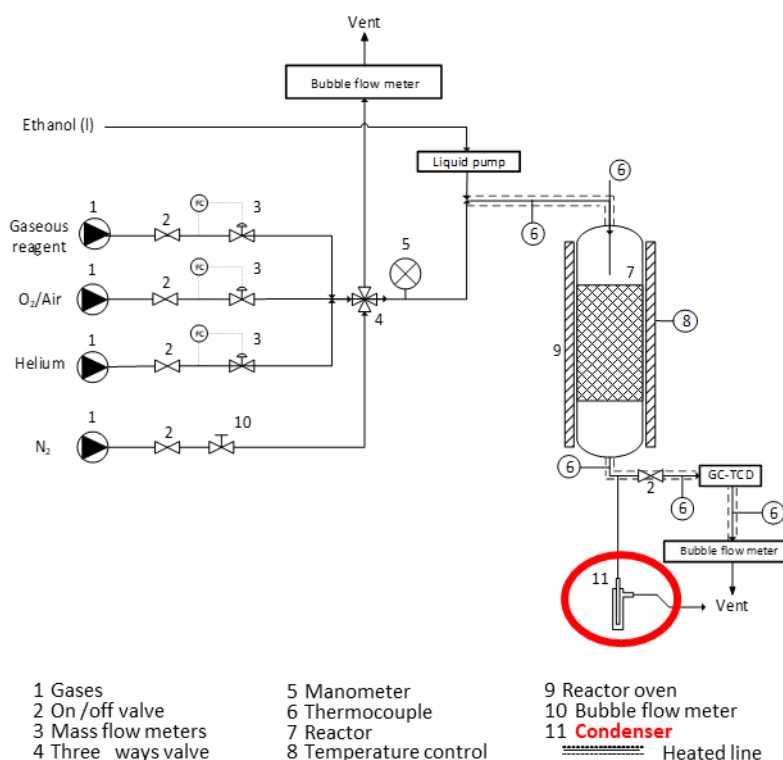


Figure 4.32 Reaction system modified, in red is highlighted the condenser.

4.1.2.4 Summary

The ion-exchanged hydroxyapatite catalysts have been tested for the ethanol gas-phase conversion at 450°C, 1 atm and 0.6 s as contact time. In summary, both Fe-HAP and Cu-HAP, showed a greater catalytic activity compared to Ca-HAP, leading to higher conversion of ethanol. However, the increased acidity of the catalysts led to the preferential formation of ethylene (and traces of butadiene) while the redox properties enhanced the formation of acetaldehyde but without promoting the desired condensation reactions. On the contrary, the Sr-HAP catalyst led to the formation of a wide distribution of compounds in the same reaction conditions, leading to formation to heavy products with longer carbon chain (up to C₁₂, Figure 4.23). Hence, the catalytic activity of this material has been investigated in depth.

In particular, with the aim of enhancing the production of compounds characterised by a longer carbon chain (i.e. >C₆), two different approaches have been considered. Firstly, the effect of increasing contact time, then the increasing ethanol feeding concentration have been evaluated. The best reaction conditions, in terms of selectivity of hydrocarbons mixture, have been located as follows: a feeding concentration of EtOH 10% v/v in He (0.6 s as contact time and a reaction temperature of 450°C). In such conditions, an ethanol conversion of ~85% has been obtained, with a product carbon balance of ~92%. The cumulative selectivity of medium (average C₆-C₁₀) and heavy (average C₁₀-C₁₄) other products at those condition was 25%, while the one of higher Guerbet

alcohols (C_6 - C_{12})~2%, C_4 compounds (alkene and aldehydes) ~9% and aromatics (C_7 - C_{10}) around 4%. By summing the selectivity of the products with a carbon chain length $>C_6$, an overall selectivity of ~31% has been obtained, corresponding to a ~26% of cumulative yield. The cumulative selectivity of lighter products (i.e., C_4 - C_6) was 29% and can be calculated considering the selectivity of *n*-butanol (~10%), the one of C_4 quantified products (i.e., olefins and aldehydes; ~9%) and the one of light other products (average C_3 - C_6 ; 10%), corresponding to a cumulative yield of ~25%.

Thus, we managed to obtain a mixture of hydrocarbons of $>C_4$ carbon chain with a cumulative yield of 50% and ethanol conversion of 85% (i.e., 60% total selectivity). The main issues were the high selectivity of acetaldehyde, that was obtained as major product (i.e., 25% of selectivity) and the high percentage of total aromatic compounds produced (34%). Nevertheless, the obtained mixture had the composition suitable to be used as gasoline (C_4 - C_{12}), in which an higher aromatic percentage is accepted (35%).¹⁰⁶

Nevertheless, with the perspective to produce a more attractive hydrocarbon mixture with composition resembling the one of jet fuel, even though Sr-HAP was active and pretty stable in the reaction conditions, the composition of the products obtained was not optimal since the production of aromatic compounds was predominant (should be below 25% in Jet Fuel composition¹⁰⁶). Indeed, by an off-line sampling and GC-MS analysis of the outlet gaseous stream it was noticed the presence of aromatics compounds in high amount. Table 4.4 reports a summary of the percentage of the aromatic compounds found in the outlet gaseous stream of the catalytic tests performed over Sr-HAP (i.e. by varying both the contact time and the inlet ethanol concentration). The amount of aromatic in the stream (reported in Table 4.4), were calculated through the peaks area obtained into the GC-MS chromatograms.

Table 4.4 Concentration of aromatic compounds in the reaction product mixture, by means of the peaks area of the GC-MS chromatograms ($A_{AROMATICS}/A_{TOTAL} \cdot 100$ [%]).

τ [s]	% EtOH in He [v/v]		
	5	10	20
0.6	28%	34%	28%
1.2	52%	45%	-

4.1.3 CONCLUSIONS

In this work, a commercial Ca-HAP has been employed and then modified (by means on in-exchange method) to study the ethanol gas-phase conversion through the Guerbet route while trying to favouring consecutive condensation reactions and obtaining longer carbon chain compounds with

potential applications as bio-fuels. To do so, attempts to optimize both the reaction parameters and the catalyst characteristics have been carried out, observing a high dependence of the overall composition of the reaction products on the reaction temperature. A reasonable balance between catalytic activity and product carbon balance has been achieved by working at 450°C and 0.6 s as contact time.

Then, Ca-HAP has been modified through ion-exchange method. The transition metals (Cu and Fe) exchanged hydroxyapatites mainly performed as acid catalysts, yielding preferentially the dehydration product of ethanol, ethylene. On the other hand, Sr-HAP lead to the production of a complex reaction mixture containing compounds different in nature and carbon chain lengths. Indeed, the mechanism of the ethanol conversion producing the hydrocarbons of different nature observed is pretty complex, involving a net of parallel, consecutive and cross reactions.

Accordingly, the Sr-HAP catalyst has been chosen to gain insight in the formation of the heaviest products. It has been observed that the product distributions is affected from the contact time and the ethanol feeding concentration, finding the best condition by working with an EtOH concentration of 10% in He and a contact time of 0.6s. In such condition it was obtained a total yield of 50% of hydrocarbons with carbon length in the range C₄-C₁₄ that could resemble the required composition of the conventional gasoline. Notwithstanding, in general the outlet streams of the product was characterized by a 30 to 45% of aromatic compounds, depending on the reaction conditions. In order to be suitable for jet-fuel, this value should be lower than 25%.

Nevertheless, the catalytic tests performed enabled to set the reaction system with the perspective of deepen the study of ethanol conversion into heavier hydrocarbon. Indeed, with the addition of a condenser in which collect the heavy products to be analysed off-line, let to better analyse the mixture composition, avoiding operational troubles.

Considering the high selectivity of acetaldehyde, always obtained as major product, and the beneficial effect observed of the decreased acidity/basicity ratio related to the Sr-exchanged HAP, it would be interesting to further modify the catalytic system in this regard.

Angelici et al. observed that the state in which copper is present on the catalyst is important not only to catalyse the dehydrogenation step, but also to affect the acid/base properties of the catalyst and favouring the consecutive aldol-condensation step, which is supposed to become the rate limiting step after copper addition.^{148,270} The way in which copper is present on the surface is strictly related to the method employed to add it on the catalyst. Consequently, changing the way by which adding a redox element (i.e., a transition metal, Fe or Cu) could be helpful in regard to favouring both the formation and consecutive condensation of acetaldehyde. Herein, Fe and Cu have been added to HAP by ion-exchange method, it could be interesting to investigate their addition by other synthesis methods (e.g., incipient wetness impregnation, wet impregnation).

When HAP exposes fewer basic sites, the catalytic activity and selectivity toward *n*-butanol decreases⁵⁹, but at the same time, acid sites are necessary to stabilize intermediate species during the aldol condensation of acetaldehyde as well as catalyse dehydration reactions.⁵⁸ Indeed, it is well known that a multifunctional catalyst is needed in order to selectively catalyse the Guerbet reaction. By taking this in mind, it could be interesting to further exploit the capacity of the crystal lattice of the HAP to undergo big distortion by incorporating ions, both cations and anions with different sizes²⁷¹, and try to synthesize other hydroxyapatite-based materials modified with diverse ions and evaluate its performance into the optimized reaction system, with particular regard to minimize the aromatic compounds formation, that could be attributable to acid-catalysed reactions²⁶⁶. Since the Sr-exchanged exhibited the most promising performance (i.e., C-C bonds formation) in our reaction system and it was the one characterized by the lowest acidity/basicity ratio (i.e., A/B ratio: 9.4, as reported in Table 4.2), it could be interesting to further modify the HAP by increasing its basicity (i.e. lowering the A/B ratio).

4.2 Ethanol transformation over zirconium oxide - based catalysts – ITQ-UPV

During the research period spent in the laboratories of the of the “Instituto de Tecnología Química” (ITQ) of the “Universitat Politecnica de Valencia” (UPV), part of the work focused on the synthesis and characterization of zirconia-based catalysts. It is well-known that pure zirconia (ZrO_2) at atmospheric pressure exhibits in three different polymorphs (i.e., monoclinic, cubic and tetragonal) and that the monoclinic one is the thermodynamically stable. Depending upon the preparation method, the final crystal structure of ZrO_2 varies and it affects its surface properties and related catalytic features. In the present work, various zirconia samples have been prepared following different procedures (i.e., precipitation and hydrothermal synthesis, variation of pH and nature of the base used, metal dopant addition) studying the effects of various synthetics parameters on the resulting zirconium oxide through several characterization techniques. Then, their catalytic activity in the ethanol gas-phase transformation have been evaluated into a bench scale continuous flow quartz reactor using as feeding a mixture of 5% Ethanol in N_2 .

4.2.1 Nomenclature

Zirconium oxide samples have been synthesized by hydrothermal or precipitation method and with or without the addition of a metal dopant (Ti or Y), in order to have an overview on the influence of this synthetic parameters on the resulting properties of the material. Then, the structural, textural and morphological properties of the synthesized catalysts will be correlated to their activity for the ethanol gas-phase conversion.

In order to facilitate the identification of the synthesized materials, a specific nomenclature has been designed. In the following scheme, the utilized nomenclature is explained, finally, an example is given.

MB-pH-DZO

M: synthesis methodology, which can be **P**recipitation or **H**ydrothermal.

B: base used in the synthesis. Could be **S**odium hydroxide (5 M solution), **A**mmonium hydroxide solution (25%w), or solid **U**rea.

The **pH** value is always indicated with its related figure since it is assumed to be a crucial parameter during the synthesis.

D: dopant element, which can be **T** for Ti, and **Y** for yttrium.

ZO is common for all the samples and indicates the ZrO_2 .

For example: *HS-13-5TZO* is related to a catalyst synthesized by **hydrothermal** method, using Sodium hydroxide as base to reach a pH of synthesis of **13**. The sample contains a 5% molar amount of **Ti** and a 95% of Zr.

4.2.2 Catalyst synthesis and characterization

TG/DSC thermal analysis has been used to analyse the zirconium hydroxide precursor in order to identify the right calcination temperature to obtain zirconium oxide. Then it has been used to investigate the presence of carbon deposits on the spent catalyst's surface after performing the catalytic tests.

The studied catalysts have been synthesized with two different methods, as explained in detail the previous section (Section 3.2.4.1):

- Hydrothermal synthesis
- Precipitation method

The precursor obtained with each of these methods has been filtered, washed, dried overnight at 100°C and then calcined in air, at 500°C for 2h, with a 10°C/min ramp.

The crystallographic phase of the obtained oxide is one of the most important parameters to study for understanding the catalytic, structural, and textural properties of the synthesized catalyst. The analysed samples at XRD can be divided in three main categories, according to the polymorph formed:

- Pure monoclinic phase
- Pure tetragonal phase
- Mixed phases

Several synthesis parameters have been investigated to evaluate their effect on the formed zirconia phase. To compare the obtained crystallographic phases, the tetragonal phase fraction (%t) has been derived from the XRD analysis of each synthesized sample. It was calculated from the ratio of the peak intensities according to the following equation ²⁴⁴:

$$\%t = \frac{It(101)}{It(101) + 1.6 Im(\bar{1}11)} \times 100$$

4.2.2.1 Calcination temperature study

Basically, the precursors obtained through the two hydrothermal and precipitation methods have been filtered, washed and dried overnight at 100°C. The dried materials obtained methods have been firstly analysed to select the proper calcination temperature. The calcination temperature is a crucial parameter when we want to produce metal oxides, the polymorphism of this kind of material can lead to the formation of a different polymorph depending on the calcination temperature. As a reference, two samples have been analysed, one for each synthesis method employed before undergoing the final calcination step.

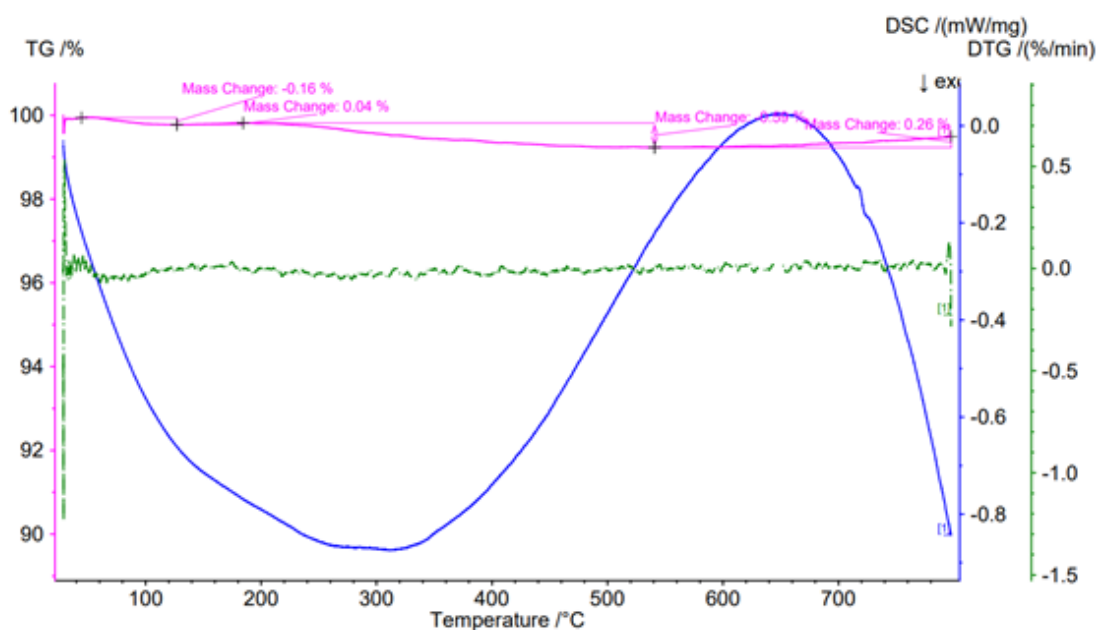


Figure 4.33 TGA-DSC analysis performed over ZrO_2 sample before performing the final thermal treatment, synthesized by hydrothermal method with NaOH, at pH = 13.

The sample synthesized by hydrothermal method did not show a significant mass loss during the experiment, as can be observed in Figure 4.33. This data can suggest that a stable zirconia phase can be formed within the hydrothermal synthesis. To prove this hypothesis, an XRD analysis of the same sample has been carried out and it is reported in Figure 4.34.

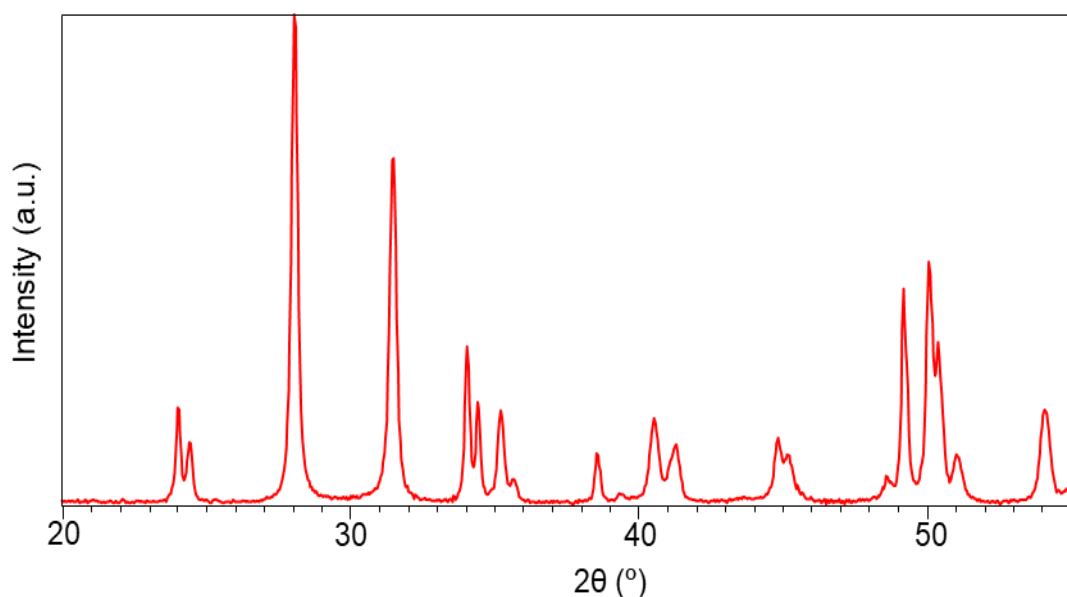


Figure 4.34 XRD analysis performed over an uncalcined ZrO_2 sample, synthesized by hydrothermal method, with NaOH, at pH = 13.

The obtained diffractogram matches the one of Baddeleyite (monoclinic zirconia, Ref. code:00-024-1165), the most stable polymorph of zirconium oxide. This approach did not allow to select a proper calcination temperature since no mass loss were observed at TGA.

In the case of the zirconia sample prepared by precipitation, as in can be observed in the XRD analysis showed in Figure 4.35, the uncalcined material appeared amorphous.

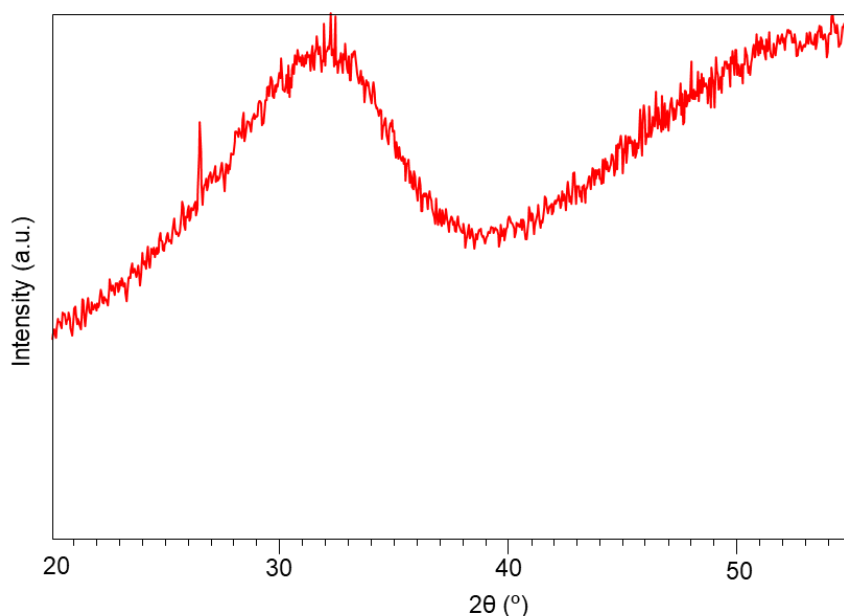


Figure 4.35 XRD analysis performed over an uncalcined ZrO_2 sample, synthesised via precipitation method, with NH_4OH 25 wt% aqueous solution, at pH = 7.6.

The change in the weight of the uncalcined sample was monitored by thermogravimetric analysis (TGA/DSC) in the flowing air from room temperature to 800 °C, the analysis results are depicted in Figure 4.36.

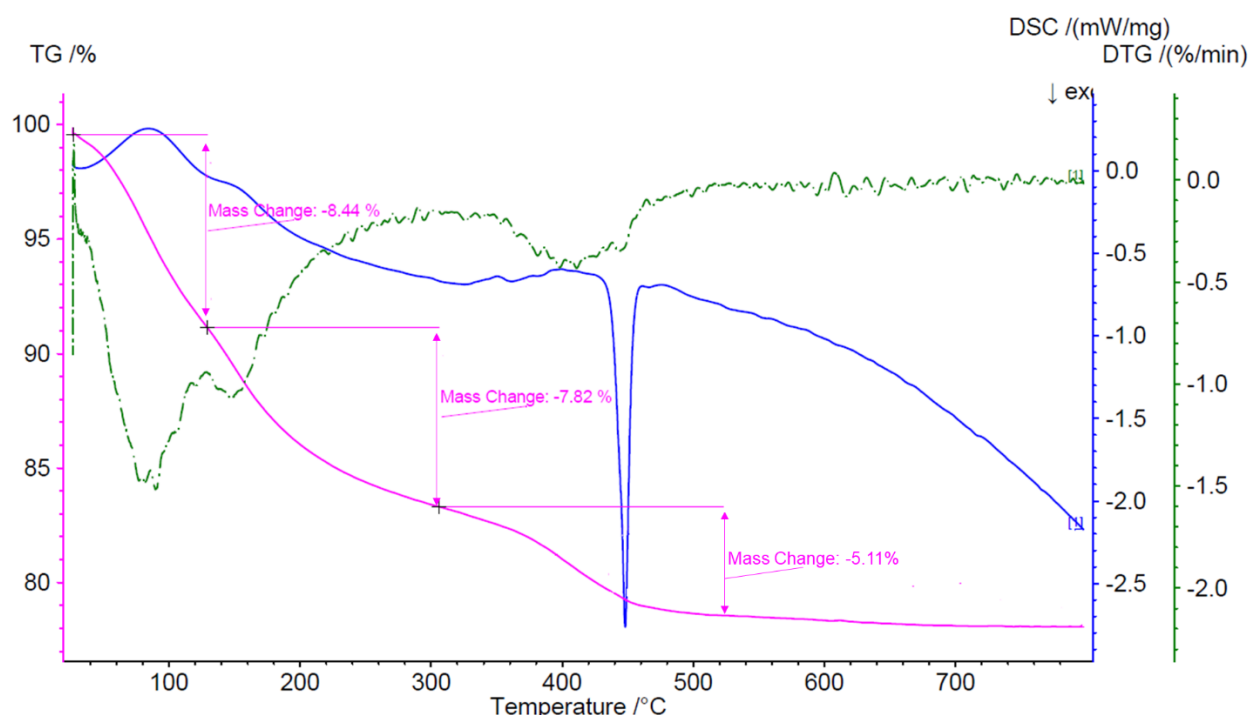


Figure 4.36 TG/DSC analysis performed over an uncalcined ZrO_2 sample, synthesized via precipitation method, with NH_4OH 25 wt% aqueous solution, at pH = 7.6.

It can be noticed that there are three weight loss steps around 40-110 °C, 110- 300 °C and 300-520 °C, nevertheless, the weight loss of the samples was from ambient up to around 520 °C.

The first two weight losses in the range starting from room temperature until 300 °C (i.e., 8.44 and 7.82 %) can be attributed to the loss of physically adsorbed water, and the partial dehydroxylation of the solid, respectively, which can be related to the two endothermic peaks observed at around 90 °C and 150 °C.²⁷² The third weight loss of 5.11%, which occurred between 300 and 450 °C, may be attributed to residual contamination from the synthesis of the material.²⁷³

The DSC profile depicted in Fig. 4.36 shows an exothermic peak around 450 °C, which was assigned to zirconia transformation from an amorphous to a crystalline phase.²⁷² Accordingly, the calcination temperature selected in this work for all the zirconia samples was 500 °C.

4.2.2.2 Zirconia phase study- pH and synthesis method effects

The value of pH is one of the most important parameters when a metal oxide catalyst is synthesized, both the $[H^+]$ and $[OH^-]$ strongly affect the properties of the forming material²⁷⁴. In the synthesis performed to prepare the zirconia samples, the pH value was varied from 7.6 to 13.0 using 3 M NaOH, NH_4OH 25 wt% aqueous solution or urea. In Figure 4.37 are reported the XRD patterns obtained of the synthesized samples. In particular, the XRD patterns of the samples obtained by hydrothermal method varying the pH (i.e., 7.5, 9.5, 10, 13) with NaOH (HS-7.5, HS-10 and HS-13) and with NH_4OH (HA-7.5 and HA-9.5) as well as the ones synthesized by precipitation method using NH_4OH (PA-7.5 and PA-9.5), urea (PU-8.5, PU-9.5 and PU-13) and NaOH (PS-13) are depicted. The samples matched with zirconia tetragonal $t-ZrO_2$ (Ref. code: 01-088-1007) or the zirconia monoclinic $m-ZrO_2$ (Ref. code: 00-024-1165), depending on the synthesis method; most of them showed to be contain both phases. The presence of tetragonal phase along with monoclinic phase indicates the crystallographic rearrangement in ZrO_2 due to the oxygen vacancies.²⁷⁵ In Fig. 4.37 the reflections of the two phases employed to compute the tetragonal fraction are highlighted (i.e., $m(\bar{1}11)$ for the monoclinic phase and $t(101)$ for the tetragonal).

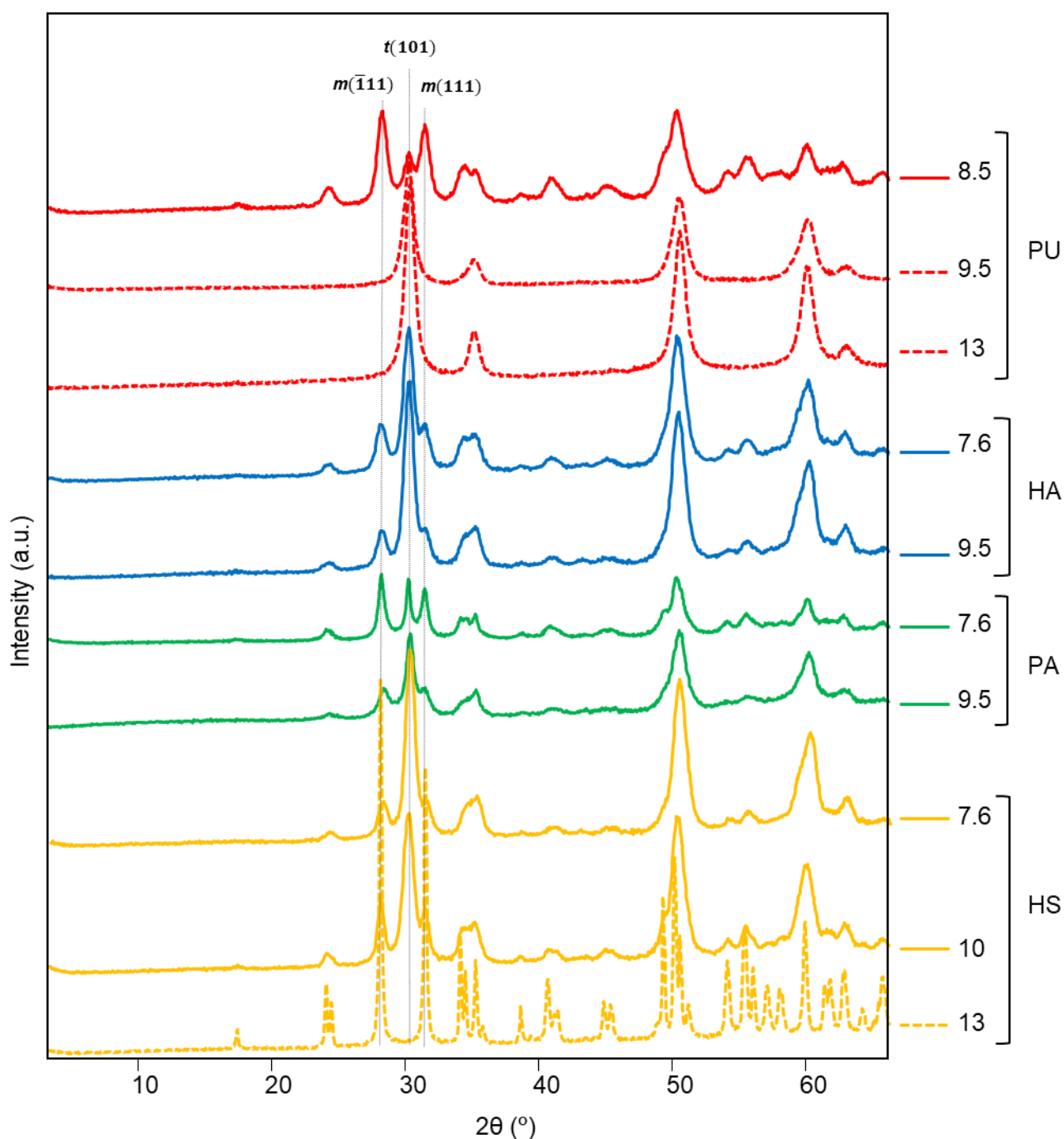


Figure 4.37 XRD patterns of the zirconia samples prepared by precipitation (P) or hydrothermal (H) methods, in the right the figures represents the pH values employed. HS: Hydrothermal synthesis using NaOH as base (yellow), HA: hydrothermal synthesis using NH_4OH as base (blue), PA: precipitation using NH_4OH as base (green), PU: precipitation using urea as base (red), and PS: precipitation using NaOH as base (X). The mixed phases are plotted with solid lines, the pure phases are plotted with dotted lines.

In the following graph reported in Figure 4.38, the pH influence on the tetragonal fraction (%) formation is showed related to the different synthesis methods and bases used.

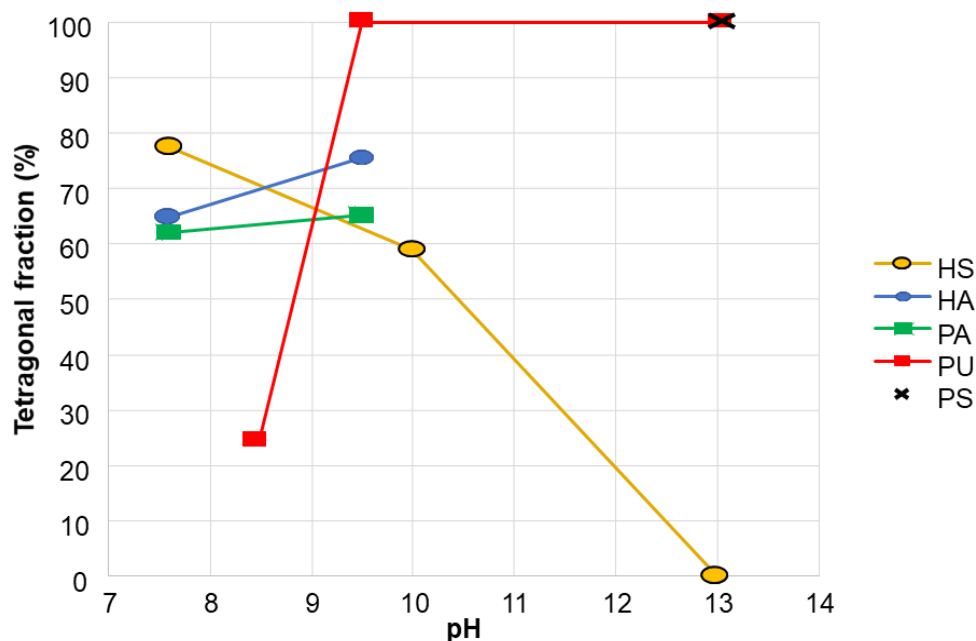


Figure 4.38 The pH influence on ZrO_2 samples tetragonal fraction. HS: Hydrothermal synthesis using NaOH as base (yellow), HA: hydrothermal synthesis using NH_4OH as base (blue), PA: precipitation using NH_4OH as base (green), PU: precipitation using urea as base (red), and PS: precipitation using NaOH as base (X).

As in can be observed into Figure 4.37 and Figure 4.38, the only case in which a pure monoclinic zirconia sample (0% tetragonal fraction) was formed is the HS-13-ZO, showed in yellow in the graph. The hydrothermal synthesis method usually favours an overall free energy decrease of the system since the samples are aging for a long time in its mother liquor. The formation of the most stable phase, the monoclinic one, can be explained according to this concept. By the way, with lower pH values, the monoclinic phase is no longer the predominant one in the formed solid. At a pH value of 7.6, the monoclinic phase obtained by hydrothermal treatment is even lower than the one obtained with the precipitation method. Using ammonium hydroxide as a base there are not relevant differences between the hydrothermal and the precipitation method, leading to the formation of mixed phases containing samples slightly more tetragonal than monoclinic. When urea was used as a basic agent, a pure tetragonal phase was formed at pH values of 13 and 9.5, while a mixed phase solid was obtained at a pH value of 8.5, with a tetragonal fraction presence of 25%. Finally, a precipitation synthesis with sodium hydroxide at a pH value of 13 was performed, obtaining a pure tetragonal sample. This data is the opposite respect to the corresponding one synthesized with the hydrothermal method. These data show that for pH values between 7 and 10 there is not a big difference between the hydrothermal method and the precipitation one in terms of phase formation. At a pH of 13 the synthesis method strongly affects the phase formation; the precipitation and the hydrothermal method show diametrically opposite results in terms of phase formation.

4.2.2.3 Zirconia phase study- Dopant effect

To evaluate the effect of dopant addition in the zirconia structure, a 5% molar amount of the doping element (Ti and Y) has been added to the precursors solution as previously described in Section 3.2.4.1. Figure 4.39 and Figure 4.40 show the effect of dopant addition on the nature of zirconia phase when using two different synthesis methods and considering two different dopants, i.e. titanium or yttrium. Since while synthesising zirconia via hydrothermal method at pH 13, pure monoclinic phase has been obtained, the dopant addition has been performed in those conditions in order to evaluate a possible tetragonal phase stabilization. Two methods have been employed to study the effect of the metal dopant effect: one via hydrothermal method at a pH value of 13 using sodium hydroxide as base and one by precipitation synthesis at a pH value of 7.6 using ammonium hydroxide as a base. Figure 4.39 reports the XRD patterns of the obtained samples, an increase of the tetragonal phase presence over the monoclinic can be noticed.

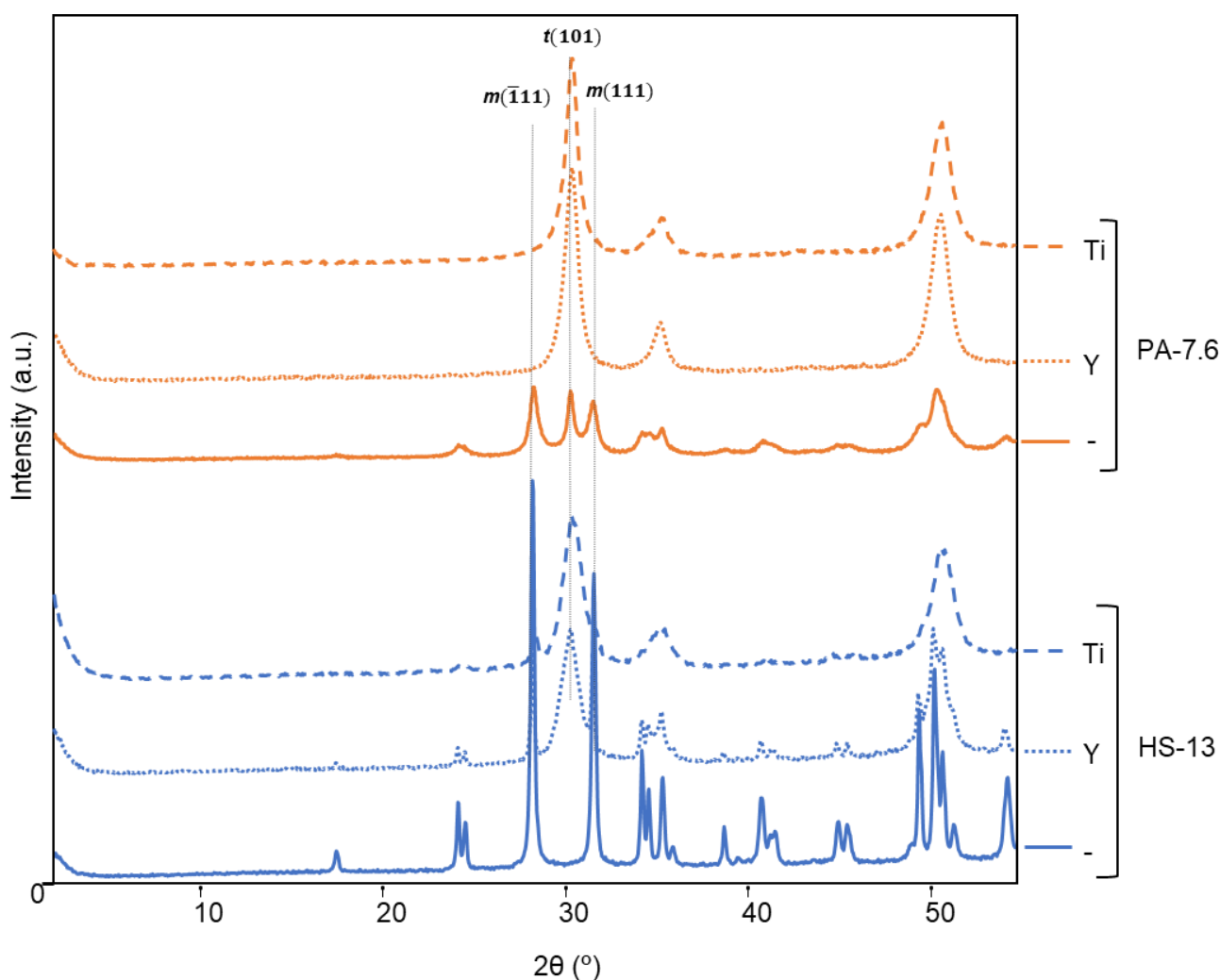


Figure 4.39 XRD patterns of the zirconia samples prepared by precipitation (PA) or hydrothermal (HS) methods, effect of the transition metal addition. **HS-13**: Hydrothermal synthesis using NaOH as base, at pH 13, undoped and doped with Ti or Y (blue lines). **PA-7.6**: precipitation synthesis using NH_4OH as base, at pH 7.6, undoped and doped with Ti or Y (orange lines).

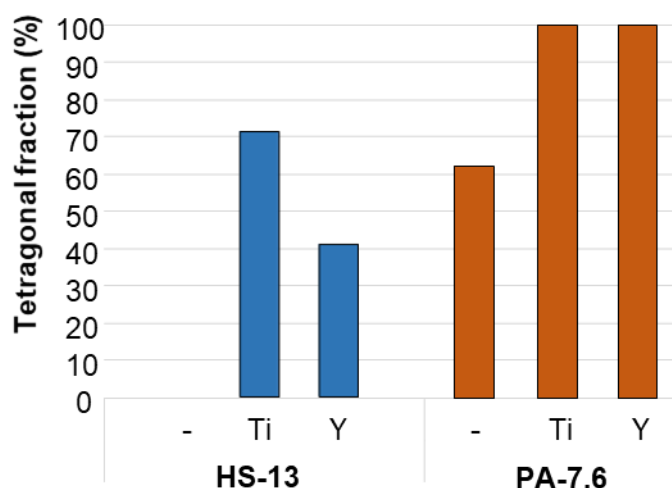


Figure 4.40 Dopant (Ti or Y) addition influence on the zirconia phase (tetragonal fraction %), on HS-13 (hydrothermal method at pH 13 with NaOH, blue) and PA-7.6 (precipitation at pH=7.6 with ammonium hydroxide, orange). **H**: hydrothermal, **P**: precipitation.

The precipitation series, plotted in orange, showed that a dopant addition might favour the tetragonal phase formation. In particular, all the doped zirconias synthesized via precipitation method (PA-7,6), appeared purely tetragonal according to the XRD analysis (summarized in Fig. 4.40 and showed in Figure 4.39). As far as the hydrothermal synthesis (HS-13) is concerned, it possible to draw some conclusions. With the absence of a dopant, no tetragonal phase formation was observed while after dopant addition, a remarkable increase of tetragonal phase has been observed. Accordingly, a dopant addition favoured the tetragonal phase stabilization; in particular when titanium is used, since high tetragonal fraction has been obtained even when the synthesis was performed by hydrothermal method (71%).

4.2.2.4 Textural analysis, nitrogen adsorption isotherms (BET)

BET surface area is a crucial parameter in heterogeneous catalysis. When a gas phase reaction on a solid catalyst occurs, just the surface atoms of the catalyst are involved in the reaction kinetics.²⁷⁶ For this reason, a measurement of the surface area of the sample can give an important information about its activity in the studied process. The collected data wants to propose a correlation between the BET surface area and the zirconia phase obtained in the analysed sample. In the following graph (Fig. 4.41), the BET surface area is plotted against the tetragonal fraction (%t) obtained by XRD experiments; Table 4.5 summarizes of the collected results.

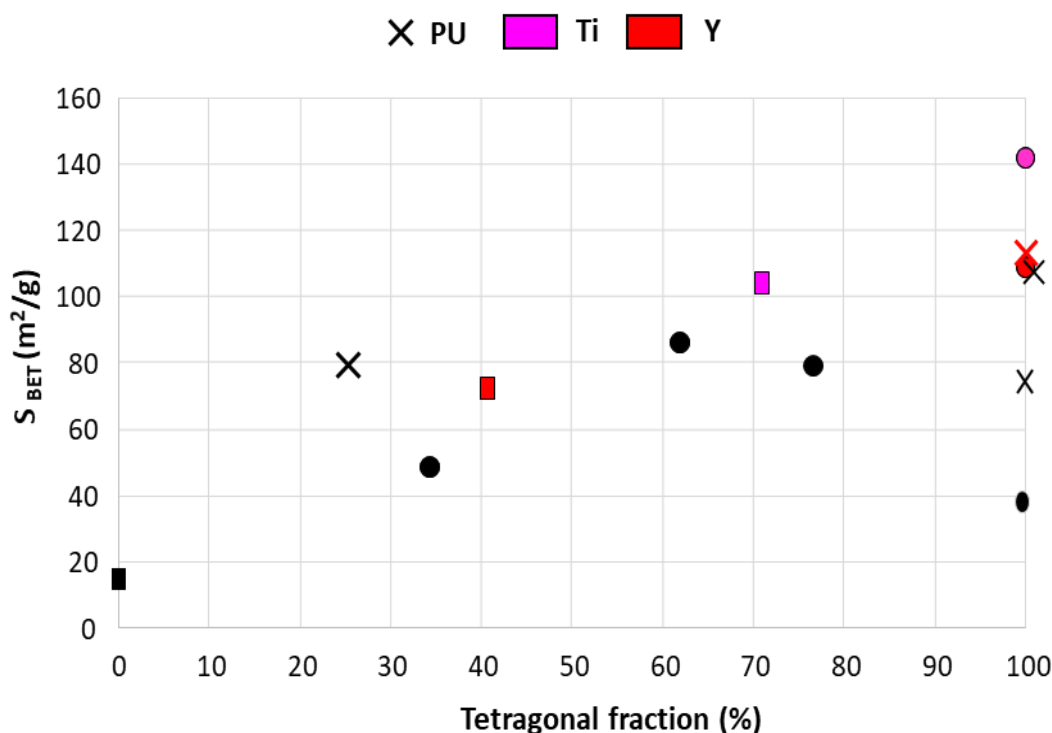


Figure 4.41 Tetragonal fraction in relation of the the BET surface area. Aamples prepared via precipitation method (●) or hydrothermal (□), with and without a metal dopant. X: precipitation with Urea; Black: pure zirconia sample; Purple: Ti; Red: Y.

As stated before, the presence of a metal dopant into the zirconia structure stabilized the tetragonal phase. Here is possible to notice a correlation between the tetragonal fraction and the surface area. From a general point of view, the BET surface area seems to increase with the tetragonal fraction within the sample's structure. All the doped catalysts, which have a higher tetragonal fraction than their corresponding pure zirconia samples, appears to have a higher surface area. This is particularly true when precipitation method is used to synthesize the zirconia samples. The titanium doped zirconia sample synthesized via precipitation employing NH_4OH to produce a pH of 7.6 (PA-7.6-TZO) is the synthesized catalyst with the highest surface area, around 141 m²/g. While the pure zirconia catalyst synthesized by hydrothermal method with NaOH at pH=13 (HS-13-ZO) presents the lower value of BET surface area (13 m²/g). These data will be useful when the catalytic behaviour of the synthesized material will be studied.

Table 4.5 BET surface data (S_{BET} [m²/g]) and tetragonal fraction (%t) of the zirconia samples. Synthesized by hydrothermal (HT) or precipitation (Ppt) methods, employing different bases (NaOH, NH₄OH and Urea) and pH values in the range: 7.6-13, and by adding a transition metal as dopant (Ti or Y).

Method	Base	pH	Dopant	%t	S_{BET} [m ² /g]
HT	NaOH	13	-	0	13
			Y	41	71
			Ti	71	104
	NH ₄ OH	7.6	-	77	69
		9.5	-	75	81
		7.6	-	65	71
Ppt	NaOH	13	-	100	37
		9.5	-	65	80
			-	62	86
	NH ₄ OH	7.6	Y	100	109
			Ti	100	142
		13	-	100	76
	Urea	9.5	-	100	108
			-	25	80
		8.5	Y	100	113

4.2.2.5 Raman spectroscopy

Assignment of cubic and tetragonal structures, based solely on the X-ray diffraction analysis, can be misleading because the cubic and tetragonal structures have very similar lattice parameters (i.e., $a_0 = 0.5124$ nm for cubic and $a_0 = 0.5094$ nm and $c_0 = 0.5177$ nm for tetragonal structures).²⁷⁷ Figure 4.42 reports the XRD patterns and the Raman profiles of the three zirconia polymorphs, where it can be observed that the reflections of tetragonal and cubic phases overlaps.²⁷⁵ While cubic structure presents only single peaks, the tetragonal one is characterized by the presence of the splitting of the diffraction peaks. Accordingly, they could be distinguished.²⁷⁷ Nevertheless, normally a significant line broadening obscures any clear distinction between the tetragonal and cubic polymorphs of ZrO₂.²⁷⁵ The XRD diffractograms of the zirconia polymorphs are shown in Fig.4.42A.

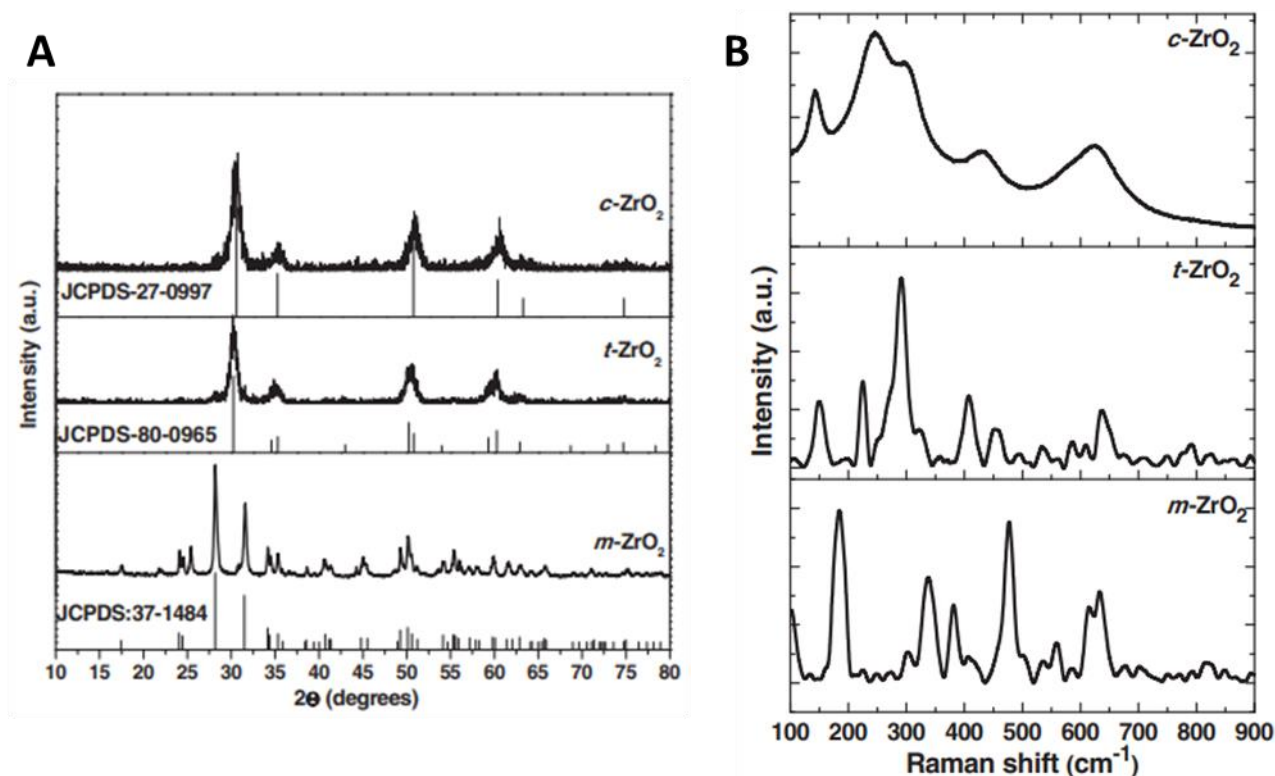


Figure 4.42 A) XRD Patterns of the zirconia polymorphs, B) Raman spectra of the zirconia polymorphs.²⁷⁵

In contrast, the monoclinic, tetragonal, and cubic zirconia structures can be readily distinguished from one another by Raman spectroscopy, as it can be observed in the representative spectra in Figure 4.42B. The monoclinic phase is characterized by the presence of a doublet at 181-190 cm^{-1} , while the tetragonal phase can be confirmed by the presence of peaks at 147 and 265 cm^{-1} . In addition, the spectrum of tetragonal phase presents relatively sharp peaks even at around 326, 474, 616 and 646 cm^{-1} . The Raman spectrum for $c\text{-ZrO}_2$ is characterized by a narrow band at 145 cm^{-1} and broad bands centred at 246, 301, 436, and 625 cm^{-1} . The Raman peak at 149 cm^{-1} is common for both the phases while cubic ZrO_2 presents a broad band between 530-670 cm^{-1} and its spectra is poorly defined due to the distorted oxygen sublattice.^{275,278}

In order to confirm the crystalline structure of the synthesized samples, some of them (i.e., PA-7.6-ZO, PA-7.6-TZO, PA-7.6-YZO, HS-10-ZO and HS-13-ZO) have been analysed by Raman spectroscopy, the results are reported in Figure 4.43. The Raman spectra obtained on the zirconia sample synthesised by hydrothermal method at pH=13 (HS-13-ZO sample, purple line) can be attributed to a monoclinic phase, in accordance with the data obtained from the XRD analysis.

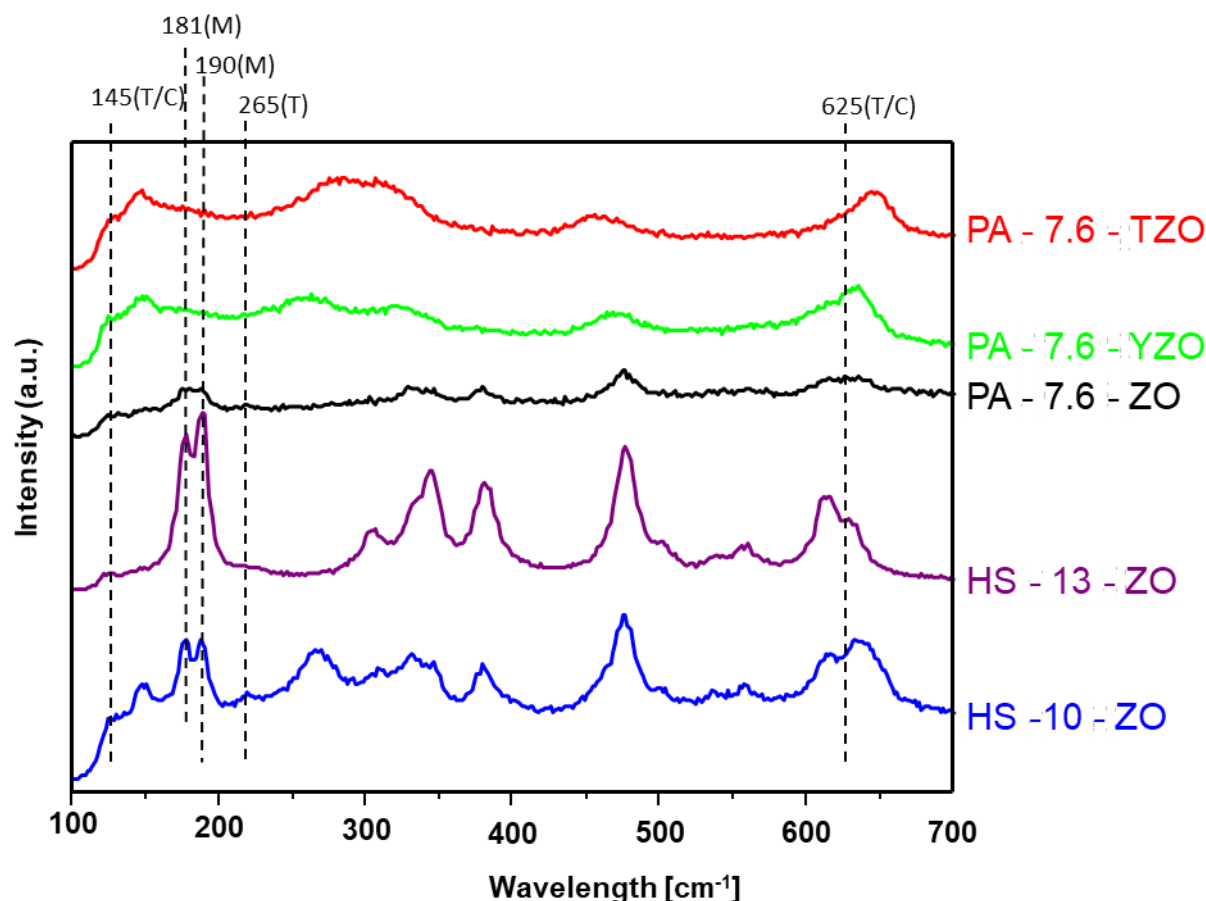


Figure 4.43 Raman spectra of the synthesized catalysts. **PA-7.6-YZO**: yttrium-doped zirconia synthesized by precipitation at pH 7.6 with NH_4OH ; **HS-13-ZO**: zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; **PA-7.6-TZO**: titanium-doped zirconia synthesized by precipitation at pH 7.6 with NH_4OH ; **HS-10-ZO**: zirconia synthesized by hydrothermal method at pH 10 with 5 M NaOH; **PA-7.6-ZO**: zirconia synthesized by precipitation at pH 7.6 with NH_4OH .

The titanium and yttrium doped zirconia samples obtained by the precipitation method (PA-7.6-TZO, red line, PA-7.6-YZO, green line) which have been considered to be purely tetragonal from the XRD analysis, showed a Raman spectra characterized by broad peaks, suggesting that they are not purely tetragonal, while probably a mixture of tetragonal and cubic phases. The zirconia sample obtained via hydrothermal method at pH=10 (HS-10-ZO, blue line) and the precipitated one at pH=7.6 (PA-7.6-ZO, black line), showed a combination between the three polymorphs, even though the one obtained through HS-10-ZO showed a predominance of the monoclinic one, in accordance with the results obtained through XRD analysis.

Overall, the presence of the cubic phase has been observed, although it is not possible to ascertain in which amount. Even though in this study the zirconia samples composition has been qualified considering only the metastable tetragonal phase, it is plausible that a combination of both tetragonal and cubic phases is incorporated in most of the samples. In order to distinguish between the tetragonal and cubic structures of zirconia, other analysis are needed (i.e., synchrotron radiation source for X-ray diffraction).²⁷⁷

4.2.2.6 Sodium presence investigation in HS catalysts

Only one sample showed a pure monoclinic phase; that is the one synthesized by hydrothermal route at pH= 13 using NaOH as base (HS-13-ZO). To give an explanation to this data, it was proposed that the sodium cation present in the utilised base (i.e., sodium hydroxide) could have entered into the zirconia structure and affected the crystal lattice composition. To investigate its presence, two different characterization method have been used on two different catalysts. ICP and SEM-EDX were performed on pure monoclinic HS-13-ZO and another catalyst synthesized with the same method but with a lower value of pH (i.e. 10), HS-10-ZO. The main difference between these two catalysts is the tetragonal fraction in the solid, which increased from 0% in the sample synthesized at a pH value of 13, to 59% in the sample synthesized at pH=10, and so by using less NaOH. SEM-EDX analysis provided a picture of the analysed samples in which the two specimens showed the presence of Na. The sodium weight percentage was estimated to be between 0.8 and 2.2 % by SEM-EDX analysis and 3.1% by ICP analysis in sample HS-10-ZO. On the other hand, sample HS-13-ZO showed a sodium weight percentage between 1.2 and 1.8 % while according to ICP analysis it was around 2.6%.

Since sodium is present in both the samples while the tetragonal fraction of the two materials is largely different, it was assumed that sodium is not promoting the monoclinic phase formation in pure zirconia samples.

4.2.2.7 Temperature programmed desorption (TPD)

The active site nature is critical in heterogeneous catalysis, several techniques allow to study the interaction of the catalyst's surface with probe molecules in gas phase which give an idea about the number and the strength of active site for that kind of interaction. Since this work mainly focuses on acid catalysis, several temperature-programmed desorption of ammonia (TPD-NH₃) analyses were carried out on the pure and doped zirconia samples. Generally, the solid acid sites can be classified according to their acid strength determined using the temperature of NH₃ desorption into three types: weak (150 - 300 °C), moderate (300 - 450°C) and strong (450 - 650 °C) acid sites.¹³⁷ Recorded spectra may be further deconvoluted by a Gaussian peak fitting method into separate peaks to be then attributed to different strength acid sites. In Table 4.6, the acidity of the samples, expressed as ammonia desorbed by weight of catalyst [$\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{CAT}}$] or surface area of the catalyst [$\mu\text{mol}_{\text{NH}_3}/\text{m}^2_{\text{CAT}}$] of adsorbed ammonia is showed together with the catalyst's specific surface area.

Table 4.6 TPD adsorbed ammonia and specific surface area of the analysed catalysts.

Catalyst Code	BET [m^2/g]	ACIDITY	
		$[\mu\text{mol}_{\text{NH}_3}/\text{m}^2_{\text{CAT}}]$	$[\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{CAT}}]$
HS-13-ZO	13	0.1	1.2
HS-13-TZO	104	1.5	22
HS-13-YZO	71	0	0
PA-7.6-ZO	76	1.5	116
PA-7.6-TZO	142	1.7	236
PU-8.5-ZO	80	1.4	114

HS-13-ZO: zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; HS-13-TZO: titanium-doped zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; HS-13-YZO: yttrium-doped zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; PA-7.6-ZO: zirconia synthesized by precipitation at pH 7.6 with NH_4OH ; PA-7.6-TZO: titanium-doped zirconia synthesized by precipitation at pH 7.6 with NH_4OH ; PU-8.5-ZO: zirconia synthesized by precipitation at pH 8.5 with urea.

The acidity of three pure zirconia samples is compared in Fig. 4.44A by plotting the trend of the ion current signal of the mass 15 m/z detected with increasing temperature in the desorption phase of the analysis. The zirconia sample synthesized by hydrothermal synthesis at pH 13 with 5 M NaOH (HS-13-ZO) did not show great acidity, maybe because of its low surface area of $13 \text{ m}^2/\text{g}$ as reported in Table 4.6. Both the samples prepared by precipitation, PA-7.6-ZO and PU-8.5-ZO, showed ammonia desorption in the temperature range from 100°C to 400°C , corresponding to weak and medium strength acid sites. The NH_3 desorption profiles of these two samples appeared to be quite similar.

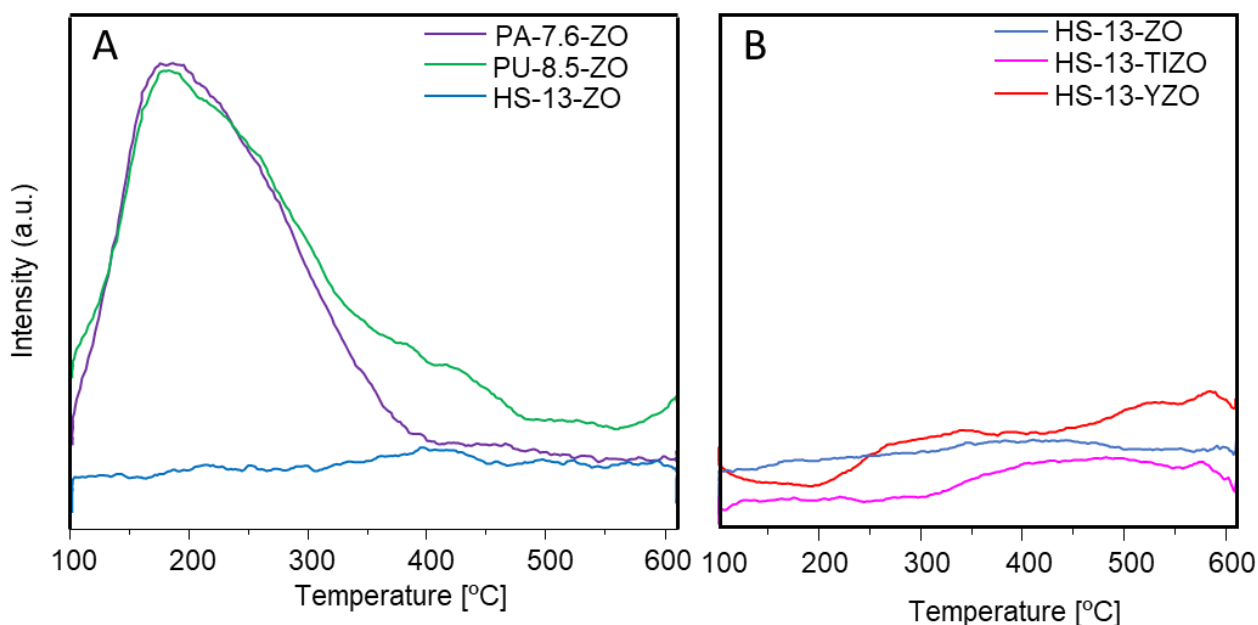


Figure 4.44 TPD- NH_3 over pure zirconia samples. A) Zirconia samples. HS-13-ZO: zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; PA-7.6-ZO: zirconia synthesized by precipitation at pH 7.6 with NH_4OH ; PU-8.5-ZO: zirconia synthesized by precipitation at pH 8.5 with urea. B) HT-Zirconia samples doped. HS-13-TZO: titanium-doped zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; HS-13-YZO: yttrium-doped zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH.

The effect of a dopant addition on the acid properties of zirconia samples obtained by hydrothermal method is depicted in Fig. 4.44B. The Ti-, Y- doped and the pure zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH did not show any peak related to ammonia desorption.

The effect of Ti doping addition to zirconia samples is shown in Fig. 4.45. Both the doped and the pure catalyst synthesized by hydrothermal method did not show ammonia desorption peaks. While when the two catalysts synthesized by precipitation method are compared, the effect of the titanium doping seemed to be important. The Ti-doped zirconia synthesized by precipitation appeared to have more and stronger acid sites respect to the pure one. In particular, it seems that some new and stronger acid sites were formed, its TPD-NH₃ desorption profile showed a broad desorption band in the temperature range 120 - 450°C, which indicates the presence of weak, medium-strength and strong acidic sites. In particular, in addition to the weak and medium strength acid sites observed in both the two samples synthesized by precipitation at pH 7.6, new stronger acid sites that desorbed at around 300°C have been observed in the sample doped with titanium.

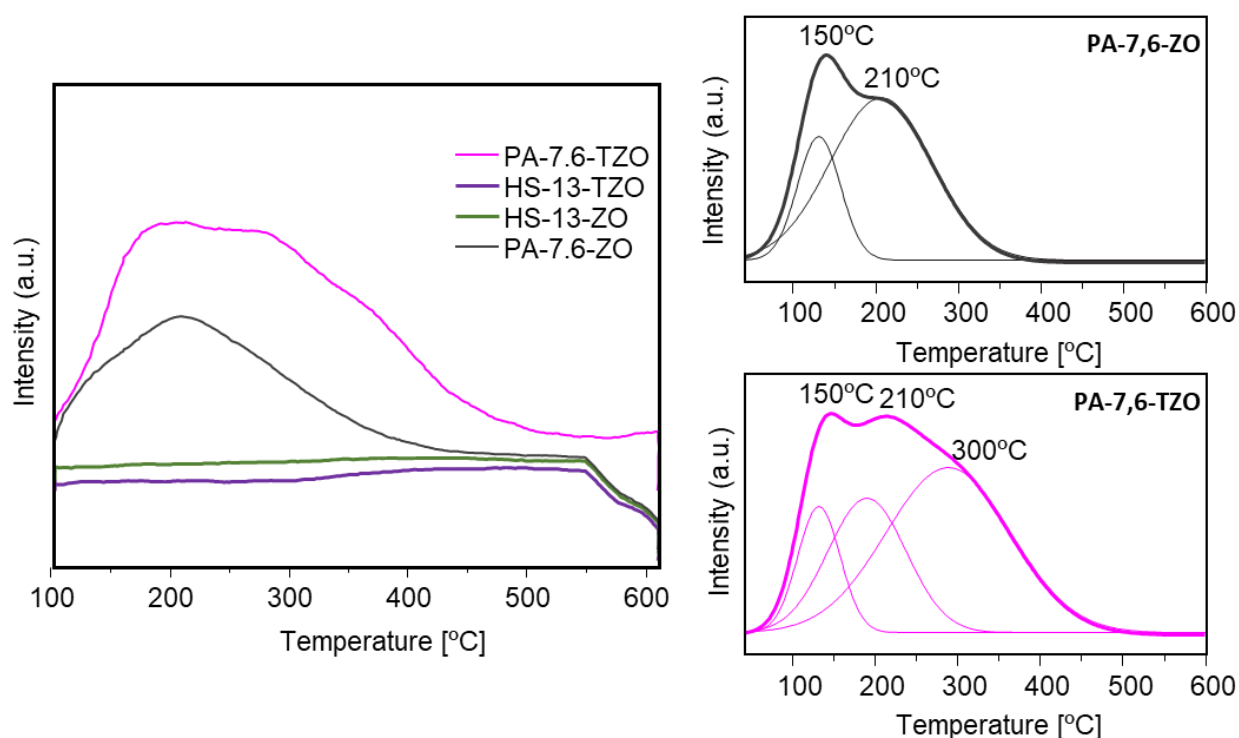


Figure 4.45 TPD-NH₃ over pure and Ti-doped zirconia samples. HS-13-ZO: zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; HS-13-TZO: titanium-doped zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; PA-7.6-ZO: zirconia synthesized by precipitation at pH 7.6 with NH₄OH; PA-7.6-TZO: titanium-doped zirconia synthesized by precipitation at pH 7.6 with NH₄OH. On the right, the signals of PA-7.6-ZO and PA-7.6-TZO deconvoluted.

4.2.3 Reactivity tests

Several catalytic tests have been performed to evaluate the catalytic activity of the synthesized samples in the gas-phase ethanol conversion. Before the reactivity tests, the synthesized catalysts have been shaped into 0.25 - 0.60 mm pellets. The pelletized catalyst has been loaded on the reactor's bed where the temperature was constantly controlled by a thermocouple. In this chapter, all the catalysts behaviour will be compared in order to give an overview on the effect of the main synthesis parameters such as the synthesis method, tetragonal fraction, and dopant presence. The pure and doped zirconia catalyst were tested at different temperatures and different contact times.

The catalytic tests on the supports have been performed in these operative conditions:

- $Feed = 5\% \text{ mol}_{EtOH} \text{ in } N_2$
- $P = 1 \text{ atm}$
- $T = 300 - 400 \text{ }^\circ\text{C}$
- $\dot{V} = 21 - 22 \text{ mL/min @ RT}$
- $W/F = 0.78 - 1.93 \left[\frac{g_{cat}}{mL_{tot}} \times s \right]$

Most of the synthesized catalysts have been tested in ethanol transformation reaction. In this chapter, the reactivity results will be compared among the catalysts synthesized with the same method, with different elemental composition. Three temperatures have been selected to study the catalytic performance at low, medium, and high conversion. The first reaction temperature was selected as 300°C, then 350 °C, and finally 400°C. In this chapter, several graphs are presented. All the synthesized catalysts will be compared in term of ethanol conversion (X) and different products selectivities (S_i) gathering them by the reaction temperature as well as the synthesis method. In Table 4.7, the tested catalysts are reported, as well as their BET surface area and their tetragonal fraction reference.

Table 4.7 Zirconia samples tested into the reaction systems together with their characteristics (i.e., surface area S_{BET} , tetragonal fraction (t, %) and acidity ($\mu\text{mol}_{\text{NH}_3}/\text{m}^2_{\text{CAT}}$)).

Precipitation Catalysts				Hydrothermal catalysts			
Catalyst Code	S_{BET} [m^2/g]	t%	Acidity [$\mu\text{mol}_{\text{NH}_3}/\text{m}^2_{\text{CAT}}$]	Catalyst Code	S_{BET} [m^2/g]	t%	Acidity [$\mu\text{mol}_{\text{NH}_3}/\text{m}^2_{\text{CAT}}$]
PA-7.6-ZO	86	62	1.5	HS-13-ZO	13	0	0.1
PA-7.6-TZO	148	100	1.7	HS-13-TZO	104	71	0.2
PA-7.6-YZO	109	100		HS-13-YZO	71	41	0
PU-8.5-ZO	80	25	1.4				
PU-8.5-TZO	109	100					
PU-8.5-YZO	113	100					

Precipitation catalysts: **PA-7.6-ZO**: zirconia synthesized by precipitation at pH 7.6 with NH_4OH ; **PA-7.6-TZO**: titanium-doped zirconia synthesized by precipitation at pH 7.6 with NH_4OH ; **PA-7.6-YZO**: yttrium-doped zirconia synthesized by precipitation at pH 7.6 with NH_4OH ; **PU-8.5-ZO**: zirconia synthesized by precipitation at pH 8.5 with urea; **PU-8.5-TZO**: titanium-doped zirconia synthesized by precipitation at pH 8.5 with urea; **PU-8.5-YZO**: yttrium-doped zirconia synthesized by precipitation at pH 8.5 with urea. *Hydrothermal catalysts:* **HS-13-ZO**: zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; **HS-13-TZO**: titanium-doped zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH; **HS-13-YZO**: yttrium-doped zirconia synthesized by hydrothermal method at pH 13 with 5 M NaOH.

4.2.3.1 Reaction temperature effect

4.2.3.1.1 Precipitation catalysts

In general, the presented values of ethanol conversion (X) and product yields (Y_i) are the mean value obtained by a series of five GC-online analysis obtained in 1.83 hours of time on stream. This was possible since the catalysts appeared stable in this time interval, showing constant values of the previously mentioned parameters. The catalyst stability will be described later in Section 4.2.3.2.

Figure 4.46 depicts the catalytic performance of the zirconia samples obtained via precipitation method (Precipitation catalysts in Table 4.7) obtained while working at a reaction temperature of 300°C.

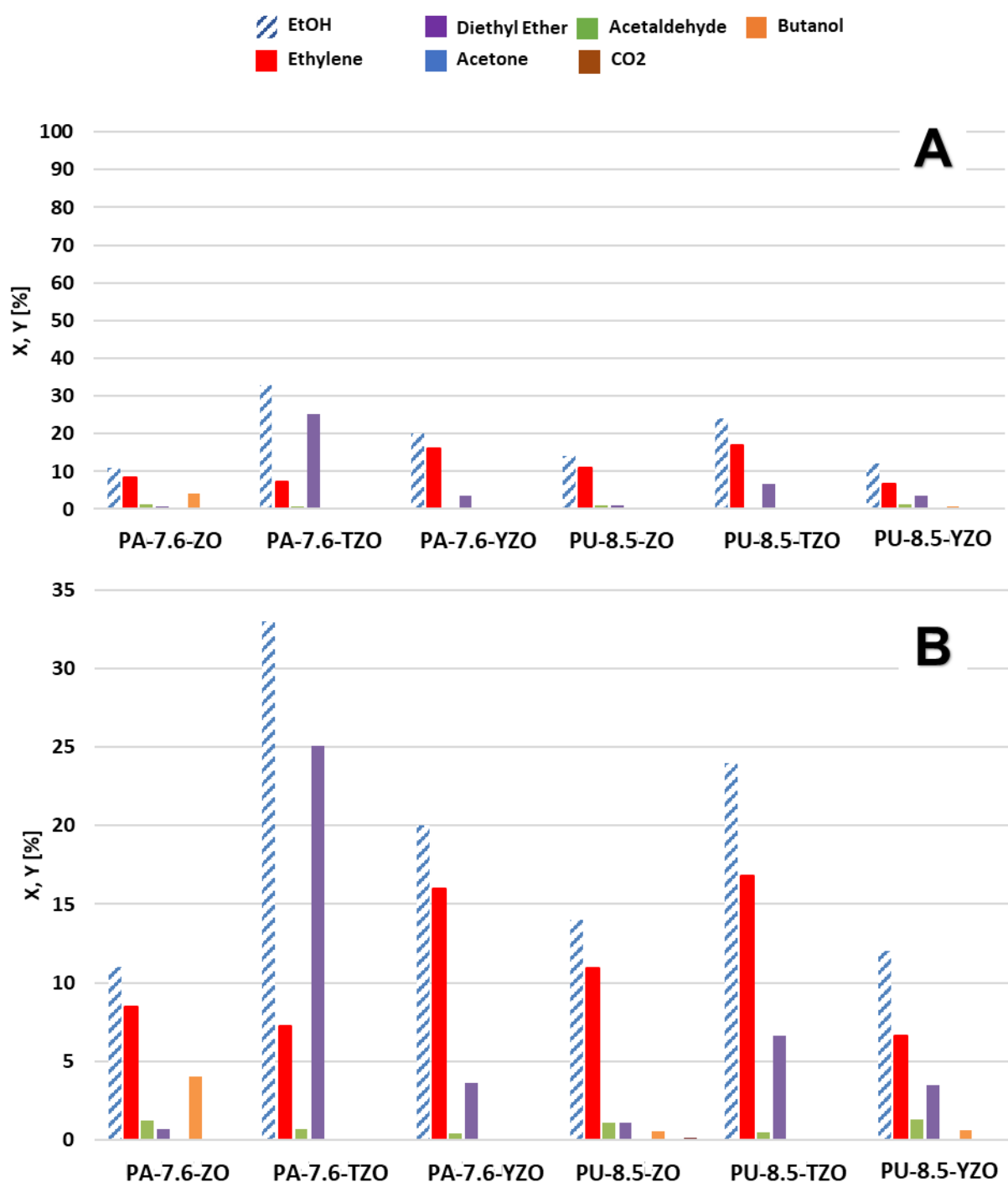


Figure 4.46 A) Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the catalysts obtained by precipitation. Reaction conditions: T: 300°C; p: 1 atm; EtOH 5%mol in N₂, $\dot{V}_{TOT}$ = 20 mL/min; W/F = 0.78 g·s/mL. B) The same results with narrowed y axis.

The titanium-doped zirconia obtained at pH 7.6 with NH₄OH (PA-7.6-TZO) shows diethyl ether as major product, the ethanol dehydration product.²⁷⁹ All the other catalysts obtained via precipitation, showed ethylene, the other dehydration product of ethanol, as major product. This difference can be explained with the nature of the acid active sites of the Ti-doped sample. As previously described in Section 4.2.2.7, the Ti-doped zirconia obtained by precipitation at pH 7.6 with ammonium hydroxide

(PA-7.6-TZO) presented stronger acid sites, which may favour diethyl ether formation respect to ethylene formation. In general, the doped samples led to a higher value of diethyl ether yields. In particular, the titanium-doped zirconia synthesized via precipitation at pH=7.6 (PA-7.6-TZO) led to the formation of diethyl ether with yield of 25% and exhibited the higher conversion of ethanol (33%) at 300°C. This higher value can be attributed to the high surface area of this catalyst which is the highest among the tested catalysts. Over pure zirconia catalyst PA-7.6-ZO, the Guerbet reaction product of ethanol,²⁸⁰ *n*-butanol, was also observed while performing the reaction at relatively low conversion of ethanol, which was not observed over the doped catalyst that acted mainly as acid catalysts. However, the rest of the zirconia-based samples presented an ethanol conversion between 10% and 25%, in accordance with their lower surface areas (Table 4.7).

Figure 4.47 reports the results obtained at higher reaction temperature, namely 350 °C. Due to the endothermic nature of this reaction, higher temperatures lead the ethylene yield to increase.²⁷⁹ The obtained products except from the already mentioned ethylene, diethyl ether and *n*-butanol are acetaldehyde and acetone. At 350 °C (Fig. 4.47) the ethylene yield increased together with the achieved ethanol conversion. Sample PA-7.6-TZO was still the most active with an ethanol conversion of 88%, at this temperature, the main product obtained with this catalyst was ethylene, a decent amount of diethyl ether was produced (Y=19%) and small amounts of butadiene and acetaldehyde, the dehydrogenation product of ethanol, have been produced too. The other catalysts still presented ethylene as major product. The other side-products obtained were acetone and CO₂, which could be formed by the ethyl acetate ketonization reaction, the formation of which could come from Tishchenko-like disproportion of acetaldehyde.⁸² Butadiene formation could occur through the mechanism proposed by Toussaint,²⁸¹ based on the aldolic condensation of acetaldehyde, even if no intermediate products have been detected into the reaction mixture.

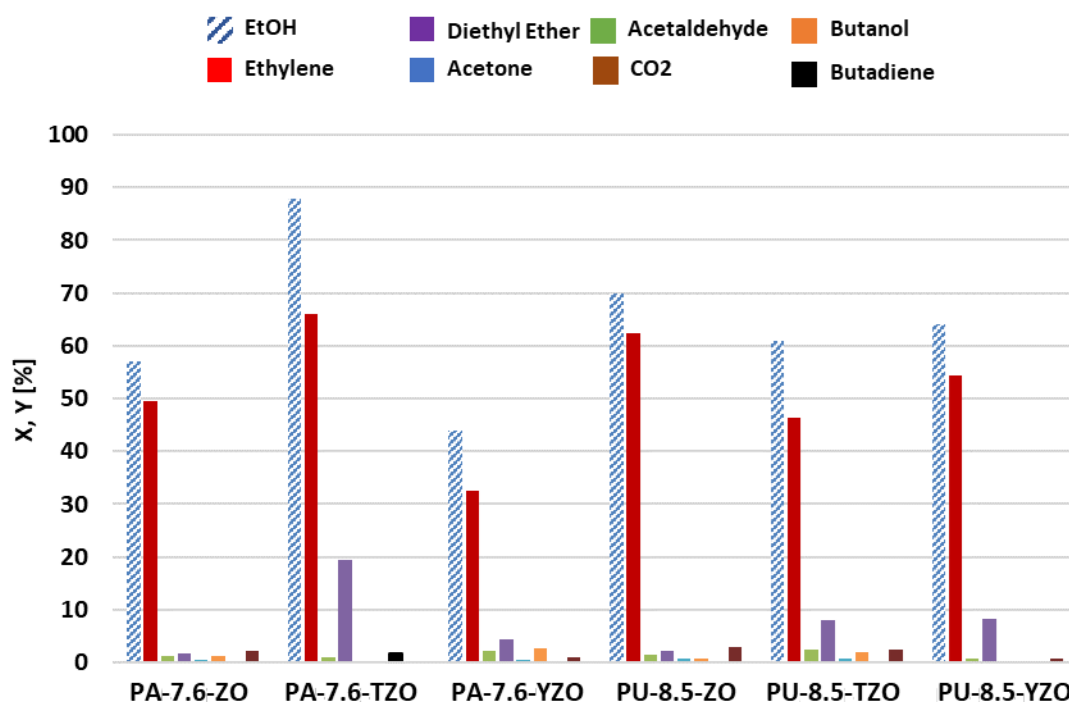


Figure 4.47 Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the catalysts obtained by precipitation. Reaction conditions: T: 350°C; p: 1 atm; EtOH 5%mol in N₂, $\dot{V}_{TOT}$ = 20 mL/min; W/F = 0.78 g·s/mL.

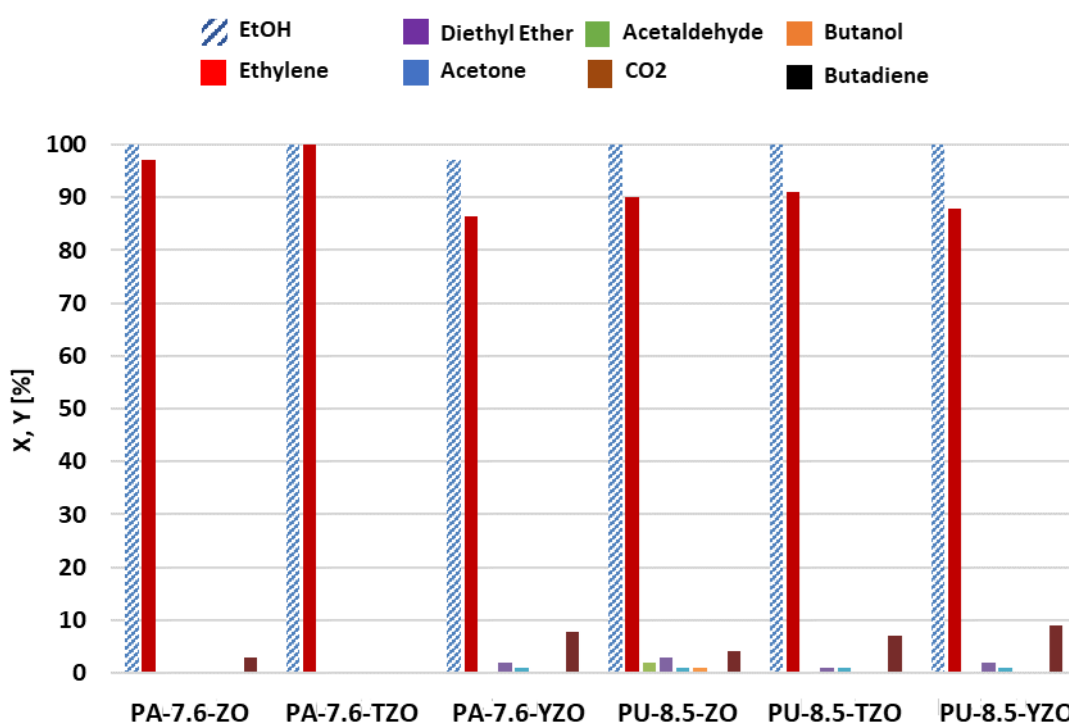


Figure 4.48 Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the catalysts obtained by precipitation. Reaction conditions: T: 400°C; p: 1 atm; EtOH 5%mol in N₂, $\dot{V}_{TOT}$ = 20 mL/min. W/F = 0.78 g·s/mL.

When the temperature is raised to 400°C (Fig. 4.48), all the catalysts exhibited a conversion higher than 95% and similar catalytic activity. Ethylene is still the major product with yields always higher than 85%. For all the tested samples, the other products yields decreased except for acetone and CO₂ whose yields slightly increased.

4.2.3.1.2 Hydrothermal catalysts

The catalysts obtained by hydrothermal synthesis (see list in Table 4.7) were tested also with the same reaction conditions to those used for catalysts prepared by precipitation, namely 1 atm, W/F= 0.78 g·s/mL, and reaction temperature range= 300-400°C. Figure 4.49 shows the variation of ethanol conversion and products yields at 300°C and 350°C. When the reaction temperature was 300°C, the catalysts presented a very low catalytic activity, never exceeding 5% of ethanol conversion (Fig 4.49A). In these conditions, the main product formed where the dehydration product of ethanol, ethylene and the dehydrogenation one, acetaldehyde, as it can be better observed in Figure 4.49B.

As it can be observed in Fig. 4.49C, even at 350°C, the catalysts obtained via hydrothermal synthesis did not exhibit a high ethanol conversion. By rising the reaction temperature, ethylene has been preferentially formed, indeed all the three samples showed in Fig 4.49C-D, presented ethylene as major product.

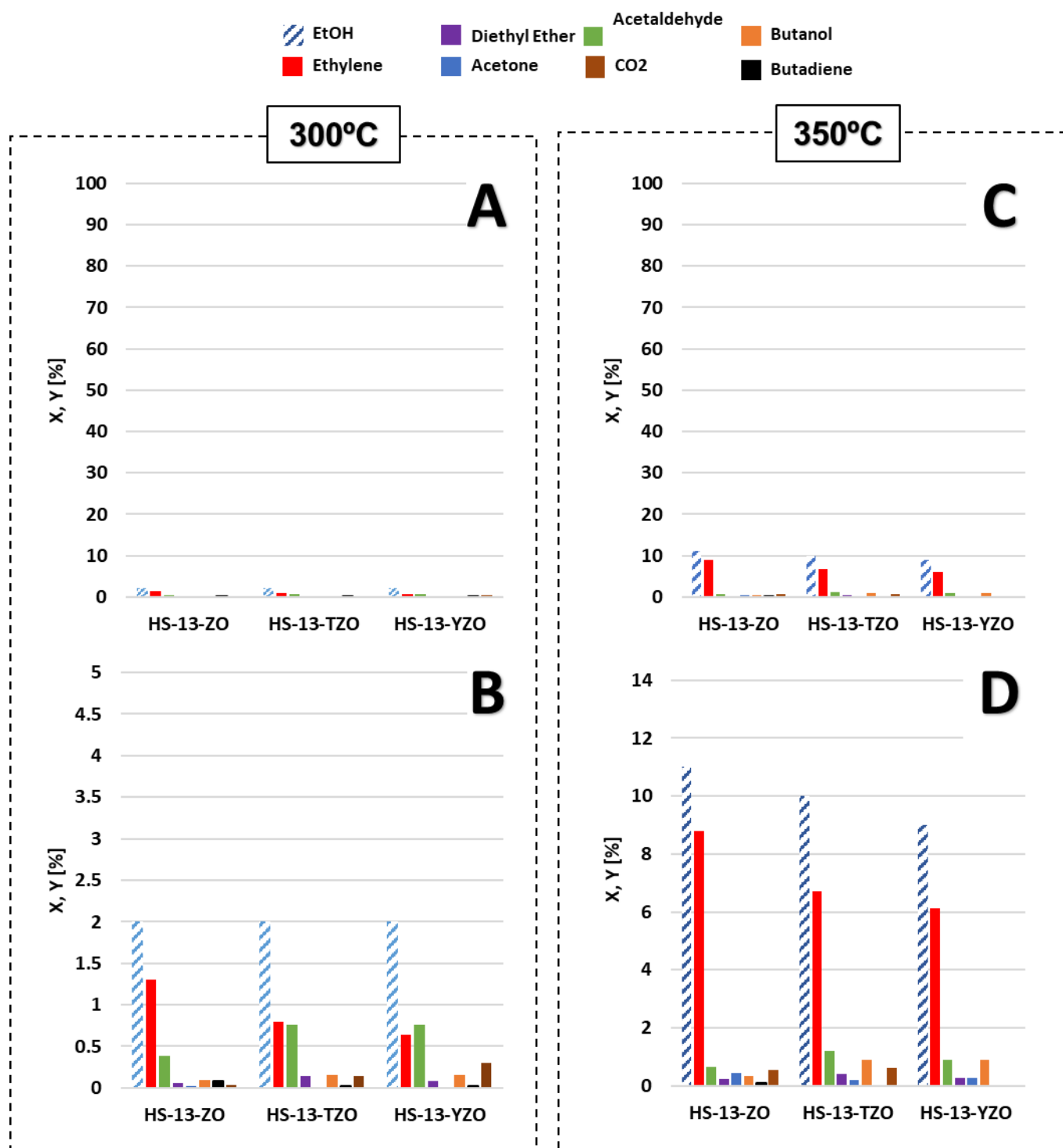


Figure 4.49 Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the catalysts obtained by hydrothermal synthesis. Reaction conditions: T: 300-350°C; p: 1 atm; EtOH 5%mol in N₂, $\dot{V}_{TOT}$ = 20 mL/min. W/F = 0.78 g·s/mL. **A)** Catalytic results obtained at 300°C; **B)** Catalytic results obtained at 300°C with narrowed y axis; **C)** Catalytic results obtained at 350°C; **D)** Catalytic results obtained at 350°C with narrowed y axis.

Higher conversion values were obtained when the catalysts were tested at 400°C converting almost half of the entering ethanol as can be seen in Fig. 4.50. The same graph shows that ethylene was still the major product of these series of catalysts in the given conditions.

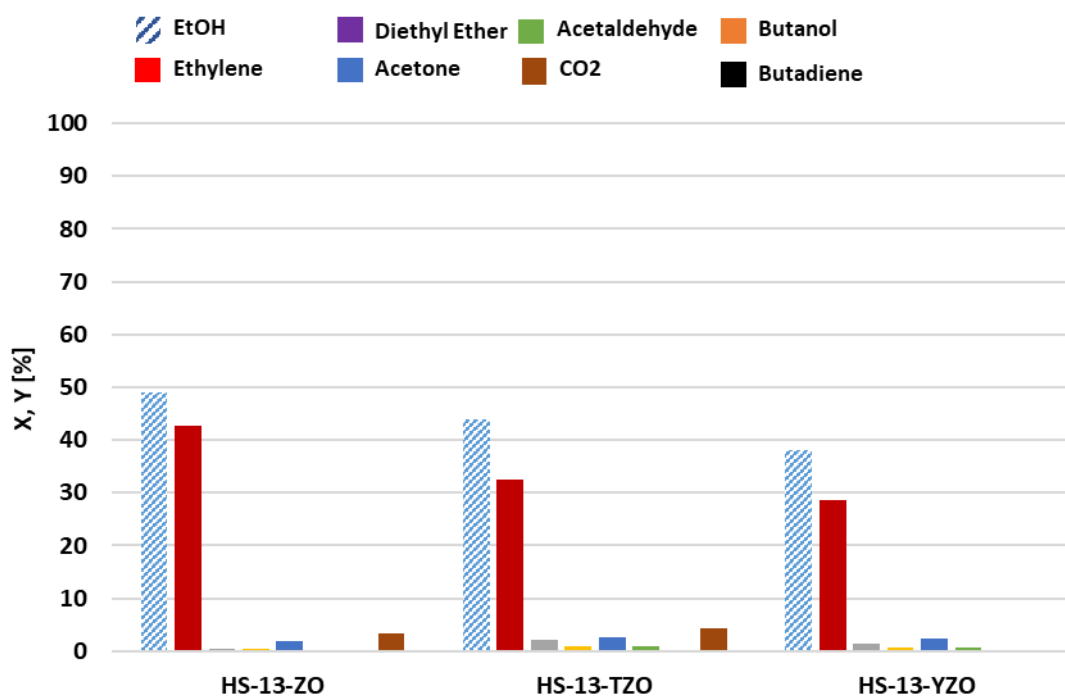


Figure 4.50 Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the catalysts obtained by hydrothermal synthesis. Reaction conditions: $T = 400^{\circ}\text{C}$; $P = 1 \text{ atm}$; EtOH 5%mol in N_2 ; $\dot{V}_{\text{TOT}} = 20 \text{ mL/min}$; $W/F = 0.78 \text{ g}\cdot\text{s/mL}$.

In summary, the catalysts obtained by precipitation have been in general more active respect to the ones synthesized via hydrothermal method in all the reaction temperature studied, namely 300°C , 350°C and 400°C . All the tested catalysts present ethylene as major product at all the tested temperatures. The titanium-doped zirconia catalyst obtained by precipitation at $\text{pH}=7.6$ appeared to be the most interesting among the tested ones, presenting higher ethanol conversion values respect to the other catalysts. Moreover, it presented diethyl ether as major product at 300°C , and a higher diethyl ether selectivity respect to the other catalysts at 350°C .

4.2.3.2 Stability tests over zirconia samples

Some of the tested zirconia samples have been chosen to investigate their stability over several hours of time on stream. In particular, the selected catalyst have been the zirconia catalyst synthesized by precipitation with ammonium hydroxide at $\text{pH}=7.6$ (PA-7.6-ZO), one sample containing Y, synthesized via precipitation with urea at $\text{pH}=8.5$ (PU-8.5-YZO) and one containing Ti (PA-7.6-TZO). The catalysts have been tested at $T: 350^{\circ}\text{C}$; $p: 1 \text{ atm}$; EtOH 5%mol in N_2 , $\dot{V}_{\text{TOT}} = 20 \text{ mL/min}$ and $W/F = 0.78 \text{ g}\cdot\text{s/mL}$. The selected time on stream was of 14.2 h. As depicted in Fig. 4.51, the zirconia catalyst synthesized by precipitation (PA-7.6-ZO) showed a decreasing in ethanol conversion from 87% to 72% after 14.2 h of time on stream, revealing a partial deactivation of the catalyst. The products distribution looked constant since all the products yields decreased with the conversion during the time on stream.

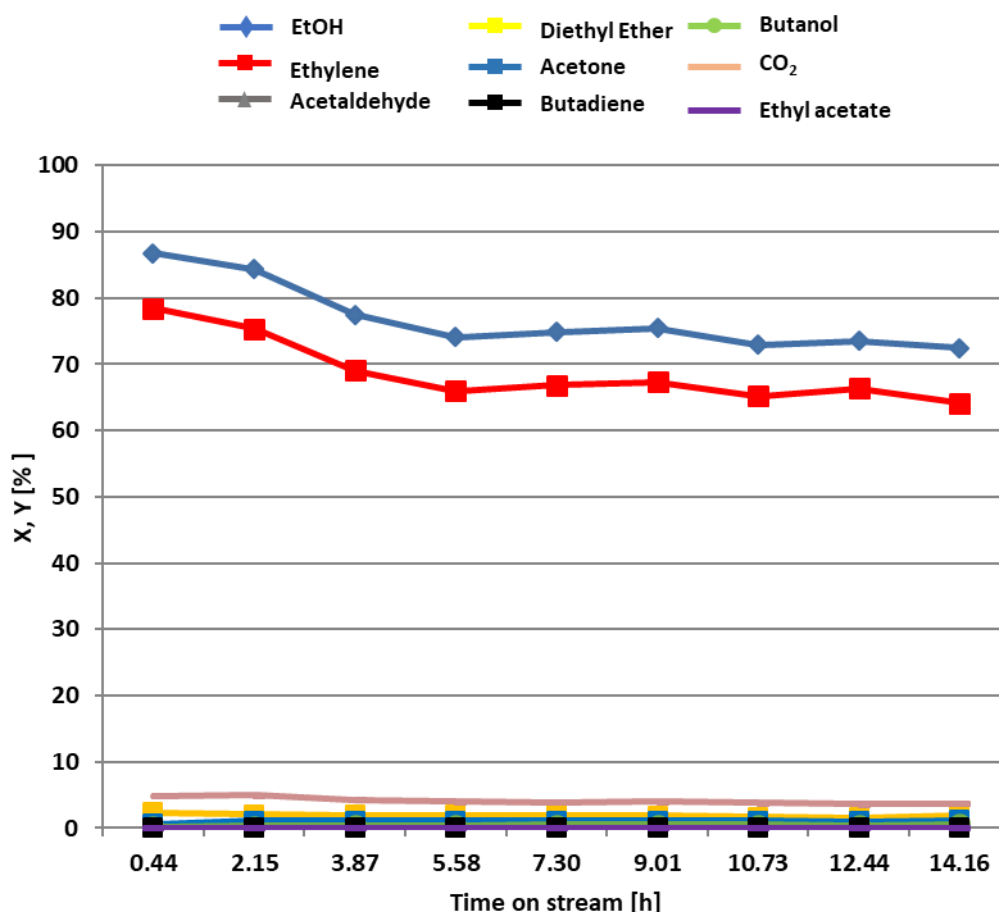


Figure 4.51 Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the zirconia catalysts obtained by precipitation with ammonium hydroxide at $\text{pH}=7.6$. (PA-7.6-ZO). Reaction conditions: T : 350°C ; p : 1 atm; EtOH 5%mol in N_2 , $\dot{V}_{\text{TOT}}=20\text{ mL/min}$; $W/F=0.78\text{ g}\cdot\text{s/mL}$.

Even the yttrium-doped zirconia samples (PU-8.5-YZO) showed a decreasing trend of ethanol conversion, dropping from 67% to 55% after 14.2 h, as shown in Fig. 4.52. All the products yields decreased with the time on stream, following the trend recorded for the ethanol conversion.

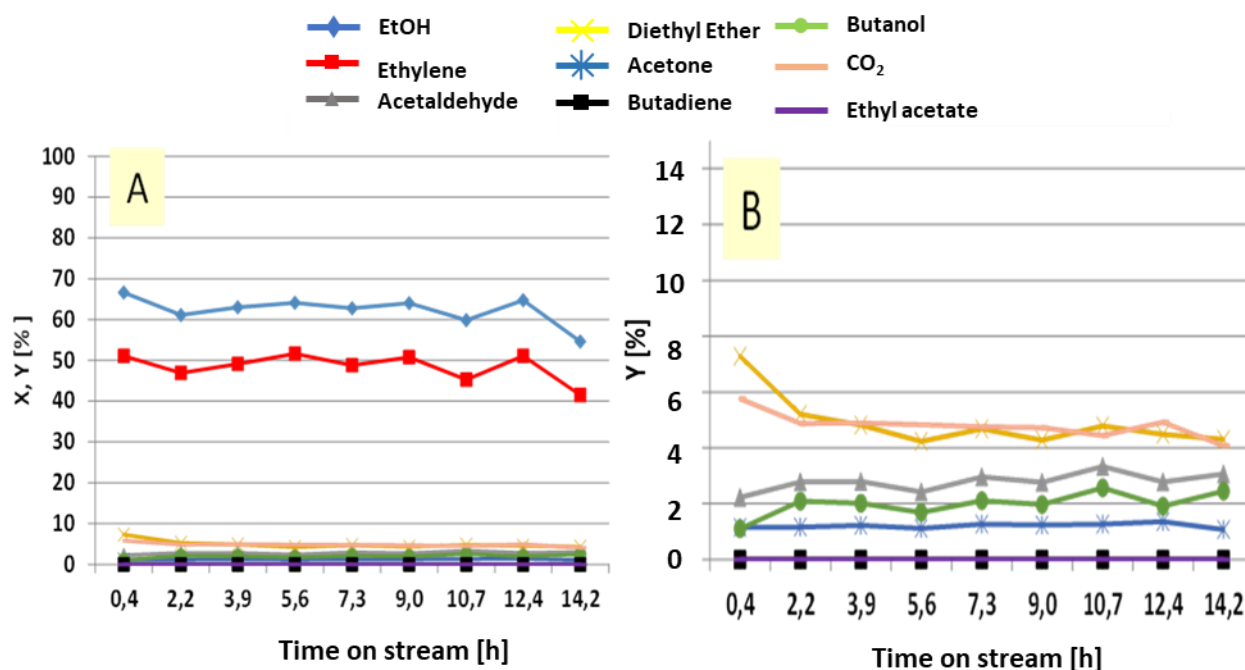


Figure 4.52 A) Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the yttrium-doped zirconia catalysts obtained by precipitation with urea at $\text{pH}=8.5$. (PU-8.5-YZO). Reaction conditions: T : 350°C ; p : 1 atm; EtOH 5%mol in N_2 , $\dot{V}_{\text{TOT}}=20\text{ mL/min}$; $W/F=0.78\text{ g}\cdot\text{s/mL}$. **B)** Yields to minority products.

Fig. 4.53 reports the conversion and yields as a function of the time on stream obtained over the titanium-doped zirconia catalyst synthesized by precipitation with ammonium hydroxide at $\text{pH } 7.6$ (PA-7.6-TZO). As can be observed, ethanol conversion appeared stable in the first 5.6 hours then decreased from 94% to 88% at 14.2 h. With this trend, ethylene yield decreased from 86% to 73% while diethyl ether yield increased from 5% to 12%, suggesting that diethyl ether could be an intermediate product yielding ethylene, indeed as the catalyst partially deactivated and the ethanol conversion decreased, the diethyl ether yield concomitantly increased slightly. This result is in accordance with the literature.²⁸²

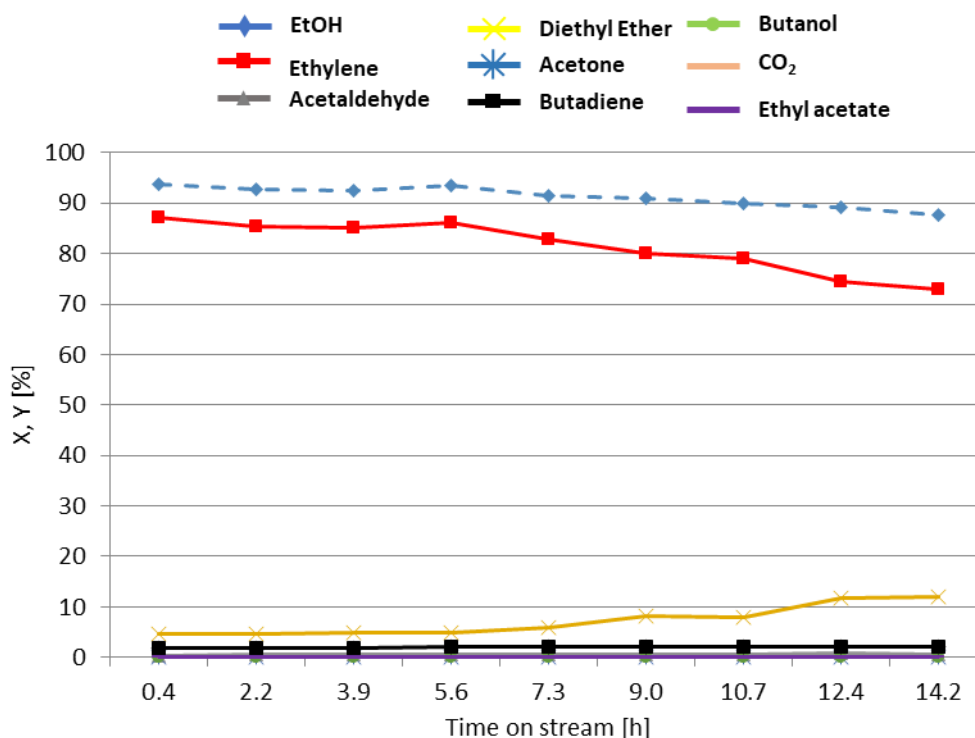


Figure 4.53 Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the titanium-doped zirconia catalysts obtained by precipitation with ammonium hydroxide at pH=7.6 (PA-7.6-TZO). Reaction conditions: T : 350°C; p : 1 atm; EtOH 5%mol in N_2 , $\dot{V}_{TOT}$ = 20 mL/min, W/F = 0.78 g·s/mL.

4.2.3.3 Study of effect of the contact time

To evaluate the effect of the contact time on the products distribution, another catalytic test with a higher mass of catalyst was performed over the titanium-doped zirconia sample obtained by precipitation with ammonium hydroxide at pH=7.6 (PA-7.6-TZO). Indeed, catalyst has been tested at the following condition: p : 1 atm; EtOH 5%mol in N_2 , $\dot{V}_{TOT}$ = 20 mL/min, and 300°C, increasing the quantity of the catalyst charged in order to obtain a W/F of 1.93 g·s/mL. Figure 4.54A depicts the results obtained in the just mentioned conditions, comparing them with the ones at lower W/F (0.78 g·s/mL). The same procedure has been performed at higher temperature, namely 350°C and the results are reported in Figure 4.54B. As can be seen in the figures, by enhancing the contact time, an increasing in the ethanol conversion was obtained, as expected. The products distribution changed as well, producing ethylene as the only product, with complete conversion of ethanol. By looking at Figure 4.54 both the effects of the contact time and the reaction temperature can be noticed, at least at the lowest contact time explored. Indeed, by working at W/F = 0.78 s·g/mL, an increase of the reaction temperature by 50°C led to an abrupt increase of the ethanol conversion from 30% to ~90%. While the main product at low temperature was diethyl ether, with a yield of ~25% (and so a selectivity > 80%), when the reaction temperature was raised to 350°C, the main product was again ethylene, reaching a value of yield of ~68%. Regardless, at the higher contact

time investigated, the same results have been obtained, complete conversion of ethanol producing ethylene as the only product.

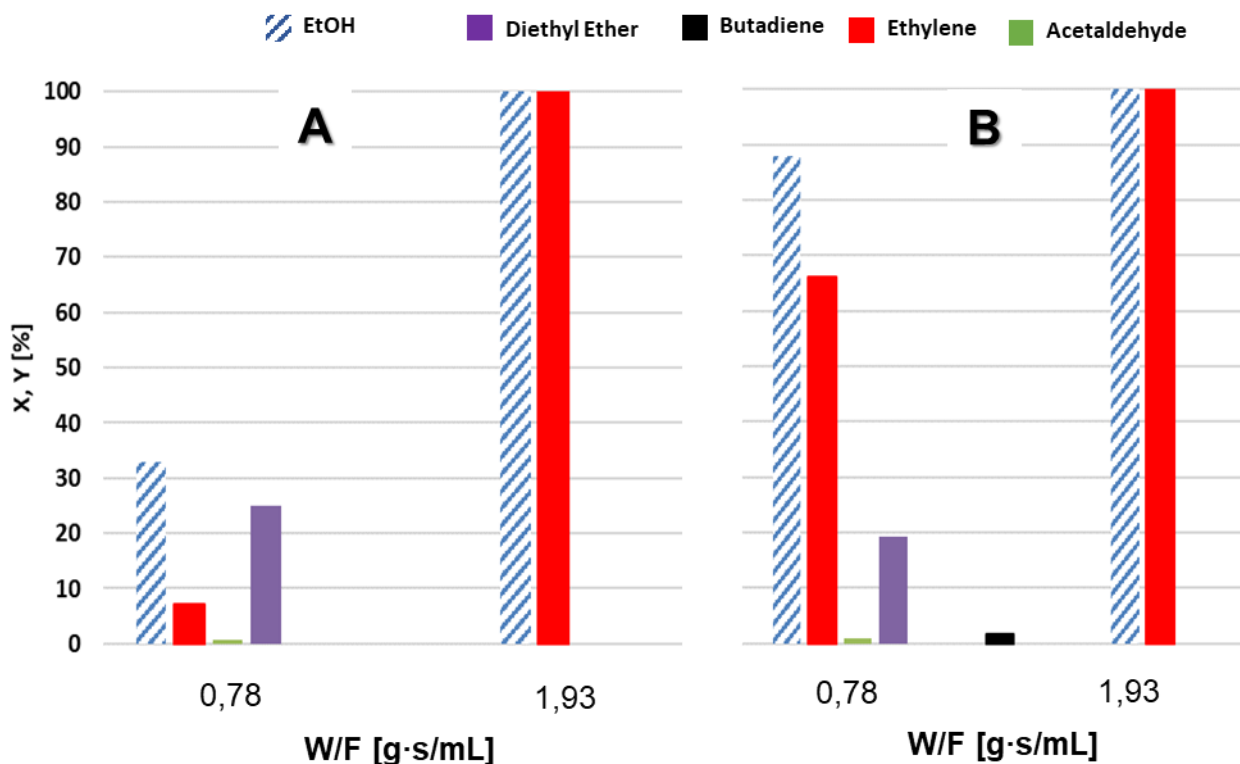


Figure 4.54 Ethanol conversion (X) and main products yields (Y) obtained from the catalytic tests performed over the titanium-doped zirconia catalysts obtained by precipitation with ammonium hydroxide at pH=7.6. (PA-7.6-TZO). A) $T_R = 300^\circ\text{C}$; B) $T_R = 350^\circ\text{C}$. Reaction conditions: $T = 300$ or 350°C ; $p = 1$ atm; EtOH 5%mol in N_2 , $\dot{V}_{TOT} = 20$ mL/min, $W/F = 0.78$ or 1.93 g·s/mL

4.2.4 Spent catalysts characterization

The TGA profiles of the analysis performed over the three catalysts which have been tested to evaluate their stability (PA-7.6-ZO, PA-7.6-TZO, and PU-8.5-YZO), are compared. TGA analysis was conducted to quantify the deposited carbon over the spent catalysts. In Figure 4.55 (pictures A, B and C) the TGA profiles illustrate the weight loss (%) as a function of temperature for the spent catalysts recovered after performing the stability tests at 350°C , $W/F = 0.78$ g·s/mL after 14.2 h on stream (see Figures 4.51, 4.52 and 4.53). In detail, the spent catalysts weighing 45-50 mg were heated from ambient temperature to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under air atmosphere, and the weight loss was recorded.

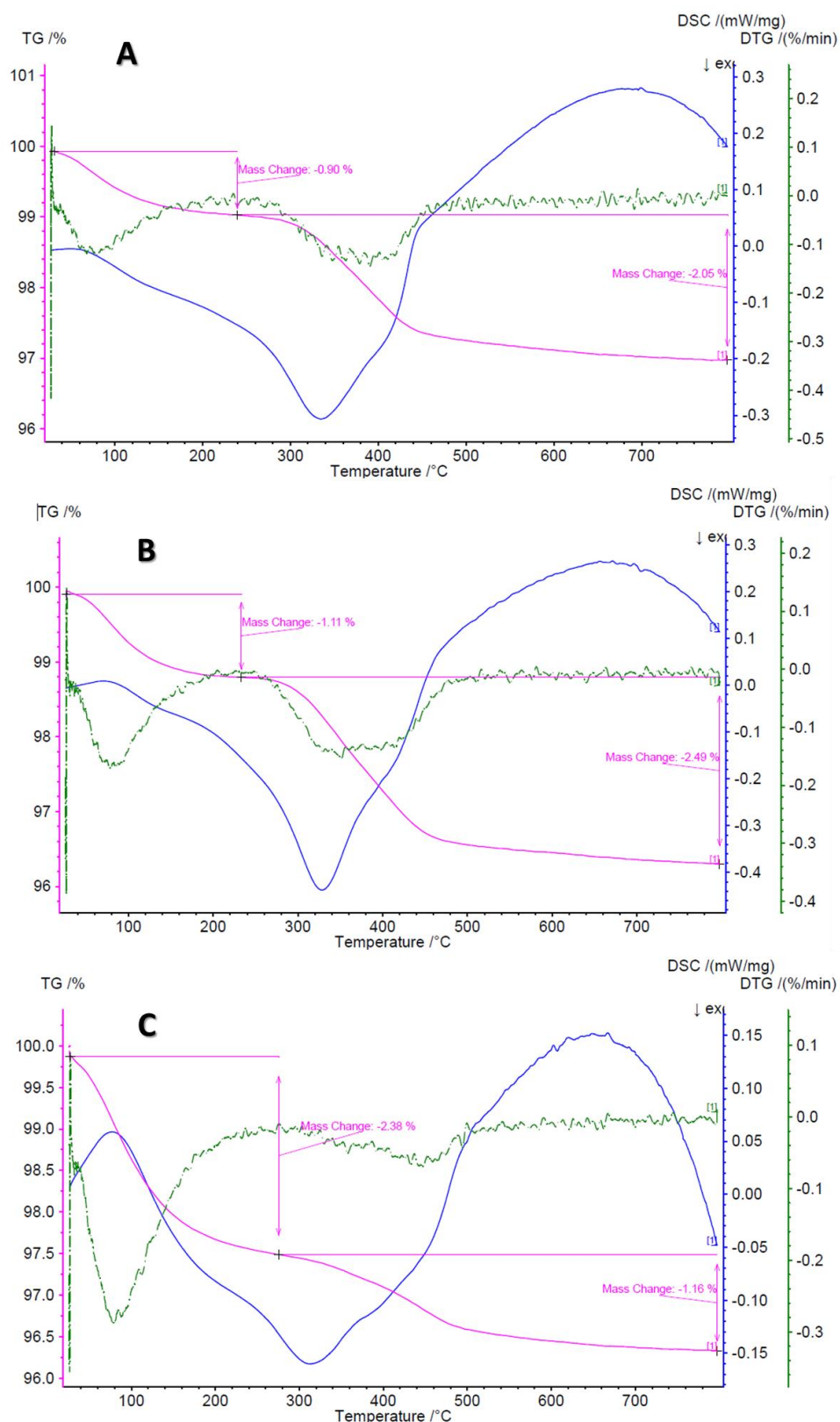


Figure 4.55 TGA/DSC profiles of spent zirconia catalyst tested at 350°C for 14.2 h of time on stream. A) Synthesized at pH=7.6 with 25%w NH_4OH solution (PA-7.6-ZO); B) The yttrium-doped zirconia sample synthesized at pH=8.5 with urea (PU-8.5-YZO); C) The titanium-doped zirconia sample synthesized at pH=7.6 with 25%w NH_4OH solution (PA-7.6-TZO).

The three TGA profiles are depicted in Fig 4.55. All of them presented two mass losses: the first one at around 100°C can be related to the loss of adsorbed water while the second one, around 400°C

showed the combustion of carbon deposits. For all catalysts, the burning of carbon starts at the same temperatures around 300 °C. All the three catalysts showed similar total mass change at the TGA. Nevertheless, what can be noticed from Fig. 4.55C is that PA-7.6-TZO mass loss at 400°C consisted in the 1.2% of the total mass, a lower amount compared to PA-7.6-ZO and PU-8.5-YZO which showed 2.0% and 2.5% respectively. This difference could have influenced the conversion loss of PA-7.6-TZO, which appeared to be lower respect to the other catalysts. Indeed, after 14.2 h of time on stream, ethanol conversion lowered by 6% on this latter catalyst compared to the ~ 15% observed for the other two catalysts under consideration. However, the total mass change was similar between the three samples because PA-7.6-TZO presented a huge loss of adsorbed water at 100°C (-2.4%) which could be related to its higher surface area (148 m²/g) compared to the other tested samples (PA-7.6-ZO and PU-8.5-YZO, 86 and 113 m²/g respectively).

Table 4.8 Ethanol conversion losses after 14.2 h of time on stream and TGA mass changes of different zirconia catalysts.

Catalyst code	ΔX_{EtOH} after 14.2 h	Δm [w%]
PA-7.6-ZO	-15%	-2.05%
PU-8.5-YZO	-12%	-2.49%
PA-7.6-TZO	-6%	-1.16%

PA-7.6-ZO: zirconia synthesized by precipitation at pH 7.6 with NH₄OH; **PA-7.6-TZO:** titanium-doped zirconia synthesized by precipitation at pH 7.6 with NH₄OH; **PU-8.5-YZO:** yttrium-doped zirconia synthesized by precipitation at pH 8.5 with urea. X_{EtOH} loss after 14.2 h has been calculated as the difference between the ethanol conversion at the first analysed point with the online GC and the one obtained after 14.2 h.

4.2.5 CONCLUSIONS

Several zirconia samples have been synthesized by hydrothermal and precipitation methods. The catalysts have been characterised in order to investigate the influence of several synthetic parameters such as the method (i.e., precipitation or hydrothermal), the base used (i.e., NaOH, NH₄OH or Urea), and pH on the catalysts characteristics. Notably, mixed crystal phases have been obtained. However, particularly at higher pH values, the catalyst preparation procedure played a crucial role over the nature of crystalline phase formation. Thus, by hydrothermal synthesis carried out at pH=13 it was obtained a sample of pure monoclinic zirconia. While, by precipitation method at the same pH value, tetragonal or cubic zirconia was formed.

Finally, the effect of the incorporation of a dopant (Y and Ti) on the nature of zirconia samples have been evaluated in both the synthetic methods employed. The main effect observed of the presence of a metal was an overall stabilization of the metastable tetragonal or cubic phases over the monoclinic one. Concomitantly, an increase of the BET surface area has been observed as well.

The synthesized zirconia-based catalysts have been tested in the gas-phase ethanol transformation in a range of temperatures from 300°C to 400°C. In general, the tested zirconia samples showed a clear acid behaviour, converting ethanol mainly into its dehydration products ethylene and diethyl ether, a well-known acid catalysed reaction. However, changes in conversion and selectivity were observed depending on the catalyst preparation procedure and/or the presence of a metal-dopant. Interestingly, the titanium-doped zirconia samples prepared by precipitation, that, according to TPD-NH₃ analysis, was the most acid between the ones analysed, allowed to obtain diethyl ether as main product while performing the reaction at relative low temperature (300°C).

In the future, would be interesting to further modify those materials by adding a redox active site, such as a transition metal, in order to increase their hydrogenation/dehydrogenation properties. Indeed, acetaldehyde, the dehydrogenation product of ethanol, has been often identified as the key product for *n*-butanol and 1,3-butadiene formation starting from ethanol, both valuable compounds with many industrial applications.

4.3 Guerbet reaction over Sepiolite based catalysts – ITQ-UPV

The topic of the whole research has been the valorisation of ethanol through its gas-phase conversion over heterogeneous catalysts into added value derivatives. This includes *n*-butanol, which is an important chemical compound with many different uses such as additive in daily use products and intermediate to produce more valuable compounds, as well as a valid alternative to gasoline. Ethanol can be converted into *n*-butanol through the so-called Guerbet reaction, which comprises a complex reaction mechanism where a fine-tuning of the acid-base catalyst properties is thought to be a key aspect to optimize.

Sepiolite is a fibrous magnesia-silicate clay mineral, with the formula structure as $(\text{Si}_{12}\text{Mg}_8\text{O}_{30})(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$. Its fibrous structure is formed by an array of parallel channels, consisting of a double layer of SiO_4 sandwiching an internal octahedral MgO_6 layer, it led to the formation of intracrystalline channels filled with coordinated water molecules and zeolitic water. The special crystal structure of sepiolite makes it have large specific areas and high surface activity and it has been applied widely in many areas including catalysis. It has been reported that sepiolite can undergo alkaline treatments for both increasing its ion-exchange capability and changing its acid/base characteristic.

In the present work, carried out in the laboratory of “Instituto de Tecnología Química” (ITQ) of the “Universitat Politècnica de Valencia” (UPV), the natural clay Sepiolite has been treated in order to obtain a bi-functional acid-base catalyst and convert bio-ethanol into *n*-butanol through the Guerbet reaction. The catalysts so prepared have been characterized by several techniques and tested in a gas-phase bench scale continuous flow quartz reactor using as feeding a mixture of 5% Ethanol in N_2 .

4.3.1 Catalysts characterization

4.3.1.1 X-ray diffraction (XRD) analysis

Catalysts crystal structure was determined by means of XRD of their powders. Figure 4.56 reports the XRD pattern of sepiolite samples, relating to their thermal treatment: no thermal treatment (SepNat) and calcined at 500°C (Sep@500) and at 700°C (Sep@700).

The XRD study (Fig. 4.56) shows that the main phase constituent of the raw material (SepNat) is a well crystallized sepiolite, as indicated by the presence of the characteristic narrow and intense diffraction peak at $2\theta=7.3^\circ$. Indeed, the XRD pattern of the raw material matched with the one of Sepiolite, Magnesium Silicate Hydroxide Hydrate (00-013-0595), $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$.

By heating the sepiolite sample up to 500°C , the peak at 7.31° disappeared, indicating that the layered structure of sepiolite collapsed with calcination. In fact, the XRD pattern of calcined sepiolite (Sep@500) contains none of the reflections peaks of the natural sample, revealing that the heating caused structural and textural changes associated with dehydration and dehydroxylation processes.²¹⁹ Accordingly, both the sepiolite samples calcined at 500°C and 700°C matched with the 00-026-1227 reference pattern related to the sepiolite anhydride (SA), Magnesium Silicate Hydroxide, $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4$. Furthermore, the slight increase of the peaks intensity at $\sim 8.9^\circ$, $\sim 11.1^\circ$ and 20.25° , corresponding to the planes (110), (120) and (031) respectively (Fig. 4.56) with calcination temperature, indicated the formation of sepiolite anhydride.²¹⁹ Those data are in accordance with the ones reported in literature.²⁸³ In addition, with increasing temperature, the presence of quartz peak at 26.7° can be observed.

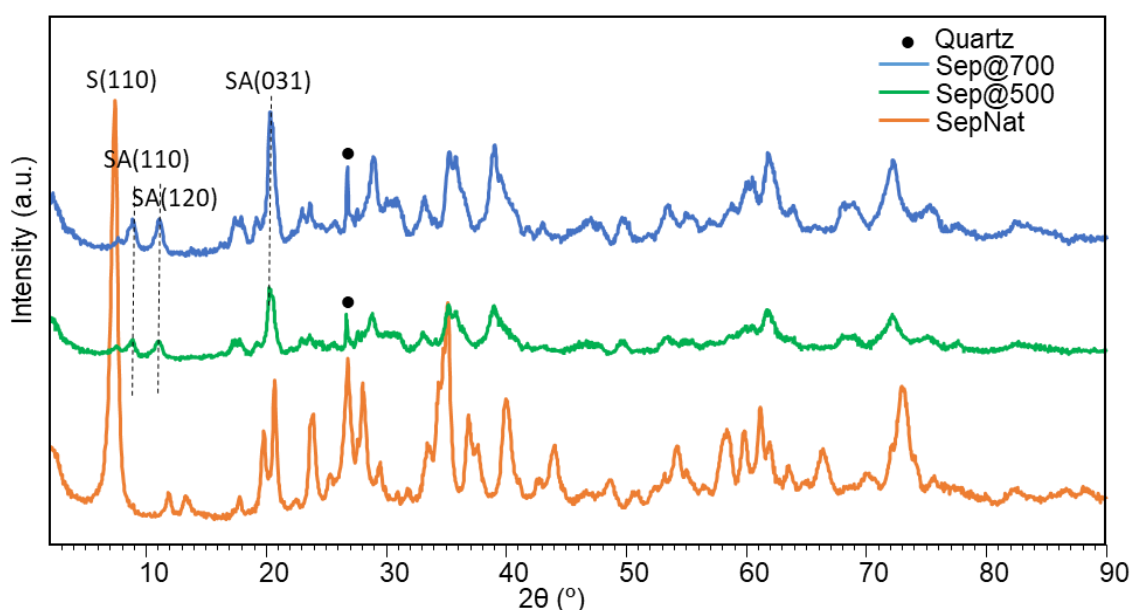


Figure 4.56 XRD patterns of sepiolite samples. Natural sepiolite (SepNat, orange line) and the two samples after calcination at 500°C (Sep@500, green line) or 700°C (Sep@700, blue line). Dot: quartz.

Table 4.9 summarizes the crystalline phases detected and the related crystallite sizes, estimated by applying Scherer's formula. The crystallite size of natural sepiolite was computed considering the peak at $2\theta= 7.3^\circ$ while for the calcined ones, relating to the sepiolite anhydride, it was considered the reflection at $2\theta= 20.25^\circ$.

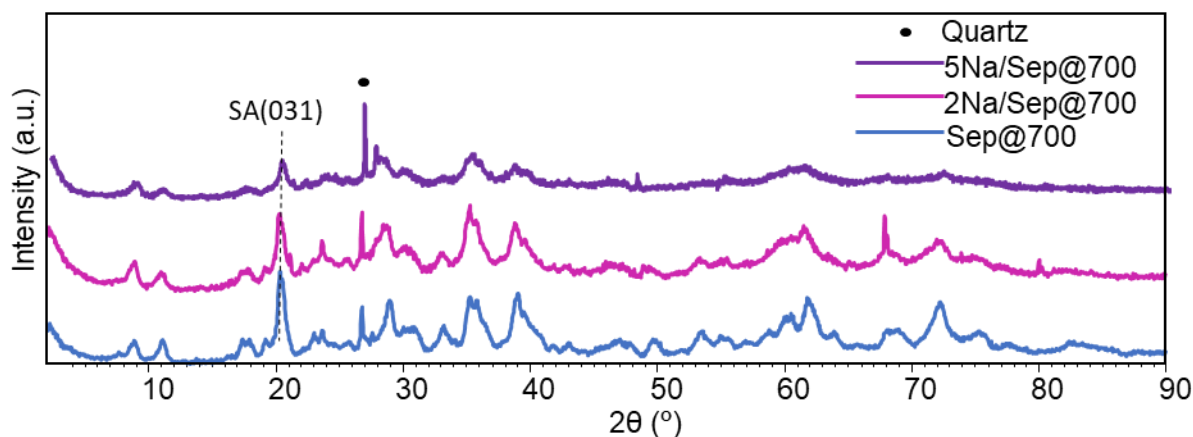
Table 4.9 Summary of information obtained from XRD analysis performed over the sepiolite samples, i.e. the natural one and those calcined at 500°C and 700°C.

Catalyst	Phase detected + Reference code	D [nm] ^a
SepNat	Magnesium Silicate Hydroxide Hydrate (00-013-0595)	14.3
Sep@500	Magnesium Silicate Hydroxide (00-026-1227)	15.9
Sep@700	Magnesium Silicate Hydroxide (00-026-1227)	16

^a Calculated through Scherrer equation.

4.3.1.1.1 Alkali metals effect

Figure 4.57 and Figure 4.58 report the XRD patterns obtained for the alkali metals-impregnated samples. Generally, it can be observed a broadening (with reference to the sepiolite support itself) and reduced intensity of the peaks, suggesting significant changes in the sepiolite crystallinity. In particular, the XRD diffractograms for samples of Na-impregnated sepiolite pre-calcined at 700°C (Sep@700) samples with different metal loading (i.e., 2 and 5 wt%) are shown in Figure 4.57. The samples are noted as XNa/Sep@700 where X denotes the weight percentage of metal loading.

**Figure 4.57** XRD patterns of sepiolite samples. Sepiolite calcined at 700°C (Sep@700) and Na-doped sepiolites with 2 and 5 wt% of Na (2Na/Sep@700 and 5Na/Sep@700).

The diffraction patterns of the Na-impregnated samples showed similar pattern to that of the parent Magnesium Silicate Hydroxide (Sepiolite Anhydride, SA), indicating that the framework structure has been retained after loaded with sodium. However, diffractograms for sample containing 5wt% of Na showed partial amorphous phase suggesting that the framework of the support have partially collapsed. Indeed, it can be observed a partial decrease of the crystallinity of the impregnated sample with increasing Na-loading.

The XRD diffractograms of the Na, K and Cs-impregnated sepiolite pre-calcined at 500°C (Sep@500) samples are shown in Figure 4.58. Even in this case, the diffraction patterns of the impregnated samples showed similar patterns to that of the parent Magnesium Silicate Hydroxide (Sepiolite Anhydride, SA), indicating that the framework structure has been retained after loaded with alkali metals. However, diffractograms for samples containing the highest amount of alkali metals showed partial amorphous phase suggesting that the framework of the support sepiolite had partially collapsed. Indeed, it can be observed a partial decreasing of the crystallinity of the impregnated samples with increasing alkali metals amount, as it is particularly evident from the decreased intensity of the reflection peak located at $2\theta = 20.25^\circ$. Figure 4.58 highlights the section of the XRD pattern in the 2θ range between 0-23 °.

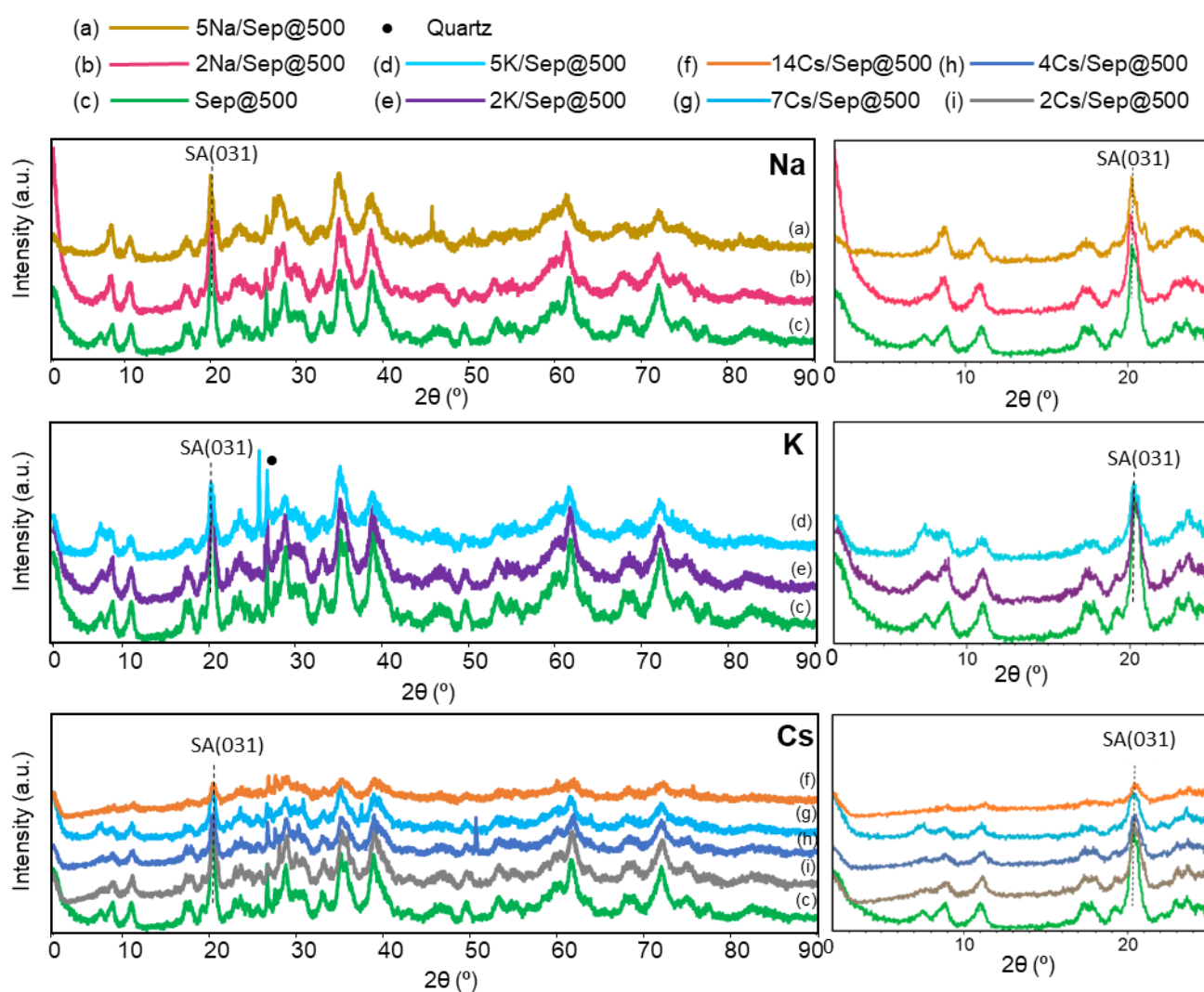


Figure 4.58 XRD patterns of sepiolite samples. a) 5K/Sep@500, b) 2K/Sep@500, c) Sep@500, d) 5Na/Sep@500, e) 2Na/Sep@500, f) 14Cs/Sep@500, g) 7Cs/Sep@500, h) 4Cs/Sep@500, i) 2Cs/Sep@500.

Pure sepiolite gave sharper peaks than the alkali-metals-doped sepiolite catalysts, indicating that the pure sepiolite samples consisted in larger crystallite sizes than the ones containing the alkali-metals. In addition, the intensity of XRD peak at $2\theta = 8^\circ$, 11° and 20.25° decreased with increasing

metal loading, indicating the decrease in the crystallinity of sepiolite dehydrate framework structure. Table 4.10 summarized the XRD data of the sepiolite samples. In general, there is no indication of the presence of any new crystalline phase other than the sepiolite dehydrate. Therefore, the alkali metal salt or oxides are well dispersed on the surface of the sepiolite calcined at 500°C.

Table 4.10 XRD data for the alkali-impregnated sepiolite samples, calculated through Scherrer equation (a), and considering the peak at 20.25° as representative for the sepiolite anhydride (ref. 00-026-1227).

Support	Metal	Metal loading [wt%]	D [nm]^a
Sep@700	-	-	16
	Na	2	13.8
		5	13.5
Sep@500	-	-	15.9
	Na	2	15.1
		5	12.7
	K	2	12.8
		5	13.3
		2	15.3
	Cs	4	15.0
		7	13.9
		14	12.6

4.3.1.1.2 Transition metal/sepiolite

4.3.1.1.2.1 Copper oxide impregnated sepiolite

To investigate the ethanol gas-phase Guerbet reaction over heterogeneous catalysts, a wide variety of basic oxides have been already employed. Between them, MgO appeared to be the most active and selective toward the Guerbet reaction and often it has been used as a reference catalyst.^{60,284} In this work we decided as well to prepare a sample of magnesium oxide and employ it as reference catalyst. Hence, it has been synthesized by precipitation as explained in detail in Section 4.2.4.2. Successful synthesis was confirmed by XRD analysis performed over the calcined sample, as shown in Figure 4.59.

Copper was added to both MgO and the sepiolite (previously calcined at 500 or 700°C), by wet impregnation as explained in Section 3.2.4.3.2. All samples after impregnation were calcined at 500°C for 3 hours with a 2°C/min heating ramp. Figure 4.59 reports the XRD patterns of MgO and the copper impregnated sample. Even if no copper oxide phases were detected, proving a good dispersion of copper over the magnesia support, a decrease of crystallinity of the MgO after impregnation can be noticed.

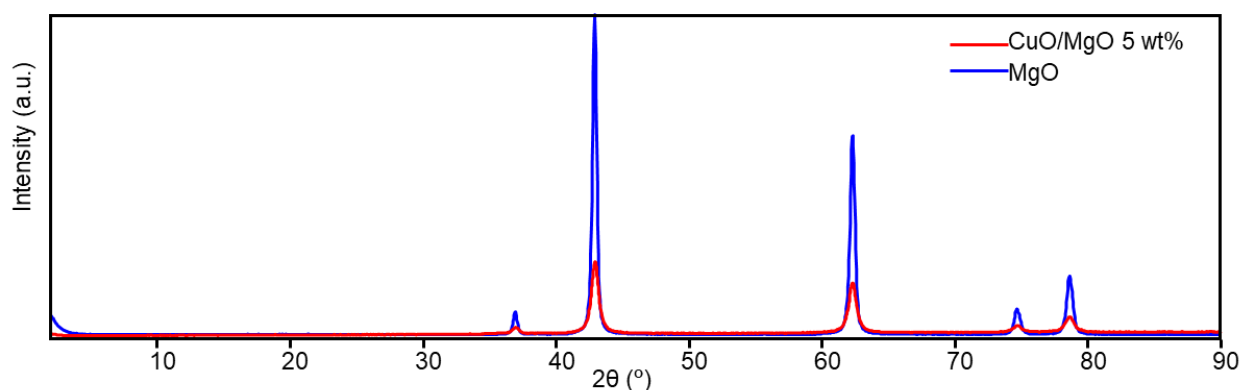


Figure 4.59 XRD of MgO and the copper oxide impregnate one (CuO/Sep@700 5 wt%).

Sepiolite sample pre-calcined at 700°C has been impregnated with 5 wt% of copper, and Fig. 4.60 shows the XRD patterns of the so-prepared samples. Upon CuO impregnation, the presence of the typical CuO (Tenorite, ref. 00-002-1040) patterns were observed at the Bragg angles, $2\theta = 35.59^\circ$, 38.78° , 48.65° , 53.5° , 58.35° and 66.23° . The first aforementioned two peaks (i.e., 35.59° , 38.78°), which are the most intense ones, coincided with the ones of the support sepiolite anhydride (00-026-1227). Therefore, the presence of the copper oxide agglomerate can be confirmed by the four less intense peaks at 48.15° , 53.5° , 58.35° , and 66.22° that corresponds to the planes (-202), (020), (202) and (022), respectively.

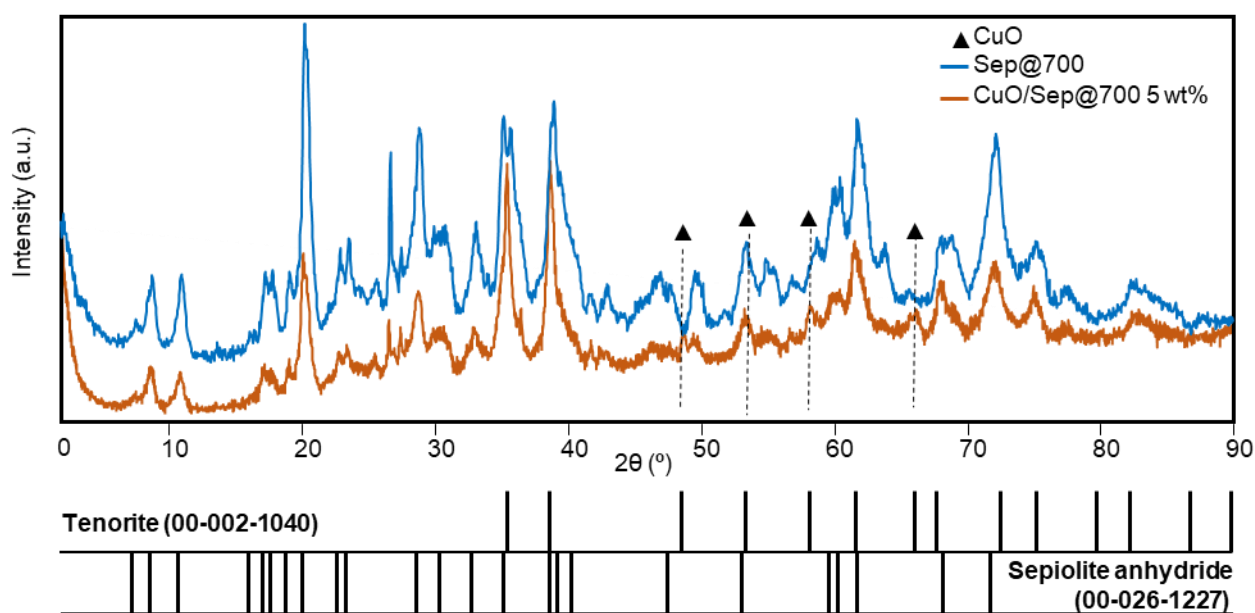


Figure 4.60 XRD of the natural sepiolite support calcined at 700°C (Sep@700) and the copper oxide impregnate one (CuO/Sep@700 5 wt%).

Then, copper has been added through wet impregnation by 5 and 10 wt% of metal loading over the sepiolite support pre-calcined at 500°C. Figure 4.61 depicts the XRD patterns obtained for those samples. Even in this case, aggregation of copper oxide can be observed by the presence of peaks at $2\theta = 48.65^\circ$, 58.35° , 66.23° and 67.86° corresponding to planes of tenorite (-202), (202), (-311) and (022), respectively. Some sepiolite samples containing sodium have been impregnated with

copper oxide, in particular the two sepiolite samples calcined at 500 and 700°C and doped with 2wt% of sodium have been impregnated with 5 or 10 wt% of CuO (i.e., CuO/2Na/Sep@700 5wt%, CuO/2Na/Sep@500 5 wt% and CuO/2Na/Sep@500 10 wt%). Likewise, the addition of copper over the sepiolite containing sodium led to similar results. The XRD analysis results of the concerned samples are depicted in Figure 4.62.

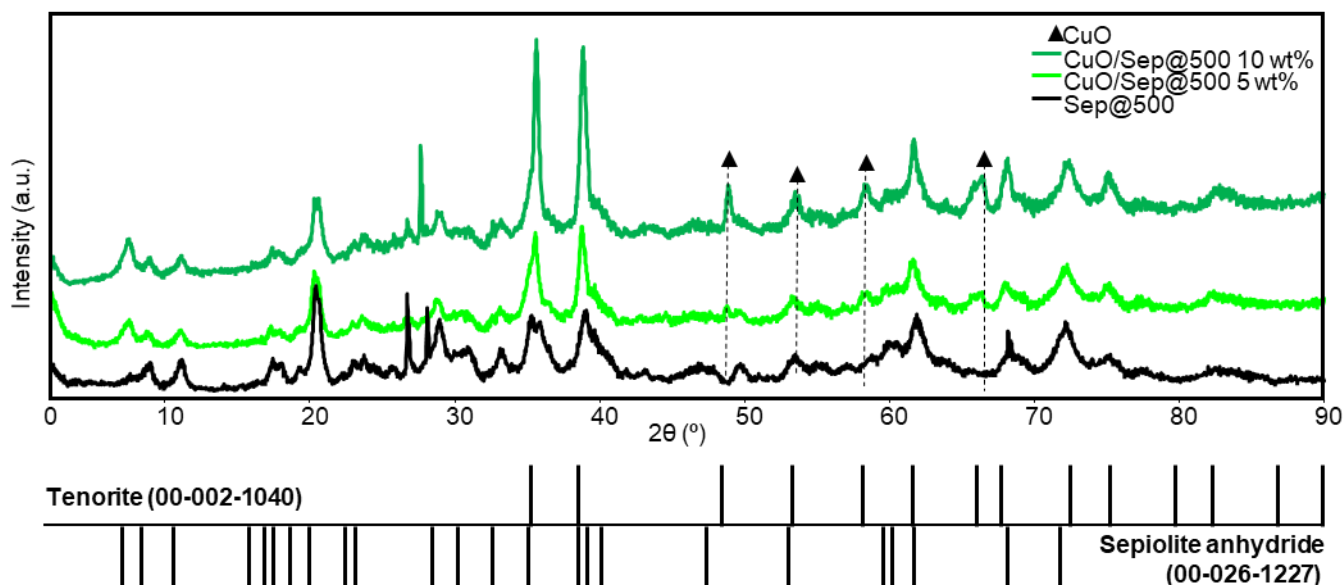


Figure 4.61 XRD of the natural sepiolite support calcined at 500°C (Sep@500) and the copper oxide impregnate ones (CuO/Sep@500 5 wt%, CuO/Sep@500 10 wt%).

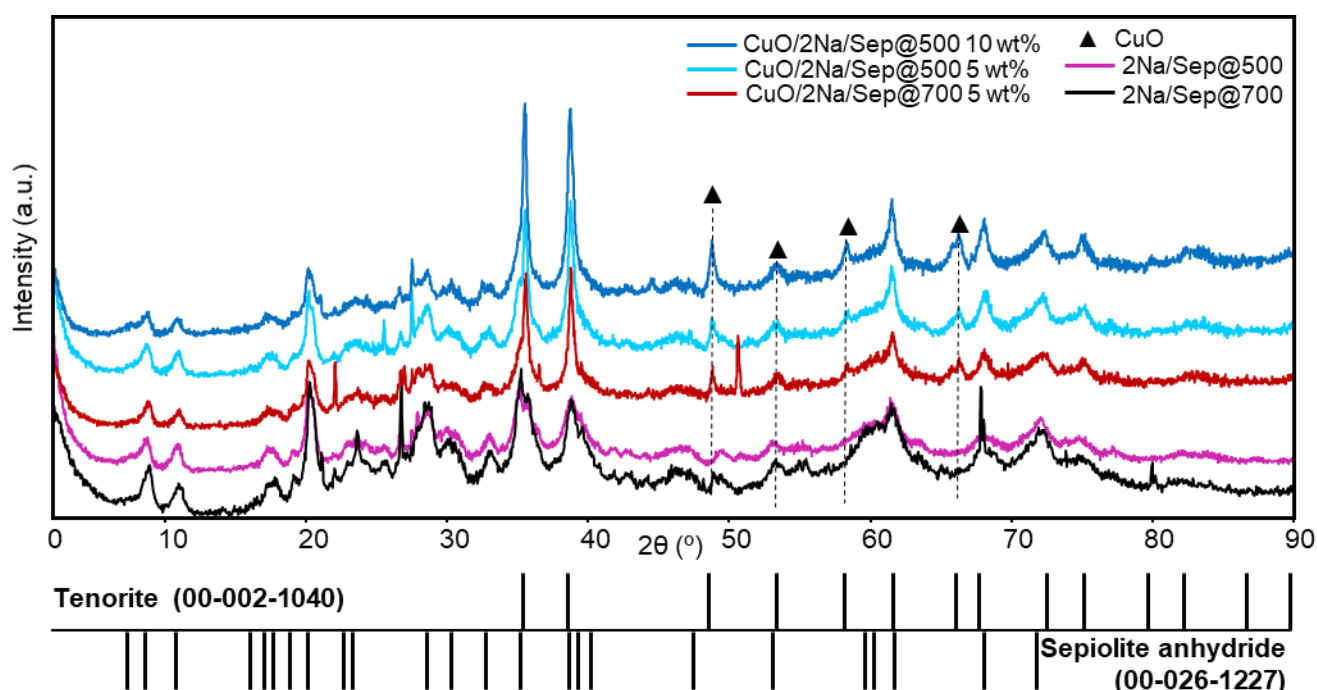


Figure 4.62 XRD of the 2 wt% Na-doped natural sepiolite samples calcined at 500°C (2Na/Sep@500) and 700°C (2Na/Sep@700) and the copper oxide impregnate ones with different metal loading (CuO/2Na/Sep@500 5 wt%, CuO/2Na/Sep@500 10 wt%, CuO/2Na/Sep@700 5 wt%).

4.3.1.1.2.2 Nickel - oxide impregnated sepiolite

A nickel-impregnated sample has been prepared as explained in Section 3.2.4.3. In particular, NiO has been supported on 2Na/Sep@500 with a metal loading of 5 wt%. The corresponding XRD pattern is presented in Fig.4.63 together with the one of the support (i.e., 2Na/Sep@500). Even in this case, the XRD patterns of the NiO supported sample displays the set of observable reflections corresponding to the sepiolite anhydride (Ref.: 00-026-1227) support. The appearance of nickel oxide (NiO, Ref.: 01-089-5881) can be noticed by the presence of the peaks at $2\theta = 43.29^\circ$ corresponding to the (400) plane and at 62.88° corresponding to (440) plane.

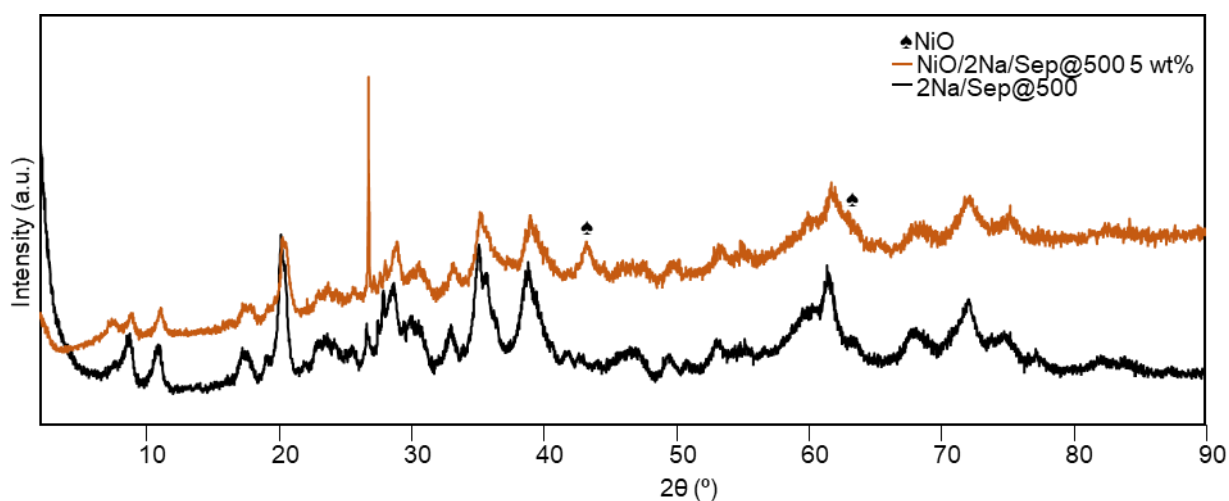


Figure 4.63 XRD of the 2 wt% Na-doped natural sepiolite samples calcined at 500°C (2Na/Sep@500) and the nickel oxide impregnated one with 5 wt% of metal loading (NiO/2Na/Sep@500 5 wt%).

4.3.1.2 Thermogravimetric analysis (TGA)

TGA analysis confirmed the removal of water with increasing temperature. From the TGA analysis results, performed in the 25 – 800°C temperature range with a 10°C/min ramp, three mass losses can be observed (Figure 4.64). These three steps (with peaks at around 100, 300 and 500°C) were accompanied with mass loss percentages of 7.6, 2.6, and 3.6%, respectively, and correspond to: i) the loss of the weakly adsorbed water on the surface (i.e., adsorbed water and zeolitic water); ii) the loss of hydration water and; iii) the loss of coordination water.²⁸⁵ Additionally, around 800°C a fourth mass loss can be also observed which, in agreement to the literature, could be related to the loss of water through dehydroxylation, leading to the formation of enstatite (MgSiO_3).^{219,286}

It is well known^{219,220} that the sepiolite dehydration takes place in two steps: i) the first one around 300°C produces sepiolite dihydrate $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_2$, ii) the second one, by heating sepiolite up until 550°C, yields sepiolite anhydride $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4$. In addition, between 600–700 °C occurs the chemical removal of the structural hydroxyls until structure collapse around 800°C.²²⁰

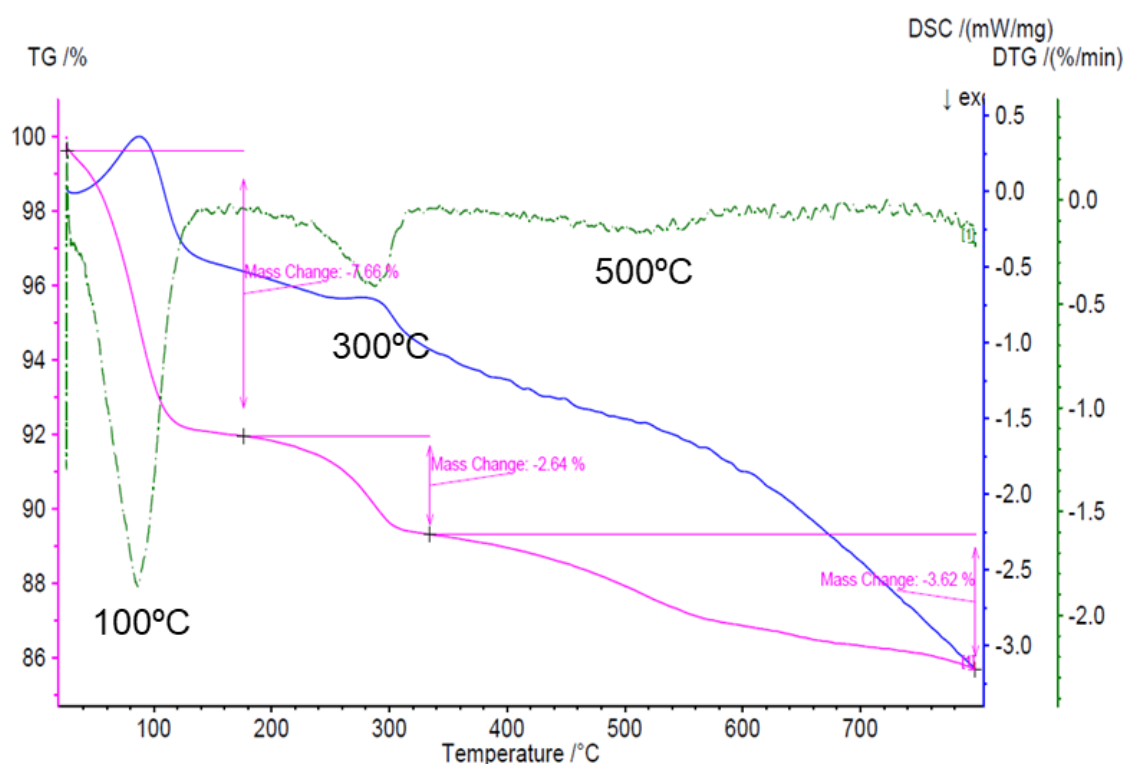


Figure 4.64 TGA analysis of natural sepiolite sample

4.3.1.3 Surface area, BET

The N₂ BET surface areas of the calcined samples were determined by N₂ physisorption isotherms, the results are listed in Table 4.11. The MgO sample had a relatively low surface area of 41 m²/g in agreement with literature values.^{287,288} On the other hand, the sepiolite samples displayed an adsorption isotherm belonging to IUPAC type IV with H-3 hysteresis loop (Figure 4.65), typical of mesoporous adsorbents.²⁸⁹ The BET surface area of the two sepiolite samples calcined at 500 and 700°C were 138 m²/g and 124 m²/g, respectively; showing a lower value of BET surface area at higher calcination temperature. The decrease in the surface area with increasing calcination temperature is a general phenomenon due to sintering of the samples at high temperatures.

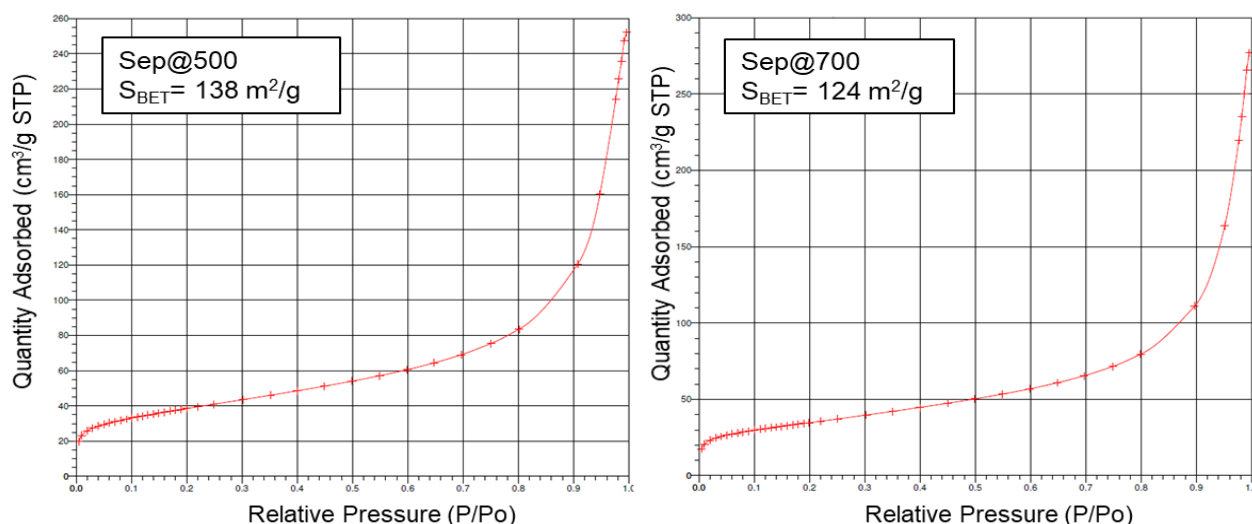


Figure 4.65 Representative adsorption isotherms and BET values for natural sepiolite calcined at 500°C (Sep@500) and at 700°C (Sep@700).

BET surface area (S_{BET}) results are in accordance with the XRD analysis. Thus, the incorporation of an alkali metal on the surface of sepiolite led to a partial degradation of the structure, confirmed by a decrease of the surface area with increasing metal loading (Table 4.11).

Table 4.11 BET analysis results of the sepiolite-based catalysts and MgO, determined by nitrogen adsorption using BET technique (a) or Determined by BJH method (b).

Support	Metal	Metal loading [%w/w]	$S_{\text{BET}}^{\text{a}}$ [m^2/g]	Pore^{b}	
				Volume [m^3/g]	Average diameter [nm]
MgO	-	-	41	0.06	11.3
Sep@700	Na	-	124	0.22	9.4
		2	126	0.18	7.7
	Na	5	102	0.15	8.0
		-	138	0.21	8.7
Sep@500	Na	2	124	0.20	9.0
		5	100	0.20	9.7
	K	2	119	0.19	9.0
		5	86	0.16	11.3
	Cs	2	130	0.17	7.9
		4	118	0.17	7.6
		7	110	0.15	8.1
		14	79	0.13	8.9

Figure 4.66 depicts the relation between the BET surface area and the metal loading for the the alkali metals-impregnated sepiolite samples calcined at 500°C. It can be observed that the surface area decreased with increasing metal loading; this decrease may reflect micropore blockage. In general, the BET surface area of sepiolite was found to decrease as the alkali-metal loading increased (Table 4.11 and Figure 4.66).

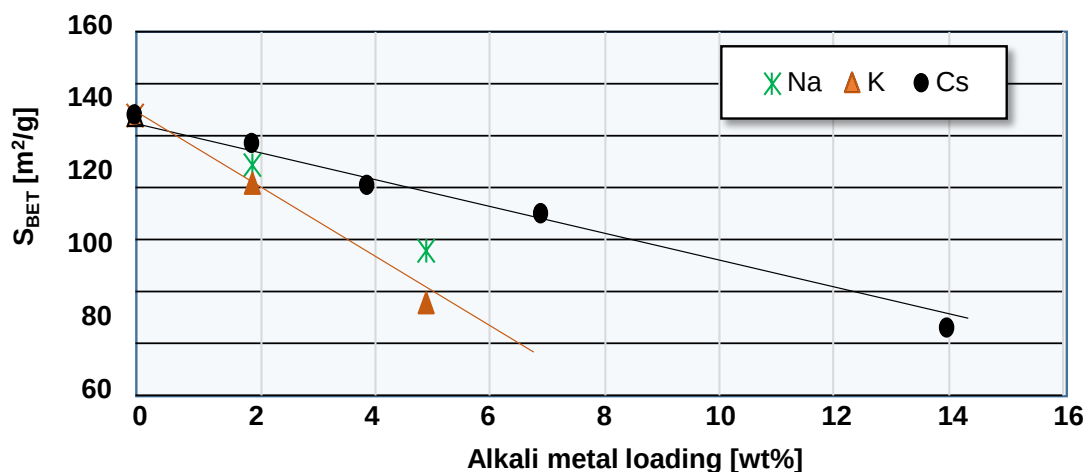


Figure 4.66 BET surface area as a function of alkali metal loading wt% over natural sepiolite calcined at 500°C.

As far as the transition metals supported sepiolite samples are concerned, the physical properties of the copper and nichel impregnated samples are reported in Table 4.12. In general, the incorporation of metal oxides on the surface of sepiolite support led to a small decrease of BET specific surface area. The increase of surface area of MgO impregnated sample is coupled to the partial loss of crystallinity of this support (probably related to changes of support during the impregnation step) as shown by the comparison of XRD patterns of pure MgO and CuO/MgO 5 wt% in Figure 4.59.

Table 4.12 BET analysis results of the MeO (CuO) impregnated samples sepiolite and MgO.

Support	Alkali metal	MeO [wt%]	S_{BET}^a	$Pore^b$	
			$[m^2/g]$	Volume $[m^3/g]$	Average diameter $[nm]$
MgO	-	-	41	0.06	11
		5	78	0.28	15
Sep@500	-	-	138	0.21	8.7
		5	138	0.18	8.5
		10	135	0.14	8.5
	2Na	-	124	0.20	9.0
		5	101	0.18	9.8
		10	101	0.16	10.2
		5*	128	0.16	7.8
Sep@700	-	-	124	0.22	9.4
		5	110	0.19	9.1
	2Na	-	126	0.18	7.7
		5	91	0.15	9.0

^a Determined by nitrogen adsorption using BET technique; ^b Determined by BJH method. *NiO

The BET surface area of sepiolite calcined at 500°C was about 138 m²/g. After impregnation with copper, and calcination, there was no significant changes of the surface area. However, when the sodium-impregnated sepiolite samples have been used as supports, the subsequent impregnation with copper led to a more significant reduction of the surface area, suggesting that the surface and pores of the support were covered. We must notice that the BET surface areas of catalysts with 5 or 10 wt.% of CuO were similar, while the diameter of CuO doped catalyst particles decreased with increasing CuO loading (Table 4.12).

4.3.1.4 SEM-EDX analysis

Successful impregnation of the sepiolite support with alkali metals was confirmed by elemental analysis EDX, the analysis results are summarized in Table 4.13 and 4.14. Figure 4.67 reports the SEM images obtained over the sodium-doped sepiolite samples, while in Figure 4.68 are reported the SEM images of the potassium and cesium – doped sepiolite samples. In general, there were no substantial alterations in the materials morphology; the typical fibrous morphology of sepiolite structure can be observed in the SEM images.

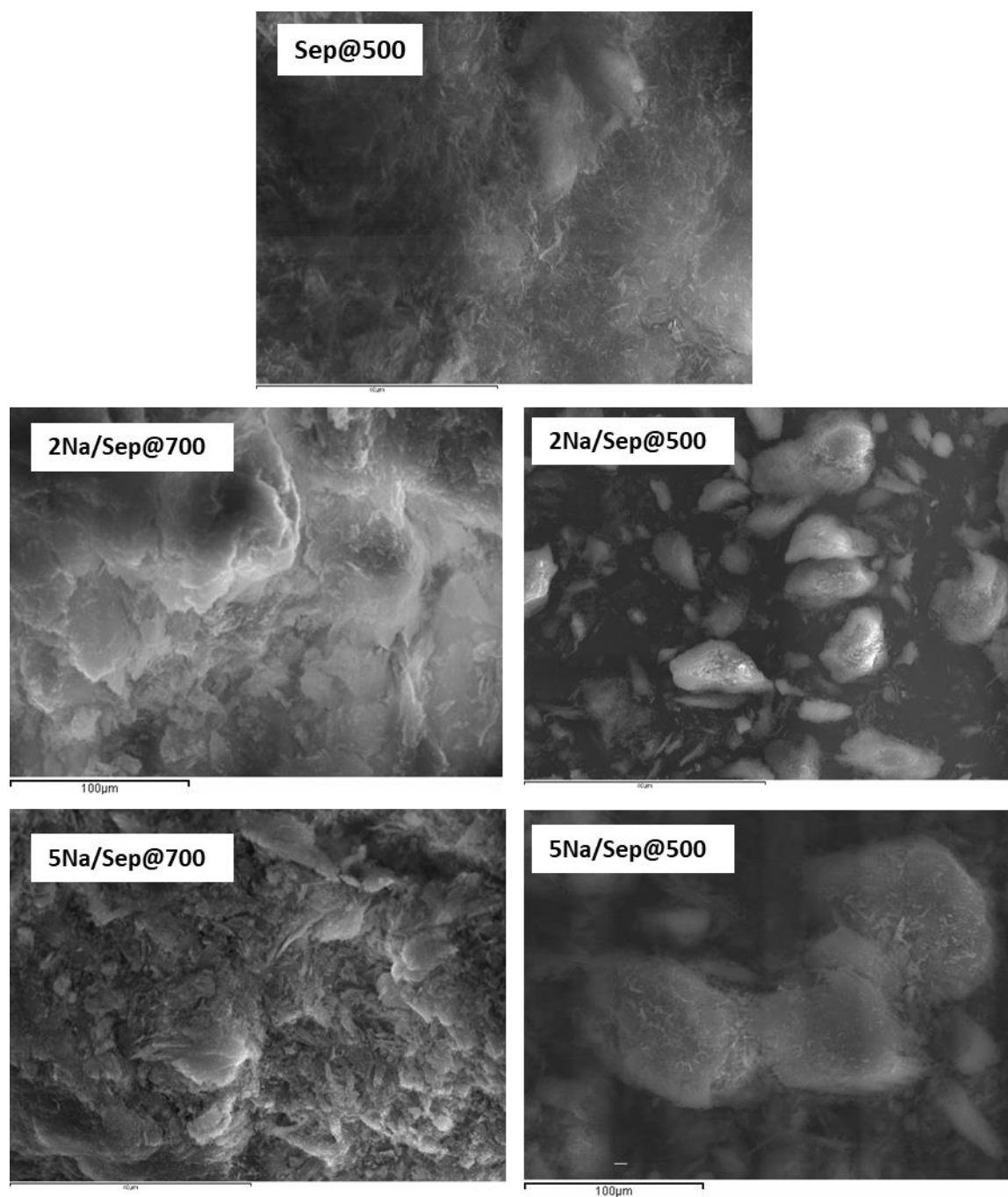


Figure 4.67 SEM micrographs of Na-impregnated sepiolite recorded at different magnifications

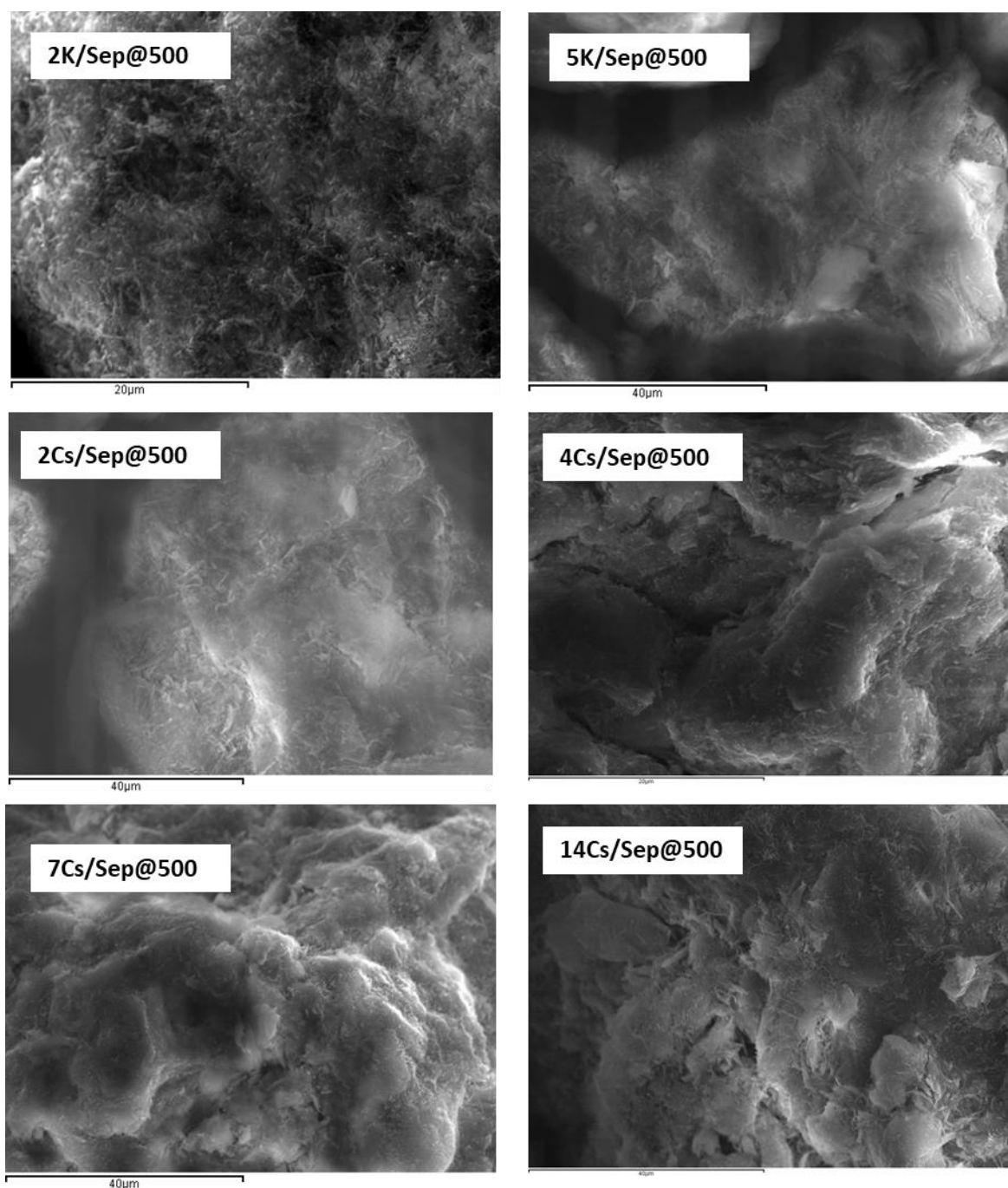


Figure 4.68 SEM micrographs of K and Cs-impregnated sepiolite recorded at different magnifications.

As an example, Fig. 4.69 shows the typical SEM–EDX micrographs of sepiolite doped with Cs_2CO_3 with a nominal cesium metal loading of 4 and 14wt%. The intensities of the peaks associated with the Cs content on the sepiolite surface increased when increasing Cs-loading in the EDX spectrum (Fig. 4.69, a and b). However, the intensities of the Si and Mg peaks decreased when increasing Cs content, as expected.

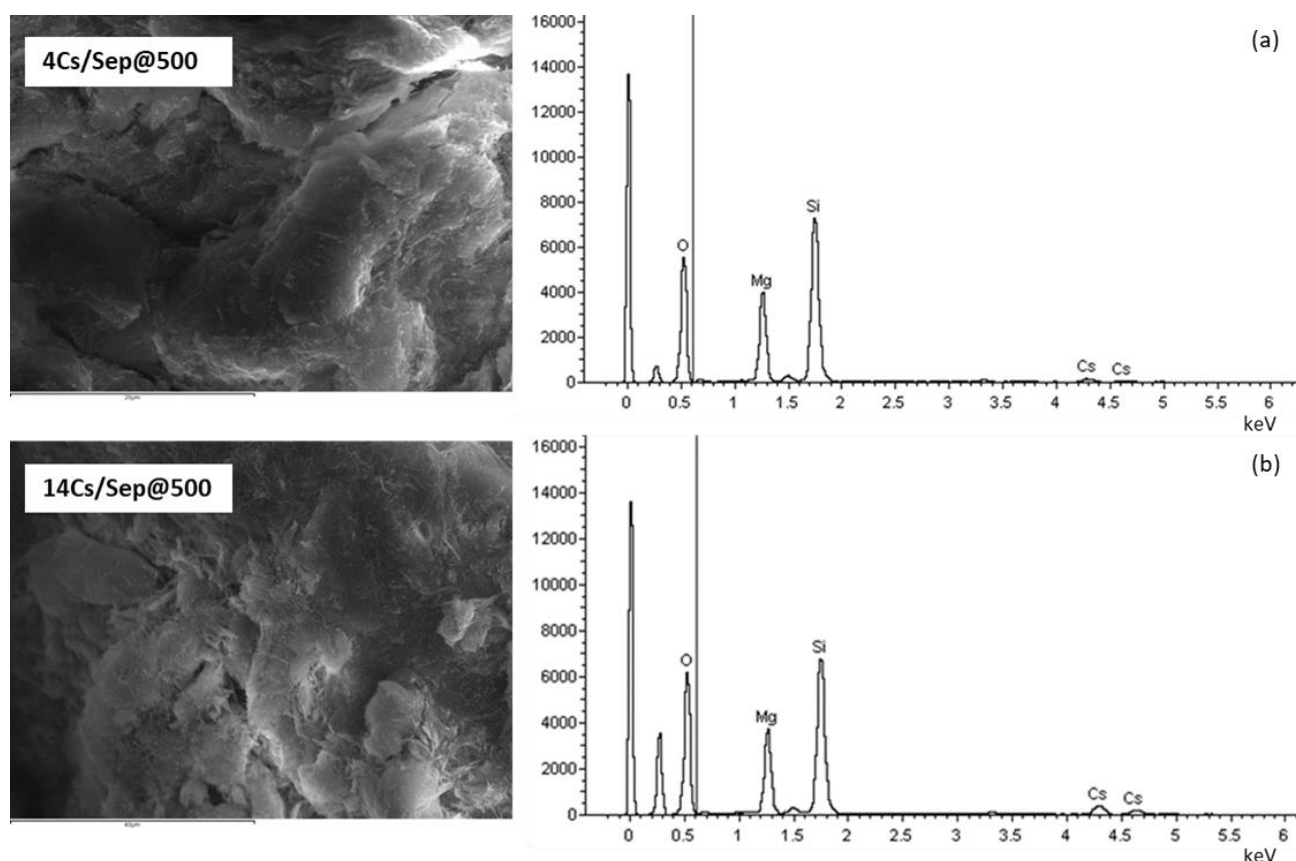


Figure 4.69 SEM photographs with EDS spectrum of (a) 4Cs/Sep@500; (b) 14Cs/Sep@500.

EDX analysis of the sepiolite and synthesized catalyst particles surface are reported in Table 4.13. Each datum reported corresponds to the average value determined from six locations on the catalyst surface.

The EDX analysis showed that the Mg/Si atomic ratio in the solids after alkali-metal impregnation of sepiolite grew with respect to the value observed in the parent sample. From the literature, this observed growing Mg/Si ratio has been attributed to the increasing desilication of sepiolite, with the amount of Mg retained by the solid remaining practically constant (Figure 4.70).²⁹⁰

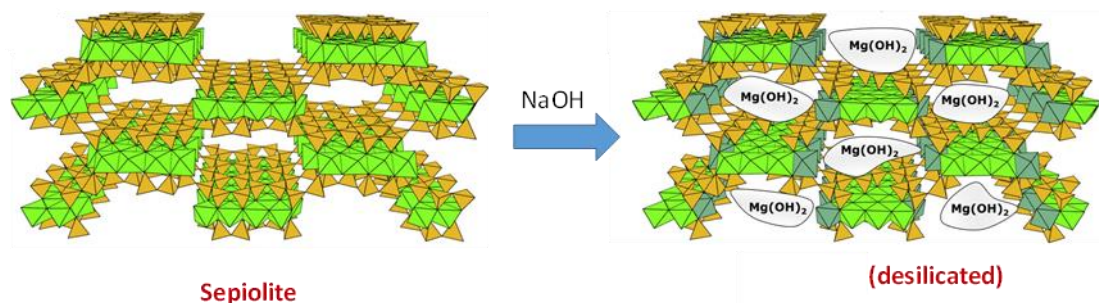


Figure 4.70 On the desilication of sepiolite. Adapted from ref.²⁹⁰

Table 4.13 EDX analysis of the surfaces of sepiolite prior to and after the impregnation with alkali metals.

<i>weight [%]</i>												
<i>Element</i>	<i>Sepiolite</i>	<i>Sep@700</i>		<i>Sep@500</i>								
		<i>2Na</i>	<i>5Na</i>	<i>1.2Na</i>	<i>2Na</i>	<i>5Na</i>	<i>2K</i>	<i>5K</i>	<i>2Cs</i>	<i>4Cs</i>	<i>7Cs</i>	<i>14Cs</i>
O	44.9	54.8	50.2	63.0	52.8	56.2	51.1	50.9	54.0	47.0	49.8	45.1
Na	-	1.6	5.6	0.6	1.3	3.7	-	-	-	-	-	-
Mg	17.0	15.0	13.7	13.3	15.5	14.7	15.5	14.7	15.1	16.1	14.3	15.8
Si	38.2	28.6	30.5	23.2	30.5	25.4	31.2	28.8	29.4	31.7	26.6	30.0
K	-	-	-	-	-	-	2.2	5.6	-	-	-	-
Cs	-	-	-	-	-	-	-	-	1.6	5.2	7.8	9.2
Mg/Si ^a	0.51	0.60	0.52	0.57	0.59	0.67	0.57	0.59	0.59	0.59	0.62	0.61

^a Mg/Si Atomic ratio in the solids.

An equal weight amount of the alkali metal amount expressed in weight % corresponds to a different moles amount. Accordingly, in order to make a more equitable comparison between diverse alkali metals, the metal loading was calculated even by the ratio between the moles of the alkali-metal and the weight of the sepiolite ($n_{\text{MET}}/w_{\text{SEP}}$, mmol/g). The results of the EDX analysis are reported in Table 4.14.

Table 4.14 EDX analysis of the surfaces of alkali-doped sepiolite catalysts.

<i>Alkali metal loading</i>						
<i>Support</i>	<i>Met</i>	<i>Nominal [wt%]</i>	<i>Measured [wt%]</i>	<i>Nominal $n_{\text{MET}}/w_{\text{SEP}}$ [mmol/g]</i>	<i>Measured $n_{\text{MET}}/w_{\text{SEP}}$ [mmol/g]</i>	<i>Measured [Atomic %]</i>
Sep@700	Na	2	1.6	0.87	0.7	1.4
		5	5.6	2.17	2.44	4.8
	Na	2	1.3	0.87	0.56	1.1
		5	3.7	2.17	1.62	3.1
Sep@500	K	2	2.2	0.51	0.56	1.1
		5	5.6	1.28	1.43	2.9
	Cs	2	1.6	0.15	0.12	0.2
		4	5.2	0.30	0.39	0.8
		7	7.8	0.53	0.59	1.2
		14	9.2	1.05	0.69	1.5

4.3.1.5 Temperature programmed desorption, TPD

From the literature emerges that a fine-tuning of both the nature and the amount of acid-base sites is crucial to obtain high *n*-butanol yield through the Guerbet conversion of ethanol.^{59,93,99,291} In this

section the acid-base properties of the sepiolite based catalysts have been studied by means of temperature desorption of probe molecules, NH_3 and CO_2 , in order to evaluate the acidity and basicity of the samples surface, respectively.

4.3.1.5.1 Acidity study - TPD- NH_3

Temperature programmed desorption of ammonia (TPD- NH_3) experiments were performed to explore the surface acidity of the samples (Fig. 4.71 - 4.73 and Table 4.15 - 4.17). The NH_3 -TPD profile can be considered as the acid sites strength distribution, while the amount of NH_3 desorbed from the catalyst is related to the number of acid sites on the catalyst, including both the Brønsted and Lewis acid sites.²⁶² Generally, the solid acid site strength can be classified according to the temperature of NH_3 desorption into three types: weak (150–300 °C), moderate (300–450°C) and strong (450–650 °C) acid sites.¹³⁷ Recorded spectra may be further deconvoluted by a Gaussian peak fitting method into separate peaks to be then attributed to different strength acid sites.

The results of TPD- NH_3 experiments performed over the two sepiolite supports, calcined at 500°C (Sep@500) and 700°C (Sep@700) are shown in Fig. 4.71. The sepiolite sample calcined at 500°C appeared more acid than the one calcined at higher temperature (i.e., 700°C). There can be noticed three different desorption peaks at 180, 260 and 350 °C reflecting the presence of acid sites of weak and medium strength while the peak at 560°C represents changes in the support nature. Calcining the sepiolite sample at 700°C led to an overall diminution of the desorption peaks and hence acidity compared to the one calcined at 500°C, from $2 \mu\text{mol}_{\text{NH}_3}/\text{m}^2$ to $1.4 \mu\text{mol}_{\text{NH}_3}/\text{m}^2$ respectively.

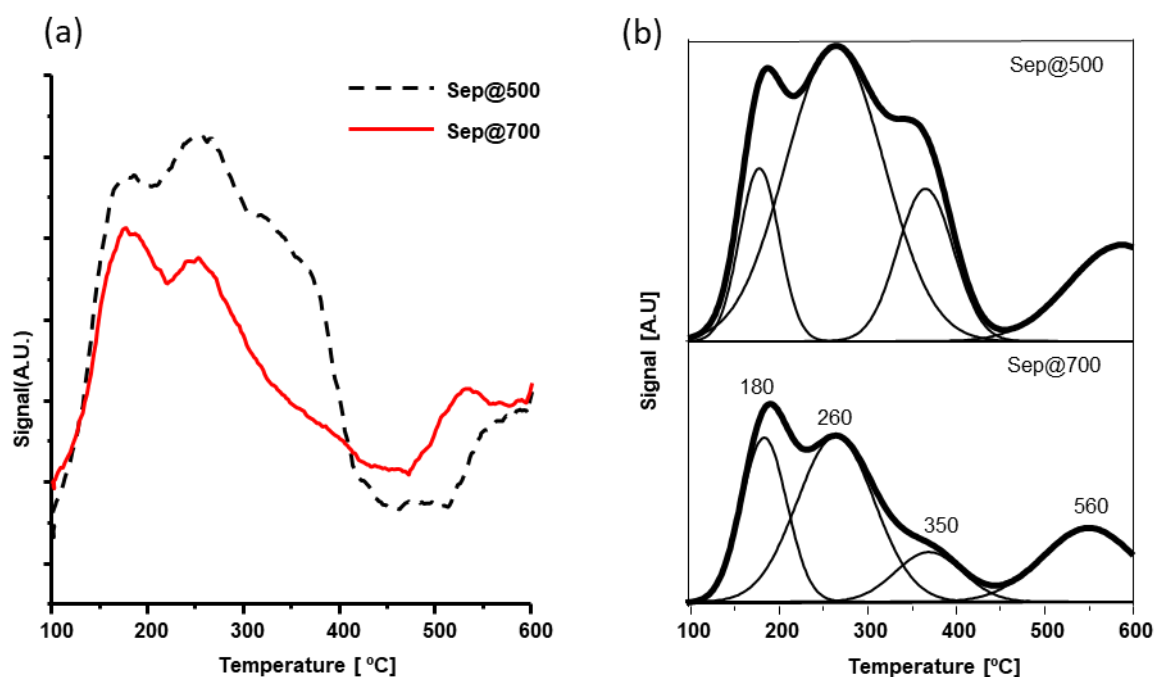


Figure 4.71 a) Profiles of temperature programmed desorption of ammonia for natural sepiolite calcined at 500 and 700°C. b) TPD- NH_3 signal in deconvoluted peaks.

The results presented in Figure 4.72 reflect the acidity changes caused by Na-modification. The addition of percentage quantities of sodium to natural sepiolite (pre-calcined at 500°C and 700°C) progressively eliminates some acid sites of the unmodified sepiolite, as determined by the TPD of NH₃. Indeed, the samples impregnated with sodium exhibited a decreased NH₃ desorption amount, showing fewer fraction of acid sites. Pure sepiolite sample showed a higher fraction of acid sites with higher strength (Figure 4.72). In Table 4.15, the results of the integration of TPD profiles are reported as moles of NH₃ both per unit weight (μmol/g) and per unit surface (μmol/m²) of the catalyst. It can be observed a general decreasing trend of the quantity of NH₃ adsorbed with increasing sodium amount.

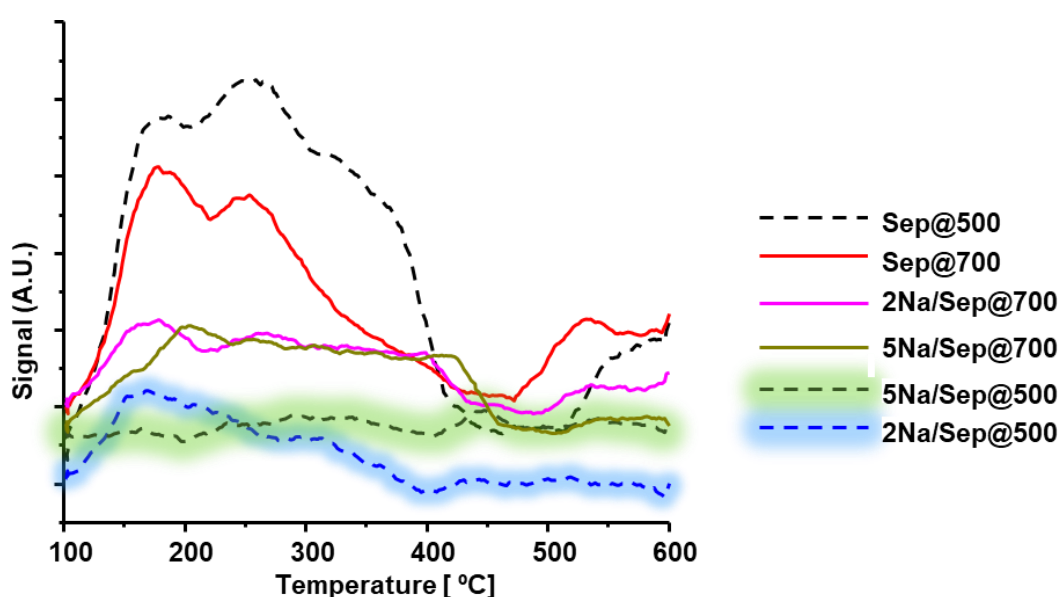


Figure 4.72 Profiles of temperature programmed desorption of ammonia for the natural sepiolite supports calcined at 500 and 700°C and the sodium-doped ones, with 2 and 5 wt% of sodium loading.

Table 4.15 Characterization results of the sepiolite supports calcined at 500 and 700°C and the sodium impregnated samples with 2 and 5 wt% metal loading.

Metal	Support	Metal loading		S_{BET}^b [m ² /g]	Pore ^c		ACIDITY ^d	
		Nominal [wt%]	Measured n_{MET}/w_{SEP} [mmol/g] ^a		Volume [m ³ /g]	Average diameter [nm]	[μmol _{NH3} /g _{CAT}]	[μmol _{NH3} /m ²]
Na	Sep@500	0	-	138	0.21	8.7	280	2.0
	Sep@700	0	-	124	0.22	9.4	175	1.4
	Sep@500	2	0.56	124	0.20	9.0	120	1.0
		5	1.62	100	0.20	9.7	54	0.5
	Sep@700	2	0.7	126	0.18	7.7	79	0.6
		5	2.44	102	0.15	8.0	32	0.3

^a Determined by EDX analysis. ^b Determined by nitrogen adsorption using BET technique; ^c Determined by BJH method; ^d Determined by TPD-NH₃ analysis.

Figure 4.73 reports the results of the TPD-NH₃ analysis performed over the alkali-metals impregnated sepiolite samples.

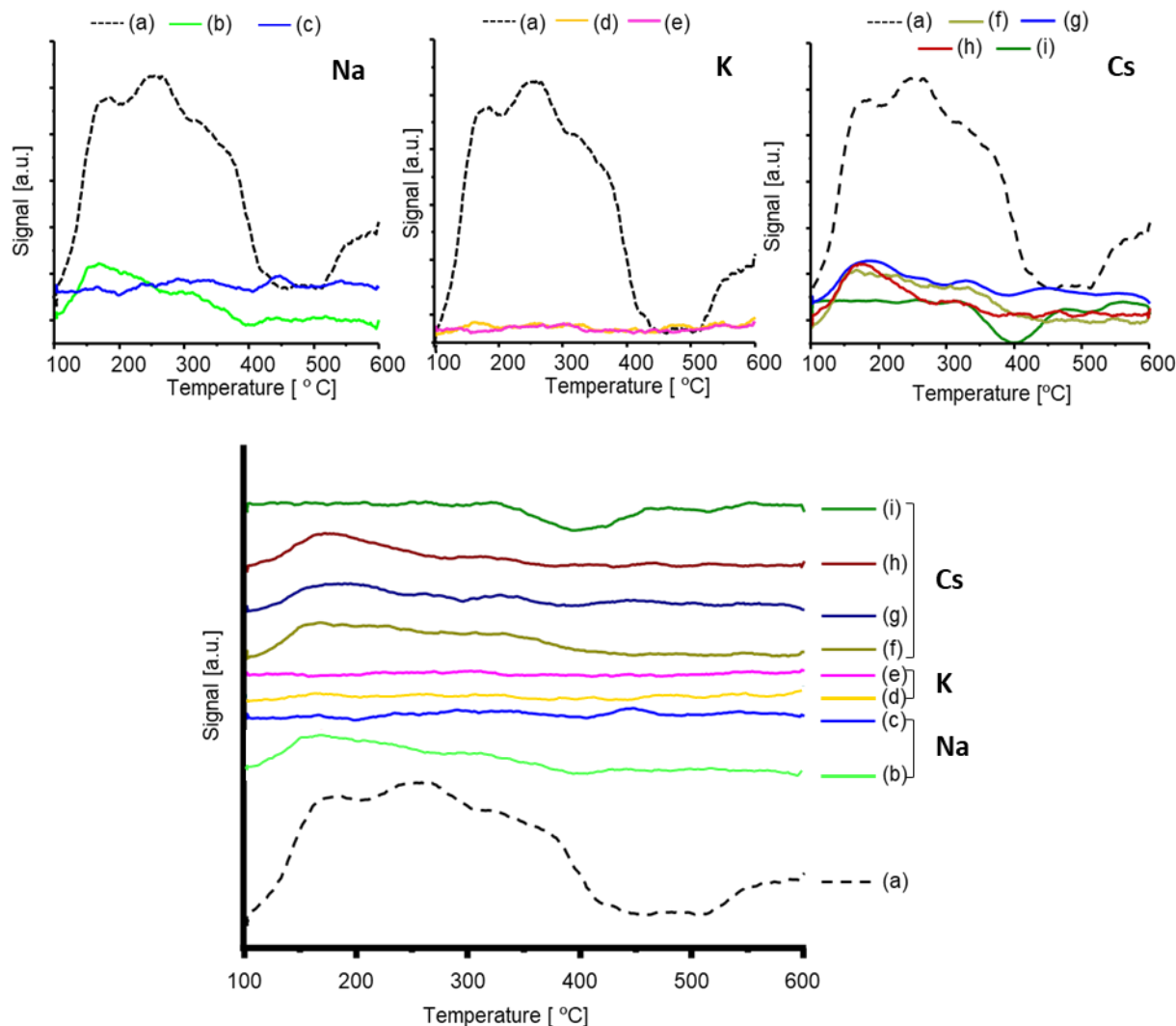


Figure 4.73 Profiles of temperature programmed desorption of ammonia for the natural sepiolite calcined at 500°C (Sep@500), and the related alkali metal-doped sepiolite samples. (a) Sep@500; (b) 2Na/Sep@500; (c) 5Na/Sep@500; (d) 2K/Sep@500; (e) 2K/Sep@500; (f) 2Cs/Sep@500; (g) 4Cs/Sep@500; (h) 7Cs/Sep@500; (i) 14Cs/Sep@500.

Accordingly, the incorporation of small amount of alkali-metals to natural sepiolite samples, pre-calcined at 500°C, progressively eliminates acid sites, as determined by the TPD of NH₃. Table 4.16 summarized the TPD-NH₃ analysis results performed over the alkali metals-doped sepiolite samples related to their surface areas.

Table 4.16 Acidic characteristics of solids determined from TPD-NH₃, expressed by μmol of NH₃ adsorbed per grams of catalyst and per surface area of catalysts.

Support	Met	Alkali metal loading		S_{BET}^b [m ² /g]	Pore ^c		ACIDITY ^d	
		Nominal [wt%]	Measured $n_{\text{MET}}/w_{\text{SEP}}$ [mmol/g] ^a		Volume [m ³ /g]	Average diameter [nm]	[$\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{CAT}}$]	[$\mu\text{mol}_{\text{NH}_3}/\text{m}^2$]
Sep@700	-	-	-	124	0.2	9.4	175.1	1.4
	Na	2	0.7	126	0.2	7.7	79.1	0.6
		5	2.44	102	0.2	8.0	32.3	0.3
Sep@500	-	-	-	138	0.2	8.7	280.2	2.0
	Na	2	0.56	124	0.2	9.0	119.7	1.0
		5	1.62	100	0.2	9.7	53.5	0.5
	K	2	0.56	119	0.2	9.0	144	1.2
		5	1.43	86	0.2	11.3	47	0.5
	Cs	2	0.12	130	0.2	7.9	203.7	1.6
		4	0.39	118	0.2	7.6	148.3	1.3
		7	0.59	110	0.1	8.1	107.8	1.0
		14	0.69	79	0.1	8.9	25.7	0.3

^a Determined by EDX analysis. ^b Determined by nitrogen adsorption using BET technique, ^c Determined by BJH method; ^d Determined by TPD-NH₃ analysis.

In order to evaluate the effect of copper oxide impregnation over the acid characteristic of the surface of the resulting sepiolite-based catalyst, a TPD-NH₃ analysis have been performed over the sample impregnated with 5 wt% of copper oxide (CuO/Sep@700 5 wt%). Figure 4.74 reports the results obtained, compared to the corresponding sepiolite support calcined at 700°C, and it can be observed that copper addition led to a slight decrease of the overall acidity. Comparing to the sepiolite support that adsorbed 1.4 $\mu\text{mol}_{\text{NH}_3}/\text{m}^2$, the CuO/Sep@700 5 wt% adsorbed 1.3 $\mu\text{mol}_{\text{NH}_3}/\text{m}^2$ (Table 4.17).

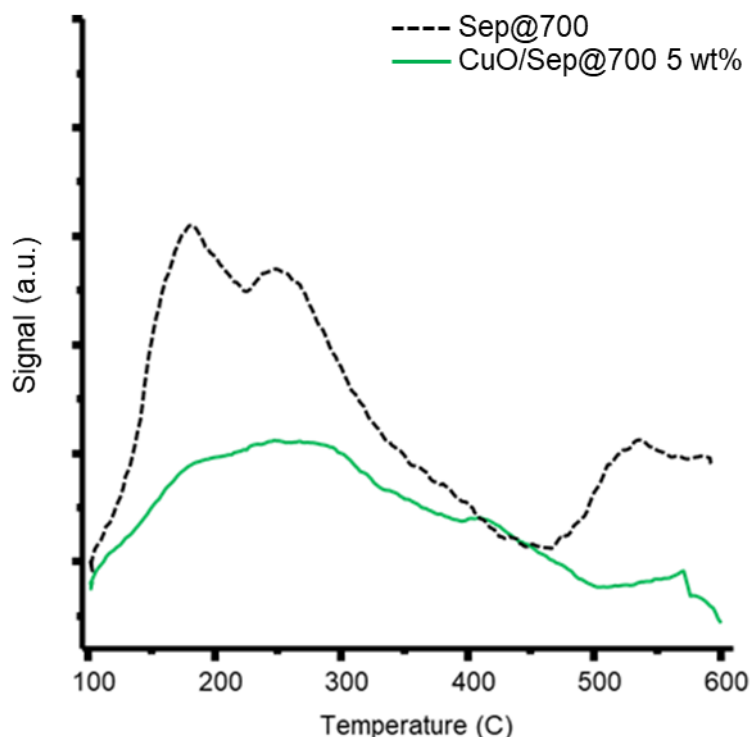


Figure 4.74 Profiles of temperature programmed desorption of ammonia for the natural sepiolite calcined at 700°C (Sep@700), and the 5 wt% copper oxide-impregnated sepiolite sample (CuO/Sep@700 5 wt%).

Table 4.17 Acidity from temperature programmed desorption of TPD-NH₃, expressed by μmol of NH₃ adsorbed per grams of catalyst and per surface area in comparison between the sepiolite support and the 5 wt% CuO-impregnated sepiolite sample.

	S_{BET}^a [m ² /g]	ACIDITY ^b	
		[$\mu\text{mol}_{\text{NH}_3}/\text{g}_{\text{CAT}}$]	[$\mu\text{mol}_{\text{NH}_3}/\text{m}^2$]
Sep@700	124	175.1	1.4
CuO/Sep@700 5 wt%	110	139.9	1.3

^a Determined by nitrogen adsorption using BET technique; ^b Determined by TPD-NH₃ analysis.

4.3.1.5.2 Basicity study – TPD-CO₂

To study the basicity of the sepiolite samples, some temperature-programmed desorption of CO₂ have been performed. The desorption profiles were deconvoluted using Gaussian curves in order to separate the weak, medium and strong basic sites. The weak strength basic sites are related to curves that show a maximum at temperature lower than 170°C, the ones between 170 and 270°C are assigned to medium strength basic sites, and finally, the ones above 270 °C are strong basic sites.⁹⁹ Table 4.18 reports the quantification of the basicity in terms of CO₂ desorbed per grams and surface area of the samples. In addition, acidity/basicity ratio (A/B) and, for the sake of clarity, the basicity/acidity ratio (B/A), are highlighted since from literature ²⁹² is reported that *n*-butanol

selectivity is strictly connected with the ratio between acid and basic centres of the catalyst surface. More in detail, the highest *n*-butanol yields were associated to low ratio between acid and basic sites.

Figure 4.75 depicts the TPD- CO_2 profiles of the natural sepiolite samples calcined at 500°C (Sep@500) and at 700°C (Sep@700). Both samples exhibited basic behaviour and their TPD-profiles showed several peaks related to basic sites of different strength. In particular, sepiolite calcined at 500°C exhibited one weak basic site related to the peak at 120°C, then two medium strength basic sites at 220 and 330°C and another strong basic sites at 420°C. Calcining the sepiolite at higher temperature led to the disposal of the medium strength basic sites at 220°C and to a lower value of overall basicity from 1.8 to 1.2 [$\mu\text{mol}_{\text{CO}_2}/\text{m}^2$]. In addition, the basic/acid sites ratio (B/A) decreased from 0.92 to 0.83 while calcining sepiolite at 500°C and 700°C, respectively. Mora et al. studied the effect of thermal treatment on sepiolite structure by means of IR analysis, finding a progressive removal of OH groups (of zeolitic water, Mg-OH groups and water octahedrally coordinated to magnesium) with increasing calcination temperature until 800°C, at which the layered structure of sepiolite collapsed and a new phase formed (estantite).²⁸³ Since exposed hydroxyl groups potentially can act both as Brønsted acid sites and basic sites,²⁹³ their changes in quantity during thermal treatment can be the cause of the acidity/basicity changes with increasing calcination temperature.

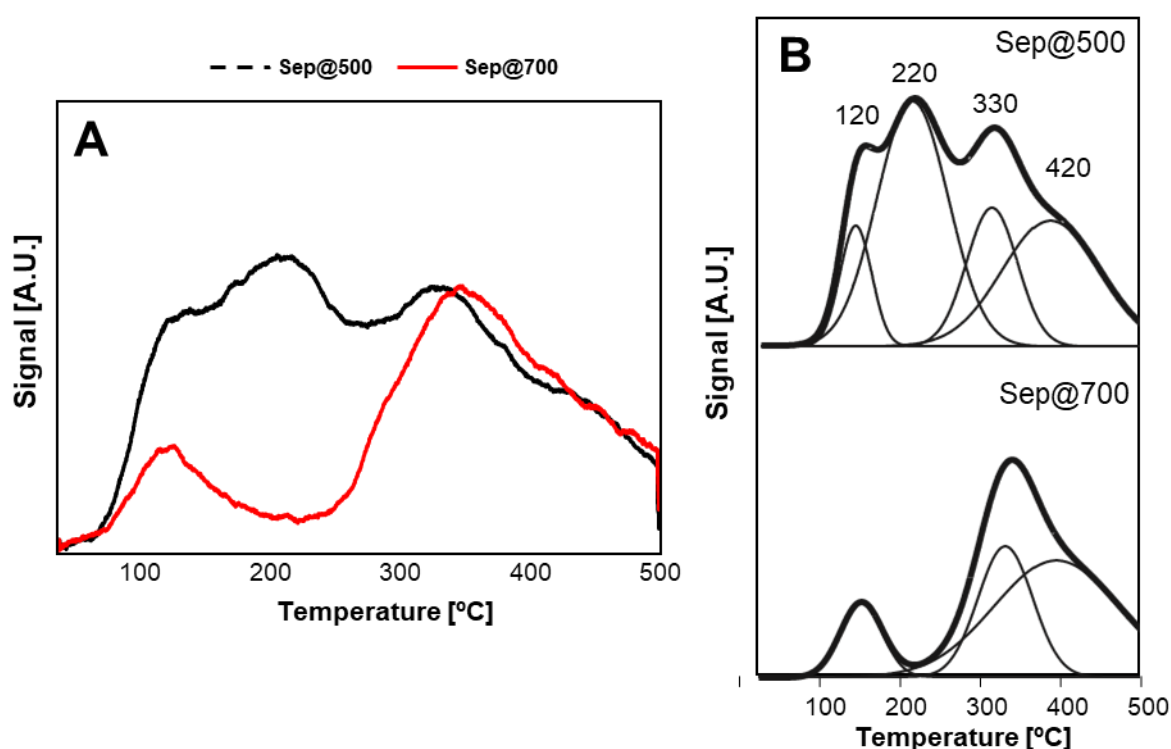


Figure 4.75 TPD - CO_2 profiles of the sepiolite catalysts calcined at 500°C (Sep@500) and at 700°C (Sep@700). (B): The profiles deconvoluted.

Table 4.18 summarizes the TPD- CO_2 analysis results obtained over the alkali-doped sepiolite samples, together with the acidity results. The *n*-butanol selectivity from the ethanol Guerbet

conversion has been found strictly related to the acid/ base properties of the catalyst, in particular to their ratio.^{164,294} Accordingly, the acidity/basicity ratio (A/B ratio) has been computed. A prevalent unexpected decrease of the overall basicity after alkali/metal addition has been observed. Nevertheless, a general decrease of the A/B ratio can be noticed with the presence of the alkali metals, linearly related with the extent of the amount added. As a consequence, a general increase of the overall basicity can be observed with increasing alkali metal loading.

Figure 4.76A depicts the TPD- CO_2 profiles of the Na, K and Cs-doped sepiolite samples containing ca. $0.6 \text{ n}_{\text{MET}}/\text{W}_{\text{SEP}}$ [mmol/g] measured (i.e. 2Na/Sep@500, 2K/Sep@500 and 7Cs/Sep@500) while Fig. 4.76B depicts the same analysis results performed over the sepiolite samples doped with the double amount of alkali metals. It is possible to observe that each alkali metal had a different effect on the nature of the basic sites of the sepiolite samples. The potassium addition led to a slight increase of basicity, as can be noted in Table 4.18. A higher amount of potassium (i.e., 5 wt%, Fig. 4.76B) led mainly to an increase of the weakest basic sites (i.e., desorption peak at 120°C) and to the disappearance of the strongest one. Regarding the cesium impregnated, the basicity increased with increasing Cs amount. Also, even the nature of the basic sites seemed affected by Cs amount. Indeed, with a metal loading of 7wt%, weak (120°C) and strong (420°C) are observed. By contrast, the main effect of increasing Cs amount was the enhancement of the density of medium basic sites (220°C), as showed in Fig.4.76B. Overall, a general effect observed is a change of the nature of the basic sites depending on the nature and amount of the alkali metal added and a decrease of the basic sites number after alkali metal addition.

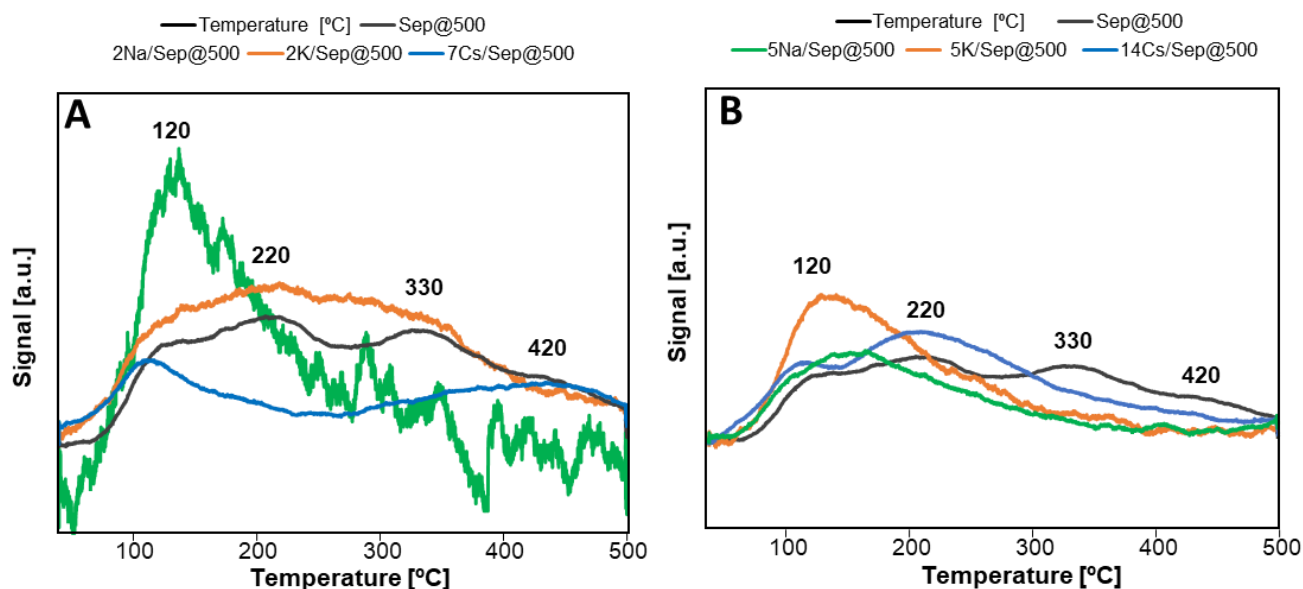


Figure 4.76 TPD- CO_2 desorption profiles of the alkali-metals impregnated sepiolite catalysts. A) 2Na, 2K and 7Cs/Sep@500; B) 5N, 5K and 14Cs/Sep@500.

Table 4.18 Acidity and basicity from temperature programmed desorption of TPD-NH₃ and TPD-CO₂, expressed by μmol of NH₃ or CO₂ adsorbed per grams of catalyst and per surface area of the sepiolite catalysts.

Support	Met	Alkali amount		S_{BET}^b [m ² /g]	ACIDITY ^c		BASICITY ^d		A/B ratio ^e	B/A ratio ^f
		Nominal [wt%]	Measured $n_{\text{MET}}/w_{\text{SEP}}$ [mmol/g] ^a		[$\mu\text{mol}_{\text{NH}_3}$ /g _{CAT}]	[$\mu\text{mol}_{\text{NH}_3}/\text{m}^2$]	[$\mu\text{mol}_{\text{CO}_2}$ /g _{CAT}]	[$\mu\text{mol}_{\text{CO}_2}/\text{m}^2$]		
Sep@700	-	0	0	124	175.1	1.4	143.6	1.2	1.69	0.83
	Na	2	0.7	126	79.1	0.6	149.2	1.2	0.30	1.98
		5	2.44	102	32.3	0.3	134.1	1.3	0.07	4.37
Sep@500	-	0	0	138	280.2	2	251.6	1.8	2.19	0.92
	Na	2	0.56	124	119.7	1	168.9	1.4	0.73	1.37
		5	1.62	100	53.5	0.5	118.9	1.2	0.21	2.38
	K	2	0.56	119	144	1.2	268.3	2.3	0.64	1.88
		5	1.43	86	47	0.5	142.1	1.7	0.15	3.31
	Cs	2	0.12	130	203.7	1.6	44.9	0.3	7.38	0.22
		4	0.39	118	148.3	1.3	120.3	1.0	1.66	0.78
		7	0.59	110	107.8	1	180.9	1.6	0.61	1.64
		14	0.69	79	25.7	0.3	154.1	2.0	0.05	6.53

^a Determined by EDX analysis; ^b Determined by nitrogen adsorption using BET technique; ^c Determined by TPD-NH₃ analysis; ^d Determined by TPD-CO₂ analysis; ^e Acidity/Basicity ratio; ^f Basicity/Acidity ratio.

The characterization results of the alkali-doped sepiolite samples are summarized in Table 4.19. The results showed that the most pronounced effect of alkali metals addition on the texture of sepiolite consisted in a fall of the specific surface area. This could be occurred maybe due to a reduction of microporosity of the sample, as can be found in literature for NaOH treated sepiolite.²⁹⁰ A. Walczyk et al. related the fall of specific surface area to the fall of micropore surface and volume by an order of magnitude explaining that with the formation and precipitation of Mg(OH)₂ from the external Mg²⁺ ions exchanged with sodium ones that have been retained into the structural micropores. Dimensions of sepiolite micropores precluded formation of long-range ordering in the precipitated clusters of magnesium hydroxide, hence no relevant reflections appeared in the XRD patterns of alkali activated solids.²⁹⁰

It is known that base strength increases with the radius of alkali cations.²⁹⁵ However, with the same amount of alkali metal added over sepiolite (i.e., ca. 0.6 mmol_{MET}/g_{SEP}), neither the acidity nor the basicity followed a linear trend with increasing alkali metal radius. No other phases or species have been detected through XRD analysis, meaning that they could be well dispersed over the catalyst surface. Thus, other characterization techniques should be needed to better understand the active sites structures (e.g. XPS, X-ray Absorption Fine Structure XAFS). Nevertheless, linear decrease of the A/B ratio of the sepiolite samples can be noticed with increasing alkali-metal loading.

Table 4.19 Textural parameters and characterization results summarized: S_{BET} , V_{PORE} , D_{PORE} , acidity from temperature programmed desorption of TPD-NH₃, for the alkali-sepiolite samples.

Support	Met	Alkali metal loading					D^b [nm]	S_{BET}^c [m ² /g]	Pore ^d Volume [m ³ /g]	Average diameter [nm]	ACIDITY ^e		BASICITY ^f		A/B ratio ^g	B/A Ratio ^h
		Nominal [wt%]	Measured [wt%] ^a	Nominal n_{MET}/w_{SEP} [mmol/g]	Measured n_{MET}/w_{SEP} [mmol/g] ^a	Measured [Atomic %] ^a					[μmol_{NH_3} /g _{CAT}]	[$\mu\text{mol}_{NH_3}/\text{m}^2$]	[μmol_{CO_2} /g _{CAT}]	[$\mu\text{mol}_{CO_2}/\text{m}^2$]		
Sep@700	-	0	-	-	-	-	16	124	0.2	9.4	175.1	1.4	143.6	1.2	1.69	0.83
	Na	2	1.6	0.87	0.7	1.1	22.2	124	0.2	9.0	119.7	1	149.2	1.2	0.30	1.98
		5	5.6	2.17	2.44	3.1	17.1	100	0.2	9.7	53.5	0.5	134.1	1.3	0.07	4.37
Sep@500	-	0	-	-	-	-	14.7	138	0.2	8.7	280.2	2	251.6	1.8	2.19	0.92
	Na	2	1.3	0.87	0.56	1.4	13.8	126	0.2	7.7	79.1	0.6	168.9	1.4	0.73	1.37
		5	3.7	2.17	1.62	4.8	13.4	102	0.2	8.0	32.3	0.3	118.9	1.2	0.21	2.38
	K	2	2.2	0.51	0.56	1.1	14.7	119	0.2	9.0	144	1.2	268.3	2.3	0.64	1.88
		5	5.6	1.28	1.43	2.9	14.7	86	0.2	11.3	47	0.5	142.1	1.7	0.15	3.31
	Cs	2	1.6	0.15	0.12	0.2	20.5	130	0.2	7.9	203.7	1.6	44.9	0.3	7.38	0.22
		4	5.2	0.30	0.39	0.8	14.7	118	0.2	7.6	148.3	1.3	120.3	1.0	1.66	0.78
		7	7.8	0.53	0.59	1.2	14.7	110	0.1	8.1	107.8	1	180.9	1.6	0.61	1.64
		14	9.2	1.05	0.69	1.5	20.5	79	0.1	8.9	25.7	0.3	154.1	2.0	0.05	6.53

^a Determined by EDX analysis; ^b Calculated through Scherrer equation, considering the peak at 20.25° for the sepiolite anhydride (ref. 00-026-1227). ^c Determined by nitrogen adsorption using BET technique; ^d Determined by BJH method; ^e Determined by TPD-NH₃ analysis; ^f Determined by TPD-CO₂ analysis; ^g Acidity/basicity ratio; ^h Basicity/acidity ratio.

4.3.2 Catalytic tests

The synthesized MgO was used as reference catalyst to compare the catalytic results obtained in the same condition over the sepiolite based-ones.

All the catalyst samples have been tested into the gas-flow reaction system well explained in the Section 3.2.2, in order to study their catalytic activity in the gas-flow ethanol conversion by feeding a gaseous mixture of EtOH 5 v/v% in N₂.

A typical reaction was performed as follows: the reactor charged with the catalyst was pre-heated at 120°C, at this temperature the vaporized ethanol was fed and analysed with the on-line GC in order to evaluate the exact starting concentration of the reagent. After that, the temperature of the furnace was set to the desired reaction temperature and when reached, the reaction started. For each reaction, fresh new catalyst was loaded inside the reactor.

Several blank tests were performed by feeding ethanol into the reactor, in the absence of the catalytic bed, in the range of the desired temperatures (250 - 450°C), and no EtOH conversion have been detected into the temperature range evaluated.

Initially, the catalytic activity of the sepiolite supports have been studied in the reaction condition of 450°C and atmospheric pressure, with a weight hourly space velocity (WHSV) of 1 g_{EtOH}/(g_{CAT}·h) (weight of ethanol fed per hour per unit weight of catalyst loaded in the reactor). Both sepiolite samples, calcined at 500°C and 700°C have been tested.

The results of the catalytic tests are shown in Fig. 4.77 and Table 4.20, where the ones obtained with MgO catalyst at 450°C are shown comparatively. It can be noted that the sepiolite samples, Sep@500 and Sep@700, are more active leading to a higher value of ethanol conversion compared to the MgO, 80%, 55% and 35%, respectively. Regardless, the thermally treated sepiolite samples mainly performed as acid catalysts leading to the formation of the dehydration products of ethanol, namely diethyl ether and ethylene. In addition, the sepiolite sample calcined at 700°C was less active than the one treated at 500°C, the lower activity can be related to the lower value of surface area (see Table 4.19).

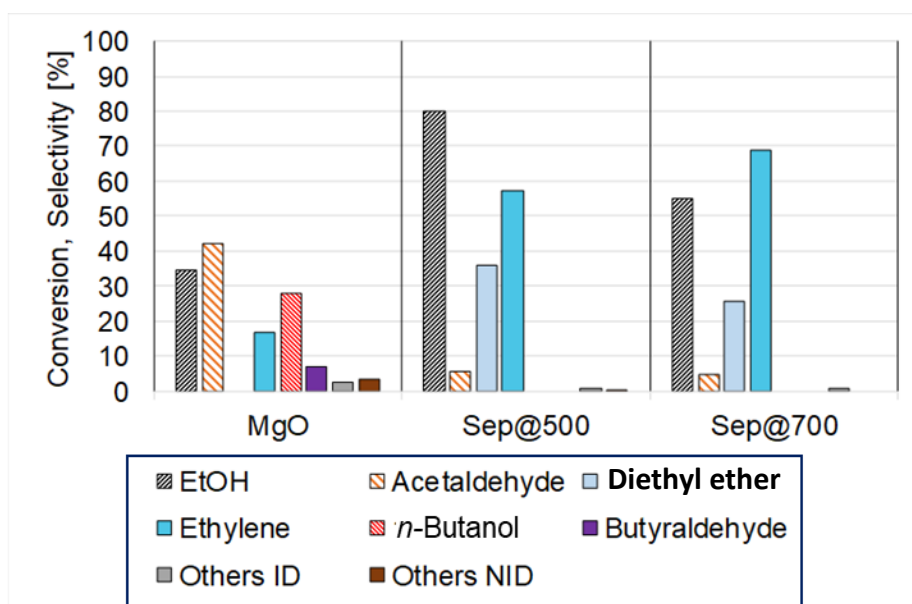


Figure 4.77 Catalytic results obtained, in terms of ethanol conversion and products selectivity, for the Ethanol gas-phase conversion over MgO and natural Sepiolite calcined at 500°C and 700°C. Others ID: acetone, CO₂, ethane. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Table 4.20 Products distributions from EtOH gas-phase conversion over MgO and natural Sepiolite calcined at 500°C and 700°C. **Others ID:** acetone, ethane, CO₂. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Selectivity [%]								
Catalyst	X EtOH [%]	AA	DEE	Ethylene	BuOH	BuA	Others ID	Others NID
MgO	35	42		17	28	7	2	3
Sep@500	80	6	36	57	0	0	1	0
Sep@700	55	5	26	69	0	0	1	0

Yield [%]								
Catalyst	X EtOH [%]	AA	DEE	Ethylene	BuOH	BuA	Others ID	Others NID
MgO	35	15	0	6	10	2	1	1
Sep@500	80	5	29	46	0	0	1	0
Sep@700	55	3	14	38	0	0	0	0

4.3.2.1 Sodium doped Sepiolite

4.3.2.1.1 Influence of Sodium loading

One possible way to decrease the dehydration rate of ethanol over sepiolite is to selectively remove, block or deactivate the acid sites responsible for dehydration by adding small amounts of alkali metal. Indeed, sodium-impregnated samples, with 2 and 5 wt% of metal loading, have been prepared (Section 3.2.4) and tested in the same reaction conditions used with the sepiolite supports, namely 450°C and atmospheric pressure and WHSV of 1 g_{EtOH}/(g_{CAT}·h).

The catalytic results are summarized in Figure 4.78 and Table 4.21, reporting them in terms of conversion of ethanol and selectivity of the main products, namely ethylene, diethyl ether, acetaldehyde, *n*-butanol and butyraldehyde. The results have been reported in relation with the sodium amount and gathered by means of the sepiolite supports calcined at different temperature, 500°C (Sep@500) and 700°C (Sep@700).

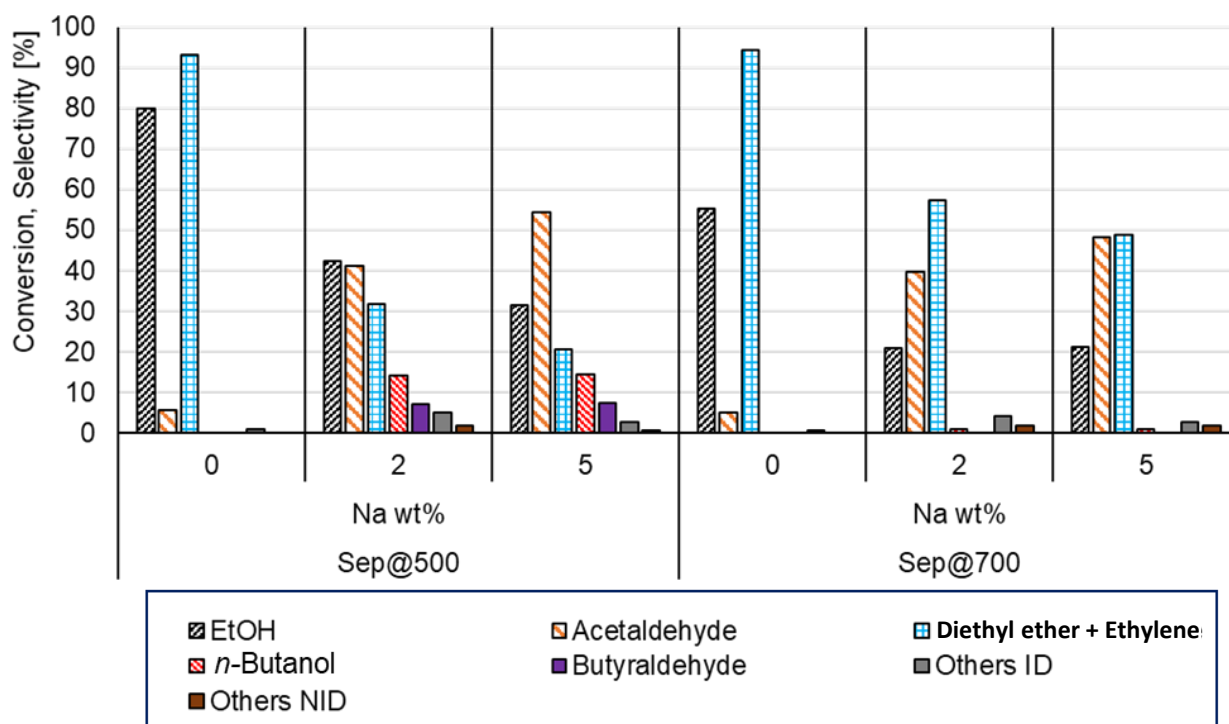


Figure 4.78 Catalytic results obtained, in terms of ethanol conversion and products selectivity, for the Ethanol gas-phase conversion over the Sepiolite supports calcined at 500°C and 700°C samples, and the sodium impregnated ones with 2 and 5 wt% of metal loading. Others ID: acetone, 2-pentanone, CO₂, ethane. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Table 4.21 Products distributions from EtOH gas-phase conversion over conversion over the Sepiolite supports calcined at 500°C and 700°C samples, and the sodium impregnated ones with 2 and 5 wt% of metal loading. Others ID: acetone, 2-pentanone, CO₂, ethane. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV= 1 g_{EtOH}/(g_{CAT}·h).

<u>Selectivity [%]</u>									
	Na wt%	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuAA	Others ID	Others NID
Sep@500	0	80	6	57	36	0	0	1	
	2	42	41	19	13	14	7	5	2
	5	31	54	13	8	14	7	3	1
Sep@700	0	55	5	69	26	0	0	1	
	2	21	40	38	13	1	0	4	2
	5	21	48	35	6	1	0	3	2
<u>Yield [%]</u>									
	Na wt%	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuAA	Others ID	Others NID
Sep@500	0	80	5	46	29	0	0	1	0
	2	42	17	8	6	6	3	2	1
	5	31	17	4	3	4	2	1	0
Sep@700	0	55	3	38	14	0	0	0	0
	2	21	8	8	3	0	0	1	0
	5	21	10	7	1	0	0	1	0

As in it can be noted from the catalytic results reported in the figure, the introduction of sodium ions Na⁺ into the sepiolite catalyst resulted in a generalized reduction in activity, leading to lower values of ethanol conversion. Subsequently and simultaneously, the selectivity of ethanol dehydration products, ethylene and diethyl ether, decreased while the dehydrogenation reaction product of ethanol, acetaldehyde, increased. This can be related to the change of acid-base properties of the catalysts, as measured by TPD-NH₃ analysis (Table 4.18), where it has been observed a decrease of the acidity with increasing alkali-metal loading. The addition of the alkali metal led to the formation of new basic sites the presence of which can be related to the formation of the dehydrogenation product of ethanol, acetaldehyde.

Interestingly, over the Sep@700 supported samples in addition of being less active, the extent of the decreasing of acid reaction products was lower than the one obtained over the Sep@500 supported samples. The overall selectivity of diethyl ether and ethylene decreased from ~95% for the support alone to ~ 50% with 5wt% of sodium for the sepiolite calcined at 700°C, while it decreased from ~95% to ~20% for the one supported over sepiolite calcined at 500°C.

Particularly noteworthy is that the Sep@500 supported catalysts led to the formation of the Guerbet reaction product of ethanol, *n*-butanol. Indeed, the 2Na/Sep@500 catalyst in the above-mentioned reaction conditions allowed to obtain *n*-butanol with a selectivity of 14%. An increase of the alkali metal loading did not lead to an increase of *n*-butanol selectivity, obtaining even in this case a selectivity of about 14%. The catalytic results are in accordance with the BET and TPD-NH₃ results.

(see Table 4.19). Indeed, the lower activity can be related to the lower BET surface area with increasing metal loading and, at the same time, the lower amount of acid sites detected by TPD analysis is in accordance with the lower amount of acid reaction products. A lowered acidity can be the reason of the formation of *n*-butanol, that requires a right balance between acid and basic sites.²⁹²

4.3.2.1.2 Contact time effect

In order to evaluate how the 2Na/Sep@700 catalyst worked at higher ethanol conversion, over the latter it was explored the effects of WHSVs variation on products distribution in the range 1, 0.5 and 0.33 g/(g_{CAT}·h), by keeping the reaction temperature at 450°C. The catalytic results are reported in Figure 4.79 and Table 4.22 as a function of 1/WHSV (g_{CAT}/g_{ETOH}·h).

Table 4.22 Catalytic results obtained, in terms of ethanol conversion (*X*,%) and products selectivity and yield, for the ethanol gas-phase conversion over **2Na/Sep@700**. Others ID: ethane, 1,3-butadiene. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV= 1.0, 0.5 or 0.33 g_{ETOH}/(g_{CAT}·h).

Selectivity [%]								
1/WHSV [h]	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID
1	21	40	38	19	1	0	4	2
2	30	33	42	21	1	0	2	0
3	46	31	40	24	2	1	3	1
Yield [%]								
1/WHSV [h]	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID
1	21	8	8	4	0.2	0	1	0.4
2	30	10	13	6	0.4	0	1	0
3	46	14	19	11	1	0.2	1	0.2

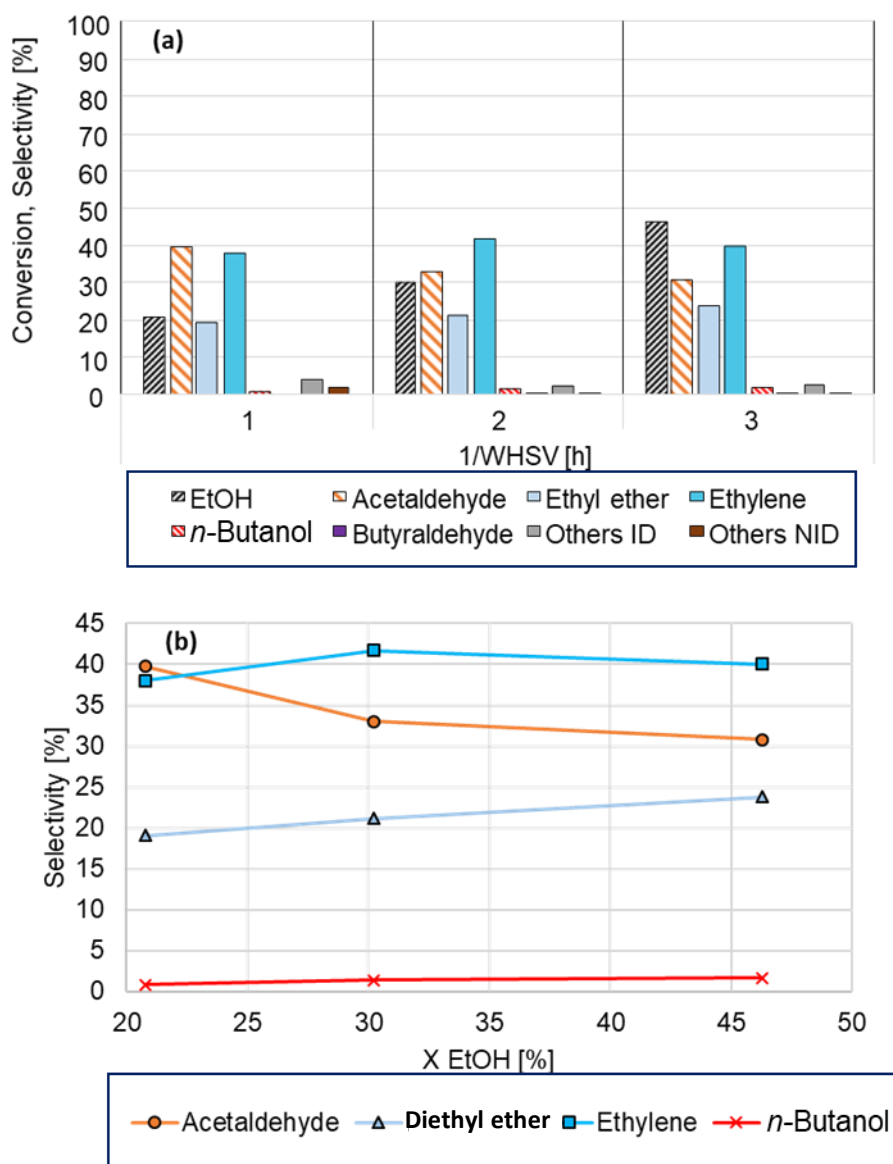


Figure 4.79 Catalytic results obtained, in terms of ethanol conversion and products selectivity, for the Ethanol gas-phase conversion over **2Na/Sep@700**. (a) EtOH conversion (X) and products selectivity in function of $1/\text{WHHSV}$. (b) Variation of selectivity of main products as a function of EtOH conversion. Others ID: ethane, 1,3-butadiene. Reaction conditions: EtOH 5% v/v in N_2 , $T = 450^\circ\text{C}$, $P = 1 \text{ atm}$, $\text{WHSV} = 1, 0.5$ and $0.33 \text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$.

In general, decreasing the WHSV (defined as the mass flow rate of ethanol divided by the weight of catalyst) and so increasing the contact time between the catalyst and the reagents, led to an increase in both ethanol conversion and selectivity of its dehydrogenation products, ethylene and diethyl ether (Figure 4.79); with concomitant decrease of acetaldehyde selectivity. A slight increase of *n*-butanol selectivity (from 1 to 2 %) was observed.

A test with lower WHSV ($0.5 \text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$) by doubling the catalyst amount has been performed even over the 5Na/Sep@500. Figure 4.80 and Table 4.23 report the results obtained over the sodium impregnated samples including the test performed at higher contact time in order to evaluate its activity at higher ethanol conversion.

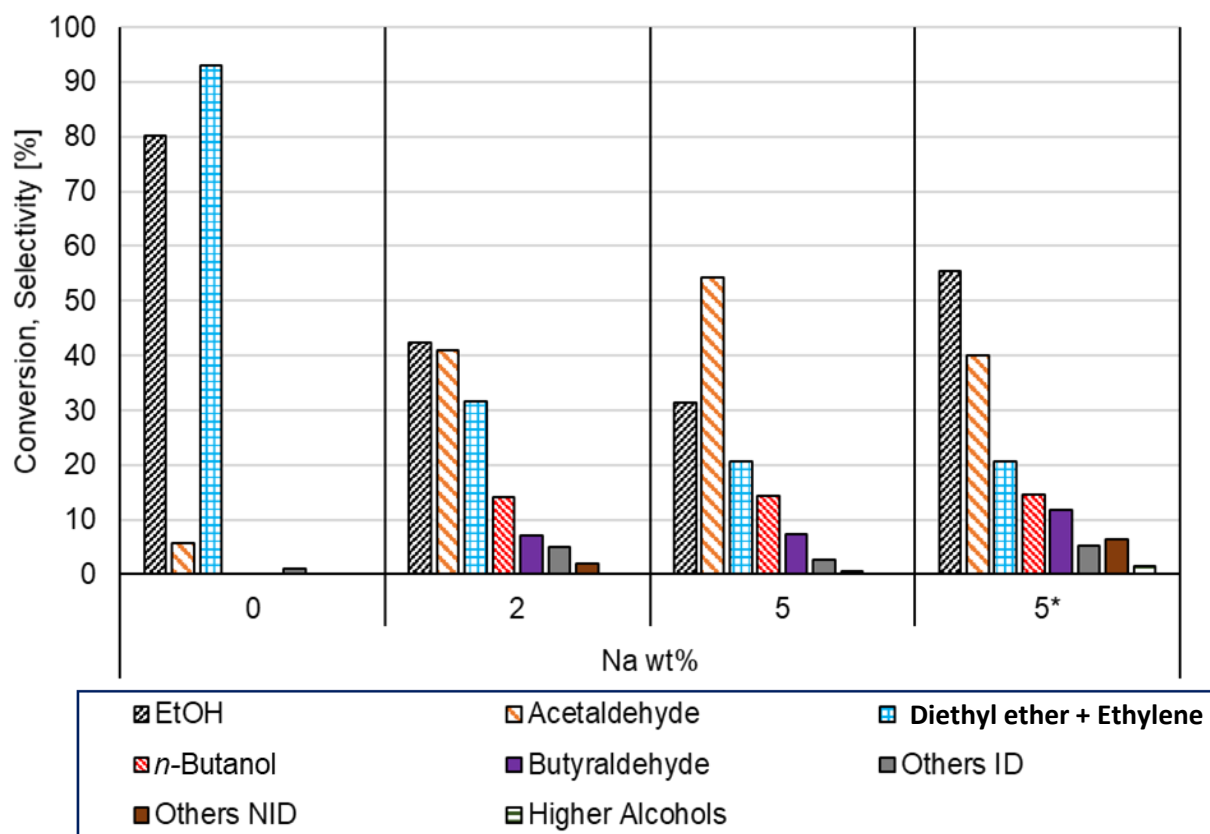


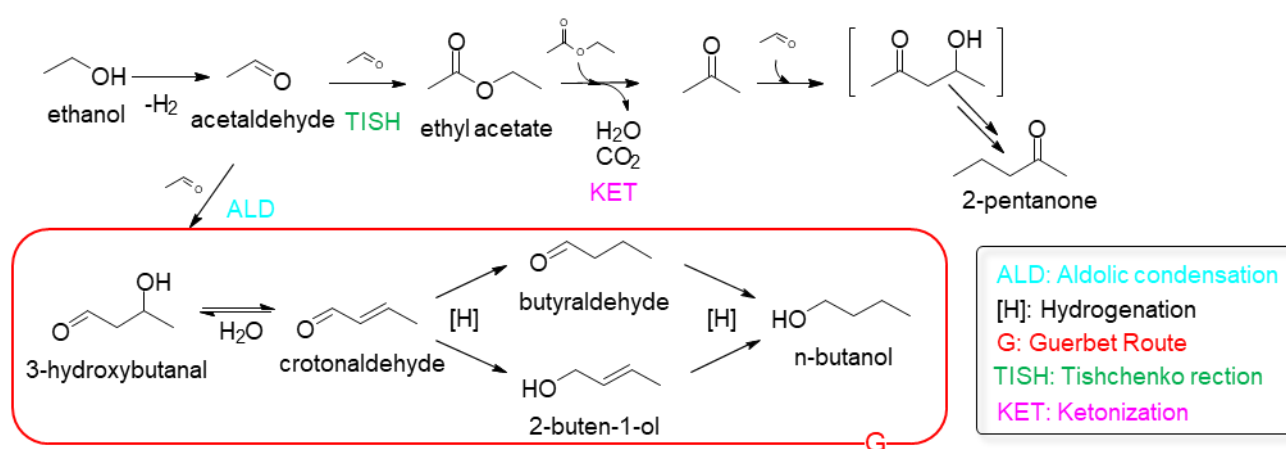
Figure 4.80 Catalytic results obtained in the Ethanol conversion over the Sepiolite supports calcined at 500°C and the sodium impregnated ones with 2 and 5 wt% of metal loading. Others ID: acetone, 2-pentanone, CO₂, ethane. Other alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm; WHSV= 1 g_{EtOH}/(g_{CAT}·h). *WHSV= 0.5 g_{EtOH}/(g_{CAT}·h).

Table 4.23 Catalytic results obtained, in terms of ethanol conversion (X%) and products selectivity and yield, for the ethanol gas-phase conversion over **2Na/Sep@700**. Others ID: ethane, 1,3-butadiene. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV= 1.0, 0.5 or 0.33 g_{EtOH}/(g_{CAT}·h).

Selectivity [%]										
WHSV [g/(g _{CAT} ·h)]	Na wt%	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
1	0	80	6	57	36	0	0	1	0	0
1	2	42	41	19	13	14	7	5	2	0
1	5	31	54	13	8	14	7	3	1	0
0.5	5*	55	40	14	7	15	12	5	6	1
Yield [%]										
WHSV [g/(g _{CAT} ·h)]	Na wt%	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
1	0	80	5	46	29	0	0	1	0	0
1	2	42	17	8	6	6	3	2	1	0
1	5	31	17	4	3	4	2	1	0	0
0.5	5*	55	22	8	4	8	6	3	3	1

A rise in contact time led to an increase of ethanol conversion, as expected, but did not affect the selectivity of *n*-butanol, that remained around 14%. It can be observed a decrease of selectivity of acetaldehyde and a concomitant increase of the selectivity of higher Guerbet alcohols as well as the

other identified (Other ID) and unidentified (Other NID) products. It can be suggested that the selectivity of *n*-butanol remained stable since it has been converted to its dehydrogenation product, butyraldehyde, whose selectivity increased from 7 to 12%, and to higher alcohols through the Guerbet route, indeed their presence has been detected at higher contact time. The same suggestion can be proposed for the lower selectivity of acetaldehyde that acted as intermediate product for side reactions that led to the formation of acetone and 2-pentanone, grouped in the other identified products “Other ID” in Fig. 4.80. Ketones can be formed through consecutive Tishchenko disproportionation reaction²⁹⁶ of acetaldehyde forming the ester (ethyl acetate, not detected) and consecutive ester ketonization reactions,¹⁰⁵ producing water and CO₂ as by-products. The reaction mechanism from which ketones can be formed starting from ethanol is depicted in Scheme 1.



Scheme 1. Reaction mechanism proposed over the Na-sepiolite catalytic system.

4.3.2.2 Transition metals supported on Sepiolite

The dehydrogenation reaction from ethanol to acetaldehyde, that is the generally accepted first step of the Guerbet reaction path (accordingly to Scheme 1), is often identified as the rate limiting step, in particular when operating at low temperatures.²⁹⁷ Catalytic systems without transition metals require higher temperature for alcohol coupling due to higher activation energy of dehydrogenation.^{67,298,299} Therefore, in order to enhance the production of acetaldehyde, frequently reported as a key intermediate product into the Guerbet mechanism, as well as the subsequent hydrogenation steps of the coupled intermediates that characterize this mechanism, some sepiolite catalyst samples have been prepared by the addition of a transition metal, namely copper and nickel. The synthesis method by means of wet impregnation has been explained in section 3.2.4.

4.3.2.2.1 Copper

Firstly, the two sepiolite supports calcined at 500°C and 700°C (Sep@500 and Sep@700) have been impregnated with copper oxide with 5 wt% of metal loading (CuO/Sep@500 5wt% and CuO/Sep@700 5 wt%). Then, even the sodium impregnated sepiolite samples with 2 wt% of Na, both calcined at 500°C and 700°C, have been impregnated with the same copper amount (CuO/2Na/Sep@500 5wt% and CuO/2Na/Sep@700 5 wt%).

The catalytic results for ethanol transformation, in terms of products distribution and ethanol conversion, obtained in the reactions performed at 450°C, atmospheric pressure and WHSV of 1 g_{ETOH}/(g_{CAT}·h) over the prepared catalysts are reported in Figure 4.81 and Table 4.24.

Regarding the Sep@700, the addition of copper raised the ethanol conversion, showing higher activity and leading to lower production of the dehydration products of ethanol with concomitant increase of acetaldehyde formation. In particular, when copper is added over the sepiolite impregnated with sodium (i.e., CuO/2Na/Sep@700 5 wt%), a selectivity of acetaldehyde of 60% has been reached. Moreover, even a slight formation of *n*-butanol can be observed over the same catalytic system. As it can be observed in Figure 4.81, a general effect of the addition of copper has been the decrease of both ethanol conversion and ethylene selectivity with a concomitant increase of acetaldehyde selectivity, as expected. The decrease of the dehydration products of ethanol reflects the decrease of the overall acidity measured by TPD-NH₃ analysis as shown in Section 4.3.1.5. This result is in accordance with Angelici et al.²⁷⁰ who explained the drop in ethylene and diethyl ether production by the poisoning activity of copper in regards of the most acidic sites of the support (i.e., SiO₂-MgO).

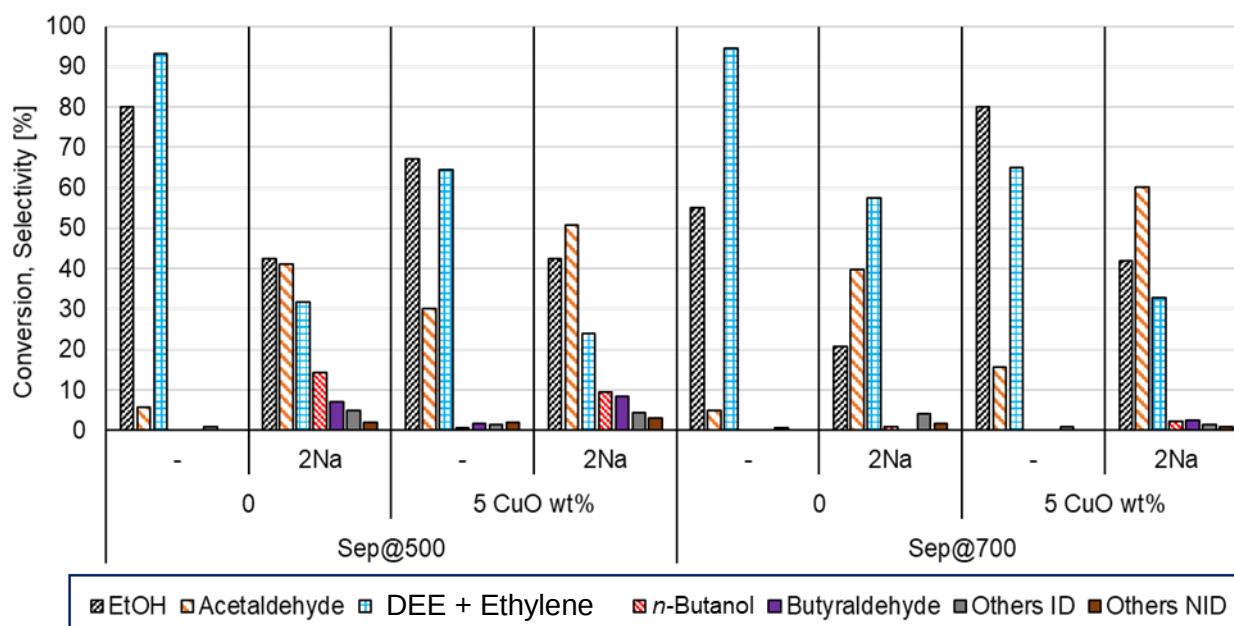


Figure 4.81 Catalytic results obtained in the Ethanol conversion over the Sepiolite supports calcined at 500°C and 700°C (Sep@500, Sep@700), the sodium impregnated ones with 2wt% of metal loading (2Na/Sep@500, 2Na/Sep@700) and the copper impregnated ones with 5wt% of CuO metal loading. Others ID: acetone, 2-pentanone, CO₂, ethane, 1,3-butadiene. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

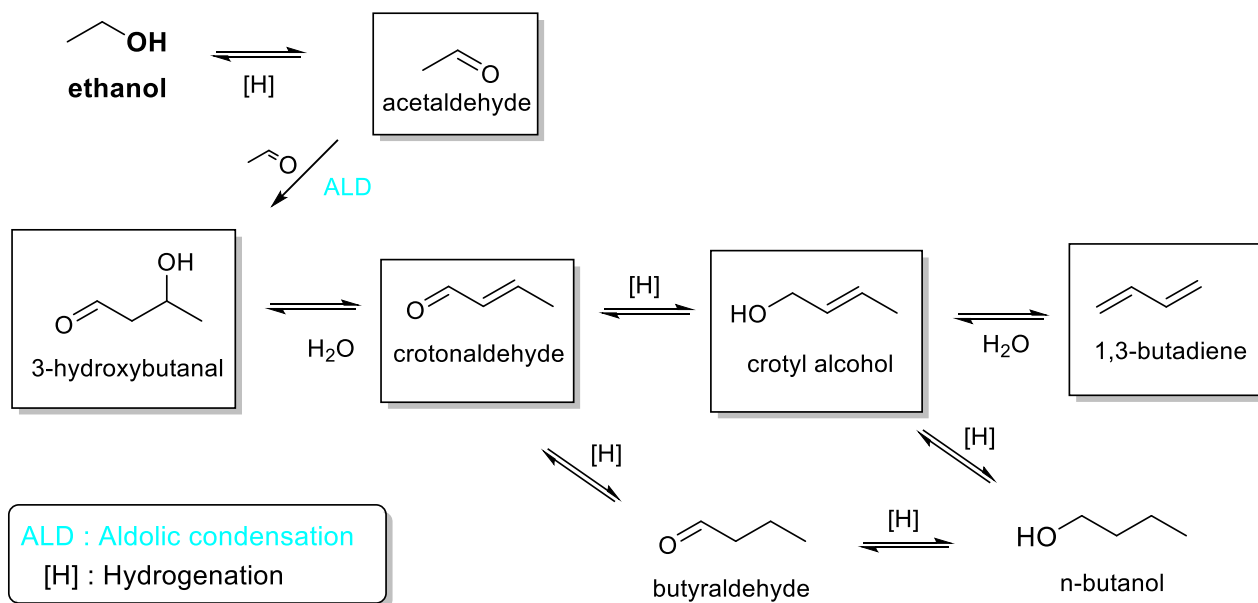
Even if the selectivity of acetaldehyde increased with copper addition, this did not lead to an increase of *n*-butanol formation, the selectivity of which instead decreased after copper addition, in all cases examined. For example, *n*-butanol selectivity obtained over 2Na/Sep@500 was 14% while after copper addition it decreased to 10%. Meanwhile, the selectivity of butyraldehyde (BuA) slightly increased from 7 to 8 %, the formation of which could be explained both by the hydrogenation of crotonaldehyde, an intermediate product of the aldol condensation route, but even by *n*-butanol dehydrogenation. Indeed, a concomitant decrease of *n*-butanol selectivity can be observed (from 14 to 10%). This could suggest that *n*-butanol formation over sepiolite could happen through a different pathway that did not involve the condensation of acetaldehyde, in contrast to the most accepted one based on aldol condensation. Indeed, *n*-butanol could be formed through the direct route, by dimerization of ethanol, for which redox catalyst properties are not required.²⁸⁴

Table 4.24 Catalytic results obtained, in terms of ethanol conversion ($X\%$) and selectivity or yield of reaction products, for the ethanol gas-phase conversion over the Sepiolite supports calcined at 500°C and 700°C (Sep@500, Sep@700), the sodium-impregnated ones with 2wt% of metal loading (2Na/Sep@500, 2Na/Sep@700) and the copper impregnated ones with 5wt% of CuO metal loading. Others ID: acetone, 2-pentanone, CO₂, ethane, 1,3-butadiene. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Selectivity [%]										
Support	CuO amount [wt%]	Na Amount [wt%]	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID
Sep@500	-	-	80	6	57	36	0	0	1	
	5	-	67	30	37	27	1	2	1	2
	-	2	42	41	19	13	14	7	5	2
	5	2	43	51	15	9	10	8	4	3
Sep@700	-	-	55	5	69	26	0	0	1	
	5	-	80	16	52	29	0	0	1	0
	-	2	21	40	38	13	1	0	4	0
	5	2	42	60	22	11	2	2	1	1
Yield [%]										
Support	CuO amount [wt%]	Na Amount [wt%]	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID
Sep@500	-	-	80	5	46	29	0	0.0	0.8	0.0
	5	-	67	20	25	18	1	1.2	0.9	1.3
	-	2	42	17	8	6	6	3.0	2.1	0.8
	5	2	43	22	7	4	4	3.6	1.9	1.3
Sep@700	-	-	55	3	38	14	0	0.0	0.4	0.0
	5	-	80	12	42	23	0	0.0	0.8	0.0
	-	2	21	8	8	3	0	0.0	0.8	0.0
	5	2	42	25	9	5	1	1.0	0.6	0.4

The presence of copper in the catalytic system did not favour *n*-butanol formation. It seems that copper only acted as dehydrogenation promoter, favouring acetaldehyde (and butyraldehyde) formation. In the literature it is reported that copper addition to a SiO₂-MgO system resulted in a change of the rate limiting step, causing the consecutive aldol condensation of acetaldehyde to become the rate-determining one in ethanol conversion into butadiene.¹⁴⁸ Angelici et al. added copper to a SiO₂-MgO material in order to promote butadiene formation from ethanol (Ostromislensky and Lebedev process).^{148,270} They stated that Cu addition had the double effect of promoting the dehydrogenation of ethanol toward acetaldehyde and of modifying the acidic/basic properties of the support, enhancing butadiene formation. Indeed, the most accepted mechanism for butadiene formation from ethanol requires a multifunctional catalyst containing both redox and acid/base active sites. The so-called Toussaint's aldol condensation mechanism by which butadiene should be formed from ethanol, consists in a parallel reaction to the Guerbet one, with acetaldehyde as key intermediate.^{300,301} The mechanism, depicted in Scheme 2, rely on of five steps: dehydrogenation of ethanol to acetaldehyde, aldol condensation or aldolization of acetaldehyde to 3-hydroxybutanal, then dehydrated to crotonaldehyde, reduction of crotonaldehyde to crotyl alcohol, dehydration of crotyl alcohol to butadiene.³⁰¹ The intermolecular hydrogen transfer between ethanol and crotonaldehyde is believed to occur via a Meerwein–Ponndorf–Verley mechanism (MPV), with ethanol acting as H-donor, which requires the participation of acid and basic sites.¹⁴⁵ Butadiene formation has not been observed over the CuO/Sep@500 5 wt% catalyst. Nevertheless, the

concomitant presence of both alkali metal and copper led to the formation of butadiene (i.e. selectivity of 2%, grouped into the “others ID” products). Thus, the presence of sodium into the catalytic system could furnish the basicity required to catalyse that step. Regardless, neither the presence of crotonaldehyde nor the one of crotyl alcohol has been detected during the catalytic tests. Besides, the “direct route” in which acetaldehyde and ethanol condensate yielding alkenols that produce butadiene by consecutive dehydration, has been suggested from the literature.³⁰² Even in this case, basicity is required to catalyse the condensation step.



Scheme 2. Ethanol conversion to 1,3-butadiene (Toussaint pathway) and to *n*-butanol (Guerbet route).

4.3.2.2.1.1 Catalytic results over the time on stream

Figure 4.82 reports the catalytic results in terms of ethanol conversion and products selectivity as a function of the time on stream (h), obtained for the reactions performed for 2.2 h, at 450°C, atmospheric pressure and WHSV of 1 h⁻¹ over the CuO/Sep@500 5wt% and the CuO/2Na/Sep@500 5wt% catalysts. As it can be noticed, ethanol conversion decreased with the time on stream, suggesting that the catalysts partially deactivated during the reaction. Regarding the catalyst CuO/Sep@500 5 wt%, with decreasing conversion (i.e., from 83 to 60%), the selectivity of the acidic products DEE and ethylene increased (i.e., from 47.5 to 70%) while the one of acetaldehyde decreased (i.e., from 33 to 27%). This could suggest that with partial deactivation of the catalyst is related to the change of active sites responsible for ethanol dehydrogenation.

Nevertheless, with regard to the CuO/2Na/Sep@500 5 wt%, ethanol conversion decreased from 55 to 40% with the time on stream. Concomitantly, the selectivity of the ethanol-Guerbet product (i.e., *n*-butanol) slightly increased and the one of its dehydrogenation product (i.e., butyraldehyde) decreased. Only a slight decrease of acetaldehyde and concomitant increase of dehydration

products (i.e., DEE and ethylene) can be observed, of around 2%, resembling the behaviour observed of the catalyst devoid of alkali metal.

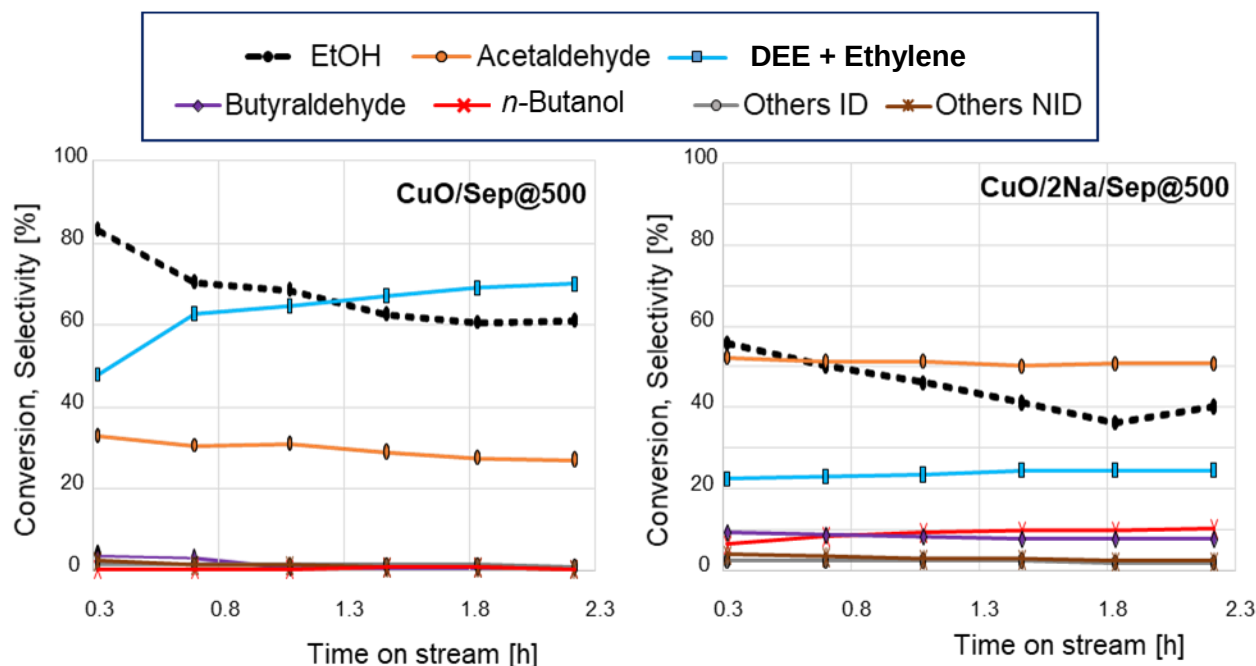


Figure 4.82 Catalytic results obtained in the Ethanol gas-phase conversion over the CuO/Sep@500-5wt% and the CuO/2Na/Sep@500-5wt% catalyst in terms of conversion of ethanol and main products selectivity as a function of the time on stream, (h). Others ID (acetone, 2-pentanone, CO₂, ethane). Reaction conditions: EtOH 5% v/v in N₂, T=450°C, P= 1 atm, WHSV= 1 g_{EtOH}/(g_{cat}·h).

4.3.2.2.1.2 Diffuse-reflectance UV-visible (DR-UV-vis) spectrometry

To shed some light on the nature of the copper species, supported catalysts with 5 wt% of metal loading were studied by means of diffuse-reflectance UV/Vis (DR-UV-vis) spectroscopy, in particular the CuO/Sep@500-5wt% and the CuO/2Na/Sep@500-5wt%. In order to evaluate the copper state after reaction, the same analysis has been performed even over the spent catalysts. Figure 4.83 reports the results obtained.

Both the fresh catalysts analysed exhibited a similar spectra, characterized by two absorption bands. The sharp one at ca. 240 nm can be assigned the ligand-to-metal charge-transfer (LMCT) from a molecular orbital primarily on O²⁻ to an orbital mainly on an isolated Cu²⁺ in octahedral coordination.³⁰³ This CT is characteristic of highly dispersed (isolated) Cu²⁺-O²⁻ in octahedral coordination of CuO oligomers (O²⁻-Cu²⁺ → O-Cu⁺ LMCT transition), showing the presence of isolated CuO species.²⁷⁰ The other band in the spectral range 600-800 nm is a relatively broad asymmetrical peak related to Cu(II) ligand field d-d transitions, in line with the reported for the bulk CuO.^{304,305} They are also indicative of Cu(II) species in a (distorted) octahedral field. Similar spectra have been reported for different Cu-zeolites, and have been discussed in terms of hydrated Cu(II) ions.^{303,304}

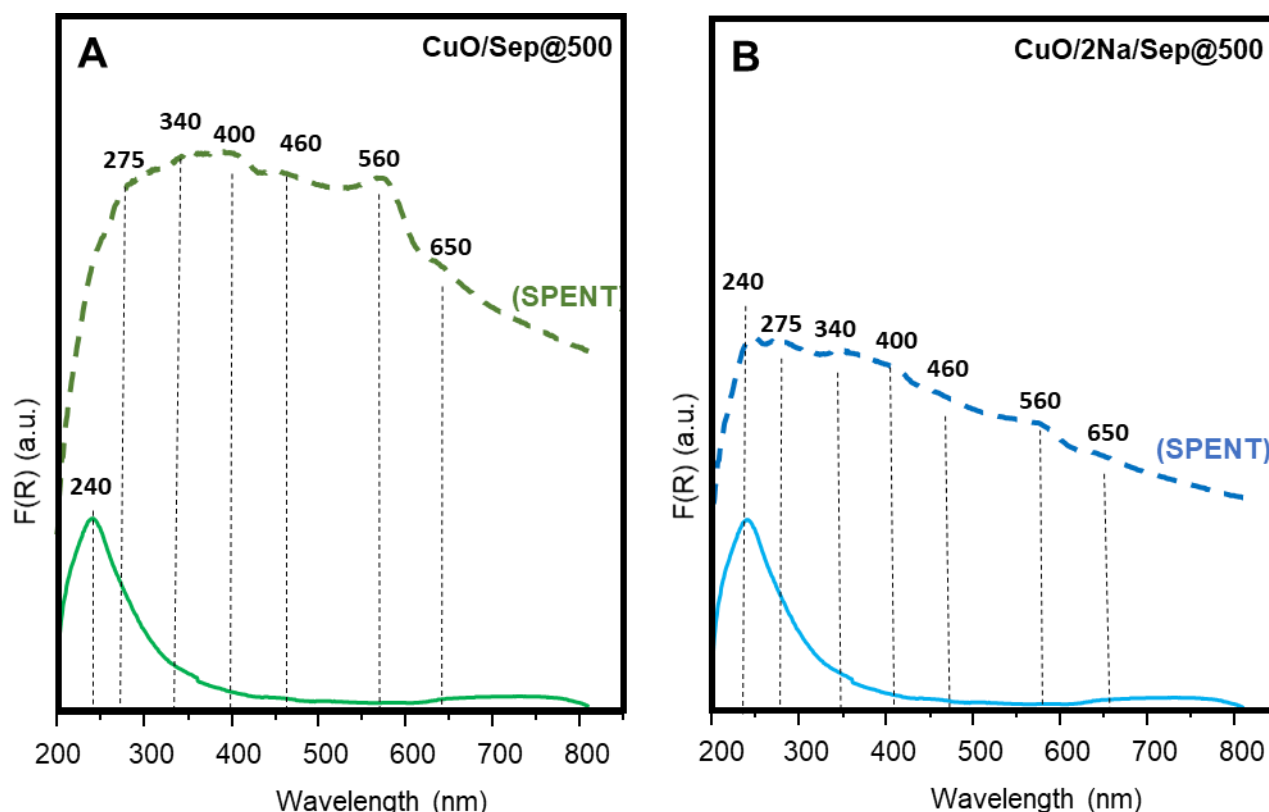


Figure 4.83 Diffuse-reflectance UV/Vis spectra of fresh and spent catalyst after reaction performed at 450°C, atmospheric pressure and WHSV of 1 h⁻¹, EtOH in N₂ 5% v/v. A): CuO/Sep@500 5 wt%; B) CuO/2Na/Sep@500 5 wt%.

The spectra of the spent catalysts obtained were quite different from the fresh ones, indicating the presence of carbonaceous materials deposits^{270,306–308} as well as a structural changes presumably via a redistribution of the Cu(II) sites.²⁷⁰ After reaction, in the spectra appeared bands at ca. 275, 340, 400, 460, 560 (6) and 650 (7) nm. From the literature, some of those signals has been assigned to carbonaceous deposits, mainly located inside the porous structure when the methanol-to-olefin reaction over zeolite catalyst is performed.^{307,308} Nevertheless, in addition to the formation of absorption bands, an increase in absorbance over the whole range of wavenumbers can be observed, which could be related to formation of larger carbonaceous deposit on the surface of the catalyst.³⁰⁶ The bands at 275 can be assigned to benzene, toluene and xylenes; the band at ca. 400 nm - to mononuclear aromatics with 4, 5 and 6 methyl groups; the broad bands at ca. 460 - to a group of binuclear aromatics with different degrees of methylation; the bands at ca. 650 nm - to aromatics with ≥3 nuclei.

In addition, the variations in the absorption bands between fresh and spent catalysts may be explained by the redox cycle undergone by Cu during the reaction. The broad bands in the range 200–800 nm presented in the spectra could suggest the appearance of cluster-like species of CuO, Cu(0) nanoparticles, as well as large size CuOx.³⁰⁹ According to the literature,³¹⁰ the signals at ca. 360, 430, 550 nm and the wide absorption in 630–660 range observed could belong to O–Cu–O (360) and Cu–O–Cu (430) complexes (charge transfer bands), plasmon resonance bands of Cu_n

nanoparticles (550) and to electron d–d transitions in Cu(II) in distorted octahedral field surrounded by oxygen in CuO particles(5), respectively. Moreover, Angelici et al. attributed the same d–d transitions to peaks observed at 700–800 nm.²⁷⁰ Thus, the band at 650 nm could be assigned to copper oxide nanoparticles of large size.³⁰⁹ The peak observed at 560 nm could be related the presence of plasmon resonance bands of Cu_n particles, suggesting that the catalytic reaction, accompanied by oxidation-reduction cycle of Cu, favoured the formation of copper metal particles.

310

From the literature²⁷⁰, the partial deactivation observed over similar catalytic system used for the ethanol conversion into butadiene, has been mainly attributed to the carbonaceous deposition over the catalyst surface, blocking active sites. The presence of carbonaceous compounds could be confirmed by the DR-UV analysis here displayed. Interestingly, carbonaceous deposits formation appeared more prominent over the catalyst devoid of sodium, showing more intense absorption bands. Indeed, the presence of sodium, which lead to lowering the acidity of the catalyst and to an overall higher B/A ratio (see Table 4.19) may be the cause of the lower ethylene formation, which is probably the intermediate product for carbonaceous compound formation^{266,311,312}, allowing the catalyst to catalyse the successive condensation reaction required for butadiene formation.

4.3.2.2.1.3 *Copper metal loading effect*

In order to evaluate the copper amount effect, some samples have been prepared by doubling the amount of copper oxide. Specifically, copper has been added with a 10 wt% of metal loading over the sepiolite calcined at 500°C support and over the one containing 2 wt% of sodium, namely CuO/Sep@500 10 wt% and CuO/2Na/Sep@500 10 wt%. The catalytic results are depicted in Figure 4.84 and Table 4.25.

Table 4.25 Catalytic results obtained, in terms of ethanol conversion ($X\%$) and products selectivity and yield, for the ethanol gas-phase conversion over the Sepiolite support calcined at 500°C (Sep@500), the sodium impregnated one with 2wt% of metal loading (2Na/Sep@500) and the copper impregnated ones with 5wt% and 10 wt% of Cu metal loading. Others ID: acetone, 2-pentanone, CO_2 , ethane. Reaction conditions: EtOH 5% v/v in N_2 , $T = 450^\circ\text{C}$, $P = 1 \text{ atm}$; $\text{WHSV} = 1 \text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$.

Selectivity [%]										
Support	CuO [wt%]	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	BD	Others ID	Others NID
Sep@500	0	80	6	57	36	0	0	0	1	
	5	67	30	37	27	1	2	0	1	2
	10	82	40	30	19	0	2	2	2	4
2Na/Sep@500	0	42	41	19	13	14	7	2	2.9	2
	5	43	51	15	9	10	8	2	2	3
	10	53	53	14	8.4	8	8	2.6	2	4
Yield [%]										
Support	CuO [wt%]	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	BD	Others ID	Others NID
Sep@500	0	80	5	46	29	0	0	0	1	0
	5	67	20	25	18	0	1	0	1	1
	10	82	33	25	16	0	1	2	1	4
2Na/Sep@500	0	42	17	8	6	6	3	1	1	1
	5	43	22	7	4	4	4	1	1	1
	10	53	28	7	4	4	4	1	1	2

By increasing the copper amount, higher value of both ethanol conversion and acetaldehyde selectivity have been obtained; simultaneously a decreasing trend of dehydration products (ethylene and diethyl ether) selectivity with copper oxide amount can be observed. Indeed, a higher amount of redox active sites led to an increased formation of the dehydrogenation product of ethanol, without affecting the overall yield of the acid-catalysed reactions products. Considering the sepiolite support alone, Sep@500, a higher amount of copper led to higher activity. Indeed, ethanol conversion increased from 67% to 82% while increasing the copper amount from 5 to 10 wt% of CuO metal loading. In addition, it can be observed the presence of 1,3-butadiene, gathered into the “Other ID” products in Figure 4.84, with a higher amount of copper. On the other hand, the presence of a 2 wt% of sodium into the catalytic system led to a small formation of ketones, acetone and 2-pentanone, with the concomitant formation of the side product CO_2 , gathered into “Other ID” in Table 4.25. The presence of sodium generally led to lower the activity of the catalyst but appeared necessary to catalyse *n*-butanol formation. It seems that the presence of copper only favoured the dehydrogenation reaction of ethanol without playing any helpful role in *n*-butanol formation, the yield of which remained stable after increasing the copper amount.

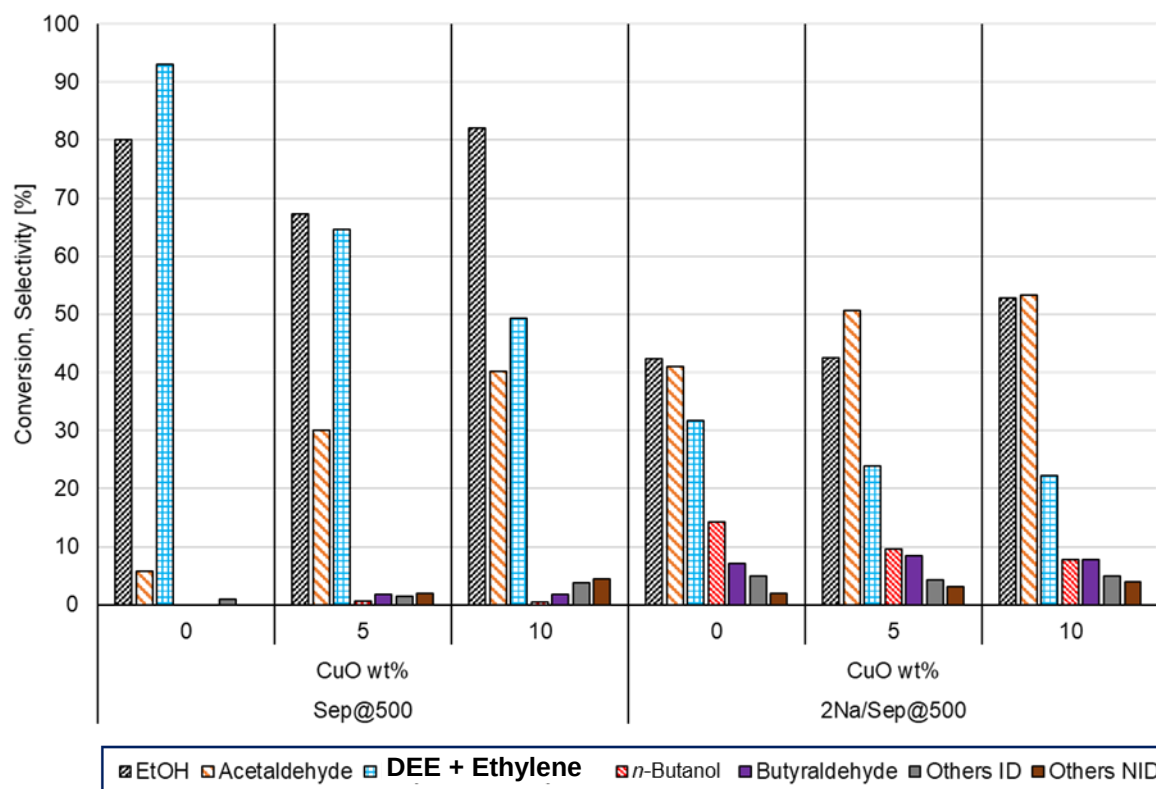


Figure 4.84 Catalytic results obtained in the Ethanol conversion over the Sepiolite support calcined at 500°C (Sep@500), the sodium impregnated one with 2wt% of metal loading (2Na/Sep@500) and the copper impregnated ones with 5wt% and 10 wt% of Cu metal loading. Others ID: acetone, 2-pentanone, CO₂, 1,3-butadiene, ethane. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

4.3.2.2.1.4 Copper reduction effect

For the purpose of evaluate the effect of the presence of copper in the metallic phase in the ethanol gas-phase conversion, some reactions have been performed over catalyst that had undergone a previous thermal treatment under hydrogen flow in order to reduce copper and obtaining it in the metallic phase. In particular, the catalyst consisting of 5wt% CuO over 2Na/Sep@500 and, for the sake of comparison, the one supported on MgO, have been previously reduced in order to obtain the metallic copper and then tested. To do so, the catalyst have been put into a vertical reactor fed by a 40mL/min hydrogen flow for three hours at 350°C in order to reduce the catalyst. After hydrogen treatment, the catalysts have been tested into the reaction system in the typical reaction condition of 450°C and atmospheric pressure and WHSV of 1 g_{EtOH}/(g_{CAT}·h). The results are reported in Figure 4.85 and Table 4.26.

Table 4.26 Catalytic results obtained, in terms of ethanol conversion (X%) and products selectivity and yield, for the ethanol gas-phase conversion over the MgO and 2Na/Sep@500 catalysts impregnated with 5 wt% of CuO and reduced to Cu after treatment at 350°C for 3h under hydrogen flow (40mL/min H₂). Others ID: acetone, 2-pentanone, CO₂, 1,3-butadiene, ethane. Guerbet alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Selectivity [%]										
Support	5 wt%	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
MgO	CuO	26	58	21	1	9	4	2	0	0
	Cu	41	43	25	5	23	8	2	11	3
2Na/Sep@500	CuO	43	51	15	9	10	8	4	3	
	Cu	46	52	8	14	10	9	5	3	
Yield [%]										
Support	5 wt%	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
MgO	CuO	26	15	5	0	2	1	0	0	0
	Cu	41	17	10	2	9	3	1	4	1
2Na/Sep@500	CuO	43	22	7	4	4	4	2	1	0
	Cu	46	24	4	6	4	4	2	1	0

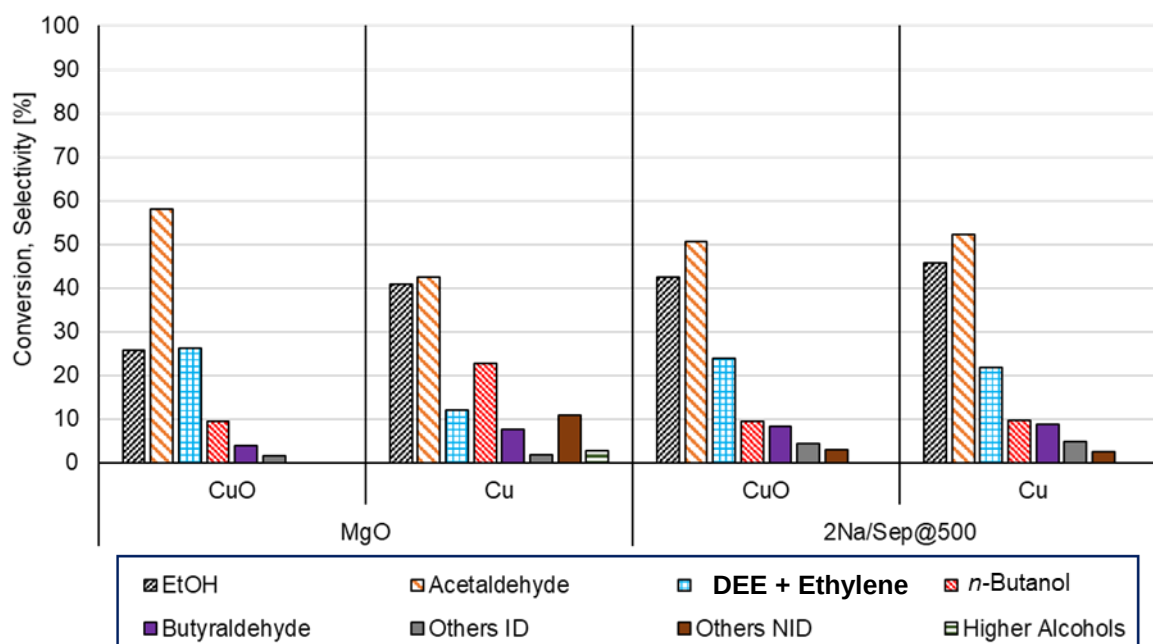


Figure 4.85 Catalytic results obtained in the Ethanol conversion over the MgO and 2Na/Sep@500 catalysts impregnated with 5 wt% of CuO and reduced to Cu after treatment at 350°C for 3h under hydrogen flow (40mL/min H₂). Others ID: acetone, 2-pentanone, CO₂, 1,3-butadiene, ethane. Guerbet alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

As far as MgO is concerned, the copper reduction led to an increase of both ethanol conversion and *n*-butanol selectivity, from 26 to 41% and from 9 to 23% respectively. The most accepted reaction mechanism for the Guerbet route encompasses two hydrogenation/dehydrogenation steps, namely the dehydrogenation of the reagent alcohol yielding the corresponding aldehyde and then the reduction of the α,β -unsaturated aldehyde (deriving from the aldol-condensation step) yielding the

higher Guerbet alcohol. The presence of the metallic copper can play a crucial role into those steps resulting in increased formation of *n*-butanol (selectivity from 9 to 23%) and even higher alcohols (selectivity from 0 to 3%).

By contrast, the reduction of copper when impregnated over the 2Na/Sep@500 sample did not lead to any effect on the catalytic results, only a slight increase of ethanol conversion and acetaldehyde selectivity can be noted. However, since the reduced catalyst after H₂ treatment was directly placed into the reaction system and then kept under inert gas flow (30 mL/min of N₂) in order to avoid the re-oxidation of copper into its oxide form, it was not possible to ascertain the successful reduction of the catalyst. Therefore, an alternative explanation for the resembling catalytic results could be an ineffective reduction treatment of the catalyst.

4.3.2.2.2 Nickel

In order to evaluate the effect of a different transition metal, a sample impregnated with nickel has been prepared. In particular, NiO has been added on 2Na/Sep@500 with a 5 wt% of metal loading through wet impregnation method (Section 3.2.4). After preparation, the catalyst has been tested in the ethanol gas-phase conversion with the reaction conditions as follows: 450°C, atmospheric pressure and WHSV of 1 g_{ETOH}/(g_{CAT}·h). In this case, the reaction temperature used has been even decreased to 400 and 350°C. Figure 4.86 reports the catalytic results obtained in terms of ethanol conversion and selectivity of the main products obtained. As it is possible to observe, while performing the reaction at the higher temperature, 450°C, the NiO/2Na/Sep@500 5 wt% catalyst led to the formation of CO and CO₂. Carbon monoxide can derive from acetaldehyde or ethanol cracking decomposition.^{136,313}

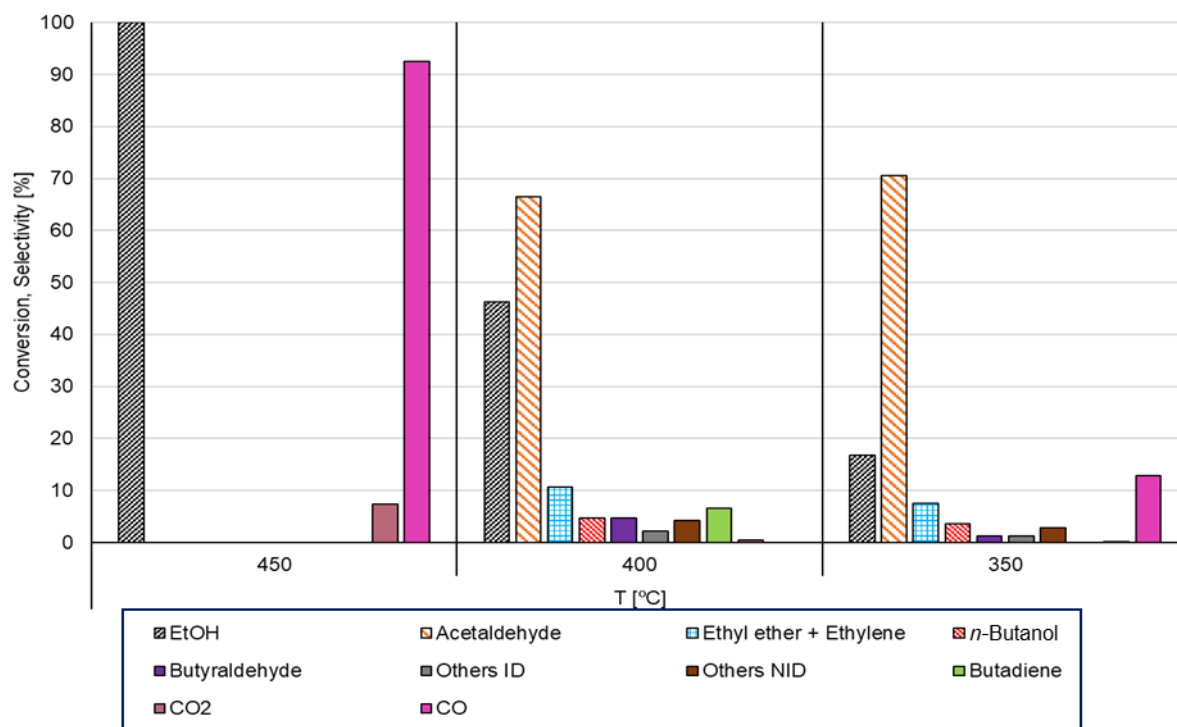


Figure 4.86 Catalytic results obtained in the Ethanol conversion over NiO/2Na/Sep@500. Others ID: acetone, 2-pentanone, ethyl acetate. Reaction conditions: EtOH 5% v/v in N₂, T=350, 400, 450°C, P= 1 atm, τ = 0.24 s; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

In order to compare the results obtained over the two different transition metal-impregnated catalysts tested (i.e., CuO/2Na/Sep@500 5 wt% and NiO/2Na/Sep@500 5 wt%) the results obtained over the nickel-supported sample that have been considered were the one obtained at 400°C. The results are compared in Figure 4.87. In the case of Sep@550, it is possible to appreciate the decreasing of ethanol conversion after impregnation with transition metal oxides. When pure sepiolite was used as catalyst support, the main products remained the dehydration products of ethanol, ethylene and diethyl ether, passing from a cumulative selectivity of 93% (57 and 36% respectively) to 65% (37 and 27%, respectively) when the CuO 5 wt% impregnated one was used. The slight decrease of the dehydration products of ethanol was balanced by an increase of its dehydrogenation product, acetaldehyde. Probably the addition of a transition metal over the catalyst covered part of the acid sites favouring the formation of the dehydrogenation product of ethanol.

On the other hand, when the sodium-doped sepiolite was used as support, the main product obtained after the impregnation with transition metal was acetaldehyde. Indeed, acetaldehyde selectivity passed from 41% over the 2Na/Sep@500 to 51 and 66 % over CuO/2Na/Sep@500 5 wt% and the NiO/2Na/Sep@500 5 wt%, respectively. Interestingly, when the sodium-doped sepiolite was used as support, even butadiene, the Lebedev reaction product of ethanol, has been detected (see Scheme 2). Moreover, after impregnation with nickel, butadiene selectivity increased from 2% over the 2Na/Sep@500 to 7% over the NiO/2Na@500 5 wt% catalyst.

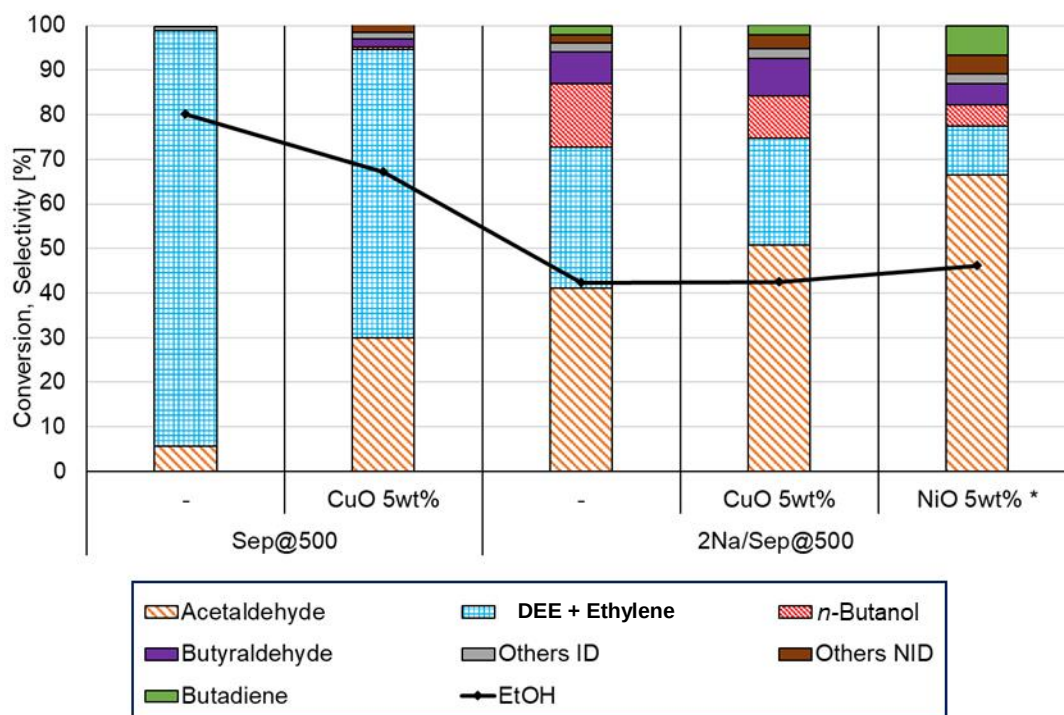


Figure 4.87 Catalytic results obtained in the Ethanol conversion over the Sep@500 and 2Na/Sep@500 supports in comparison with the CuO and NiO 5wt% impregnated samples. Others ID: acetone, 2-pentanone, CO₂, ethyl acetate. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C (*400°C), P= 1 atm; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Table 4.27 Catalytic results obtained, in terms of ethanol conversion (X%) and products selectivity and yield, for the ethanol gas-phase conversion over the Sep@500 and 2Na/Sep@500 supports in comparison with the CuO and NiO 5 wt% impregnated samples. Others ID: acetone, 2-pentanone, CO₂, ethyl acetate. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Selectivity [%]										
Support	Transition metal [5 wt%]	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	BD	Others ID	Others NID
Sep@500	-	80	6	57	36	0	0	0	1	0
	CuO	67	30	37	27	1	2	0	1	2
2Na/Sep@500	-	42	41	19	13	14	7	2	2	2
	CuO	43	51	15	9	10	8	2	2	3
	NiO*	46	66	5	6	5	5	7	2	4
Yield [%]										
Support	Transition metal [5 wt%]	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	BD	Others ID	Others NID
Sep@500	-	80	5	46	29	0	0	0	1	0
	CuO	67	20	25	18	0	1	0	1	1
2Na/Sep@500	-	42	17	8	6	6	3	1	1	1
	CuO	43	22	7	4	4	4	1	1	1
	NiO*	46	31	2	3	2	2	3	1	2

4.3.2.3 Alkali metals doped sepiolite

The highest selectivity of *n*-butanol (14%) was obtained over the catalyst consisting in sepiolite calcined at 500°C impregnated with 2wt% of sodium. So, the presence of an alkali metal showed to be crucial in favouring the *n*-butanol formation pathway. Its presence led to an overall decrease of the sepiolite acidity probably generating the right acidity/basicity ratio required to induce *n*-butanol formation. It was reported that base strength increases with the radius of alkali cations.²⁹⁵ In order to evaluate the effect of bigger and more electropositive alkali metals, other sepiolite samples have been prepared adding potassium and cesium by incipient wetness impregnation. The synthesis method has been explained in section 3.2.4.

4.3.2.3.1 K-doped sepiolite

Two samples impregnated with 2 and 5 wt% of potassium have been synthesized by incipient wet impregnation and then have been tested into the reaction system for the ethanol gas-phase conversion at 450°C, atmospheric pressure and WHSV of 1 g_{EtOH}/(g_{CAT}·h). The catalytic results are reported in Figure 4.88 and Table 4.28.

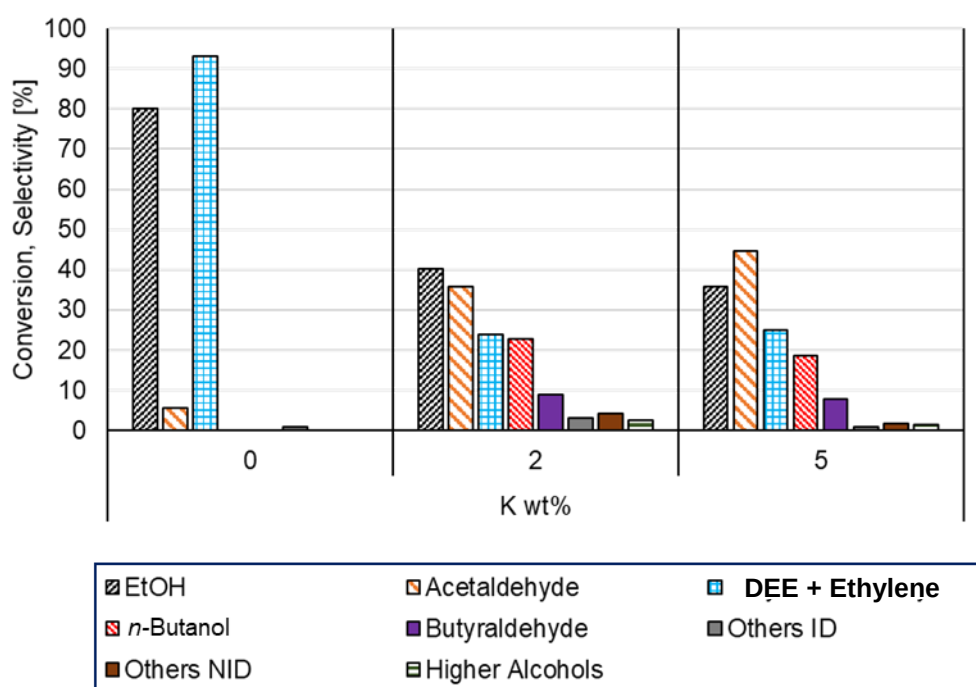


Figure 4.88 Catalytic results obtained in the Ethanol conversion over the Sep@500 support and the impregnated samples with 2 and 5 wt% of K. Others ID: acetone, 2-pentanone, CO₂, ethyl acetate. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N₂, T=450°C, P= 1 atm, WHSV= 1 g/(g_{CAT}·h).

Table 4.28 Catalytic results obtained, in terms of ethanol conversion (X , %) and products selectivity and yield, for the ethanol gas-phase conversion over the Sep@500 support and the impregnated samples with 2 and 5 wt% of K. Others ID: acetone, 2-pentanone, CO_2 , ethyl acetate. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N_2 , $T=450^\circ\text{C}$, $P=1\text{ atm}$, $\text{WHSV}=1\text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$.

Selectivity [%]									
$K\text{ wt\%}$	$X\text{ EtOH [\%]}$	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
0	80	6	57	36	0	0	1	0	0
2	40	36	12	12	23	9	3	4	2
5	36	45	15	10	19	8	1	2	1
Yield [%]									
$K\text{ wt\%}$	$X\text{ EtOH [\%]}$	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
0	80	5	46	29	0	0	1	0	0
2	40	14	5	5	9	4	1	2	1
5	36	16	5	4	7	3	0	1	0

By impregnating sepiolite calcined at 500°C with potassium, it was possible to obtain n -butanol with higher selectivity comparing the results obtained over the sodium impregnated samples. Indeed, over the 2K/Sep@500 catalyst, n -butanol has been obtained with a 23% of selectivity, ~10% more than the analogous sample impregnated with sodium, i.e. 14% (see Figure 4.78 and Table 4.21). Interestingly, over that catalyst even longer chain alcohols (i.e., 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol) started to be produced. The formation of higher alcohols comes from consecutive Guerbet reactions from n -butanol condensing with it-self (2-ethyl hexanol), with ethanol (1-hexanol, 2-ethyl butanol) and from condensation of hexanol with ethanol (1 octanol). (Scheme 3).

Over the just mentioned potassium-doped catalyst (i.e., 2K/Sep@500), a stability test have been performed by feeding the EtOH 5 v/v% in N_2 gaseous mixture into the reaction system for ca. 4 hours, in Figure 4.89 are depicted the catalytic results as a function of the time on stream (h).

From Figure 4.89 it can be noted no changes in activity of the catalyst over the time on stream, where ethanol conversion fluctuated around 40%. With the time on stream, acetaldehyde selectivity increased a bit from ~34% to 37% while ethylene selectivity decreased from 27 to ~23%. This could be related to changes in the nature of active sites (basic and acid sites), probably due to the formation of carbonaceous compounds (coke) partially covering the catalyst surface. The selectivity to n -butanol was not affected by the time on stream, staying constant at 23% with all the time on stream under consideration.

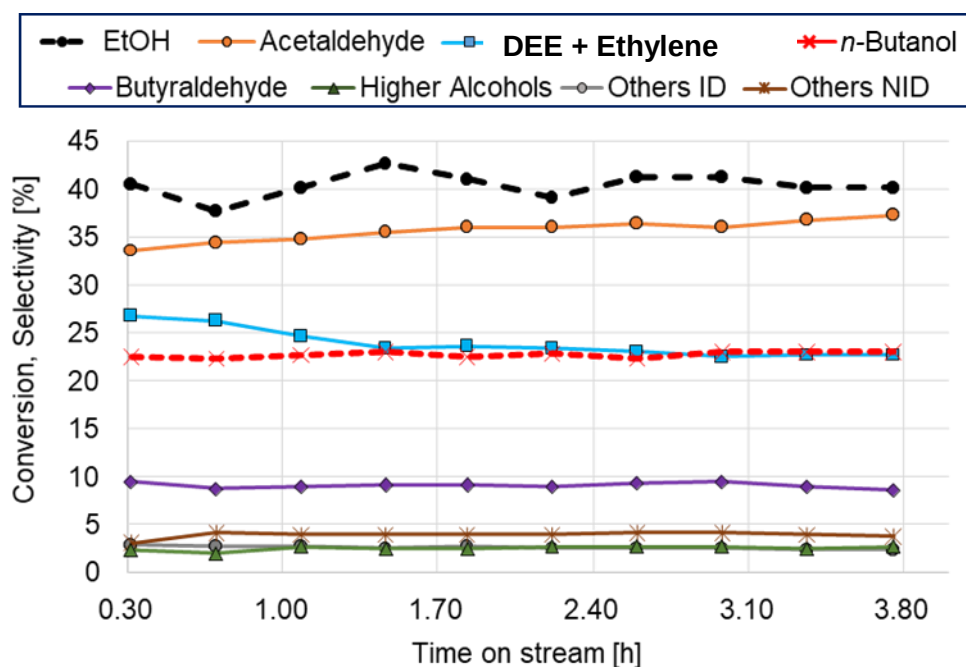


Figure 4.89 Catalytic results obtained in the Ethanol gas-phase conversion over the 2K/Sep@500 in terms of conversion of ethanol and main products selectivity as a function of the time on stream (h). Others ID: acetone, 2-pentanone, CO₂, ethyl acetate. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N₂, T=450°C, P= 1 atm, WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Interestingly, even in the case of potassium doped sepiolite, a higher amount of potassium over the catalyst was not beneficial for *n*-butanol production neither catalytic activity (Fig. 4.88). Indeed, by increasing the K metal loading from 2 to 5 wt%, *n*-butanol selectivity decreased from 23 to 19% as well as ethanol conversion, from 40 to 36%. The fact that they both decreased by the same extent could suggest that *n*-butanol is a primary kinetic product. Nevertheless, with increasing potassium amount, acetaldehyde formation increased reaching a selectivity value of 45% (see Figure 4.88 and Table 4.28).

4.3.2.3.2 Cs-doped sepiolite

The metal loading expressed by weight percent of the different alkali metals corresponds to a different molar amount of them. Therefore, in order to do a better comparison between the alkali metals-doped samples, it has been computed the alkali-metal molar ratios over the weight of sepiolite $n_{\text{MET}}/w_{\text{SEP}}$ [mmol_{METAL}/g_{SEPIOLITE}]. In addition, after SEM-EDX analysis, even the concrete alkali amount impregnated over the sepiolite has been measured (Table 4.29). Due to the higher molar mass of Cesium (i.e., M(Na):22.99 g/mol; M(K):39.10 g/mol and M(Cs):132.91 g/mol), some samples with higher metal loading (wt%) but with comparable $n_{\text{MET}}/w_{\text{SEP}}$ ratio values have been prepared.

Table 4.29 EDX analysis of the surfaces of alkali-doped sepiolite catalysts.

Support	Met	Alkali metal loading				
		Nominal [wt%]	Measured [wt%]	Nominal $n_{\text{MET}}/w_{\text{SEP}}$ [mmol/g]	Measured $n_{\text{MET}}/w_{\text{SEP}}$ [mmol/g]	Measured [Atomic %]
Sep@500	Na	2	1.3	0.87	0.56	1.1
		5	3.7	2.17	1.62	3.1
	K	2	2.2	0.51	0.56	1.1
		5	5.6	1.28	1.43	2.9
	Cs	2	1.6	0.15	0.12	0.2
		4	5.2	0.30	0.39	0.8
		7	7.8	0.53	0.59	1.2
		14	9.2	1.05	0.69	1.5

Figure 4.90 and Table 4.29 report the catalytic results obtained over the Cs-doped catalysts for the ethanol gas-phase conversion of ethanol performed at 450°C, 1 atm and WHSV= 1 g_{EtOH}/(g_{CAT}·h).

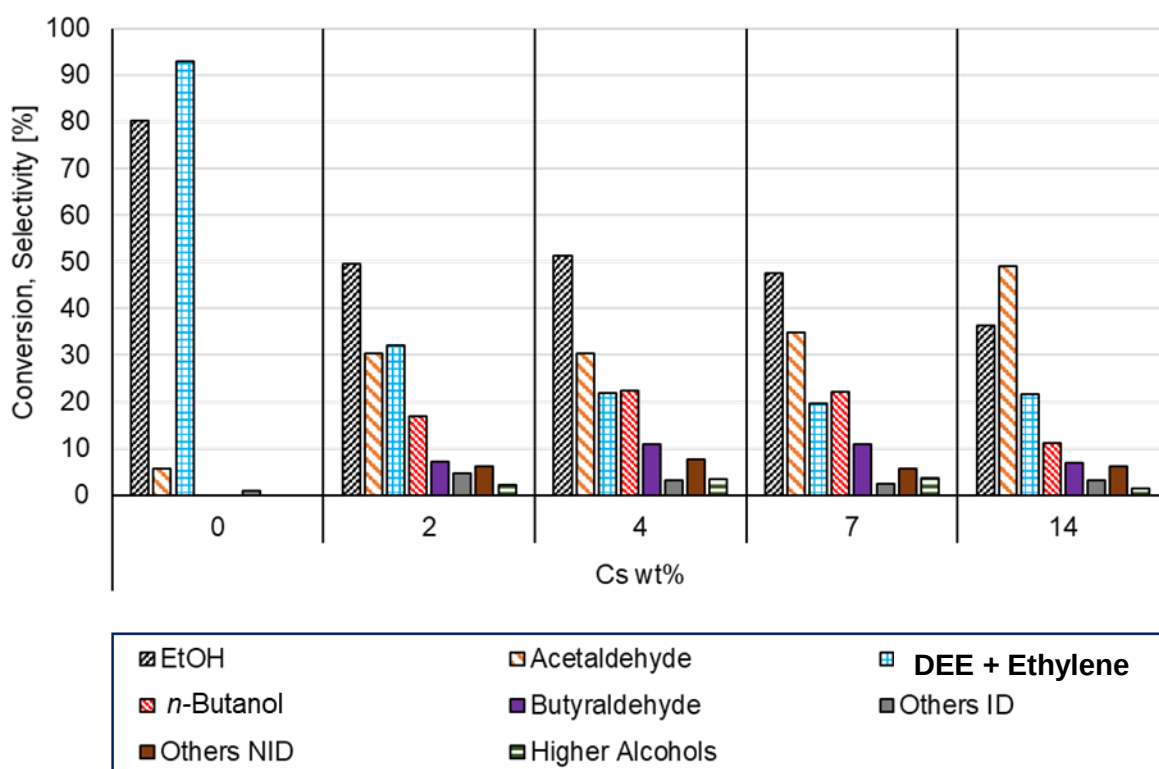


Figure 4.90 Catalytic results obtained in the Ethanol conversion over the Sep@500 support and the impregnated samples with 2, 4, 7 and 14 wt% of Cs. Others ID: acetone, 2-pentanone, CO₂, ethyl acetate. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Table 4.30 Catalytic results obtained, in terms of ethanol conversion (X %) and products selectivity and yield, for the ethanol gas-phase conversion over the Sep@500 support and the impregnated samples with 2, 4, 7 and 14 wt% of Cs. Others ID: acetone, 2-pentanone, CO_2 , ethyl acetate. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N_2 , $T = 450^\circ\text{C}$, $P = 1$ atm, $\text{WHSV} = 1 \text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}} \cdot \text{h})$.

Cs wt%	X_{EtOH} [%]	Selectivity [%]							
		AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
0	80	6	57	36	0	0	1	0	0
2	50	30	12	20	17	7	5	6	2
4	51	30	9	13	22	11	3	8	4
7	47	35	10	10	22	11	3	6	4
14	36	49	17.6	4.1	11	7	3	6	2
Cs wt%	X_{EtOH} [%]	Yield [%]							
		AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
0	80	5	46	29	0	0	1	0	0
2	50	24	10	16	14	6	4	5	2
4	51	16	4	7	12	6	2	4	2
7	47	17	5	5	10	5	1	3	2
14	36	18	6	1	4	3	1	2	1

From the results reported in Figure 4.90 and Table 4.30 it can be noticed the effect of the cesium amount over the catalytic activity and product distribution. Indeed, with increasing cesium amount, ethanol conversion decreased, as well as ethylene and DEE selectivity, probably due to the increasing amount of cesium that had neutralized part of the active acid sites of sepiolite, as observed by TPD- NH_3 analysis (Section 4.3.1.5). While n -butanol selectivity (together with BuA and higher alcohols) showed a maximum over the 4Cs/Sep@500 and 7Cs/Sep@500, acetaldehyde selectivity showed an increasing trend with increasing cesium loading.

4.3.2.3.3 Effect of the alkali-metals loading

Figure 4.91 summarizes the catalytic results obtained over the alkali-doped (Na, K, Cs) sepiolite samples prepared with different metal loading (2, 5 or 7 wt%). In particular, the trends of ethanol conversion ($X\%$) and main products selectivity ($S\%$) are depicted as a function of the nominal molar metal loading, expressed as moles of the metals (mmol) divided by the weight of the sepiolite (g), $n_{\text{METAL}}/W_{\text{SEP}}$.

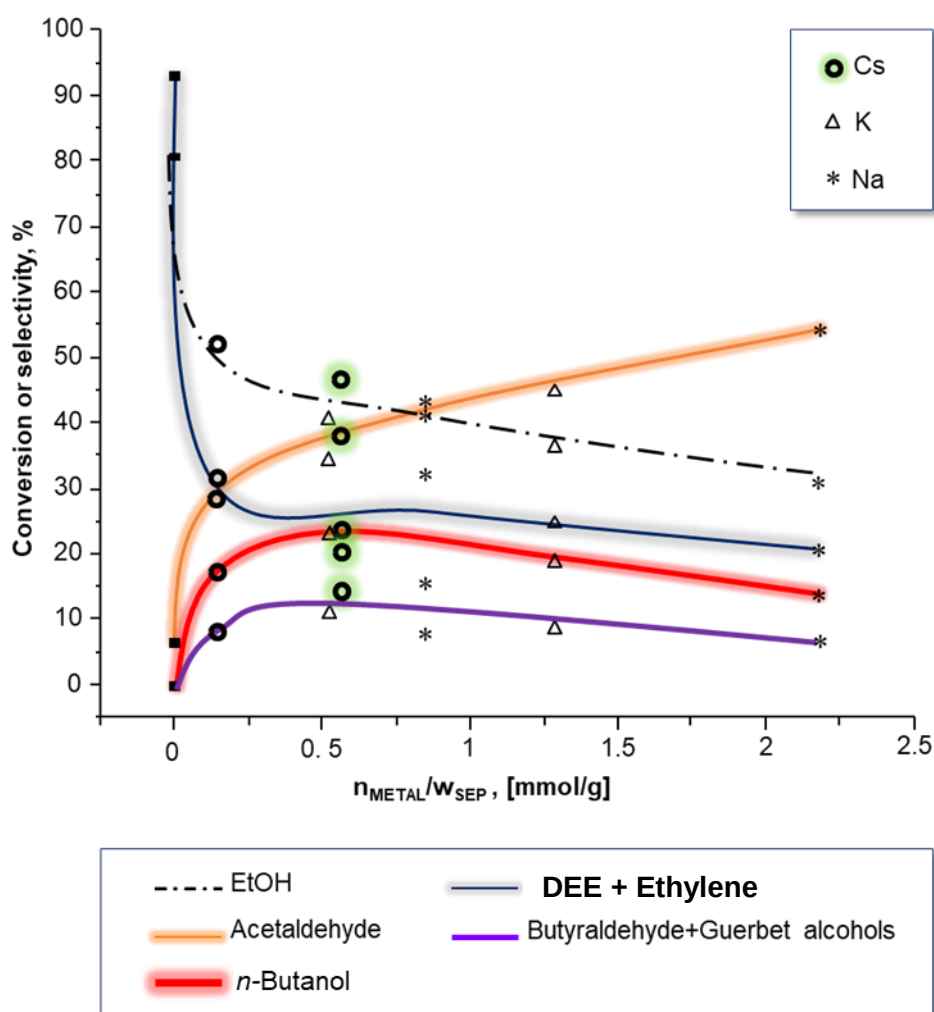


Figure 4.91 Influence of alkali metal loading ($\text{mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$) on the conversion of ethanol and the selectivity of the main reaction products. (■) Natural Sepiolite calcined at 500°C; (▲): K/Sep@500 (2 and 5 wt%; 0.51 and 1.28 $\text{mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$); (*): Na/Sep@500 (2 and 5 wt%, 0.87 and 2.17 $\text{mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$); (○): Cs/Sep@500 catalysts (2, 7 wt%, 0.15 and 0.53 $\text{mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$). Guerbet alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N_2 , Temperature= 450 °C; WHSV= 1 $\text{g}_{\text{EtOH}}/(\text{g}_{\text{CAT}} \cdot \text{h})$.

In general, it is possible to observe that with increasing metal loading, the ethanol conversion decreased. The dehydrogenation of ethanol seemed favoured by a higher alkali metal amount since acetaldehyde selectivity increased. By contrast, the selectivity of the dehydration products of ethanol, ethylene and diethyl ether, decreased with increasing metal loading, while the ones of *n*-butanol, butyraldehyde and higher alcohols showed a maximum around 0.6 $\text{mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$ and then, with a higher metal loading, decreased.

In Figure 4.92 the catalytic results obtained over the different alkali-impregnated sepiolite are shown in terms of ethanol conversion and the main products selectivity, as previously showed. Here, the catalytic results are reported in relation to the measured alkali metals amount by SEM-EDX analysis.

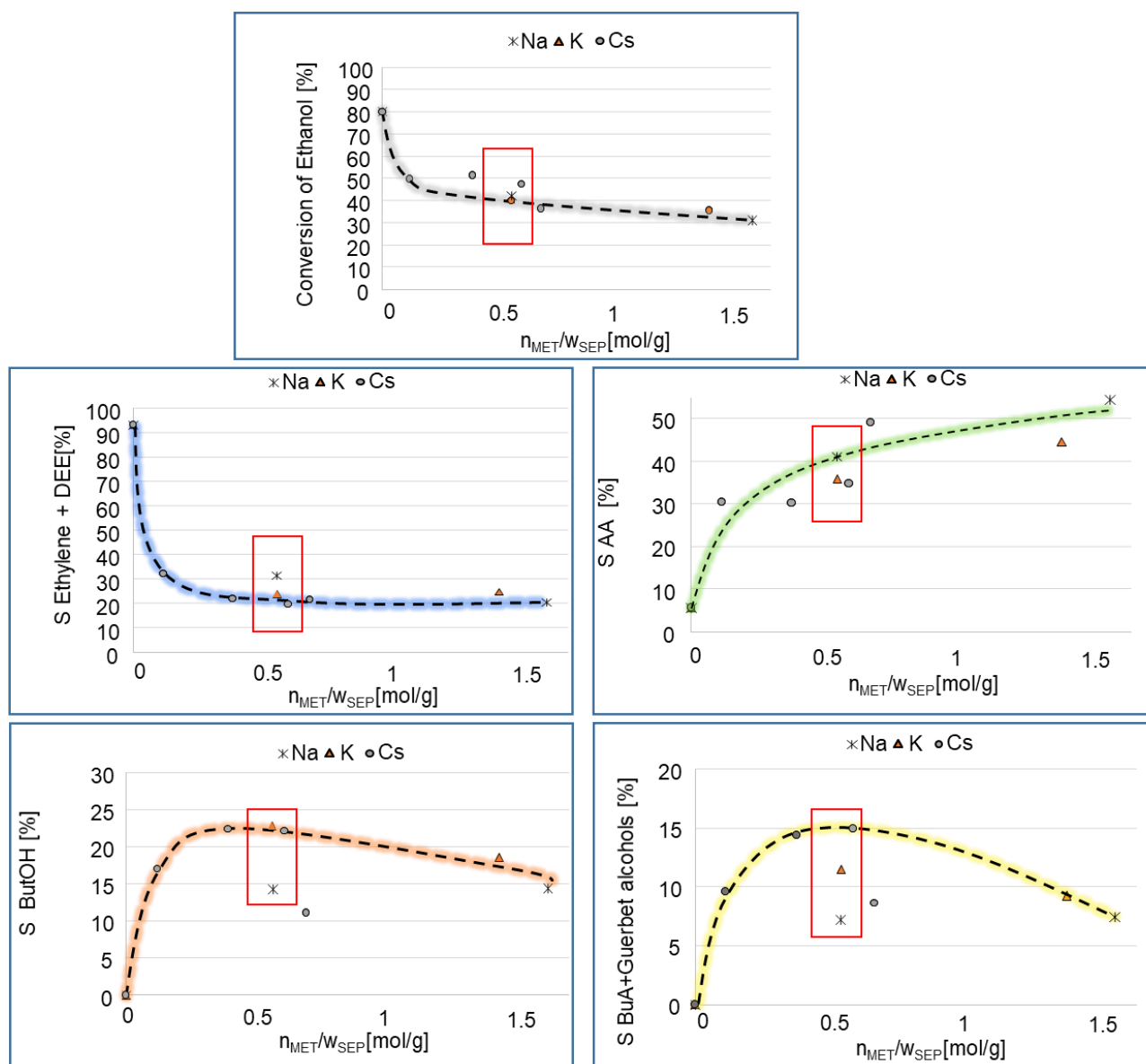


Figure 4.92 Influence of alkali metal loading ($\text{mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$) on the conversion of the ethanol and the selectivity to the main reaction products. AA: acetaldehyde; BuA: butyraldehyde; Guerbet alcohols: 2-ethylbutanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N_2 , Temperature= 450 °C; $W/F= 0.3 \text{ g}_{\text{CAT}}/(\text{mL/s})$ and $\text{WHSV}= 1 \text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$.

From results in Fig. 4.92, it is possible to observe a trend of the ethanol conversion and products distributions with the molar amount of the alkali metals over sepiolite support. Ethanol conversion and its dehydration products, ethylene and diethyl ether, decreased with increasing alkali-metal amount, showing a linear correlation between activity and acidity. On the other hand, acetaldehyde selectivity increased. The trends of *n*-butanol selectivity as well as the one of butyraldehyde and higher alcohols, is affected by, not only the nature of the metal impregnated to the support, but even its quantity. Indeed, both *n*-butanol and the consecutive Guerbet higher alcohols presented a maximum value of selectivity in relation with the alkali metal loading, namely around $\sim 0.6 \text{ mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$. The maximum value of *n*-butanol selectivity obtained was around 22% over the 2K/Sep@500 and 7Cs/Sep@500 catalysts that contained the same molar amount of alkali metal,

namely $\sim 0.6 \text{ mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$. It is worth noting that the acidity/basicity ratio (A/B ratio) measured by TPD analysis for both catalysts was quite similar, 0.64 and 0.61, respectively (see section 4.3.1.5).

Fig. 4.93 highlights the effect of the nature of the alkali metal over the EtOH conversion (X,%) and the selectivity to the main products (S%) obtained over the catalysts containing ca. $0.6 \text{ mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$ (i.e., 2Na/Sep@500, 2K/Sep@500 and 7Cs/Sep@500), that are the ones which led to achieve the highest BuOH selectivity (i.e., 22%). As far as the dehydration products formation is concerned, bigger alkali metal atom led to lower production of them in accordance with the lower acidity of the catalyst. In addition, it can be noted that cesium containing sample favoured the formation of higher alcohols and butyraldehyde. Nevertheless, the best results in terms of activity (X_{EtOH} : 47%) and *n*-butanol selectivity (S_{BuOH} : 22%), and so in terms of *n*-butanol yield, have been obtained over the 7Cs/Sep@500.

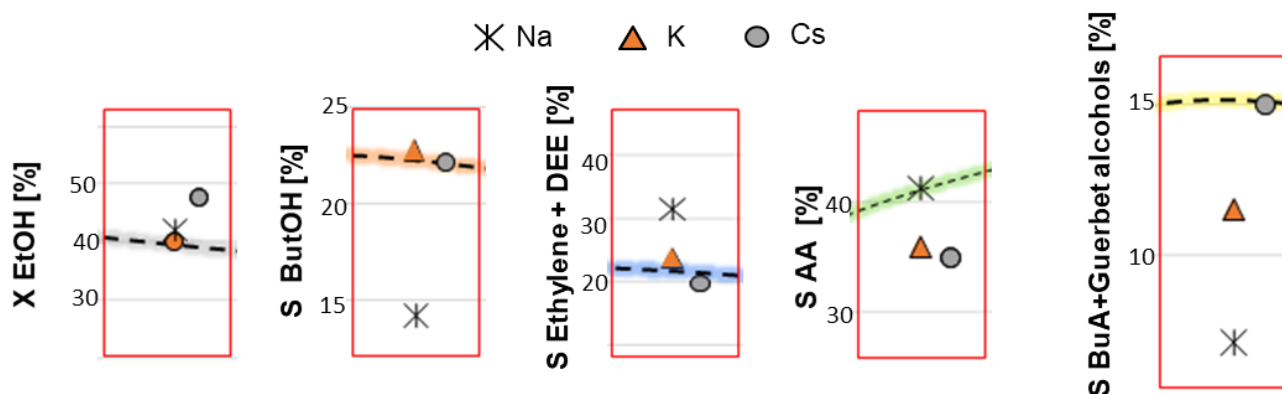


Figure 4.93 Conversion of the ethanol (X %) and the selectivity (S %) to the main reaction products over the alkali-metal doped catalyst with $\sim 0.6 \text{ mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$ of molar metal loading ($n_{\text{MET}}/W_{\text{SEP}}$). AA: acetaldehyde; BuOH: butanol; BuA: butyraldehyde; Guerbet alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Reaction conditions: EtOH 5% v/v in N_2 , Temperature= 450 °C; W/F= $0.3 \text{ g}_{\text{CAT}}/(\text{mL}\cdot\text{s})$ and WHSV= $1 \text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$.

The ethanol conversion and the selectivities to the main products for the gas-phase Guerbet reaction of ethanol over sepiolite-based catalysts calcined at 500°C (Sep@500) are summarized in Figure 4.94. For the sake of comparison, the catalytic results obtained over MgO and the sepiolite support, in the same reaction conditions, i.e. 450°C, 1 atm and WHSV= $1 \text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$, are reported as well.

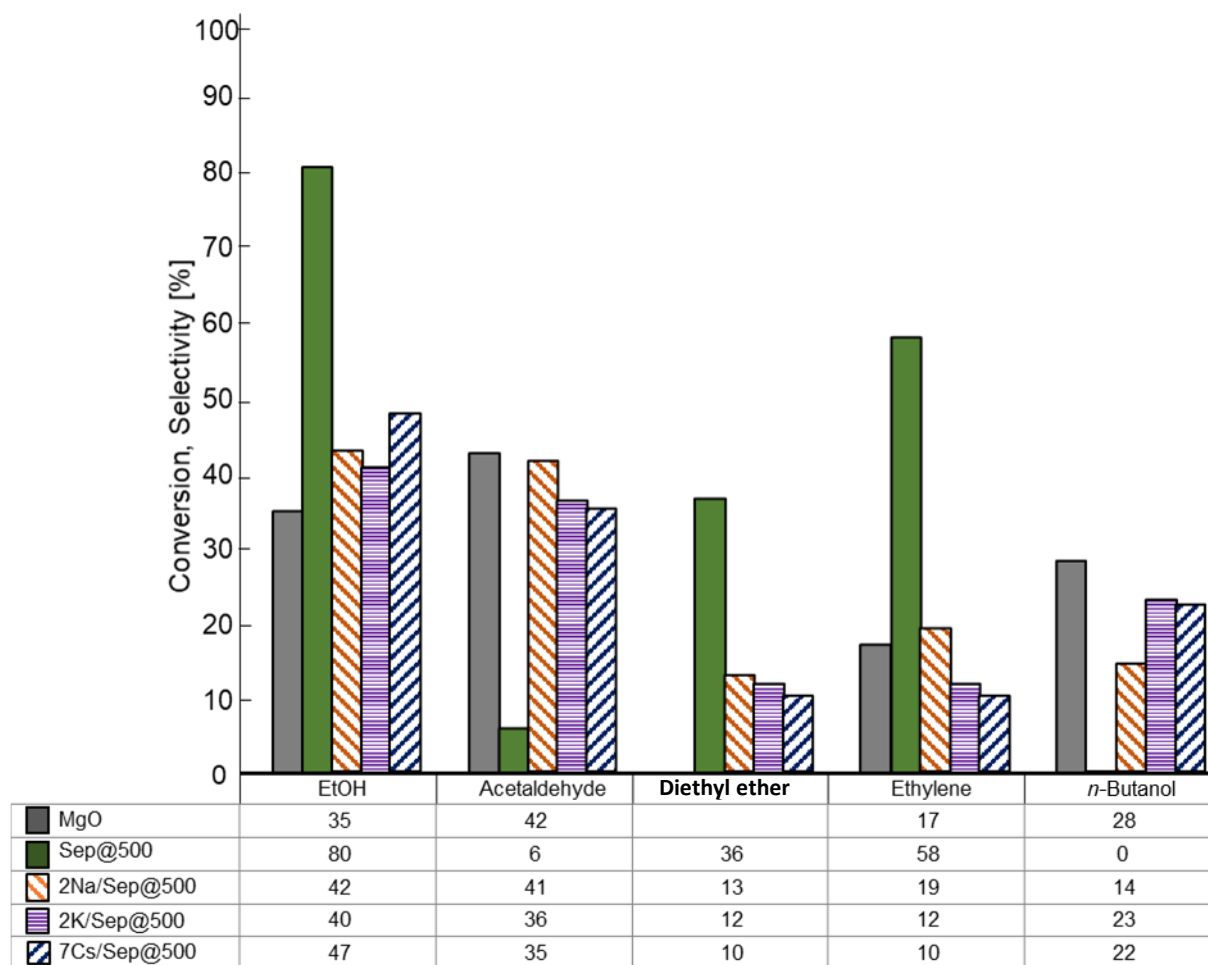


Figure 4.94 Comparison of the catalytic results, in terms of EtOH conversion and products selectivity, for the gas-phase ethanol conversion over MgO and natural sepiolite calcined at 500°C based catalysts. Reaction conditions: EtOH 5% v/v in N₂, Temperature= 450 °C; in all cases using a WHSV= 1 g_{EtOH}/(g_{CAT}·h).

4.3.2.4 7Cs/Sepiolite, optimization of experimental conditions

In order to monitor the conversions and selectivities, a typical way is to vary the reaction temperature or the contact time between the catalyst and the reagents. The main aim of the optimization study was to maximize the ethanol conversion while enhancing *n*-butanol and higher Guerbet alcohols selectivity, and thus their yields. Therefore, the ethanol gas-phase conversion was performed at different WHSVs and reaction temperatures accordingly to find the optimal conditions.

After a first catalysts screening, focusing on favouring the Guerbet reaction pathway, the best performances in terms of ethanol conversion (47%) and *n*-butanol selectivity (22%) have been obtained over the catalyst Cs/Sep@500 7 wt%. Accordingly, this catalyst has been chosen to investigate the effects of the main reaction parameters, namely the reaction temperature and the contact time on ethanol conversion and products distributions.

4.3.2.4.1 Effect of temperature and space time on ethanol gas-phase conversion

In order to study the effect of the reaction temperature for the ethanol gas-phase conversion over 7Cs/Sep@500, the temperature was varied in the range of 300–450 °C by keeping the WHSV (weight hourly space velocity) and the contact time, W/F, constant under otherwise similar conditions. On the other hand, the effect of the WHSV in the range of 1.7 to 0.11 $\text{g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$ has been investigated by keeping the other reaction parameters constant.

4.3.2.4.1.1 Temperature effect at $\text{WHSV}=1\text{ h}^{-1}$

Firstly, the effect of the reaction temperature on the ethanol conversion have been investigated at a W/F of 0.4 $\text{g}_{\text{CAT}}/\text{mL}\cdot\text{s}$ ($\text{WHSV} = 1\text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$). In particular, the reaction has been performed at 350, 400 and 450°C by keeping the other reaction parameters constant. Figure 4.95 and Table 4.31 report the results obtained in terms of ethanol conversion (X,%) and main products selectivity (S,%).

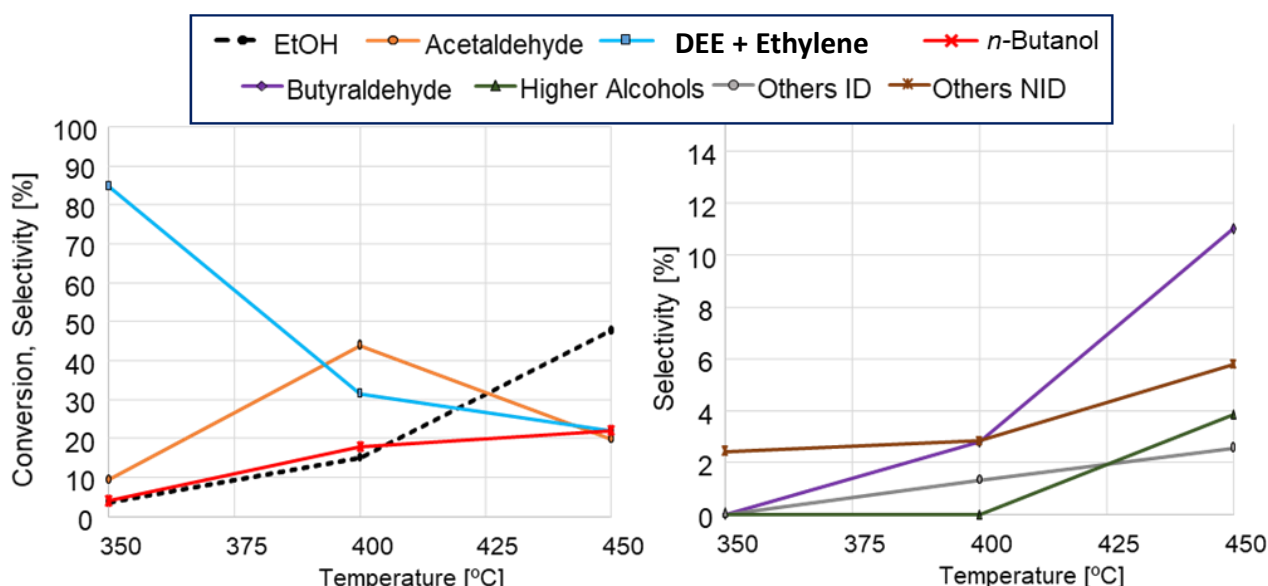


Figure 4.95 Influence of the temperature on the ethanol conversion and products selectivities over the 7Cs/Sep@500 catalyst. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Others ID: acetone, 2-pentanone, CO_2 , ethyl acetate. Reaction conditions: EtOH 5% v/v in N_2 ; $T=350, 400$ or 450°C ; $P=1\text{ atm}$, $\text{W/F}=0.4\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$; $\text{WHSV}=1\text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$.

Table 4.31 Influence of the temperature on the ethanol conversion and products selectivities over the 7Cs/Sep@500 catalyst. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Others ID: acetone, 2-pentanone, CO₂, ethyl acetate. Reaction conditions: EtOH 5% v/v in N₂, T=350, 400, 450°C, P= 1 atm, W/F= 0.4 g_{CAT}/mL·s; WHSV= 1 g_{EtOH}/(g_{CAT}·h).

Selectivity [%]									
<i>T</i> [°C]	<i>X</i> EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
350	4	9	10	75	4	0	0	2	0
400	15	44	13	18	18	3	1	3	0
450	47	20	10	10	22	11	3	6	4
Yield [%]									
<i>T</i> [°C]	<i>X</i> EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
350	4	0.3	0.4	2.7	0.1	0.0	0.0	0.1	0.0
400	15	6.5	1.9	2.7	2.7	0.4	0.2	0.4	0.0
450	47	9.4	4.6	4.8	10.5	5.2	1.2	2.7	1.8

As expected, ethanol conversion increased with increasing temperature. While working at 350°C, with an ethanol conversion of 4% a high, diethyl ether was the main product, with a selectivity of 75%. Diethyl ether formation, being exothermic, was favoured at lower temperature.¹³⁸ Interestingly, at higher temperature, acetaldehyde selectivity decreased from 44% at 400°C to 20 % at 450°C. Concomitantly, *n*-butanol selectivity increased a bit from 18 to 22% as well as butyraldehyde selectivity from 3 to 11% and higher alcohols (4%). Even the selectivity of the other products, Other ID and Other NID increased with increasing temperature. The nature of the reaction products gathered in the group named “Others NID” products should be of heavier products forming by consecutive reactions, being related to peaks obtained into the GC-online chromatogram a high retention times. Nevertheless, the decrease of acetaldehyde selectivity with reaction temperature and concomitant increase of *n*-butanol selectivity as well as the one of the other products suggested that the acetaldehyde acted as intermediate product converting in consecutive products, e.g. *n*-butanol, acetone, 2-pentanone (grouped in “Other ID”).

4.3.2.4.1.2 WHSVs effect at 450°C

At the highest temperature used in the previous trials (450°C) it was studied the effect of increasing contact time W/F or decreasing WHSV. In particular, the reactions have been performed with W/F: 0.4, 1 and 3 g_{CAT}/mL·s or WHSV= 0.9, 0.3, 0.11 g_{EtOH}/(g_{CAT}·h); the results are reported in Figure 4.96 and Table 4.32.

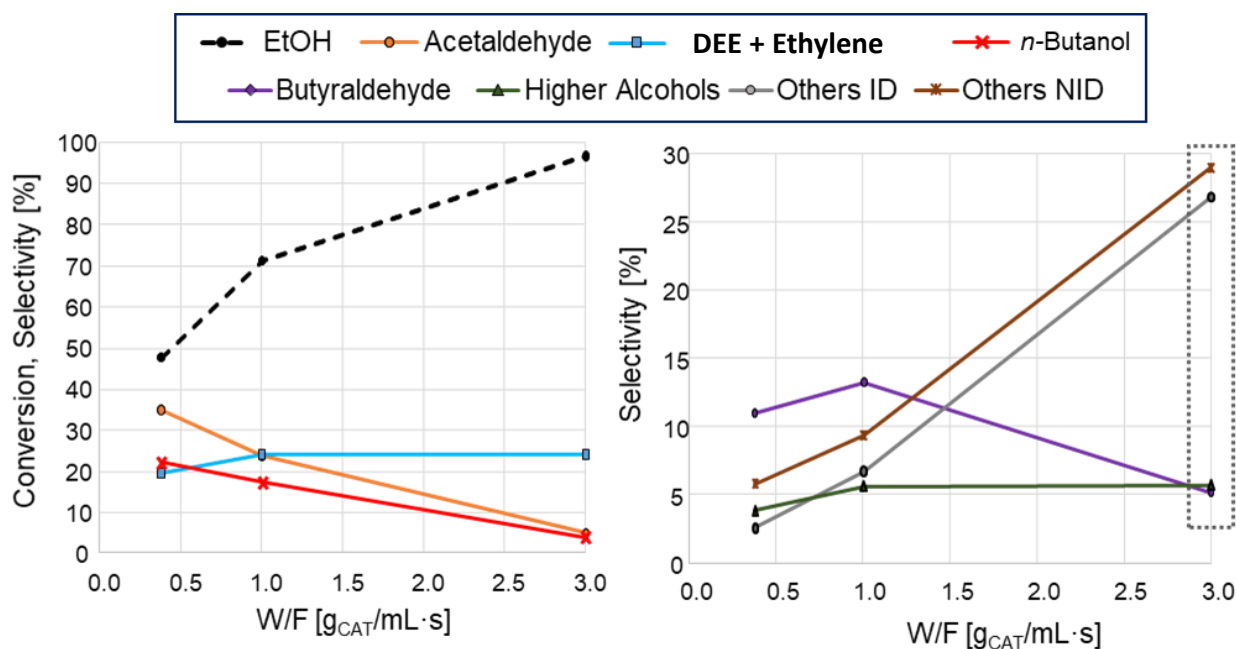


Figure 4.96 Influence of the contact time (W/F , $g_{CAT}/mL \cdot s$) on the ethanol conversion and products selectivities over the 7Cs/Sep@500 catalyst. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Others ID: acetone, 2-pentanone, CO_2 , 1,3-butadiene, ethane. Reaction conditions: EtOH 5% v/v in N_2 , $T=450^\circ C$, $P=1$ atm, W/F : 0.4, 1, 3 $g_{CAT}/mL \cdot s$; $WHSV=0.9, 0.3, 0.11$ $g_{EtOH}/(g_{CAT} \cdot h)$.

Table 4.32 Influence of the contact time (W/F , $g_{CAT}/mL \cdot s$) on the ethanol conversion and products selectivities over the 7Cs/Sep@500 catalyst. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Others ID: acetone, 2-pentanone, CO_2 , 1,3-butadiene, ethane. Reaction conditions: EtOH 5% v/v in N_2 , $T=450^\circ C$, $P=1$ atm, W/F : 0.4, 1, 3 $g_{CAT}/mL \cdot s$; $WHSV=0.9, 0.3, 0.11$ $g_{EtOH}/(g_{CAT} \cdot h)$.

Selectivity [%]									
W/F [$g_{CAT}/mL \cdot s$]	X_{EtOH} [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
0.4	47.5	34.9	9.7	10.1	22.1	11.0	2.6	5.8	3.8
1.0	71.3	23.6	16.0	8.2	17.2	13.3	6.7	9.4	5.6
3.0	96.7	5.1	14.2	9.8	4.1	5.2	26.8	29.0	5.7
Yield [%]									
W/F [$g_{CAT}/mL \cdot s$]	X_{EtOH} [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
0.4	47.5	17	5	5	10	5	1	3	2
1.0	71.3	17	11	6	12	9	5	7	4
3.0	96.7	5	14	9	4	5	26	28	6

With increasing contact time, ethanol conversion increased as expected, from 47.5 to 96.7%. On the other hand, it is possible to notice a decreasing trend for the selectivity of acetaldehyde, n -butanol and butyraldehyde, from 34.9% to 5.1%, 22.1 to 4.1 and 11 to 5.2% respectively, with increasing contact time from 0.4 to 3 $g_{CAT}/mL \cdot s$. At the same time, while the selectivity of higher alcohols remained constant with increasing contact time, by contrast, an abrupt increase of selectivity of both ID (i.e., acetone, 2-pentanone, CO_2 , butadiene and ethane) and NID others products can be observed, from 2.6 to 26.8% and from 5.8 to 29%, confirming their nature as consecutive products

that could come from the conversion of acetaldehyde or *n*-butanol. Figure 4.97 depicts the trends of the just mentioned products selectivity with increasing contact time. The values of the selectivity obtained at the highest value of W/F examined, 3 g_{CAT}/mL·s, have been framed. Interestingly, the selectivity of 1-3-butadiene obtained at the highest contact time was as high as 14.6%. In addition, even ketones selectivity increased with increasing contact time. The formation of both side-products involves acetaldehyde as intermediate product (see Scheme 1 and Scheme 2).

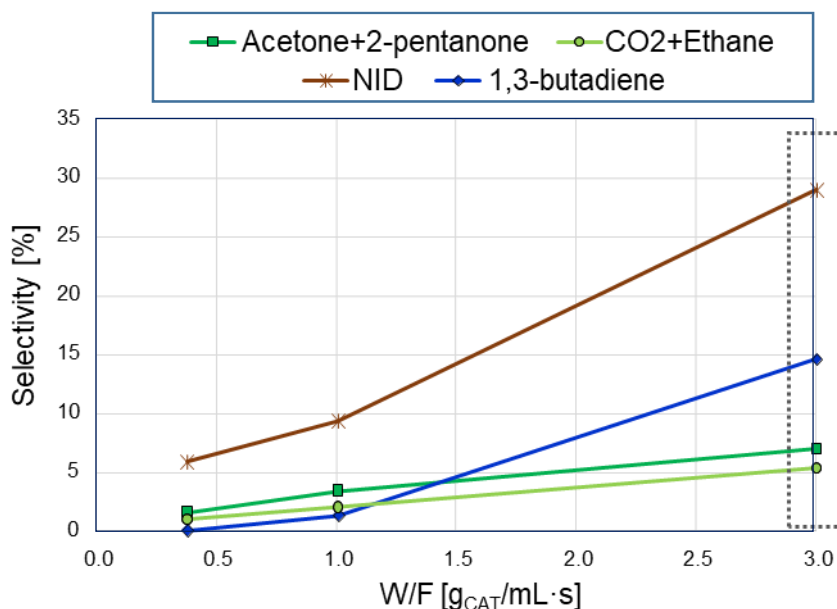


Figure 4.97 Influence of the contact time (W/F, g_{CAT}/mL·s) on side products selectivities over the 7Cs/Sep@500 catalyst. Reaction conditions: EtOH 5% v/v in N₂, T=450°C, P= 1 atm, W/F: 0.4, 1, 3 g_{CAT}/mL·s; WHSV= 0.9, 0.3, 0.11 g_{EtOH}/(g_{cat}·h).

Table 4.33 Influence of the contact time (W/F, g_{CAT}/mL·s) on side products selectivities over the 7Cs/Sep@500 catalyst. Reaction conditions: EtOH 5% v/v in N₂, T=450°C, P= 1 atm, W/F: 0.4, 1, 3 g_{CAT}/mL·s; WHSV= 0.9, 0.3, 0.11 g_{EtOH}/(g_{cat}·h).

W/F [g _{CAT} /mL·s]	Selectivity [%]					
	Others NID	Acetone	2-Pentanone	BD	CO ₂	Ethane
0.4	5.8	0.7	0.9	0.0	0.3	0.7
1.0	9.4	1.5	1.8	1.4	0.8	1.2
3.0	29.0	2.9	4.1	14.6	2.6	2.7

W/F [g _{CAT} /mL·s]	Yield [%]					
	Others NID	Acetone	2-Pentanone	BD	CO ₂	Ethane
0.4	2.7	0.3	0.4	0.0	0.1	0.3
1.0	6.7	1.1	1.3	1.0	0.5	0.9
3.0	28.1	2.8	3.9	14.1	2.5	2.6

Since with the highest contact time, 3 g_{CAT}/mL·s, ethanol conversion was almost completed (97%) and the unknown products (Others NID) were produced in high quantity (with an overall selectivity of 29%), an attempt to better identify the nature of those products was performed by collecting them by condensation and then injecting a sample into the GC-MS system. In detail, the out-flowing line of the reaction system has been connected to a trap kept at 0 °C. In this way, the heaviest products have been accumulated by condensation. The collected liquid mixture so obtained was diluted with

acetonitrile and then injected into a GC-MS system. The qualitative analysis led to notice the nature of some of the NID, i.e. a mixture of aromatics and ketones organic compounds. Interestingly, between the major compounds detected (in relation of the peaks areas obtained), higher ketones have been detected (i.e., 4-nonanone and 4-undecanone). Those results suggest that in such harsh condition with high temperature (450°C) and contact time ($W/F=3 \text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$), the ethanol conversion over the catalyst 7Cs/Sep@500 led to the formation of heavier products following mainly two reaction paths: the ketonization and aromatization. The latter could come from: i) ethylene aromatization, ii) radical or Diels-Alder type reactions between conjugated dienes compounds (such as butadiene) and a dienophile (such as ethylene) and subsequent dehydrogenation of the cyclic compounds.

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In accordance with the literature, at high ethanol conversion it is difficult to control the Guerbet products selectivity. Indeed, the produced primary alcohols undergoes further condensation to produce heavier alcohols and other heavier byproducts.³¹⁵ Nevertheless, these heavier products/alcohols mixtures can be used as fuel additives, solvents or plasticizers, after some separation steps, if needed.⁶¹

4.3.2.4.1.3 Temperature effect at $WHSV=0.3 \text{ h}^{-1}$

The effect of the temperature reaction in the range 300-450°C has been studied by keeping the contact time constant at $1 \text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$ ($WHSV=0.3 \text{ h}^{-1}$), that is the one which led to the formation of the highest yield of *n*-butanol (12%, at 450°C). The results, in terms of ethanol conversion and product selectivity are depicted in Figure 4.98 and Table 4.34.

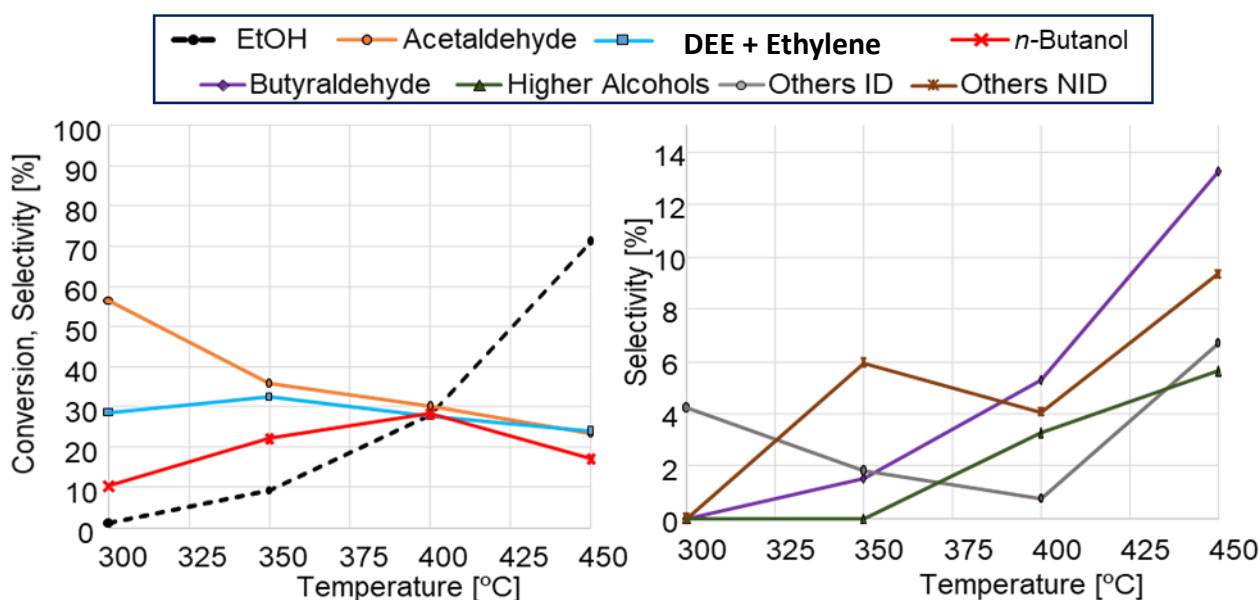


Figure 4.98 Influence of the temperature on the ethanol conversion and products selectivities over the 7Cs/Sep@500 catalyst. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Others ID: acetone, 2-pentanone, CO_2 , ethyl acetate. Reaction conditions: EtOH 5% v/v in N_2 , $T=300, 350, 400, 450^\circ\text{C}$, $P=1 \text{ atm}$, $W/F=1 \text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$; $WHSV=0.3 \text{ g}_{\text{EtOH}}/(\text{gcat}\cdot\text{h})$.

Table 4.34 Influence of the temperature on the ethanol conversion and products selectivities over the 7Cs/Sep@500 catalyst. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Others ID: acetone, 2-pentanone, CO₂, ethyl acetate. Reaction conditions: EtOH 5% v/v in N₂, T=300, 350, 400, 450°C, P= 1 atm, W/F= 1 g_{CAT}/mL·s; WHSV= 0.3 g_{EtOH}/(gcat·h).

Selectivity [%]									
$T\ [^{\circ}\text{C}]$	$X\ \text{EtOH}\ [\%]$	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
300	1	57	7	22	10	0	4	0	0
350	9	36	11	22	22	2	2	6	0
400	28	30	12	16	28	5	1	4	3
450	71	24	16	8	17	13	7	9	6
Yield [%]									
$T\ [^{\circ}\text{C}]$	$X\ \text{EtOH}\ [\%]$	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols
300	1	1	0	0	0	0	0	0	0
350	9	3	1	2	2	0	0	1	0
400	28	9	3	4	8	1	0	1	1
450	71	17	11	6	12	9	5	7	4

By studying the reaction temperature effect at a higher value of contact time than the previous conditions (Figure 4.95, Table 4.31), namely 1 g_{CAT}/mL·s instead of 0.4 g_{CAT}/mL·s, the trends observed of the reaction results changed. Ethanol conversion increased with increasing temperature as expected, while both acetaldehyde and dehydration products of ethanol selectivity decreased with increasing temperature. At the lowest temperature studied (i.e., 300°C), with an ethanol conversion of 1%, *n*-butanol was already detected with a selectivity value of 10%. Then, *n*-butanol selectivity presented a maximum at 400°C reaching 28%, which decreased to 17% at 450°C. This suggests that at higher temperature *n*-butanol is converted to other products. Indeed, at higher temperature the butyraldehyde (the dehydrogenation reaction product of *n*-butanol) and higher alcohols (Guerbet reaction products) selectivity increased, reaching 13% and 6%, respectively. Accordingly, the effect of the contact time at 400°C has been investigated, the results are presented in the next section.

4.3.2.4.1.4 WHSVs effect at 400°C

The influence of the contact time on the products distribution has been evaluated at 400°C. The amount of catalyst in the system was adjusted in order to reach a contact time of 0.2, 0.35, 1.0, 2.0 or 3.0 g_{CAT}/mL·s (WHSV= 1.7, 1.0, 0.3, 0.17 or 0.11 g_{EtOH}/(gcat·h)); the results are depicted in Figure 4.99 and Table 4.35.

Figure 4.100 reports the catalytic results by means of the dependence of the products selectivity on the ethanol conversion.

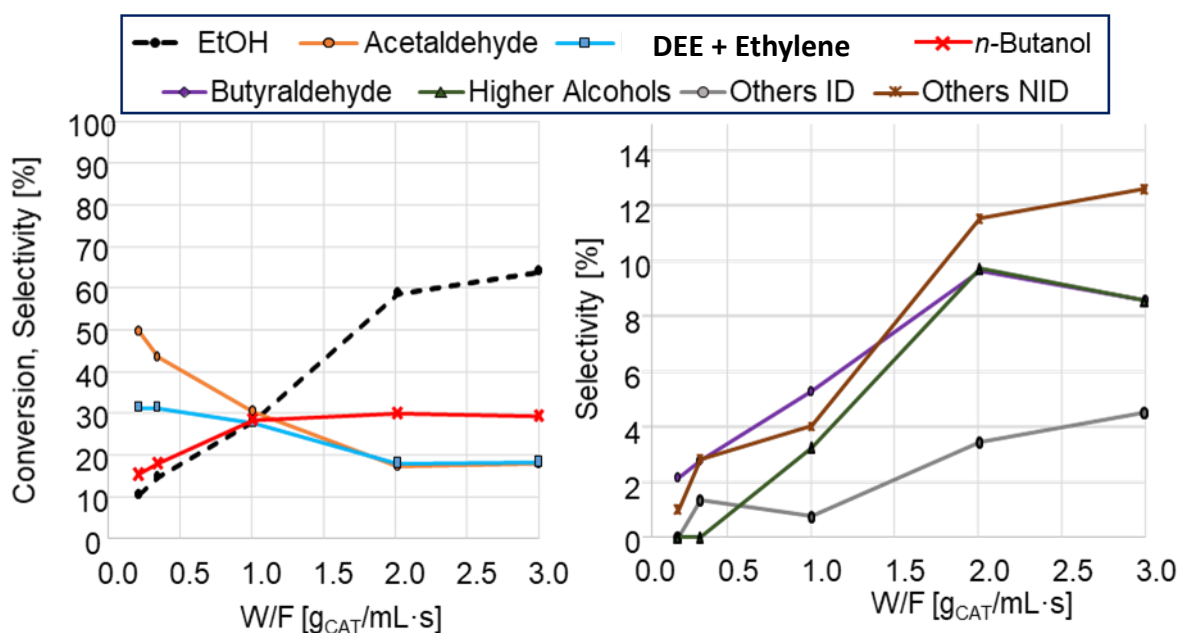


Figure 4.99 Ethanol conversion and products selectivities as a function of the contact time (W/F , g_{CAT}/mL·s) for the reaction performed over the 7Cs/Sep@500 catalyst. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Others ID: acetone, 2-pentanone, CO₂, ethyl acetate. Reaction conditions: EtOH 5% v/v in N₂, $T=400^{\circ}\text{C}$, $P=1\text{ atm}$, $W/F=0.2, 0.35, 1.0, 2.0, 3.0\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$; $\text{WHSV}=1.7, 1, 0.3, 0.17, 0.11\text{ g}_{\text{EtOH}}/(\text{g}_{\text{cat}}\cdot\text{h})$.

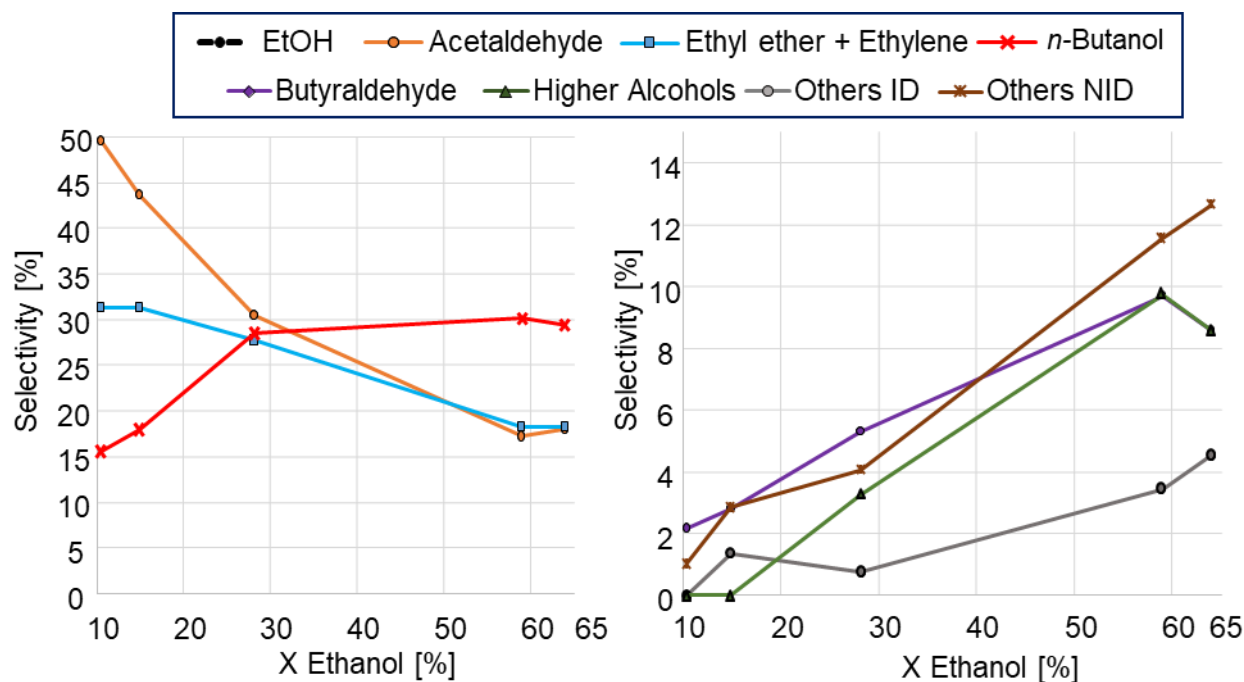


Figure 4.100 Products selectivity as a function of ethanol conversion over the 7Cs/Sep@500 catalyst. Higher alcohols: 2-ethyl-butanol, 1-hexanol, 2-ethyl-hexanol, 1-octanol. Others ID: acetone, 2-pentanone, CO₂, ethyl acetate, ethane. Reaction conditions: EtOH 5% v/v in N₂, $T=400^{\circ}\text{C}$, $P=1\text{ atm}$; $W/F=0.2, 0.3, 1.0, 2.0, 3.0\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$.

By increasing the contact time, ethanol conversion increased, reaching the value of 65% at $W/F\ 3.0\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$. The selectivity to *n*-Butanol reached a maximum value of 30% while working at $W/F\ 2.0\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$ then dropped slightly to 29% at $W/F=3.0\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$. Selectivity of both higher alcohols and BuA followed the same trend. By increasing the contact time, the selectivity of both the dehydration

products of ethanol and acetaldehyde decreased, and concomitantly, the ones of the other products increased. Accordingly, the formation of Others NID products was favoured at higher contact time suggesting that their formation could come from consecutive side reactions. As stated before (Section 4.3.2.4.1.2), thanks to GC-MS analysis, their nature could be mainly aromatics and longer chains ketones. The quite specular trend of acetaldehyde and *n*-butanol selectivity with increasing ethanol conversion could suggest the nature of acetaldehyde as intermediate product for *n*-butanol formation.

Table 4.35 Variation of products selectivities with contact time W/F [$g_{CAT}/mL \cdot s$] and the ethanol conversion over the 7Cs/Sep@500 catalyst. Guerbet alcohols = *n*-butanol, higher alcohols (*n*-hexanol, 2-ethyl butanol, *n*-octanol, 2-ethyl hexanol); Others= others NID and ID (acetone, 2-pentanone, CO_2 , ethyl acetate, ethane). Reaction conditions: EtOH 5% v/v in N_2 , $T=400^\circ C$, $P=1$ atm, $W/F=0.2, 0.3, 1.0, 2.0$ or 3.0 $g_{CAT}/mL \cdot s$.

Selectivity [%]											
W/F [$g_{CAT}/mL \cdot s$]	X_{EtOH} [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols	Guerbet Alcohols	Dehydration products
0.2	10	50	14	18	16	2	0	1	0	16	31
0.3	15	44	13	18	18	3	1	3	0	18	31
1.0	28	30	12	16	28	5	1	4	3	32	28
2.0	59	17	6	12	30	10	3	12	10	40	18
3.0	64	18	7	12	29	9	5	13	9	38	18
Yield [%]											
W/F [$g_{CAT}/mL \cdot s$]	X_{EtOH} [%]	AA	Ethylene	DEE	BuOH	BuA	Others ID	Others NID	Higher Alcohols	Guerbet Alcohols	Dehydration products
0.2	10	5	1	2	2	0	0	0	0	2	3
0.3	15	6	2	3	3	0	0	0	0	3	5
1.0	28	9	3	4	8	1	0	1	1	9	8
2.0	59	10	3	7	18	6	2	7	6	23	11
3.0	64	12	4	7	19	5	3	8	5	25	12

Regardless, a relative high value of *n*-butanol selectivity has been obtained. From the point of view of the overall Guerbet alcohols production, the total alcohols selectivity followed the same trends manifested by *n*-butanol: the maximum value was reached at $W/F=2$ $g_{CAT}/mL \cdot s$ with a cumulative selectivity of 40% (Figure 4.101). At that value of contact time, the Guerbet reactions seemed faster than the dehydration of ethanol.

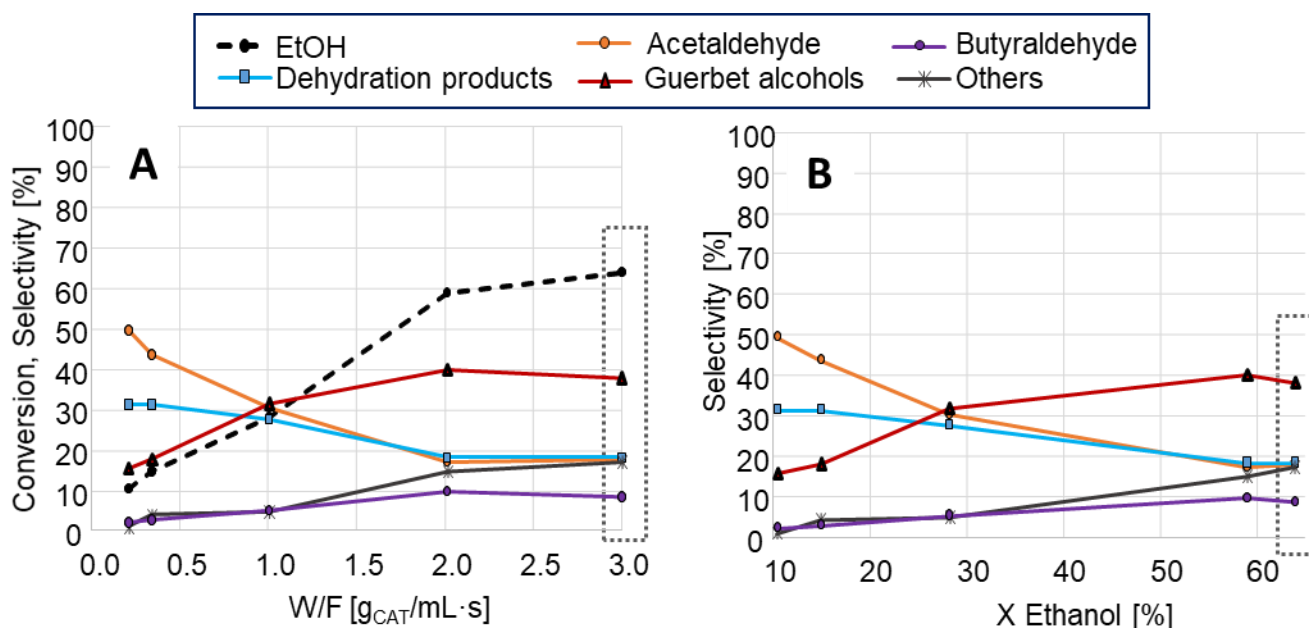


Figure 4.101 Variation of products selectivities with contact time W/F [$\text{g}_{\text{CAT}}/\text{mL}\cdot\text{s}$] (A) and the ethanol conversion (B) over the 7Cs/Sep@500 catalyst. Guerbet alcohols = *n*-butanol, higher alcohols (*n*-hexanol, 2-ethyl butanol, *n*-octanol, 2-ethyl hexanol); Others= others NID and ID (acetone, 2-pentanone, CO_2 , ethyl acetate, ethane). Reaction conditions: EtOH 5% v/v in N_2 , $T=400^\circ\text{C}$, $P=1\text{ atm}$, $W/F=0.2, 0.3, 1, 2, 3\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$.

4.3.2.4.1.5 Stability Test

Finally, in order to evaluate the catalyst stability and deactivation, a 7.5 h test was carried out at 400°C and $3.0\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$, the same reaction conditions with the highest contact time used in the previous tests (framed in Figure 4.101). To do so, the reaction has been performed by keeping the reaction parameters constant over a time on stream of 7.5 hours, the results are depicted in Figure 4.102.

The stability has been reached after 0.5 h of time on stream (TOS), with an ethanol conversion of around 60%, it can be noticed a slight decrease of conversion after 7.5 h to 55%. The trend can be related to partial deactivation of the catalyst due to coke formation. While the overall Guerbet products selectivity has not changed, a simultaneous slight decrease of other products (e.g., others NID and ID, acetone, 2-pentanone, CO_2 , ethyl acetate, ethane) selectivity can be observed, suggesting that their production is related to reaction paths other than the Guerbet route.

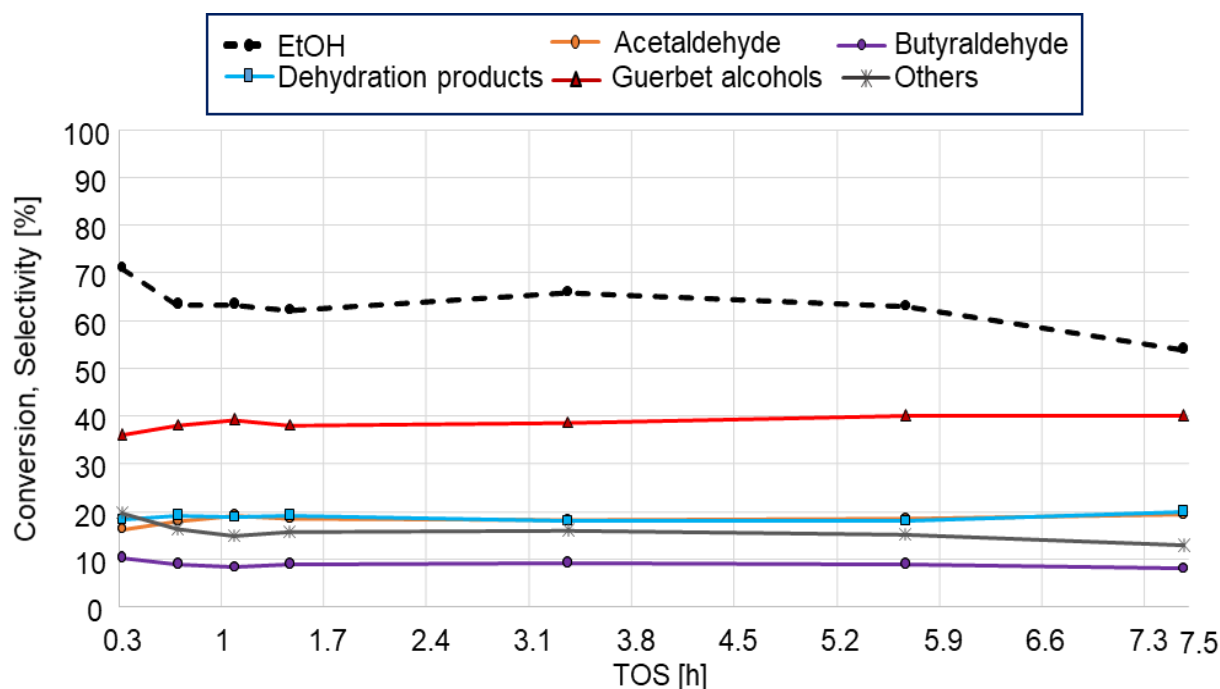


Figure 4.102 Catalytic results obtained in the Ethanol gas-phase conversion over the 7Cs/Sep@500 in terms of conversion of ethanol and main products selectivity as a function of the time on stream, TOS (h). Guerbet products= *n*-butanol, butyraldehyde, higher alcohols (*n*-hexanol, 2-ethyl butanol, *n*-octanol, 2-ethyl hexanol); Others= others NID and ID (acetone, 2-pentanone, CO₂, ethyl acetate, ethane). Reaction conditions: EtOH 5% v/v in N₂; T=400°C; P= 1 atm; W/F =3 g_{CAT}/mL·s; WHSV= 0.11 g_{EtOH}/(g_{CAT}·h).

4.3.2.4.1.6 Effect of reaction temperature and W/F, overview.

Figure 4.103 summarizes the results obtained while studying the effect of the reaction temperature and contact time on the catalyst activity and the product distribution. In particular, the effect of the contact time studied (i.e., 0.2, 0.35, 1.0, 2.0, 3.0 g_{CAT}/mL·s), at 400 and 450°C, on the ethanol conversion and the selectivity to main reaction products, is depicted. It can be noticed a different behaviour of the product distribution with increasing contact time according to the reaction temperature employed. In particular, higher temperature (i.e., 450°C) seemed to favour *n*-butanol conversion to consecutive reactions while rising the contact time employed, indeed its selectivity decreased with increasing contact time.

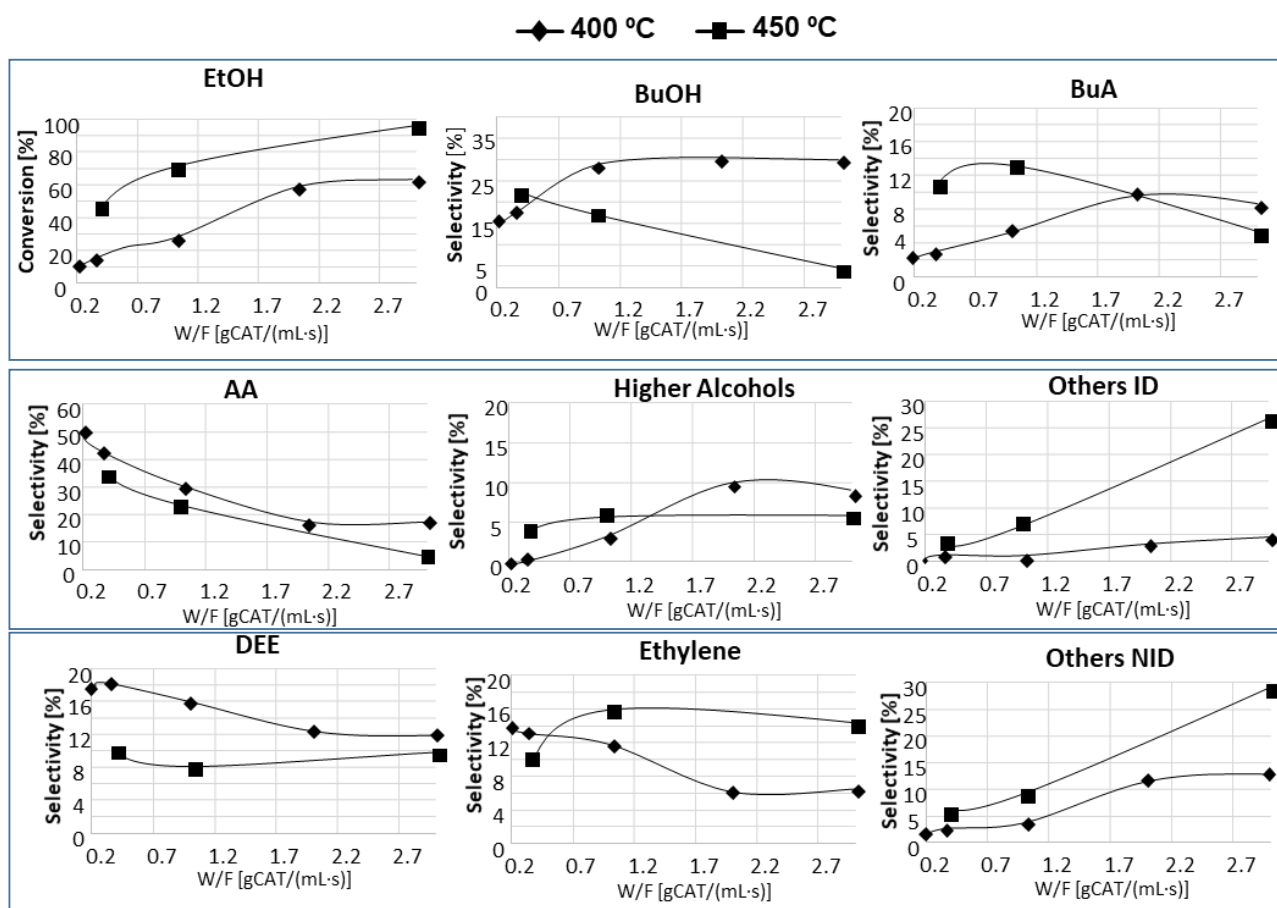


Figure 4.103 Conversion and selectivity of the main products as a function of the contact time W/F . (Others NID= other products unidentified; Others ID (acetone, 2-pentanone, CO_2 , ethyl acetate, ethane). Reaction conditions: EtOH 5% v/v in N_2 ; $T=400^\circ\text{C}$; 450°C ; $P=1\text{ atm}$; $W/F=0.2, 0.35, 1.0, 2.0, 3.0\text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$.

The selectivity of the other unknown products (Other NID) is not completely trustworthy since they have been quantified through an artificial response factor (see Section 3.2.3.1) that could overestimate or underestimate some products, according to their nature and number of carbon atoms.

Regardless, since the selectivity to *n*-butanol calculated at short contact time seemed to be higher than zero, it is reasonable to claim that this compound is a kinetic primary product. Thus, the reaction mechanism of its formation could not follow the one based on aldol condensation. The reaction mechanism that could take place over the alkali doped sepiolite will be discussed in the final section (Section 4.3.3).

4.3.2.5 Catalytic double bed

For the production of *n*-butanol from ethanol, two main reaction mechanism has been proposed. The main accepted one relies on aldol condensation, with acetaldehyde as key intermediate, while the second one involves the direct condensation of two molecules of ethanol.^{46,65,284,291,302} To gain more insight into the reaction pathway, a reaction over the most performing catalyst (7Cs/Sep@500) has been carried out by feeding a mixture of ethanol and acetaldehyde. Since acetaldehyde is difficult to

handle at room temperature due to its low boiling point (20.2°C), another strategy has been adopted, i.e. it has been produced in-situ. Therefore, aiming to study the effect of the presence of acetaldehyde in the feeding mixture, a reaction has been performed by using two catalysts, shaping a catalytic “double bed”. The first catalyst used was the CuO/2Na/Sep@500 10 wt%, since by using it at 450°C and 0.24 s of contact time, the ethanol conversion and acetaldehyde selectivity obtained where both 51% (see section 4.3.2.2.1.3). In this way, a gaseous solution containing 2.5 v/v of ethanol and 1.25 v/v of acetaldehyde (EtOH:AA 2:1) was fed through the second catalyst, namely 7Cs/Sep@500. The reaction has been performed at 450°C and with 1 g_{EtOH}/(g_{CAT}·h) as WHSV for each catalyst. The results obtained in terms of ethanol conversion and products yields are reported in Figures 4.104 and 4.105, as well as in Table 4.36.

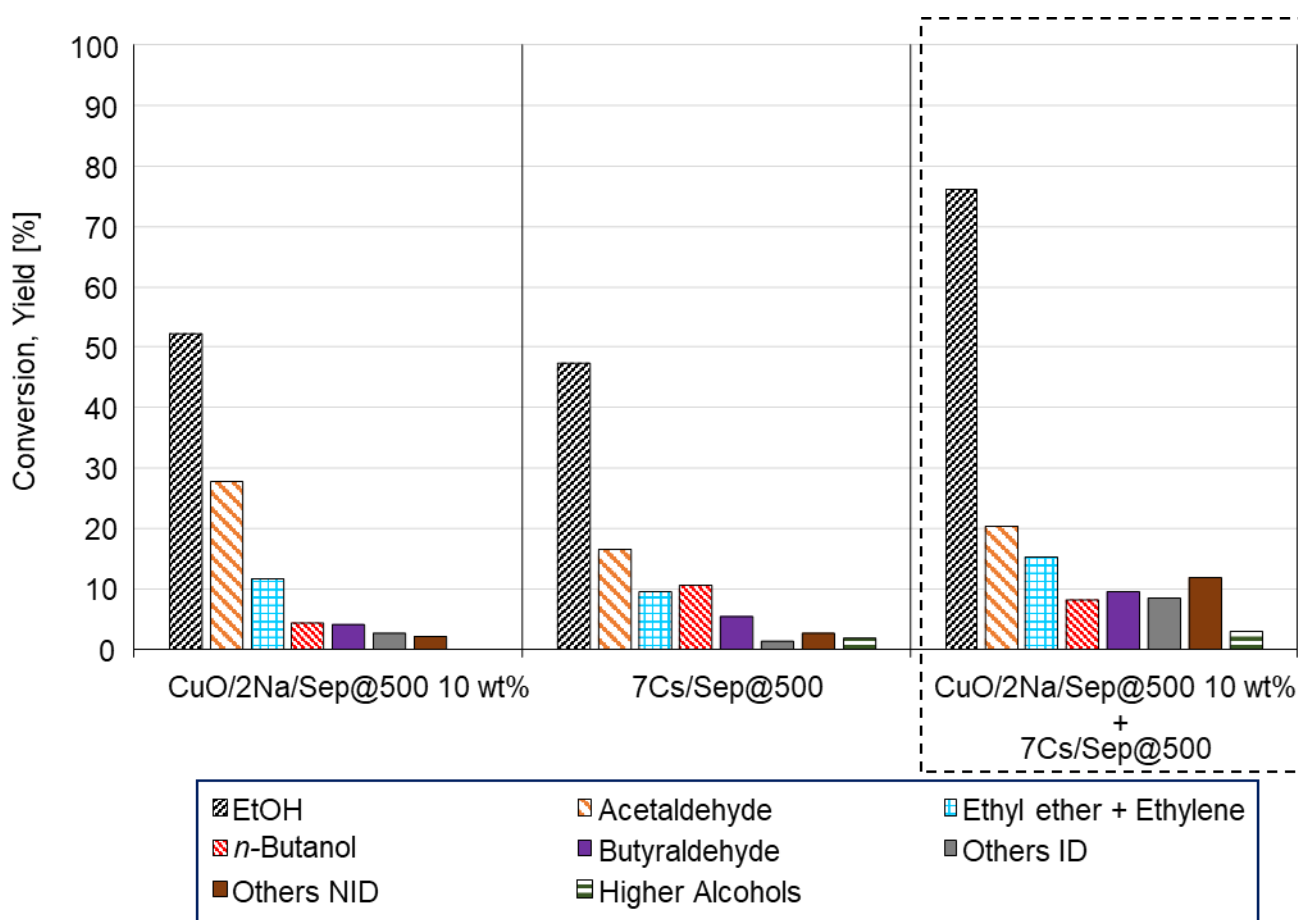


Figure 4.104 Products yield and ethanol conversion obtained for the ethanol gas-phase conversion over CuO/2Na/Sep@500 10 wt%, 7Cs/Sep@500 and the dual bed catalysts. Higher alcohols: *n*-hexanol, 2-ethyl butanol, *n*-octanol, 2-ethyl hexanol; Others ID: acetone, 2-pentanone, CO₂, 1,3-butadiene, ethane. Others NID: other products unidentified. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV₁= 1 g_{EtOH}/(g_{CAT}·h), WHSV₂= 1 g_{EtOH}/(g_{CAT}·h).

Table 4.36 Catalytic results obtained in the Ethanol gas-phase conversion over CuO/2Na/Sep@500 10 wt%, 7Cs/Sep@500 and the dual bed catalysts. Higher alcohols: *n*-hexanol, 2-ethyl butanol, *n*-octanol, 2-ethyl hexanol; Others ID: acetone, 2-pentanone, CO₂, 1,3-butadiene (BD), ethane. Others NID: other products unidentified. Reaction conditions: EtOH 5% v/v in N₂, T= 450°C, P= 1 atm, WHSV₁= 1 g_{EtOH}/(g_{CAT}·h), WHSV₂= 1 g_{EtOH}/(g_{CAT}·h).

Catalyst	Yield[%]							
	X EtOH [%]	AA	Ethylene	DEE	BuOH	BuA	Others NID	Higher Alcohols
CuO/2Na/Sep@500 10 wt%	52	28	4	7	4	4	2	0
7Cs/Sep@500	47	17	5	5	10	5	3	2
CuO/2Na/Sep@500 10 wt% + 7Cs/Sep@500	76	20	5	10	8	10	12	3

Catalyst	X EtOH [%]	Others ID					Total Others ID
		Acetone	2-Pentanone	BD	CO ₂	Etane	
CuO/2Na/Sep@500 10 wt%	52	0.5	0.2	1.3	0.1	0.4	3
7Cs/Sep@500	47	0.3	0.4	0.0	0.1	0.3	1
CuO/2Na/Sep@500 10 wt% + 7Cs/Sep@500	76	1.5	2.0	3.4	0.6	0.9	8

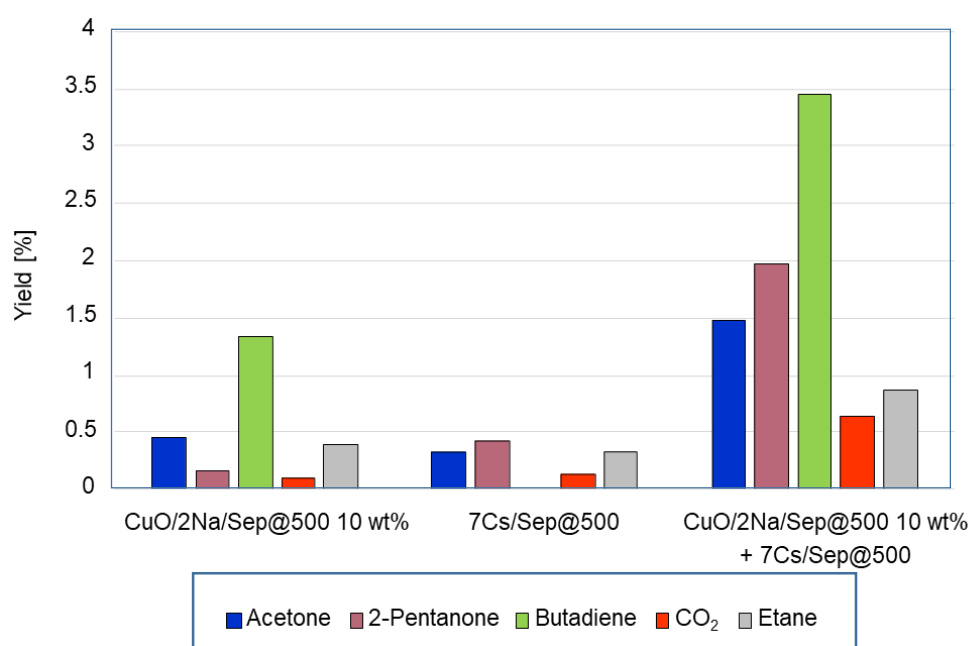
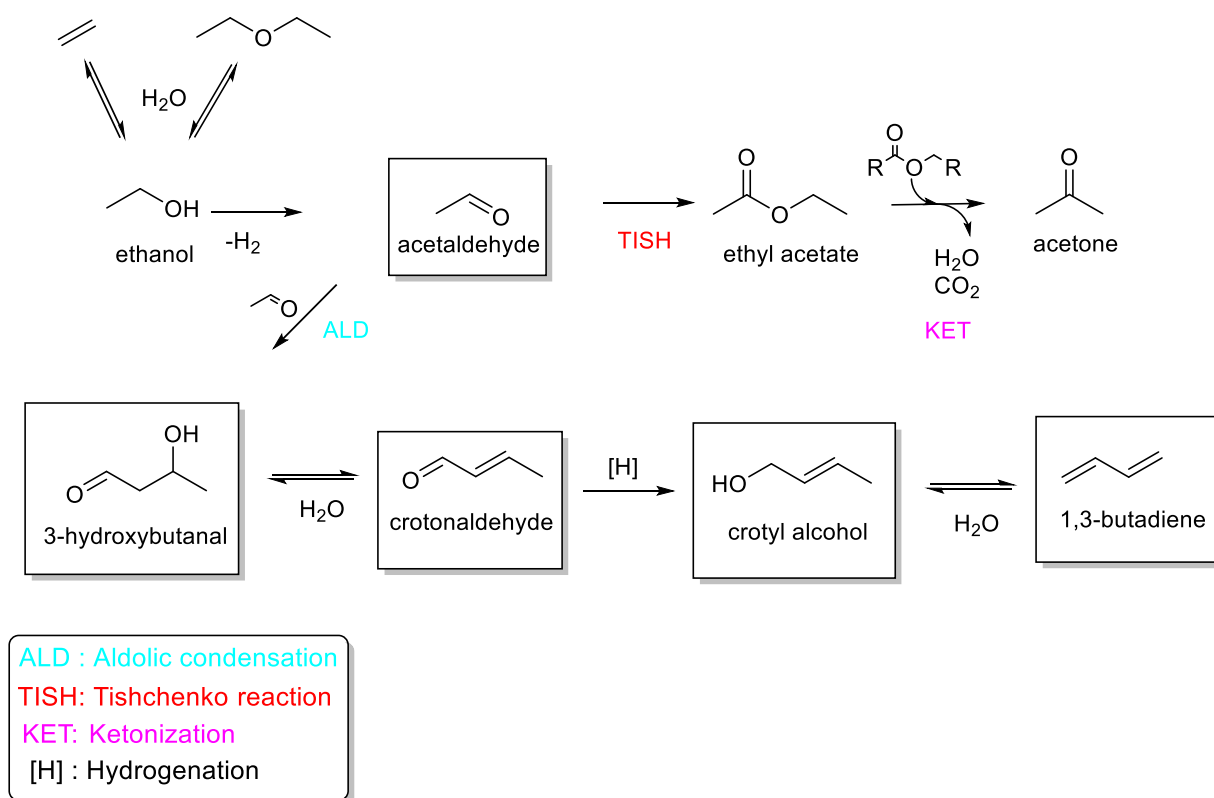


Figure 4.105 Catalytic results obtained, in terms of products yields (ID others), in the Ethanol gas-phase conversion over CuO/2Na/Sep@500 10 wt%, 7Cs/Sep@500 and the dual bed catalysts. EtOH 5% v/v in N₂; T= 450°C; P= 1 atm; WHSV₁= 1 g_{EtOH}/(g_{CAT}·h), WHSV₂= 1 g_{EtOH}/(g_{CAT}·h).

It can be noticed that by feeding acetaldehyde with ethanol the formation of *n*-butanol has not been favoured. On the contrary, a slight decrease of *n*-butanol yield was obtained. Considering that *n*-butanol was present in the “feeding” mixture obtained over the first catalyst, a decrease of *n*-butanol yield could be explained by its subsequent conversion over the second catalyst. Indeed, the yield of both higher alcohols and butyraldehyde increased, the formation of which can be explained by

consecutive Guerbet reactions and dehydrogenation of *n*-butanol, respectively. Acetaldehyde yield slightly increased, comparing the results between the ones obtained over 7Cs/Sep@500 and the dual bed set. On the other hand, the just-mentioned selectivity decreased if compared to the one obtained while performing the reaction over the CuO/2Na/Sep@500 10 wt% catalyst alone. Its final yields is a combination of the two catalytic results, but the fact that it has decreased could be related to its conversion to form other products. In particular, in Figure 4.105 are reported the yields obtained of the other identified products, namely acetone, 2-pentanone, CO₂, 1,3-butadiene, ethane. Except for ethane, the hydrogenation product of ethylene, the other products came from consecutive reactions that involve acetaldehyde as intermediate products (ketonization and Toussaint reactions, see Scheme 4).³⁰⁰ Moreover, it is well-known that acetaldehyde has a beneficial effect on 1,3-butadiene yield, which is why this aldehyde is recycled into the reactor in the industrial process.³¹⁶ Indeed, acetaldehyde has been reported as key intermediate product in ethanol conversion into butadiene.³⁰¹ The Ostromislensky process³¹⁷ consists of two reactors system, a first one for partial dehydrogenation of ethanol to acetaldehyde followed by a second one, allocated to the conversion of the as-obtained ethanol–acetaldehyde mixtures to butadiene.



Scheme 4. Toussaint mechanism for ethanol conversion to butadiene. Some side reactions are depicted.

4.3.2.6 Catalysts screening in the best reaction conditions

From the previous catalytic tests, the highest *n*-butanol selectivity obtained, 30%, was reached by performing the reaction at 400°C with a contact time of 2 g_{CAT}/mL·s over the catalyst 7Cs/Sep@500. At the same time, it has been observed that the best alkali-metal:sepiolite moles/weight ratio was

the one at around $0.6 \text{ mmol}_{\text{MET}}/\text{g}_{\text{SEP}}$. Accordingly, the catalysts containing this amount of sodium and potassium have been prepared and tested in the most performing reaction conditions in order to evaluate the effect of the different alkali metals. More specifically, catalytic tests at 400°C , 1 atm and $2 \text{ g}_{\text{CAT}}/\text{mL}\cdot\text{s}$, have been performed over the catalysts 2K/Sep@500 and 1.2Na/Sep@500 and the results obtained have been compared to the ones obtained over the 7Cs/Sep@500 catalyst. The results in terms of ethanol conversion and products selectivity are reported in Figure 4.106 and Table 4.37.

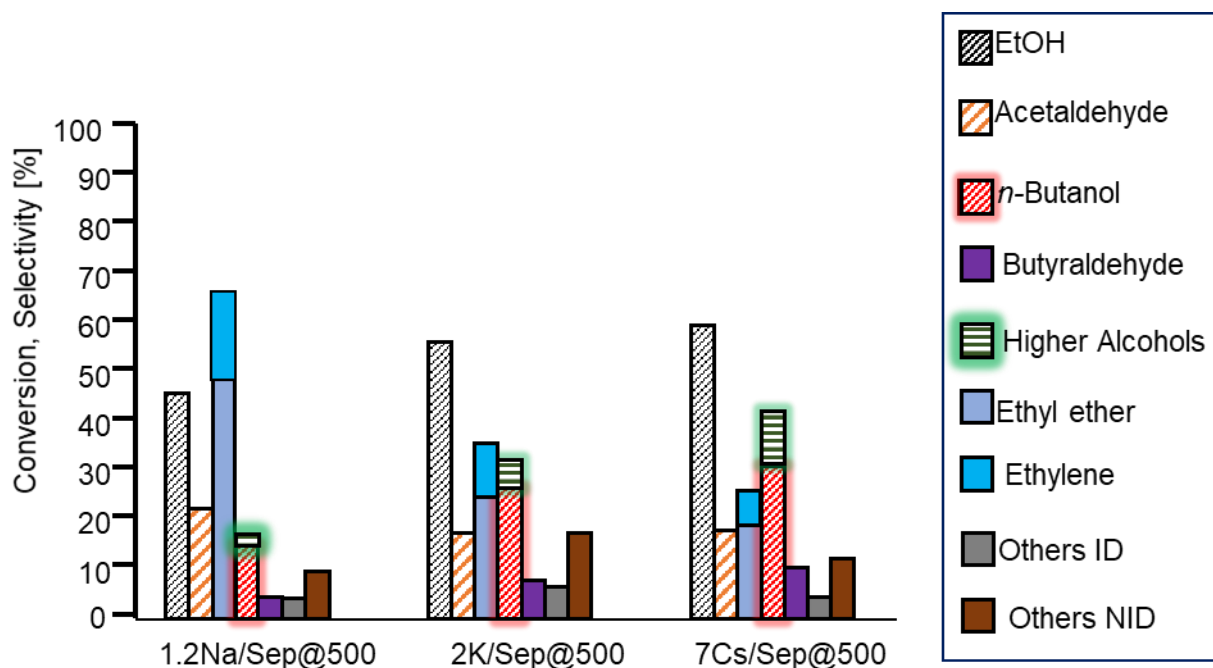


Figure 4.106 Catalytic results obtained, in terms of EtOH conversion and main products selectivity, in the Ethanol gas-phase conversion over the impregnated sepiolite samples with 1.2 wt% of Na (1.2Na/Sep@500), 2wt% of K (2K/Sep@500) and 7 wt% of Cs (7Cs/Sep@500). Higher alcohols: *n*-hexanol, 2-ethyl butanol, *n*-octanol, 2-ethyl hexanol; Others ID: acetone, 2-pentanone, CO_2 , ethyl acetate; Others NID: other products unidentified. Reaction conditions: EtOH 5% v/v in N_2 , $T = 400^\circ\text{C}$, $P = 1 \text{ atm}$, $W/F = 2 \text{ g/mL}\cdot\text{s}$; $WHSV = 0.2 \text{ g}_{\text{EtOH}}/(\text{g}_{\text{CAT}}\cdot\text{h})$.

Table 4.37 Catalytic results obtained, in terms of EtOH conversion and main products selectivity and yields, in the Ethanol gas-phase conversion over the impregnated sepiolite samples with 1.2 wt% of Na (1.2Na/Sep@500), 2wt% of K (2K/Sep@500) and 7 wt% of Cs (7Cs/Sep@500). AA: acetaldehyde, BuA: butyraldehyde Higher alcohols: *n*-hexanol, 2-ethyl butanol, *n*-octanol, 2-ethyl hexanol; Others ID: acetone, 2-pentanone, CO₂, ethyl acetate; Others NID: other products unidentified. Guerbet alcohols: *n*-butanol + higher alcohols. Reaction conditions: EtOH 5% v/v in N₂, T= 400°C, P= 1 atm, W/F= 2 g/mL·s; WHSV= 0.2 g_{EtOH}/(g_{CAT}·h).

Selectivity [%]										
<i>Metal</i>	<i>EtOH</i>	<i>AA</i>	<i>DEE</i>	<i>Ethylene</i>	<i>BuOH</i>	<i>BuA</i>	<i>Higher Alcohols</i>	<i>Guerbet alcohols</i>	<i>Others ID</i>	<i>Others NID</i>
1.2Na	45.2	21.5	47.7	17	13.9	3.5	1.2	15.1	3.4	8.8
2K	55.7	16.6	24.0	9.8	25.8	6.9	4.9	30.7	5.7	16.6
7Cs	59.0	17.2	18.2	5.9	30.1	9.7	9.8	39.9	3.5	11.5
Yields [%]										
<i>Metal</i>	<i>EtOH</i>	<i>AA</i>	<i>DEE</i>	<i>Ethylene</i>	<i>BuOH</i>	<i>BuA</i>	<i>Higher Alcohols</i>	<i>Guerbet alcohols</i>	<i>Others ID</i>	<i>Others NID</i>
1.2Na	45.2	9.7	21.6	7.7	6.3	1.6	0.5	6.8	1.5	4.0
2K	55.7	9.2	13.4	5.5	14.4	3.8	2.7	17.1	3.2	9.2
7Cs	59.0	10.2	10.7	3.5	17.8	5.7	5.7	23.5	2.0	6.8

The nature of the alkali metal exerts a great effect on ethanol conversion (Figure 4.106), especially with regards of the products distribution. Ethanol conversion obtained over the cesium-doped sepiolite is greater than the one containing sodium and potassium by 14% and 4% respectively. The products distribution could reflect the basicity of the metal ions. Accordingly, the selectivity of dehydration products (diethyl ether and ethylene) decreased while the ones of *n*-butanol and higher alcohols increased. Butyraldehyde and others NID products formation seemed to be favoured over the 7Cs/Sep@500 catalyst as well.

4.3.3 Reaction mechanism

Along the aldol-condensation-based pathway for the Guerbet reaction mechanism, the intermediates that are formed starting from the aldol condensation of two molecules of acetaldehyde are the acetaldol (3-hydroxy-butanal), its dehydration product, the α,β -unsaturated aldehyde (crotonaldehyde) and then its hydrogenation products. From the hydrogenation of the double bond is formed butyraldehyde, while from the hydrogenation of the carbonyl group, crotyl alcohol is formed. Crotyl alcohol is reported to be a key product for butadiene formation, that should come from its dehydration.⁵⁸ Butadiene have been detected mainly when transition metals (copper and nickel) were added to sepiolite, favouring acetaldehyde formation, suggesting that acetaldehyde is a key compound for the formation of butadiene. Nevertheless, neither crotonaldehyde nor

crotylalcohol have been detected or quantified while conducting the catalytic tests. Then, the formation of butadiene could follow another route different from the aldol-condensation one.

The fact that the addition of a transition metal only favoured the formation of acetaldehyde without favouring *n*-butanol formation could suggest that acetaldehyde is not the major intermediate in the mechanism of its formation, instead, it favoured the formation of the side product 1,3-butadiene. Nevertheless, it is reported in literature that after transition metal addition, the aldol condensation step becomes the rate-limiting one.¹⁴⁸

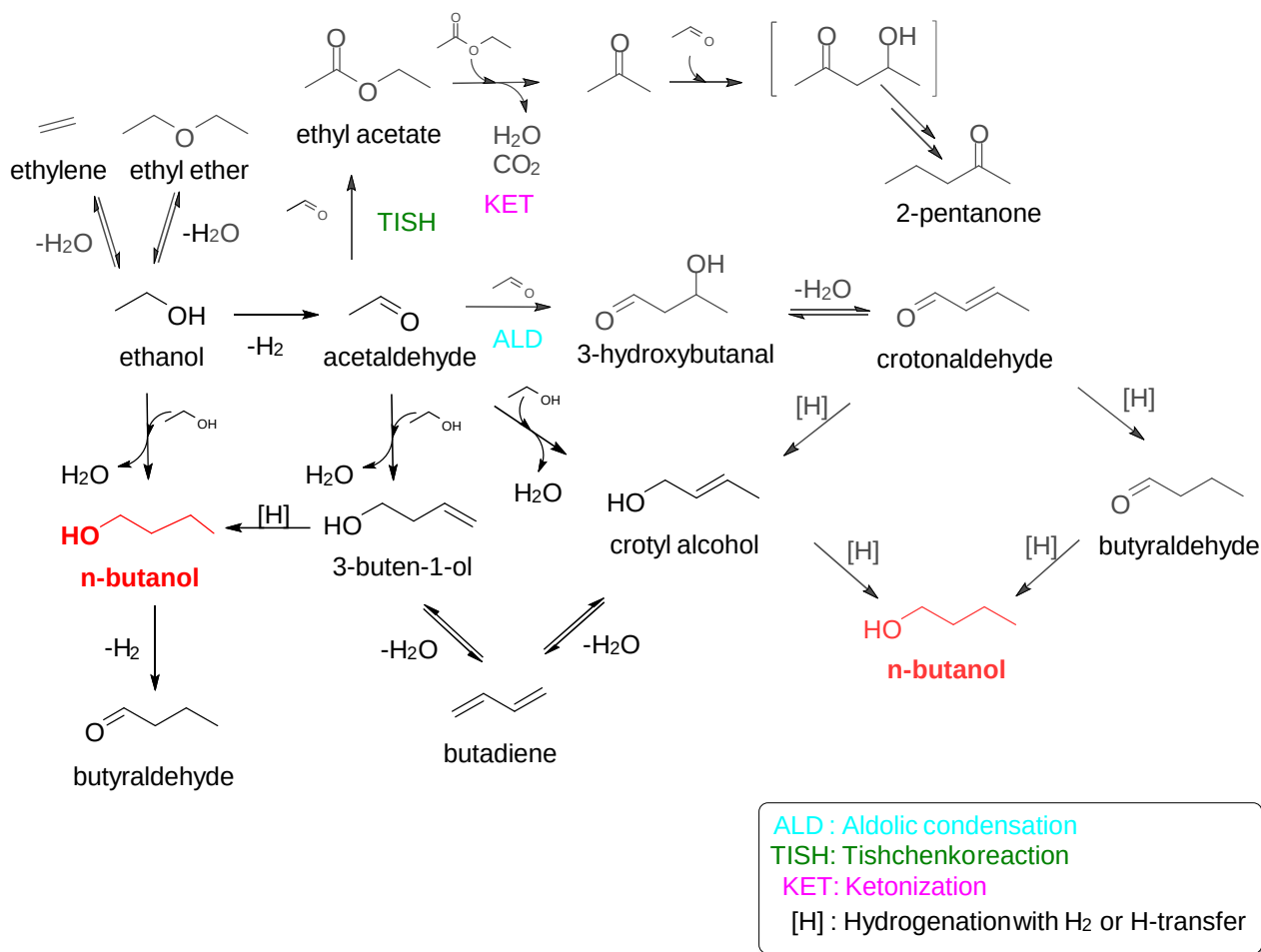
From the literature, along with the aldol-condensation based mechanism, another way to produce *n*-butanol from ethanol has been proposed by several authors, and it is based on the formation of *n*-butanol directly from two molecules of ethanol by condensation without any intermediates, the so-called “direct route”.^{46,65,284,291,302} Yang and et al. in 1993 proposed a mechanism in which ethanol undergoes H-abstraction from a β - carbon atom generating a nucleophilic centre that attacks another molecule of ethanol, condensing to *n*-butanol and water.⁴⁶ Ndou et al. stated that the basic sites on the surface of the catalyst are necessary to activate the C-H bond in the β -position in ethanol in order to condense with another molecule of ethanol by dehydration to form *n*-butanol.²⁸⁴ Accordingly, the addition of the basic alkali metal ions Na⁺, K⁺ and Cs⁺ promoted *n*-butanol formation. Indeed, by adding alkali metals it has been observed a related formation of new basic sites with different strength, which led to a general decrease of the acidity of the sepiolite surface and consequently lower values of the A/B ratios (see Table 4.18). Many authors reported how important it is to tune the quantity and ratio of basic and acid sites of the catalyst in order to promote *n*-butanol formation from ethanol, regardless the overall activity differs from one catalyst to another due to its nature and side reactions that can take place over its specific surface.^{59,257}

Scalbert et al. reported that at least two reaction pathways take place simultaneously, the direct route and a secondary condensation reaction between ethanol and acetaldehyde (formed from ethanol dehydrogenation) to form butenols, which are dehydrogenated to *n*-butanol by H-transfer from a sacrificial ethanol molecule.⁶⁵ Also, Chieregato et al. stated that even the condensation features of the catalyst need to be adjusted by means of the distance of the active sites in order to adequately accommodate the intermediates that lead selectively to *n*-butanol formation. Using DRIFTS and DFT calculations they proposed a different reaction mechanism. They studied the Guerbet reaction mechanism over a basic heterogeneous catalyst, MgO, and they claimed that the *n*-butanol formation from ethanol occurs through the formation of a carbanion intermediate formed over the surface of the catalyst that directly yield *n*-butanol. If vicinal adsorbed acetaldehyde reacts with the carbanion, butadiene is formed. Moreover, the mechanism they proposed do not involve hydrogenation reactions by H-transfer (Meerwein-Ponndorf-Verley).³⁰²

As far as the side product butyraldehyde is concerned, some of the catalytic results obtained suggested its formation derived from consecutive dehydrogenation of *n*-butanol, rather than being an intermediate (as it should be considering the aldol condensation route). For instance, considering the effect of the contact time on the products distribution obtained at 400°C (see Fig.4.99, 4.100 and 4.103), the increasing trend of the selectivity of butyraldehyde with the contact time suggested its nature of consecutive product. Nevertheless, considering the complexity of the reaction mechanism it is difficult to draw certain conclusions. Indeed, butyraldehyde may be formed even by direct

condensation of a molecule of ethanol and one of acetaldehyde, then its hydrogenation could lead to form *n*-butanol.^{46,284}

By combining the catalytic results together with the reaction mechanisms proposed from literature, a reaction mechanism for the Guerbet route that could take place over the alkali metal doped sepiolite catalysts has been proposed and is depicted in Scheme 5. Further evidence will be required to support this proposal.



Scheme 5. Reaction mechanism hypothesized over the alkali-doped sepiolite catalyst.

4.3.4 CONCLUSIONS

The natural clay Sepiolite has been modified with the addition of alkali metals (i.e. Na, K and Cs) by incipient wetness impregnation with different amount (i.e., 2, 4, 5, 7, 14 wt%) and of transition metal oxides (i.e., CuO and NiO) with a metal loading of 5 or 10 wt%. The catalysts as prepared have then been tested for the ethanol continuous flow gas-phase conversion into a lab-scale quartz reactor.

Since it is known that copper as a dopant could significantly speed up the rate of ethanol dehydrogenation, which is supposed to be the first step toward the formation of *n*-butanol, some samples impregnated with copper have been prepared and tested. The results obtained were not promising regarding the Guerbet pathway, since its addition only favoured acetaldehyde formation. Nevertheless, an interesting synergic effect has been observed between transition metal and alkali metal leading to higher acetaldehyde formation, to butadiene formation and even to a lower overall carbonaceous deposit formation over the catalyst surface. The formation of the latter has been linked to the ethylene oligomerization and consecutive coke formation.^{266,311,312} Hence, the concomitant presence of transition metal and alkali metal should be better investigated with the focus of enhancing selectivity to butadiene, an important chemical compound for the polymer industry. In addition, the catalyst impregnated with nickel (i.e., NiO/2Na/Sep@500 5 wt%) has been more active and led to a slight increase of 1,3-butadiene formation, reaching a butadiene selectivity of 7% while performing the reaction at 400°C and 1 g_{EtOH}/(g_{CAT}·h).as WHSV.

Generally, it has been observed that the presence of an alkali metal over sepiolite favoured the formation of the Guerbet product of ethanol, *n*-butanol. Simultaneously, a decrease in the strength and concentration of acid sites responsible for the occurrence of the side reactions of dehydration of ethanol to ethylene or diethyl ether has been observed. It is worth to note that the calcination temperature of the heating treatment of sepiolite was crucial, showing better results when calcined at 500°C. Indeed, regarding the sodium-impregnated sepiolite, the best results in terms of *n*-butanol selectivity have been obtained over the 2Na/Sep@500, namely 14%, a 13% higher than the one obtained over 2Na/Sep@700, when tested in the same conditions.

Even the amount and the nature of the alkali metals played a role in enhancing the *n*-butanol selectivity. The catalytic results obtained with the different alkali metals have been compared through the molar amount of the metals per weight of sepiolite (mmol_{MET}/g_{SEP}), finding an optimal amount of ca. 0.6 mmol_{MET}/g_{SEP}. Indeed, with that amount, the selectivity of *n*-butanol has been maximized, regardless the nature of the alkali metals. Among them, the greatest yield of *n*-butanol, namely 10.3%, has been obtained over the cesium-impregnated one (i.e., 7Cs/Sep@500, feeding a gaseous mixture of EtOH 5% v/v in N₂, at 450 °C and using a WHSV= 1 g_{EtOH}/(g_{CAT}·h)). This catalyst had an acid/base sites ratio of 1.6, containing both of medium and strong basic sites. In contrast with the ones doped with sodium or potassium that, with the same alkali metal amount, showed a different basic sites distribution. The reason of such difference should be better investigated since the nature of the basic sites could be responsible for the enhanced *n*-butanol formation.

The subsequent reaction condition optimization performed over the catalyst 7Cs/Sep@500 (i.e., 400°C, atmospheric pressure and 0.2 g_{EtOH}/(g_{CAT}·h).as WHSV) led to the achievement of a maximum

selectivity of *n*-butanol equal to 30% with 59% of ethanol conversion, corresponding to a 18% of *n*-butanol yield. Figure 4.107 summarizes the catalytic results obtained by several authors for the ethanol gas-phase conversion through the Guerbet route performed at atmospheric pressure.^{59,61,97,99,181,284,292,318} It can be noticed an inverse relation between *n*-butanol selectivity and ethanol conversion, indeed the best result in terms of *n*-butanol selectivity (~80%) was obtained with an ethanol conversion of 4% over a strontium phosphate hydroxyapatite catalyst.⁹⁷ The results obtained over the 7Cs/Sep@500 let it be placed in a promising position.

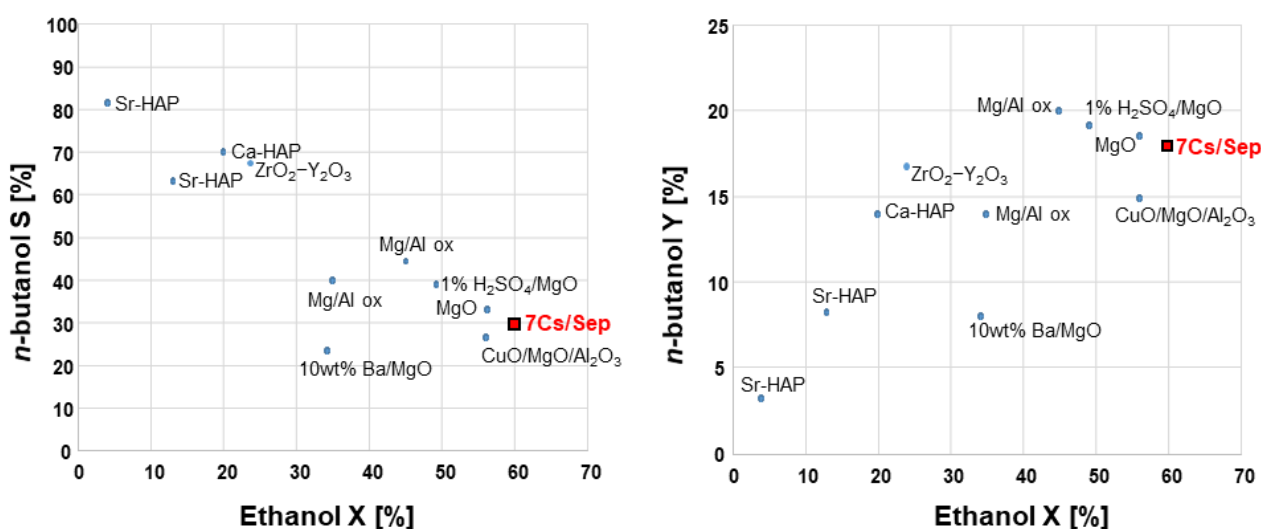


Figure 4.107 Dependence of selectivity (S, %) and yield (Y, %) of *n*-butanol with ethanol conversion (X, %) for the best performing heterogeneous catalysts in the vapour-phase Guerbet reaction performed at atmospheric pressure and in the temperature range 260-450°C.^{59,61,97,99,181,284,292,318}

In addition, considering the cumulative selectivity of *n*-butanol and higher Guerbet alcohols, which find suitability for advanced biofuel and lubricants applications, it was possible to reach a total Guerbet alcohols selectivity of 40%, corresponding to a total yield of ~24%.

A reaction mechanism by which the Guerbet reaction took place over the alkali-doped sepiolite catalyst has been proposed. Further studies are needed to better understand the overall reaction mechanism. To shed more light on the reaction mechanism over the alkali-sepiolite catalysts, it could be useful to perform reactions by feeding some intermediate molecules, such as butyraldehyde. Then, it would be interesting to perform in situ Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy analysis over the sepiolite surface.

5 CONCLUSIONS

This Thesis, which represents the summary of the results collected during the three years of my PhD, reports the investigation of the catalytic, gas-phase, continuous-flow, upgrading of ethanol to a wide range of added-value molecules. Three main topics have been addressed, with regards to the nature of the materials used as heterogeneous catalysts: hydroxyapatite, zirconium oxide and the natural clay sepiolite.

As far as the ion-exchanged hydroxyapatite-based catalysts are concerned, the Sr-HAP system has been employed to study the formation of heavier products from ethanol in order to obtain a hydrocarbon mixture suitable for biofuel application. With this proposal, harsh reaction conditions such as high ethanol feeding concentration or relatively long contact time have been used. A final hydrocarbon mixture with composition resembling the one of gasoline has been obtained with a total yield of ca.50%. Nevertheless, the main product obtained was the acetaldehyde, a dehydrogenation product of ethanol. Another issue encountered was the percentage of aromatics products obtained, which should be diminished in order to reach the limits of 25% claimed in standard specification for jet fuel application.¹⁰⁶ Nevertheless, the reaction system has been upgraded in order to perform further investigations for this purpose.

The effect of various synthetic parameters over the zirconia phase formation have been evaluated. The incorporation of a 5% molar of a metal dopant (Ti and Y) permitted the stabilization of the metastable phases cubic and tetragonal over the monoclinic one. However, all the synthesized samples acted mainly as acid catalysts, promoting diethyl ether and ethylene formation, both dehydration products of ethanol. From the perspective of favouring the Guerbet mechanism, it would be interesting to study the effect of the addition of a redox element, such as a transition metal, over the catalyst surface in order to catalyse the acetaldehyde formation, often reported as the rate-limiting step of the Guerbet reaction.

Natural sepiolite has been also studied as an alternative heterogeneous catalyst for the gas-phase ethanol selective conversion through the Guerbet route. It has been observed that the incorporation of an alkali metal as promoter (by means of incipient wetness impregnation) changes the acid-base properties of the catalysts favouring the formation of *n*-butanol from ethanol. In particular, it was possible to obtain *n*-butanol with a selectivity of 30% and ethanol conversion of 59% over the 7Cs/Sep@500 catalyst (with 7 wt% of Cs). Those results are interesting since, from the perspective of the “Green and Sustainable Development” concept, the use of naturally abundant clay minerals like sepiolite as catalyst has economical, eco-friendly and nontoxic advantages.³¹⁹ In this study, sepiolite has been used for the first time as heterogeneous catalyst for performing ethanol gas-phase

5. CONCLUSIONS

Guerbet conversion into higher alcohols with reasonable yields, opening new perspectives for future catalyst engineering for this kind of complex reaction mechanism.

6 REFERENCES

1. Martin Alonso, D., Q. Bond, J., and A. Dumesic, J. "Catalytic conversion of biomass to biofuels," *Green Chemistry*, V. 12, No. 9, 2010, pp. 1493–513.
2. Anastas, P. T., and Warner, J. C. "Green Chemistry: Theory and Practice," Oxford University Press: New York, 1998.
3. Poliakoff, M., Licence, P., and George, M. W. "UN sustainable development goals: How can sustainable/green chemistry contribute? By doing things differently," *Current Opinion in Green and Sustainable Chemistry*, V. 13, 2018, pp. 146–9.
4. Cavani, F., Centi, G., Perathoner, S., et al., eds. "Sustainable Industrial Chemistry: Principles, Tools and Industrial Examples," 1st edition, Weinheim, Wiley-VCH, 2009, 621 pp.
5. Sun, J., Wang, Y., Li, J., et al. "H₂ production from stable ethanol steam reforming over catalyst of NiO based on flowerlike CeO₂ microspheres," *International Journal of Hydrogen Energy*, V. 35, No. 7, 2010, pp. 3087–91.
6. Hülsey, M. J. "Shell biorefinery: A comprehensive introduction," *Green Energy & Environment*, V. 3, No. 4, 2018, pp. 318–27.
7. Carioca, J. O. B. "Biofuels: Problems, challenges and perspectives," *Biotechnology Journal*, V. 5, No. 3, 2010, pp. 260–73.
8. Mohan, D., Pittman, C. U., and Steele, P. H. "Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review," *Energy & Fuels*, V. 20, No. 3, 2006, pp. 848–89.
9. Bolyos, E., Lawrence, D., and Nordin, A. "BIOMASS AS AN ENERGY SOURCE: THE CHALLENGES AND THE PATH FORWARD," *Proceedings from the Third International Disposal Conference*, 2003, p. 7.
10. "Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC (Text with EEA relevance)," v. vol. 140, 2009.
11. Clark, J. H. "Chapter 1: Green and Sustainable Chemistry: An Introduction." *Green and Sustainable Medicinal Chemistry*. 2016. pp. 1–11.
12. "Innovating for Sustainable Growth: A Bioeconomy for Europe," *Industrial Biotechnology*, V. 8, No. 2, 2012, pp. 57–61.
13. Ubando, A. T., Felix, C. B., and Chen, W.-H. "Biorefineries in circular bioeconomy: A comprehensive review," *Bioresource Technology*, V. 299, 2020, p. 122585.
14. Centi, G., and van Santen, R. A., eds. "Catalysis for Renewables: From Feedstock to Energy Production," 1st edition, Wiley, 2007.
15. Nogueira, L., Seabra, J., Best, G., et al. "Sugarcane based bioethanol: energy for sustainable development," 1st edition, Banco Nacional de Desenvolvimento Econômico e Social, 2008.
16. Dumeignil, F., Capron, M., Katryniok, B., et al. "Biomass-derived Platform Molecules Upgrading through Catalytic Processes: Yielding Chemicals and Fuels," *Journal of the Japan Petroleum Institute*, V. 58, No. 5, 2015, pp. 257–73.
17. Lanzafame, P., Perathoner, S., Centi, G., et al. "Grand challenges for catalysis in the Science and Technology Roadmap on Catalysis for Europe: moving ahead for a sustainable future," *Catalysis Science & Technology*, V. 7, No. 22, 2017, pp. 5182–94.
18. Gómez, J. M., Romero, M. D., and Callejo, V. "Heterogeneous basic catalysis for upgrading of biofuels," *Catalysis Today*, V. 218–219, 2013, pp. 143–7.
19. Zhang, L., Xu, C. (Charles), and Champagne, P. "Overview of recent advances in thermochemical conversion of biomass," *Energy Conversion and Management*, V. 51, No. 5, 2010, pp. 969–82.
20. Robak, K., and Balcerek, M. "Review of Second Generation Bioethanol Production from Residual Biomass," *Food Technology and Biotechnology*, V. 56, No. 2, 2018, pp. 174–87.
21. Dias De Oliveira, M. E., Vaughan, B. E., and Rykiel, E. J. "Ethanol as Fuel: Energy, Carbon Dioxide Balances, and Ecological Footprint," *BioScience*, V. 55, No. 7, 2005, pp. 593–602.
22. Service, R. F. "Is There a Road Ahead for Cellulosic Ethanol?," *Science*, V. 329, No. 5993, 2010, pp. 784–5.

23. Tsuchida, T., Sakuma, S., Takeguchi, T., et al. "Direct Synthesis of n-Butanol from Ethanol over Nonstoichiometric Hydroxyapatite," *Industrial & Engineering Chemistry Research*, V. 45, No. 25, 2006, pp. 8634–42.
24. Cardona, C. A., and Sánchez, O. J. "Fuel ethanol production: process design trends and integration opportunities," *Bioresource Technology*, V. 98, No. 12, 2007, pp. 2415–57.
25. Panella, L. "Sugar Beet as an Energy Crop," *Sugar Tech*, V. 12, No. 3, 2010, pp. 288–93.
26. Goh, C. S., and Lee, K. T. "A visionary and conceptual macroalgae-based third-generation bioethanol (TGB) biorefinery in Sabah, Malaysia as an underlay for renewable and sustainable development," *Renewable and Sustainable Energy Reviews*, V. 14, No. 2, 2010, pp. 842–8.
27. John, R. P., Anisha, G. S., Nampoothiri, K. M., et al. "Micro and macroalgal biomass: a renewable source for bioethanol," *Bioresource Technology*, V. 102, No. 1, 2011, pp. 186–93.
28. Menetrez, M. Y. "An Overview of Algae Biofuel Production and Potential Environmental Impact," *Environmental Science & Technology*, V. 46, No. 13, 2012, pp. 7073–85.
29. Menon, V., and Rao, M. "Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept," *Progress in Energy and Combustion Science*, V. 38, No. 4, 2012, pp. 522–50.
30. Saxena, R. C., Adhikari, D. K., and Goyal, H. B. "Biomass-based energy fuel through biochemical routes: A review," *Renewable and Sustainable Energy Reviews*, V. 13, No. 1, 2009, pp. 167–78.
31. Singh, A., Nigam, P. S., and Murphy, J. D. "Renewable fuels from algae: An answer to debatable land based fuels," *Bioresource Technology*, V. 102, No. 1, 2011, pp. 10–6.
32. Ezinkwo, G. O., Tretyakov, V. P., Aliyu, A., et al. "Fundamental Issues of Catalytic Conversion of Bio-Ethanol into Butadiene," *ChemBioEng Reviews*, V. 1, No. 5, 2014, pp. 194–203.
33. Spivey, J. J., and Egbebi, A. "Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas," *Chemical Society Reviews*, V. 36, No. 9, 2007, pp. 1514–28.
34. Bengelsdorf, F. R., Straub, M., and Dürre, P. "Bacterial synthesis gas (syngas) fermentation," *Environmental Technology*, V. 34, Nos. 13–14, 2013, pp. 1639–51.
35. Phillips, J. R., Klasson, K. T., Clausen, E. C., et al. "Biological production of ethanol from coal synthesis gas. Medium development studies," *Applied Biochemistry and Biotechnology*, V. 37, No. 39/40, 1993, pp. 559–71.
36. Henstra, A. M., Sipma, J., Rinzema, A., et al. "Microbiology of synthesis gas fermentation for biofuel production," *Current Opinion in Biotechnology*, V. 18, No. 3, 2007, pp. 200–6.
37. Griffin, D. W., and Schultz, M. A. "Fuel and chemical products from biomass syngas: A comparison of gas fermentation to thermochemical conversion routes," *Environmental Progress & Sustainable Energy*, V. 31, No. 2, 2012, pp. 219–24.
38. Köpke, M., Mihalcea, C., Bromley, J. C., et al. "Fermentative production of ethanol from carbon monoxide," *Current Opinion in Biotechnology*, V. 22, No. 3, 2011, pp. 320–5.
39. Huber, G. W., Iborra, S., and Corma, A. "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering," *Chemical Reviews*, V. 106, No. 9, 2006, pp. 4044–98.
40. Rostrup-Nielsen, J. R. "Fuels and Energy for the Future: The Role of Catalysis," *Catalysis Reviews*, V. 46, Nos. 3–4, 2004, pp. 247–70.
41. Harvey, B. G., and Meylemans, H. A. "The role of butanol in the development of sustainable fuel technologies," *Journal of Chemical Technology & Biotechnology*, V. 86, No. 1, 2011, pp. 2–9.
42. Johansson, R., Hruby, S. L., Rass-Hansen, J., et al. "The Hydrocarbon Pool in Ethanol-to-Gasoline over HZSM-5 Catalysts," *Catalysis Letters*, V. 127, No. 1, 2008, p. 1.
43. Coombs, J. "Production of fuel alcohol from biomass," *Enzyme and Microbial Technology*, V. 3, No. 2, 1981, pp. 171–3.
44. Cardona Alzate, C. A., and Sánchez Toro, O. J. "Energy consumption analysis of integrated flowsheets for production of fuel ethanol from lignocellulosic biomass," *Energy*, V. 31, No. 13, 2006, pp. 2447–59.
45. Taherzadeh, M. J., and Karimi, K. "ACID-BASED HYDROLYSIS PROCESSES FOR ETHANOL FROM LIGNOCELLULOSIC MATERIALS: A REVIEW," *BioResources*, V. 2, No. 3, 2007, pp. 472–99.
46. Yang, C., and Meng, Z. Y. "Bimolecular Condensation of Ethanol to 1-Butanol Catalyzed by Alkali Cation Zeolites," *Journal of Catalysis*, V. 142, No. 1, 1993, pp. 37–44.

47. Ed. Kirk-Othmer. "Encyclopedia of Chemical Technology," John Wiley & Sons, 2001.
48. Ndou, A. S., Plint, N., and Coville, N. J. "Dimerisation of ethanol to butanol over solid-base catalysts," *Applied Catalysis A: General*, V. 251, No. 2, 2003, pp. 337–45.
49. Green, E. M. "Fermentative production of butanol—the industrial perspective," *Current Opinion in Biotechnology*, V. 22, No. 3, 2011, pp. 337–43.
50. Jin, C., Yao, M., Liu, H., et al. "Progress in the production and application of n-butanol as a biofuel," *Renewable and Sustainable Energy Reviews*, V. 15, No. 8, 2011, pp. 4080–106.
51. Miller, R. E., and Bennett, G. E. "Manufacture of alcohols by guerbet condensation." US2762847A, 1956.
52. O'Lenick, A. J. "Guerbet chemistry," *Journal of Surfactants and Detergents*, V. 4, No. 3, 2001, pp. 311–5.
53. Xie, Y., Ben-David, Y., Shimon, L. J. W., et al. "Highly Efficient Process for Production of Biofuel from Ethanol Catalyzed by Ruthenium Pincer Complexes," *Journal of the American Chemical Society*, V. 138, No. 29, 2016, pp. 9077–80.
54. Campos-Fernández, J., Arnal, J. M., Gómez, J., et al. "A comparison of performance of higher alcohols/diesel fuel blends in a diesel engine," *Applied Energy*, V. 95, 2012, pp. 267–75.
55. Liu, Q., Xu, G., Wang, X., et al. "Highly Selective Upgrading of Biomass-Derived Alcohol Mixtures for Jet/Diesel-Fuel Components," *ChemSusChem*, V. 9, No. 24, 2016, pp. 3465–72.
56. Pang, J., Yin, M., Wu, P., et al. "Advances in catalytic dehydrogenation of ethanol to acetaldehyde," *Green Chemistry*, V. 23, No. 20, 2021, pp. 7902–16.
57. Injongkol, Y., Maihom, T., Choomwattana, S., et al. "A mechanistic study of ethanol transformation into ethene and acetaldehyde on an oxygenated Au-exchanged ZSM-5 zeolite," *RSC Advances*, V. 7, No. 60, 2017, pp. 38052–8.
58. Ho, C. R., Shylesh, S., and Bell, A. T. "Mechanism and Kinetics of Ethanol Coupling to Butanol over Hydroxyapatite," *ACS Catalysis*, V. 6, No. 2, 2016, pp. 939–48.
59. Tsuchida, T., Kubo, J., Yoshioka, T., et al. "Reaction of ethanol over hydroxyapatite affected by Ca/P ratio of catalyst," *Journal of Catalysis*, V. 259, No. 2, 2008, pp. 183–9.
60. Gabriëls, D., Hernández, W. Y., Sels, B., et al. "Review of catalytic systems and thermodynamics for the Guerbet condensation reaction and challenges for biomass valorization," *Catalysis Science & Technology*, V. 5, No. 8, 2015, pp. 3876–902.
61. Silvester, L., Lamonier, J.-F., Lamonier, C., et al. "Guerbet Reaction over Strontium-Substituted Hydroxyapatite Catalysts Prepared at Various (Ca+Sr)/P Ratios," *ChemCatChem*, V. 9, No. 12, 2017, pp. 2250–61.
62. de Graauw, C. F., Peters, J. A., van Bekkum, H., et al. "Meerwein-Ponndorf-Verley Reductions and Oppenauer Oxidations: An Integrated Approach," *Synthesis*, V. 1994, No. 10, 1994, pp. 1007–17.
63. Chieriegato, A., Velasquez Ochoa, J., Bandinelli, C., et al. "On the Chemistry of Ethanol on Basic Oxides: Revising Mechanisms and Intermediates in the Lebedev and Guerbet reactions," *ChemSusChem*, V. 8, No. 2, 2015, pp. 377–88.
64. Weizmann, C., Bergmann, E., and Sulzbacher, M. "Further observations on the guerbet reaction," *The Journal of Organic Chemistry*, V. 15, No. 1, 1950, pp. 54–7.
65. Scalbert, J., Thibault-Starzyk, F., Jacquot, R., et al. "Ethanol condensation to butanol at high temperatures over a basic heterogeneous catalyst: How relevant is acetaldehyde self-aldolization?," *Journal of Catalysis*, V. 311, 2014, pp. 28–32.
66. Di Cosimo, J. I., Apestegui, C. R., Ginés, M. J. L., et al. "Structural Requirements and Reaction Pathways in Condensation Reactions of Alcohols on MgyAlOx Catalysts," *Journal of Catalysis*, V. 190, No. 2, 2000, pp. 261–75.
67. Kozłowski, J. T., and Davis, R. J. "Sodium modification of zirconia catalysts for ethanol coupling to 1-butanol," *Journal of Energy Chemistry*, V. 1, No. 22, 2013, pp. 58–64.
68. Jordison, T. L., Lira, C. T., and Miller, D. J. "Condensed-Phase Ethanol Conversion to Higher Alcohols," *Industrial & Engineering Chemistry Research*, V. 54, No. 44, 2015, pp. 10991–1000.
69. Tsuchida, T., Yoshioka, T., Sakuma, S., et al. "Synthesis of Biogasoline from Ethanol over Hydroxyapatite Catalyst," *Industrial & Engineering Chemistry Research*, V. 47, No. 5, 2008, pp. 1443–52.
70. Di Cosimo, J. I., Díez, V. K., Xu, M., et al. "Structure and Surface and Catalytic Properties of Mg-Al Basic Oxides," *Journal of Catalysis*, V. 178, No. 2, 1998, pp. 499–510.

71. Ciftci, A., Varisli, D., Cem Tokay, K., et al. "Dimethyl ether, diethyl ether & ethylene from alcohols over tungstophosphoric acid based mesoporous catalysts," *Chemical Engineering Journal*, V. 207–208, 2012, pp. 85–93.
72. Fan, D., Dai, D.-J., and Wu, H.-S. "Ethylene Formation by Catalytic Dehydration of Ethanol with Industrial Considerations," *Materials*, V. 6, No. 1, 2013, pp. 101–15.
73. Morschbacker, A. "Bio-Ethanol Based Ethylene," *Polymer Reviews*, V. 49, No. 2, 2009, pp. 79–84.
74. Makshina, E. V., Dusselier, M., Janssens, W., et al. "Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene," *Chemical Society Reviews*, V. 43, No. 22, 2014, pp. 7917–53.
75. Santacesaria, E., Carotenuto, G., Tesser, R., et al. "Ethanol dehydrogenation to ethyl acetate by using copper and copper chromite catalysts," *Chemical Engineering Journal*, V. 179, 2012, pp. 209–20.
76. Liu, H., and Eisen, M. S. "Facile Coupling of Aldehydes with Alcohols: An Evolved Tishchenko Process for the Preparation of Unsymmetrical Esters: Facile Coupling of Aldehydes with Alcohols: An Evolved Tishchenko Process for the Preparation of Unsymmetrical Esters," *European Journal of Organic Chemistry*, V. 2017, No. 32, 2017, pp. 4852–8.
77. Sad, M. E., Neurock, M., and Iglesia, E. "Formation of C–C and C–O Bonds and Oxygen Removal in Reactions of Alkanediols, Alkanols, and Alkanals on Copper Catalysts," *Journal of the American Chemical Society*, V. 133, No. 50, 2011, pp. 20384–98.
78. Idriss, H., Kim, K. S., and Barteau, M. A. "Carbon–Carbon Bond Formation via Aldolization of Acetaldehyde on Single Crystal and Polycrystalline TiO₂ Surfaces," *Journal of Catalysis*, V. 139, No. 1, 1993, pp. 119–33.
79. Gliński, M., Szymański, W., and Łomot, D. "Catalytic ketonization over oxide catalysts: X. Transformations of various alkyl heptanoates," *Applied Catalysis A: General*, V. 281, No. 1, 2005, pp. 107–13.
80. Plint, N., Ghavalas, D., Vally, T., et al. "Catalysed synthesis of 4-heptanone from 1-butanol," *Catalysis Today*, V. 49, No. 1, 1999, pp. 71–7.
81. Plint, N. D., Coville, N. J., Lack, D., et al. "The catalysed synthesis of symmetrical ketones from alcohols," *Journal of Molecular Catalysis A: Chemical*, V. 165, Nos. 1–2, 2001, pp. 275–81.
82. Orozco, L. M., Renz, M., and Corma, A. "Carbon-Carbon Bond Formation and Hydrogen Production in the Ketonization of Aldehydes," *ChemSusChem*, V. 9, No. 17, 2016, pp. 2430–42.
83. Gangadharan, A., Shen, M., Sooknoi, T., et al. "Condensation reactions of propanal over CexZr1–xO₂ mixed oxide catalysts," *Applied Catalysis A: General*, V. 385, No. 1, 2010, pp. 80–91.
84. Aitchison, H., Wingad, R. L., and Wass, D. F. "Homogeneous Ethanol to Butanol Catalysis—Guerbet Renewed," *ACS Catalysis*, V. 6, No. 10, 2016, pp. 7125–32.
85. Koda, K., Matsu-ura, T., Obora, Y., et al. "Guerbet Reaction of Ethanol to n-Butanol Catalyzed by Iridium Complexes," *Chemistry Letters*, V. 38, No. 8, 2009, pp. 838–9.
86. Tanaka, Y., and Utsunomiya, M. "Process of producing alcohol." US8318990B2, 2012.
87. Cesari, C., Gagliardi, A., Messori, A., et al. "Boosting the guerbet reaction: A cooperative catalytic system for the efficient bio-ethanol refinery to second-generation biofuels," *Journal of Catalysis*, V. 405, 2022, pp. 47–59.
88. Farnetti, E. "Homogeneous and Heterogeneous Catalysis," *INORGANIC CHEMISTRY*, n.d., p. 10.
89. Lam, M. K., and Lee, K. T. "Chapter 12 - Scale-Up and Commercialization of Algal Cultivation and Biofuel Production." In: Pandey, A., Lee, D.-J., Chisti, Y. et al., eds. *Biofuels from Algae*. Amsterdam, Elsevier, 2014. pp. 261–86.
90. Ueda, W., Ohshida, T., Kuwabara, T., et al. "Condensation of alcohol over solid-base catalyst to form higher alcohols," *Catalysis Letters*, V. 12, No. 1, 1992, pp. 97–104.
91. Ndou, A. S., and Coville, N. J. "Self-condensation of propanol over solid-base catalysts," *Applied Catalysis A: General*, V. 275, No. 1, 2004, pp. 103–10.
92. Kozłowski, J. T., and Davis, R. J. "Heterogeneous Catalysts for the Guerbet Coupling of Alcohols," *ACS Catalysis*, V. 3, No. 7, 2013, pp. 1588–600.

93. Hanspal, S., Young, Z. D., Shou, H., et al. "Multiproduct Steady-State Isotopic Transient Kinetic Analysis of the Ethanol Coupling Reaction over Hydroxyapatite and Magnesia," *ACS Catalysis*, V. 5, No. 3, 2015, pp. 1737–46.
94. Marcu, I.-C., Tanchoux, N., Fajula, F., et al. "Catalytic Conversion of Ethanol into Butanol over M–Mg–Al Mixed Oxide Catalysts (M = Pd, Ag, Mn, Fe, Cu, Sm, Yb) Obtained from LDH Precursors," *Catalysis Letters*, V. 143, No. 1, 2013, pp. 23–30.
95. Riittonen, T., Toukoniitty, E., Madnani, D. K., et al. "One-Pot Liquid-Phase Catalytic Conversion of Ethanol to 1-Butanol over Aluminium Oxide—The Effect of the Active Metal on the Selectivity," *Catalysts*, V. 2, No. 1, 2012, pp. 68–84.
96. Young, Z. D., and Davis, R. J. "Hydrogen transfer reactions relevant to Guerbet coupling of alcohols over hydroxyapatite and magnesium oxide catalysts," *Catalysis Science & Technology*, V. 8, No. 6, 2018, pp. 1722–9.
97. Ogo, S., Onda, A., and Yanagisawa, K. "Selective synthesis of 1-butanol from ethanol over strontium phosphate hydroxyapatite catalysts," *Applied Catalysis A: General*, V. 402, No. 1, 2011, pp. 188–95.
98. Earley, J. H., Bourne, R. A., Watson, M. J., et al. "Continuous catalytic upgrading of ethanol to n-butanol and >C4 products over Cu/CeO₂ catalysts in supercritical CO₂," *Green Chemistry*, V. 17, No. 5, 2015, pp. 3018–25.
99. Carvalho, D. L., de Avillez, R. R., Rodrigues, M. T., et al. "Mg and Al mixed oxides and the synthesis of n-butanol from ethanol," *Applied Catalysis A: General*, V. 415–416, 2012, pp. 96–100.
100. Ordonsky, V. V., Sushkevich, V. L., and Ivanova, I. I. "Study of acetaldehyde condensation chemistry over magnesia and zirconia supported on silica," *Journal of Molecular Catalysis A: Chemical*, V. 333, No. 1, 2010, pp. 85–93.
101. Díaz-Pérez, M. A., and Serrano-Ruiz, J. C. "Catalytic Production of Jet Fuels from Biomass," *Molecules*, V. 25, No. 4, 2020, p. 802.
102. Pradelle, F., Braga, S. L., Martins, A. R. F. A., et al. "Gum Formation in Gasoline and Its Blends: A Review," *Energy & Fuels*, V. 29, No. 12, 2015, pp. 7753–70.
103. Stratiev, D. "D. Stratiev, 'Effect of gasoline hydrocarbon composition on the properties of the blend gasoline/bioethanol', Oxidation communications 34, No1, 183-192, 2011," *Oxidation Communications*, V. 34, 2011, pp. 183–92.
104. ExxonMobil. "Outlook for energy: A view to 2040," 2017.
105. Jamalzade, E., Kashkooli, K., Griffin, L., et al. "Production of jet-fuel-range molecules from biomass-derived mixed acids," *Reaction Chemistry & Engineering*, V. 6, No. 5, 2021, pp. 845–57.
106. Eagan, N. M., Kumbhalkar, M. D., Buchanan, J. S., et al. "Chemistries and processes for the conversion of ethanol into middle-distillate fuels," *Nature Reviews Chemistry*, V. 3, No. 4, 2019, pp. 223–49.
107. Brooks, K. P., Snowden-Swan, L. J., Jones, S. B., et al. "Chapter 6 - Low-Carbon Aviation Fuel Through the Alcohol to Jet Pathway." In: Chuck, C. J., ed. *Biofuels for Aviation*. Academic Press, 2016. pp. 109–50.
108. Yang, J., Xin, Z., He, Q. (Sophia), et al. "An overview on performance characteristics of bio-jet fuels," *Fuel*, V. 237, 2019, pp. 916–36.
109. Wang, M., Dewil, Raf., Maniatis, K., et al. "Biomass-derived aviation fuels: Challenges and perspective," *Progress in Energy and Combustion Science*, V. 74, 2019, pp. 31–49.
110. Biello, D. "'Fatted Eagle' Joins 'Green Hornet' in U.S. Military's Alternative Fuels Fighter Fleet." *Scientific American*. Available at: <https://www.scientificamerican.com/article/fatted-eagle-biofuel-flight-air-force-fighter/>.
111. James D. Kinder., and Timothy Rahmes. "Evaluation of Bio-Derived Synthetic Paraffinic Kerosenes," 2009.
112. "Naphthalene Removal Assessment – Ascent." Available at: <https://ascent.aero/project/naphthalene-removal-assessment/>.
113. Ford, J. P., Immer, J. G., and Lamb, H. H. "Palladium Catalysts for Fatty Acid Deoxygenation: Influence of the Support and Fatty Acid Chain Length on Decarboxylation Kinetics," *Topics in Catalysis*, V. 55, Nos. 3–4, 2012, pp. 175–84.

114. Serrano-Ruiz, J. C., Ramos-Fernández, E. V., and Sepúlveda-Escribano, A. "From biodiesel and bioethanol to liquid hydrocarbonfuels: new hydrotreating and advanced microbial technologies," *Energy Environ. Sci.*, V. 5, No. 2, 2012, pp. 5638–52.
115. Nikolaev, S. A., Chistyakov, A. V., Chudakova, M. V., et al. "Novel gold catalysts for the direct conversion of ethanol into C₃+ hydrocarbons," *Journal of Catalysis*, V. 297, 2013, pp. 296–305.
116. Viswanadham, N., Saxena, S. K., Kumar, J., et al. "Catalytic performance of nano crystalline H-ZSM-5 in ethanol to gasoline (ETG) reaction," *Fuel*, V. 95, 2012, pp. 298–304.
117. "Alliance BioEnergy Plus, Vertimass sign technology license agreement." Canadian Biomass Magazine. Available at: <https://www.canadianbiomassmagazine.ca/alliance-bioenergy-plus-vertimass-sign-technology-license-agreement/>.
118. "Gevo Flies High with USAF Alcohol-to-Jet Test Flight." Available at: <https://www.businesswire.com/news/home/20120703005409/en/Gevo-Flies-High-with-USAF-Alcohol-to-Jet-Test-Flight>.
119. Ben Tayeb, K., Pinard, L., Touati, N., et al. "Ethanol transformation into higher hydrocarbons over HZSM-5 zeolite: Direct detection of radical species by in situ EPR spectroscopy," *Catalysis Communications*, V. 27, 2012, pp. 119–23.
120. Galadima, A., and Muraza, O. "Zeolite catalysts in upgrading of bioethanol to fuels range hydrocarbons: A review," *Journal of Industrial and Engineering Chemistry*, V. 31, 2015, pp. 1–14.
121. Svelle, S., Kolboe, S., and Swang, O. "Theoretical Investigation of the Dimerization of Linear Alkenes Catalyzed by Acidic Zeolites," *The Journal of Physical Chemistry B*, V. 108, No. 9, 2004, pp. 2953–62.
122. Hannon, J. "One-Step High-Yield Production of Fungible Gasoline, Diesel, and Jet Fuel Blend Stocks from Ethanol without Added Hydrogen.," https://www.energy.gov/sites/prod/files/2017/05/f34/thermochem_hannon_2.3.1.201.pdf, n.d.
123. "ExxonMobil." Available at: <https://corporate.exxonmobil.com/>.
124. Ramasamy, K. K., and Wang, Y. "Ethanol conversion to hydrocarbons on HZSM-5: Effect of reaction conditions and Si/Al ratio on the product distributions," *Catalysis Today*, V. 237, 2014, pp. 89–99.
125. Ramasamy, K. K., Zhang, H., Sun, J., et al. "Conversion of ethanol to hydrocarbons on hierarchical HZSM-5 zeolites," *Catalysis Today*, V. 238, 2014, pp. 103–10.
126. Lopez, J. S., Dagle, R. A., Dagle, V. L., et al. "Oligomerization of ethanol-derived propene and isobutene mixtures to transportation fuels: catalyst and process considerations," *Catalysis Science & Technology*, V. 9, No. 5, 2019, pp. 1117–31.
127. Bryant, D. E., and Kranich, W. L. "Dehydration of alcohols over zeolite catalysts," *Journal of Catalysis*, V. 8, No. 1, 1967, pp. 8–13.
128. Phillips, C. B., and Datta, R. "Production of Ethylene from Hydrous Ethanol on H-ZSM-5 under Mild Conditions," *Industrial & Engineering Chemistry Research*, V. 36, No. 11, 1997, pp. 4466–75.
129. Dossumov, K., Churina, D. Kh., Yergaziyeva, G. Y., et al. "Conversion of Bio-ethanol over Zeolites and Oxide Catalysts," *International Journal of Chemical Engineering and Applications*, V. 7, No. 2, 2016, pp. 128–32.
130. Mohsenzadeh, A., Zamani, A., and Taherzadeh, M. J. "Bioethylene Production from Ethanol: A Review and Techno-economical Evaluation," *ChemBioEng Reviews*, V. 4, No. 2, 2017, pp. 75–91.
131. Zhang, M., and Yu, Y. "Dehydration of Ethanol to Ethylene," *Industrial & Engineering Chemistry Research*, V. 52, No. 28, 2013, pp. 9505–14.
132. Kito-Borsa, T., Pacas, D. A., Selim, S., et al. "Properties of an Ethanol–Diethyl Ether–Water Fuel Mixture for Cold-Start Assistance of an Ethanol-Fueled Vehicle," *Industrial & Engineering Chemistry Research*, V. 37, No. 8, 1998, pp. 3366–74.
133. Takahara, I., Saito, M., Inaba, M., et al. "Dehydration of Ethanol into Ethylene over Solid Acid Catalysts," *Catalysis Letters*, V. 105, Nos. 3–4, 2005, pp. 249–52.
134. Varisli, D., Dogu, T., and Dogu, G. "Ethylene and diethyl-ether production by dehydration reaction of ethanol over different heteropolyacid catalysts," *Chemical Engineering Science*, V. 62, No. 18, 2007, pp. 5349–52.

135. Corma, A., and Perez-Pariente, J. "Catalytic activity of modified silicates: I. Dehydration of ethanol catalysed by acidic sepiolite," *Clay Minerals*, V. 22, No. 4, 1987, pp. 423–33.
136. Garbarino, G., Pampararo, G., Phung, T. K., et al. "Heterogeneous Catalysis in (Bio)Ethanol Conversion to Chemicals and Fuels: Thermodynamics, Catalysis, Reaction Paths, Mechanisms and Product Selectivities," *Energies*, V. 13, No. 14, 2020, p. 3587.
137. Almohalla, M., Rodríguez-Ramos, I., and Guerrero-Ruiz, A. "Comparative study of three heteropolyacids supported on carbon materials as catalysts for ethylene production from bioethanol," *Catalysis Science & Technology*, V. 7, No. 9, 2017, pp. 1892–901.
138. de Oliveira, T. K. R., Rosset, M., and Perez-Lopez, O. W. "Ethanol dehydration to diethyl ether over Cu-Fe/ZSM-5 catalysts," *Catalysis Communications*, V. 104, 2018, pp. 32–6.
139. Bokade, V. V., and Yadav, G. D. "Heteropolyacid supported on montmorillonite catalyst for dehydration of dilute bio-ethanol," *Applied Clay Science*, V. 53, No. 2, 2011, pp. 263–71.
140. Morrow, N. L. "The industrial production and use of 1,3-butadiene.," *Environmental Health Perspectives*, V. 86, 1990, pp. 7–8.
141. White, W. C. "Butadiene production process overview," *Chemico-Biological Interactions*, V. 166, Nos. 1–3, 2007, pp. 10–4.
142. Cavani, F., Albonetti, S., Basile, F., et al. "Chemicals and Fuels from Bio-Based Building Blocks," Wiley-VCH Verlag GmbH & Co. KGaA, 2016.
143. Angelici, C., Weckhuysen, B. M., and Bruijninx, P. C. A. "Chemocatalytic Conversion of Ethanol into Butadiene and Other Bulk Chemicals," *ChemSusChem*, V. 6, No. 9, 2013, pp. 1595–614.
144. Quattlebaum, W. M., Toussaint, W. J., and Dunn, J. T. "Deoxygenation of Certain Aldehydes and Ketones: Preparation of Butadiene and Styrene¹," *Journal of the American Chemical Society*, V. 69, No. 3, 1947, pp. 593–9.
145. Niiyama, H., Morii, S., and Echigoya, E. "Butadiene Formation from Ethanol over Silica-Magnesia Catalysts," *Bulletin of the Chemical Society of Japan*, V. 45, No. 3, 1972, pp. 655–9.
146. Pomalaza, G., Capron, M., Ordonsky, V., et al. "Recent Breakthroughs in the Conversion of Ethanol to Butadiene," *Catalysts*, V. 6, No. 12, 2016, p. 203.
147. Velasquez Ochoa, J., Bandinelli, C., Vozniuk, O., et al. "An analysis of the chemical, physical and reactivity features of MgO–SiO₂ catalysts for butadiene synthesis with the Lebedev process," *Green Chemistry*, V. 18, No. 6, 2016, pp. 1653–63.
148. Angelici, C., Velthoen, M. E. Z., Weckhuysen, B. M., et al. "Effect of Preparation Method and CuO Promotion in the Conversion of Ethanol into 1,3-Butadiene over SiO₂–MgO Catalysts," *ChemSusChem*, V. 7, No. 9, 2014, pp. 2505–15.
149. Patel, A. D., Meesters, K., Uil, H. den., et al. "Sustainability assessment of novel chemical processes at early stage: application to biobased processes," *Energy & Environmental Science*, V. 5, No. 9, 2012, pp. 8430–44.
150. Bhat, S. S., Waghmare, U. V., and Ramamurty, U. "First-Principles Study of Structure, Vibrational, and Elastic Properties of Stoichiometric and Calcium-Deficient Hydroxyapatite," *Crystal Growth & Design*, V. 14, No. 6, 2014, pp. 3131–41.
151. Agbeboh, N. I., Oladele, I. O., Daramola, O. O., et al. "Environmentally sustainable processes for the synthesis of hydroxyapatite," *Heliyon*, V. 6, No. 4, 2020, p. e03765.
152. Ferri, M., Campisi, S., Scavini, M., et al. "In-depth study of the mechanism of heavy metal trapping on the surface of hydroxyapatite," *Applied Surface Science*, V. 475, 2019, pp. 397–409.
153. Fihri, A., Len, C., Varma, R. S., et al. "Hydroxyapatite: A review of syntheses, structure and applications in heterogeneous catalysis," *Coordination Chemistry Reviews*, V. 347, 2017, pp. 48–76.
154. Silvester, L., Lamonier, J.-F., Vannier, R.-N., et al. "Structural, textural and acid–base properties of carbonate-containing hydroxyapatites," *Journal of Materials Chemistry A*, V. 2, No. 29, 2014, pp. 11073–90.
155. Dobosz, J., Hull, S., and Zawadzki, M. "Calcium Hydroxyapatite Supported Cobalt Catalysts for Ethanol Steam Reforming: Effect of the Incorporation Method of Active Phase," *Studia Universitatis Babeş-Bolyai Chimia*, V. 63, 2018, pp. 215–37.

156. Diallo-Garcia, S., Laurencin, D., Krafft, J.-M., et al. "Influence of Magnesium Substitution on the Basic Properties of Hydroxyapatites," *The Journal of Physical Chemistry C*, V. 115, No. 49, 2011, pp. 24317–27.
157. Robles-Águila, M. J., Reyes-Avendaño, J. A., and Mendoza, M. E. "Structural analysis of metal-doped (Mn, Fe, Co, Ni, Cu, Zn) calcium hydroxyapatite synthesized by a sol-gel microwave-assisted method," *Ceramics International*, V. 43, No. 15, 2017, pp. 12705–9.
158. Campisi, S., Galloni, M. G., Bossola, F., et al. "Comparative performance of copper and iron functionalized hydroxyapatite catalysts in NH₃-SCR," *Catalysis Communications*, V. 123, 2019, pp. 79–85.
159. Chen, G., Zheng, X., Wang, C., et al. "A postsynthetic ion exchange method for tunable doping of hydroxyapatite nanocrystals," *RSC Advances*, V. 7, No. 89, 2017, pp. 56537–42.
160. Ho, C. R., Zheng, S., Shylesh, S., et al. "The mechanism and kinetics of methyl isobutyl ketone synthesis from acetone over ion-exchanged hydroxyapatite," *Journal of Catalysis*, V. 365, 2018, pp. 174–83.
161. Pai, S., Kini, M. S., and Selvaraj, R. "A review on adsorptive removal of dyes from wastewater by hydroxyapatite nanocomposites," *Environmental Science and Pollution Research*, V. 28, No. 10, 2021, pp. 11835–49.
162. Galloni, M. G., Campisi, S., Marchetti, S. G., et al. "Environmental Reactions of Air-Quality Protection on Eco-Friendly Iron-Based Catalysts," *Catalysts*, V. 10, No. 12, 2020, p. 1415.
163. Kibby, C. L., and Hall, W. K. "Dehydrogenation of alcohols and hydrogen transfer from alcohols to ketones over hydroxyapatite catalysts," *Journal of Catalysis*, V. 31, No. 1, 1973, pp. 65–73.
164. Silvester, L., Lamonier, J.-F., Faye, J., et al. "Reactivity of ethanol over hydroxyapatite-based Ca-enriched catalysts with various carbonate contents," *Catalysis Science & Technology*, V. 5, No. 5, 2015, pp. 2994–3006.
165. Shuji Sakuma, Tsuchida, and Tetsuya Yoshioka "METHOD FOR PRODUCING COMPOSITION USING ALCOHOL AS STARTING MATERIAL." US 8,187,347 B2, 2012.
166. Lovón-Quintana, J. J., Rodríguez-Guerrero, J. K., and Valença, P. G. "Carbonate hydroxyapatite as a catalyst for ethanol conversion to hydrocarbon fuels," *Applied Catalysis A: General*, V. 542, 2017, pp. 136–45.
167. Tret'yakov, V. F., Makarfi, Yu. I., Tret'yakov, K. V., et al. "The catalytic conversion of bioethanol to hydrocarbon fuel: A review and study," *Catalysis in Industry*, V. 2, No. 4, 2010, pp. 402–20.
168. Han, Y., and Zhu, J. "Surface Science Studies on the Zirconia-Based Model Catalysts," *Topics in Catalysis*, V. 56, Nos. 15–17, 2013, pp. 1525–41.
169. Porter, D. L., and Heuer, A. H. "Microstructural development in MgO-partially stabilized zirconia (Mg-PSZ)," *Journal of the American Ceramic Society*, V. 62, Nos. 5–6, 1979, pp. 298–305.
170. Basahel, S. N., Ali, T. T., Mokhtar, M., et al. "Influence of crystal structure of nanosized ZrO₂ on photocatalytic degradation of methyl orange," *Nanoscale Research Letters*, V. 10, No. 1, 2015, p. 73.
171. Murase, Y., and Kato, E. "Role of Water Vapor in Crystallite Growth and Tetragonal-Monoclinic Phase Transformation of ZrO₂," *Journal of the American Ceramic Society*, V. 66, No. 3, 1983, pp. 196–200.
172. Nielsen, R. H., and Wilfing, G. "Zirconium and Zirconium Compounds." In: Wiley-VCH Verlag GmbH & Co. KGaA, ed. Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany, Wiley-VCH Verlag GmbH & Co. KGaA, 2010. p. a28_543.pub2.
173. Muñoz, M. C., Gallego, S., Beltrán, J. I., et al. "Adhesion at metal–ZrO₂ interfaces," *Surface Science Reports*, V. 61, No. 7, 2006, pp. 303–44.
174. Grau-Crespo, R., Hernández, N. C., Sanz, J. F., et al. "Theoretical Investigation of the Deposition of Cu, Ag, and Au Atoms on the ZrO₂ (111) Surface," *The Journal of Physical Chemistry C*, V. 111, No. 28, 2007, pp. 10448–54.
175. Teufer, G. "The crystal structure of tetragonal ZrO₂," *Acta Crystallographica*, V. 15, No. 11, 1962, pp. 1187–1187.
176. Smith, D. K., and Newkirk, W. "The crystal structure of baddeleyite (monoclinic ZrO₂) and its relation to the polymorphism of ZrO₂," *Acta Crystallographica*, V. 18, No. 6, 1965, pp. 983–91.
177. Pissenberger, A., and Gritzner, G. "Preparation and properties of niobia- and tantalum-doped orthorhombic zirconia," *Journal of Materials Science Letters*, V. 14, No. 22, 1995, pp. 1580–2.

178. Sugizaki, Y., Yamaguchi, S., Hashimoto, S., et al. "Neutron Diffraction Study on the Short-Range Order in $\text{ZrO}_{0.30}$ Interstitial Solid Solution," *Journal of the Physical Society of Japan*, V. 54, No. 7, 1985, pp. 2543–51.
179. Abriata, J. P., Garcés, J., and Versaci, R. "The O–Zr (Oxygen-Zirconium) system," *Bulletin of Alloy Phase Diagrams*, V. 7, No. 2, 1986, pp. 116–24.
180. Mercera, P. D. L., Van Ommen, J. G., Doesburg, E. B. M., et al. "Zirconia as a support for catalysts: Evolution of the texture and structure on calcination in air," *Applied Catalysis*, V. 57, No. 1, 1990, pp. 127–48.
181. Vlasenko, N. V., Kyriienko, P. I., Valihura, K. V., et al. "Yttria-Stabilized Zirconia as a High-Performance Catalyst for Ethanol to *n*-Butanol Guerbet Coupling," *ACS Omega*, V. 4, No. 25, 2019, pp. 21469–76.
182. Yamaguchi, T. "Application of ZrO_2 as a catalyst and a catalyst support," *Catalysis Today*, V. 20, No. 2, 1994, pp. 199–217.
183. Benedetti, A., Fagherazzi, G., and Pinna, F. "Preparation and Structural Characterization of Ultrafine Zirconia Powders," *Journal of the American Ceramic Society*, V. 72, No. 3, 1989, pp. 467–9.
184. Turlier, P., Dalmon, J. A., Martin, G. A., et al. "Non-porous stabilized ZrO_2 particles as support for catalysts," *Applied Catalysis*, V. 29, No. 2, 1987, pp. 305–10.
185. Zhang, W., Wang, Z., Huang, J., et al. "Zirconia-Based Solid Acid Catalysts for Biomass Conversion," *Energy & Fuels*, V. 35, No. 11, 2021, pp. 9209–27.
186. Campbell, C. T., and Peden, C. H. F. "Oxygen Vacancies and Catalysis on Ceria Surfaces," *Science*, V. 309, No. 5735, 2005, pp. 713–4.
187. Vlasenko, N. V., Kyriienko, P. I., Yanushevska, O. I., et al. "The Effect of Ceria Content on the Acid–Base and Catalytic Characteristics of ZrO_2 – CeO_2 Oxide Compositions in the Process of Ethanol to *n*-Butanol Condensation," *Catalysis Letters*, V. 150, No. 1, 2020, pp. 234–42.
188. Nakano, Y., Iizuka, T., Hattori, H., et al. "Surface properties of zirconium oxide and its catalytic activity for isomerization of 1-butene," *Journal of Catalysis*, V. 57, No. 1, 1979, pp. 1–10.
189. Apxuac, S., Aramendía, M. A., Hidalgo-Carrillo, J., et al. "Study of structure–performance relationships in Meerwein–Ponndorf–Verley reduction of crotonaldehyde on several magnesium and zirconium-based systems," *Catalysis Today*, V. 187, No. 1, 2012, pp. 183–90.
190. Vásquez, P. B., Tabanelli, T., Monti, E., et al. "Gas-Phase Catalytic Transfer Hydrogenation of Methyl Levulinate with Ethanol over ZrO_2 ," *ACS Sustainable Chemistry & Engineering*, V. 7, No. 9, 2019, pp. 8317–30.
191. Tai, J., and Davis, R. J. "Synthesis of methacrylic acid by aldol condensation of propionic acid with formaldehyde over acid–base bifunctional catalysts," *Catalysis Today*, V. 123, No. 1, 2007, pp. 42–9.
192. Angeles Aramendía, M., Boráu, V., Jiménez, C., et al. "Synthesis and characterization of ZrO_2 as an acid–base catalyst Dehydration–dehydrogenation of propan-2-ol," *Journal of the Chemical Society, Faraday Transactions*, V. 93, No. 7, 1997, pp. 1431–8.
193. Ferino, I., Casula, M. F., Corrias, A., et al. "4-Methylpentan-2-ol dehydration over zirconia catalysts prepared by sol-gel," *Physical Chemistry Chemical Physics*, V. 2, No. 8, 2000, pp. 1847–54.
194. Cutrufello, M. G., Ferino, I., Monaci, R., et al. "Acid-Base Properties of Zirconium, Cerium and Lanthanum Oxides by Calorimetric and Catalytic Investigation," *Topics in Catalysis*, V. 19, No. 3, 2002, pp. 225–40.
195. Tanabe, K., and Yamaguchi, T. "Acid-base bifunctional catalysis by ZrO_2 and its mixed oxides," *Catalysis Today*, V. 20, No. 2, 1994, pp. 185–97.
196. Comotti, M., Li, W.-C., Spliethoff, B., et al. "Support Effect in High Activity Gold Catalysts for CO Oxidation," *Journal of the American Chemical Society*, V. 128, No. 3, 2006, pp. 917–24.
197. Zhang, X., Shi, H., and Xu, B.-Q. "Comparative study of Au/ZrO_2 catalysts in CO oxidation and 1,3-butadiene hydrogenation," *Catalysis Today*, V. 122, No. 3, 2007, pp. 330–7.
198. Zhang, X., Wang, H., and Xu, B.-Q. "Remarkable Nanosize Effect of Zirconia in Au/ZrO_2 Catalyst for CO Oxidation," *The Journal of Physical Chemistry B*, V. 109, No. 19, 2005, pp. 9678–83.
199. Li, J., Ta, N., Song, W., et al. " Au/ZrO_2 catalysts for low-temperature water gas shift reaction: Influence of particle sizes," *Gold Bulletin*, V. 42, No. 1, 2009, pp. 48–60.

200. Pinna, F., Olivo, A., Trevisan, V., et al. "The effects of gold nanosize for the exploitation of furfural by selective oxidation," *Catalysis Today*, V. 203, 2013, pp. 196–201.
201. Zhang, X., Shi, H., and Xu, B.-Q. "Catalysis by Gold: Isolated Surface Au³⁺ Ions are Active Sites for Selective Hydrogenation of 1,3-Butadiene over Au/ZrO₂ Catalysts," *Angewandte Chemie*, V. 117, No. 43, 2005, pp. 7294–7.
202. B. Nagy., and W. Bradle. "The structural scheme of sepiolite," *The structural scheme of sepiolite*, V. 40, 1955, pp. 885–92.
203. Tian, G., Han, G., Wang, F., et al. "3 - Sepiolite Nanomaterials: Structure, Properties and Functional Applications." In: Wang, A., Wang, W., eds. *Nanomaterials from Clay Minerals*. Elsevier, 2019. pp. 135–201.
204. Jones, B. F., and Galan, E. "Chapter 16. SEPIOLITE AND Palygorskite." Chapter 16. *SEPIOLITE AND Palygorskite*. De Gruyter, 2018. pp. 631–74.
205. Galán, E., and Pozo, M. "Chapter 6 - Palygorskite and Sepiolite Deposits in Continental Environments. Description, Genetic Patterns and Sedimentary Settings." In: Galán, E., Singer, A., eds. *Developments in Clay Science*, vol. 3. Elsevier, 2011. pp. 125–73.
206. Galan, E., and Castillo, A. "Sepiolite - Palygorskite in Spanish Tertiary Basins: Genetical Patterns in Continental Environments**Presented at the International Clay Conference 1981." In: Singer, A., Galan, E., eds. *Developments in Sedimentology*, vol. 37. Elsevier, 1984. pp. 87–124.
207. Dutta, D. K. "9 - Clay mineral catalysts." In: Schoonheydt, R., Johnston, C. T., Bergaya, F., eds. *Developments in Clay Science*, vol. 9. Elsevier, 2018. pp. 289–329.
208. Dandy, A. J., and Nadiye-Tabbiruka, M. S. "Surface properties of sepiolite from Amboseli, Tanzania and its catalytic activity for ethanol decomposition," *Clays Clay Miner.*, V. 30, No. 5, 1982, pp. 347–52.
209. Berenguer, A. A., and Martin, C. B. "Process for bleaching and increasing the ion-exchange capability of sepiolite." US5051202A, 1991.
210. Mora, M., Isabel López, M., Ángeles Carmona, M., et al. "Study of the thermal decomposition of a sepiolite by mid- and near-infrared spectroscopies," *Polyhedron*, V. 29, No. 16, 2010, pp. 3046–51.
211. Kitayama, Y., and Abe, A. "Catalytic Conversion of Ethanol into 1,3-Butadiene over ZnO-supported Sepiolite," *Nippon Kagaku Kaishi*, V. 1989, No. 11, 1989, pp. 1824–9.
212. Suárez, M., and García-Romero, E. "Chapter 2 - Advances in the Crystal Chemistry of Sepiolite and Palygorskite." In: Galán, E., Singer, A., eds. *Developments in Clay Science*, vol. 3. Elsevier, 2011. pp. 33–65.
213. Duquesne, E., Moins, S., Alexandre, M., et al. "How can Nanohybrids Enhance Polyester/Sepiolite Nanocomposite Properties?," *Macromolecular Chemistry and Physics*, V. 208, No. 23, 2007, pp. 2542–50.
214. McCabe, R. W., and Adams, J. M. "Chapter 4.3 - Clay Minerals as Catalysts." In: Bergaya, F., Lagaly, G., eds. *Developments in Clay Science*, vol. 5. Elsevier, 2013. pp. 491–538.
215. Weir, M. R., Rutinduka, E., Detellier, C., et al. "Fabrication, characterization and preliminary testing of all-inorganic ultrafiltration membranes composed entirely of a naturally occurring sepiolite clay mineral," *Journal of Membrane Science*, V. 182, No. 1, 2001, pp. 41–50.
216. Nehra, R., Maiti, S. N., and Jacob, J. "Poly(lactic acid)/(styrene-ethylene-butylene-styrene)-g-maleic anhydride copolymer/sepiolite nanocomposites: Investigation of thermo-mechanical and morphological properties," *Polymers for Advanced Technologies*, V. 29, No. 1, 2018, pp. 234–43.
217. Chen, H., Zheng, M., Sun, H., et al. "Characterization and properties of sepiolite/polyurethane nanocomposites," *Materials Science and Engineering: A*, V. 445, 2007, pp. 725–30.
218. Dandy, A. J., and Nadiye-tabbiruka, M. S. "Surface Properties of Sepiolite from Amboseli, Tanzania, and Its Catalytic Activity for Ethanol Decomposition," n.d.
219. Hojati, S., and Hossein, K. "Thermal behavior of a natural sepiolite from northeastern Iran.," *Journal of Sciences, Islamic Republic of Iran*, V. 24, 2013, pp. 129–34.
220. Sarıkaya, Y., Önal, M., and Pekdemir, A. D. "Kinetic and thermodynamic approaches on thermal degradation of sepiolite crystal using XRD-analysis," *Journal of Thermal Analysis and Calorimetry*, V. 140, No. 6, 2020, pp. 2667–72.

221. Tian, G., Han, G., Wang, F., et al. "3 - Sepiolite Nanomaterials: Structure, Properties and Functional Applications." In: Wang, A., Wang, W., eds. *Nanomaterials from Clay Minerals*. Elsevier, 2019. pp. 135–201.
222. Rodriguez, M. A. V., Gonzalez, J. D. D. L., and Muñoz, M. A. B. "Acid activation of a Spanish sepiolite: physico-chemical characterization, free silica content and surface area of products obtained," *Clay Minerals*, V. 29, No. 3, 1994, pp. 361–7.
223. Myriam, M., Suárez, M., and Martín-Pozas, J. M. "Structural and Textural Modifications of Palygorskite and Sepiolite Under Acid Treatment," *Clays and Clay Minerals*, V. 46, No. 3, 1998, pp. 225–31.
224. Pérez Pariente, J., Fornés, V., Corma, A., et al. "The surface acidity and hydrothermal stability of sepiolite derivatives," *Applied Clay Science*, V. 3, No. 4, 1988, pp. 299–306.
225. Corma, A. C., Mifsud, A. C., and Perez, J. P. "Silicates with high ion exchange capacity derived from sepiolite and processes for their production." US4542002A, 1985.
226. Corma, A., and Martín-Aranda, R. M. "Alkaline-substituted sepiolites as a new type of strong base catalyst," *Journal of Catalysis*, V. 130, No. 1, 1991, pp. 130–7.
227. Corma, A., García, H., Leyva, A., et al. "Alkali-exchanged sepiolites containing palladium as bifunctional (basic sites and noble metal) catalysts for the Heck and Suzuki reactions," *Applied Catalysis A: General*, V. 257, No. 1, 2004, pp. 77–83.
228. Corma, A., and Martín-Aranda, R. M. "Application of solid base catalysts in the preparation of prepolymers by condensation of ketones and malononitrile," *Applied Catalysis A: General*, V. 105, No. 2, 1993, pp. 271–9.
229. Degirmenbasi, N., Boz, N., and Kalyon, D. M. "Biofuel production via transesterification using sepiolite-supported alkaline catalysts," *Applied Catalysis B: Environmental*, V. 150–151, 2014, pp. 147–56.
230. Kitayama, Y., and Michishita, A. "Catalytic activity of fibrous clay mineral sepiolite for butadiene formation from ethanol," *Journal of the Chemical Society, Chemical Communications*, No. 9, 1981, p. 401.
231. Gruver, V., Sun, A., and Fripiat, J. J. "Catalytic properties of aluminated sepiolite in ethanol conversion," *Catalysis Letters*, V. 34, No. 3, 1995, pp. 359–64.
232. Arundale, E., and Mikeska, L. A. "The Olefin-Aldehyde Condensation. The Prins Reaction.," *Chemical Reviews*, V. 51, No. 3, 1952, pp. 505–55.
233. Chen, M., Wang, C., Wang, Y., et al. "Hydrogen production from ethanol steam reforming: Effect of Ce content on catalytic performance of Co/Sepiolite catalyst," *Fuel*, V. 247, 2019, pp. 344–55.
234. Zilm, M. E., Chen, L., Sharma, V., et al. "Hydroxyapatite substituted by transition metals: experiment and theory," *Physical Chemistry Chemical Physics*, V. 18, No. 24, 2016, pp. 16457–65.
235. Matsumura, Y., Moffat, J. B., Sugiyama, S., et al. "Selective oxidative coupling of methane catalysed over hydroxyapatite ion-exchanged with lead," *Journal of the Chemical Society, Faraday Transactions*, V. 90, No. 14, 1994, pp. 2133–40.
236. Schiavoni, M., Campisi, S., Carniti, P., et al. "Focus on the catalytic performances of Cu-functionalized hydroxyapatites in NH₃-SCR reaction," *Applied Catalysis A: General*, V. 563, 2018, pp. 43–53.
237. Campisi, S., Galloni, M. G., Bossola, F., et al. "Comparative performance of copper and iron functionalized hydroxyapatite catalysts in NH₃-SCR," *Catalysis Communications*, V. 123, 2019, pp. 79–85.
238. Burton, A. W., Ong, K., Rea, T., et al. "On the estimation of average crystallite size of zeolites from the Scherrer equation: A critical evaluation of its application to zeolites with one-dimensional pore systems," *Microporous and Mesoporous Materials*, V. 117, Nos. 1–2, 2009, pp. 75–90.
239. Sasaki, T., Sakai, Y., Iizuka, A., et al. "Evaluation of the Capacity of Hydroxyapaptite Prepared from Concrete Sludge to Remove Lead from Water," *Industrial & Engineering Chemistry Research*, V. 50, No. 16, 2011, pp. 9564–8.
240. Okada, M., Fujiwara, K., Uehira, M., et al. "Expansion of nanosized pores in low-crystallinity nanoparticle-assembled plates via a thermally induced increase in solid-state density," *Journal of Colloid and Interface Science*, V. 405, 2013, pp. 58–63.

241. "Investigation of HA Nanocrystallite Size Crystallographic Characterizations in NHA, BHA and HA Pure Powders and their Influence on Biodegradation of HA | Scientific.Net." Available at: <https://www.scientific.net/AMR.829.314>.
242. Locardi, B., Pazzaglia, U. E., Gabbi, C., et al. "Thermal behaviour of hydroxyapatite intended for medical applications," *Biomaterials*, V. 14, No. 6, 1993, pp. 437–41.
243. Kumari, L., Li, W., and Wang, D. "Monoclinic zirconium oxide nanostructures synthesized by a hydrothermal route," *Nanotechnology*, V. 19, No. 19, 2008, p. 195602.
244. Corma, A., Fornés, V., Juan-Rajadell, M. I., et al. "Influence of preparation conditions on the structure and catalytic properties of SO₄²⁻/ZrO₂ superacid catalysts," *Applied Catalysis A: General*, V. 116, No. 1, 1994, pp. 151–63.
245. Corma, A., Nieto, J. M. L., and Paredes, N. "Influence of the Preparation Methods of V-Mg-O Catalysts on Their Catalytic Properties for the Oxidative Dehydrogenation of Propane," *Journal of Catalysis*, V. 144, No. 2, 1993, pp. 425–38.
246. Gauna, M., Conconi, S., Gómez, S., et al. "Monoclinic-tetragonal zirconia quantification of commercial nanopowder mixtures by XRD and DTA," *Ceramics Silikaty*, V. 59, 2015, pp. 318–25.
247. Gardiner, D. J. "Introduction to Raman Scattering." In: Gardiner, D. J., Graves, P. R., eds. *Practical Raman Spectroscopy*. Berlin, Heidelberg, Springer, 1989. pp. 1–12.
248. Skoog, D. A., Holler, F. J., and Crouch, S. R. "Principles of Instrumental Analysis," 6th edition, Belmont, CA, Cengage Learning, 2006, 1056 pp.
249. Ebnesajjad, S. "Surface and Material Characterization Techniques." *Surface Treatment of Materials for Adhesive Bonding*. Elsevier, 2014. pp. 39–75.
250. Neikov, O. D., and Yefimov, N. A. "Powder Characterization and Testing." *Handbook of Non-Ferrous Metal Powders*. Elsevier, 2019. pp. 3–62.
251. Colpan, C. O., Nalbant, Y., and Ercelik, M. "4.28 Fundamentals of Fuel Cell Technologies." *Comprehensive Energy Systems*. Elsevier, 2018. pp. 1107–30.
252. Srinivasan, P. D., Nitz, S. R., Stephens, K. J., et al. "Modified Harrick reaction cell for in situ/operando fiber optics diffuse reflectance UV–visible spectroscopic characterization of catalysts," *Applied Catalysis A: General*, V. 561, 2018, pp. 7–18.
253. Hummel, R. e. "Differential Reflectance Spectroscopy in Analysis of Surfaces." *Encyclopedia of Analytical Chemistry*. John Wiley & Sons, Ltd, 2006.
254. Benomar, S., Chieriegato, A., Masso, A., et al. "Al₂O₃-Supported W–V–O bronze catalysts for oxidative dehydrogenation of ethane," *Catalysis Science & Technology*, V. 10, No. 23, 2020, pp. 8064–76.
255. Costa, E., Uguina, A., Aguado, J., et al. "Ethanol to gasoline process: effect of variables, mechanism, and kinetics," *Industrial & Engineering Chemistry Process Design and Development*, V. 24, No. 2, 1985, pp. 239–44.
256. Wang, W.-C., and Tao, L. "Bio-jet fuel conversion technologies," *Renewable and Sustainable Energy Reviews*, V. 53, 2016, pp. 801–22.
257. Brasil, H., Bittencourt, A. F. B., Yokoo, K. C. E. S., et al. "Synthesis modification of hydroxyapatite surface for ethanol conversion: The role of the acidic/basic sites ratio," *Journal of Catalysis*, No. 404, 2021, pp. 802–13.
258. Hanspal, S., Young, Z. D., Prillaman, J. T., et al. "Influence of surface acid and base sites on the Guerbet coupling of ethanol to butanol over metal phosphate catalysts," *Journal of Catalysis*, V. 352, 2017, pp. 182–90.
259. Liao, C.-J., Lin, F.-H., Chen, K.-S., et al. "Thermal decomposition and reconstitution of hydroxyapatite in air atmosphere," *Biomaterials*, V. 20, No. 19, 1999, pp. 1807–13.
260. Tönsuaadu, K., Gross, K. A., Plüdduma, L., et al. "A review on the thermal stability of calcium apatites," *Journal of Thermal Analysis and Calorimetry*, V. 110, No. 2, 2012, pp. 647–59.
261. Khachani, M., Kacimi, M., Ensueque, A., et al. "Iron–calcium–hydroxyapatite catalysts: Iron speciation and comparative performances in butan-2-ol conversion and propane oxidative dehydrogenation," *Applied Catalysis A: General*, V. 388, No. 1, 2010, pp. 113–23.
262. Sasidharan, M., Hegde, S. G., and Kumar, R. "Surface acidity of Al-, Ga- and Fe-silicate analogues of zeolite NCL-1 characterized by FTIR, TPD (NH₃) and catalytic methods," *Microporous and Mesoporous Materials*, V. 24, No. 1, 1998, pp. 59–67.

263. Lovón-Quintana, J. J., Rodriguez-Guerrero, J. K., and Valença, P. G. "Carbonate hydroxyapatite as a catalyst for ethanol conversion to hydrocarbon fuels," *Applied Catalysis A: General*, V. 542, 2017, pp. 136–45.
264. Rodrigues, E. G., Keller, T. C., Mitchell, S., et al. "Hydroxyapatite, an exceptional catalyst for the gas-phase deoxygenation of bio-oil by aldol condensation," *Green Chemistry*, V. 16, No. 12, 2014, pp. 4870–4.
265. Silvester, L., Lamonier, J.-F., Lamonier, C., et al. "Guerbet Reaction over Strontium-Substituted Hydroxyapatite Catalysts Prepared at Various (Ca+Sr)/P Ratios," *ChemCatChem*, V. 9, No. 12, 2017, pp. 2250–61.
266. A. Uslamin, E., Saito, H., Kosinov, N., et al. "Aromatization of ethylene over zeolite-based catalysts," *Catalysis Science & Technology*, V. 10, No. 9, 2020, pp. 2774–85.
267. Tret'yakov, V. F., Makarfi, Yu. I., Tret'yakov, K. V., et al. "The catalytic conversion of bioethanol to hydrocarbon fuel: A review and study," *Catalysis in Industry*, V. 2, No. 4, 2010, pp. 402–20.
268. Tsuchida, T., Sakuma, S., Takeguchi, T., et al. "Direct Synthesis of n-Butanol from Ethanol over Nonstoichiometric Hydroxyapatite," *Industrial & Engineering Chemistry Research*, V. 45, No. 25, 2006, pp. 8634–42.
269. Pilusa, T. J., and Muzenda, E. "Pyrolytic Tyre Derived Fuel: A Review," 2013.
270. Angelici, C., Meirer, F., van der Eerden, A. M. J., et al. "Ex Situ and Operando Studies on the Role of Copper in Cu-Promoted SiO₂–MgO Catalysts for the Lebedev Ethanol-to-Butadiene Process," *ACS Catalysis*, V. 5, No. 10, 2015, pp. 6005–15.
271. "Hydroxyapatite and Nonstoichiometric Apatites." *Studies in Inorganic Chemistry*, vol. 18. Elsevier, 1994. pp. 111–89.
272. Gorsd, M., Pizzio, L., and Blanco, M. "Trifluoromethanesulfonic acid immobilized on zirconium oxide obtained by the sol–gel method as catalyst in paraben synthesis," *Applied Catalysis A: General*, V. 400, No. 1, 2011, pp. 91–8.
273. Silva, G. L. J. P. da., Silva, M. L. C. P. da., and Caetano, T. "Preparation and Characterization of Hydrous Zirconium Oxide Formed by Homogeneous Precipitation," *Materials Research*, V. 5, 2002, pp. 149–53.
274. Dahman, Y. "Chapter 6 - Nanopolymers**By Yaser Dahman, Kevin Deonanan, Timothy Dontos, and Andrew Iammatteo." In: Dahman, Y., ed. *Nanotechnology and Functional Materials for Engineers*. Elsevier, 2017. pp. 121–44.
275. Basahel, S. N., Ali, T. T., Mokhtar, M., et al. "Influence of crystal structure of nanosized ZrO₂ on photocatalytic degradation of methyl orange," *Nanoscale Research Letters*, V. 10, No. 1, 2015, p. 73.
276. Rothenberg, G. "Catalysis: concepts and green applications," Weinheim, WILEY-VCH, 2008, 279 pp.
277. Srinivasan, R., De Angelis, R. J., Ice, G., et al. "Identification of tetragonal and cubic structures of zirconia using synchrotron x-radiation source," *Journal of Materials Research*, V. 6, No. 6, 1991, pp. 1287–92.
278. Chervin, C. N., Clapsaddle, B. J., Chiu, H. W., et al. "Aerogel Synthesis of Ytria-Stabilized Zirconia by a Non-Alkoxide Sol–Gel Route," *Chemistry of Materials*, V. 17, No. 13, 2005, pp. 3345–51.
279. Mohsenzadeh, A., Zamani, A., and Taherzadeh, M. J. "Bioethylene Production from Ethanol: A Review and Techno-economical Evaluation," *ChemBioEng Reviews*, V. 4, No. 2, 2017, pp. 75–91.
280. Gabriëls, D., Hernández, W. Y., Sels, B., et al. "Review of catalytic systems and thermodynamics for the Guerbet condensation reaction and challenges for biomass valorization," *Catalysis Science & Technology*, V. 5, No. 8, 2015, pp. 3876–902.
281. Jones, M. D. "Catalytic transformation of ethanol into 1,3-butadiene," *Chemistry Central Journal*, V. 8, No. 1, 2014, p. 53.
282. Corma, A., and Perez-Pariente, J. "Catalytic activity of modified silicates: I. Dehydration of ethanol catalysed by acidic sepiolite," *Clay Minerals*, V. 22, No. 4, 1987, pp. 423–33.
283. Mora, M., Isabel López, M., Ángeles Carmona, M., et al. "Study of the thermal decomposition of a sepiolite by mid- and near-infrared spectroscopies," *Polyhedron*, V. 29, No. 16, 2010, pp. 3046–51.

284. Ndou, A. "Dimerisation of ethanol to butanol over solid-base catalysts," *Applied Catalysis A: General*, V. 251, No. 2, 2003, pp. 337–45.
285. Hojati, S., and Khademi, H. "Thermal Behavior of a Natural Sepiolite from Northeastern Iran," *Journal of Sciences, Islamic Republic of Iran*, V. 24, No. 2, 2013, pp. 129–34.
286. d'Azevedo, C. A., Garrido, F. M. S., and Medeiros, M. E. "The effect of mechanochemical activation on the reactivity in the MgO–Al₂O₃–SiO₂ system," *Journal of Thermal Analysis and Calorimetry*, V. 83, No. 3, 2006, pp. 649–55.
287. Nagaraja, B. M., Siva Kumar, V., Shashikala, V., et al. "Effect of method of preparation of copper – magnesium oxide catalyst on the dehydrogenation of cyclohexanol," *Journal of Molecular Catalysis A: Chemical*, V. 223, No. 1, 2004, pp. 339–45.
288. Putanov, P., Kis, E., Boskovic, G., et al. "Effects of the method of preparation of MgC₂O₄ as a support precursor on the properties of iron/magnesium oxide catalysts," *Applied Catalysis*, V. 73, No. 1, 1991, pp. 17–26.
289. Sing, K. S. W. "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984)," *Pure and Applied Chemistry*, V. 57, No. 4, 1985, pp. 603–19.
290. Walczyk, A., Michalik, A., Napruszewska, B. D., et al. "New insight into the phase transformation of sepiolite upon alkali activation: Impact on composition, structure, texture, and catalytic/sorptive properties," *Applied Clay Science*, V. 195, 2020, p. 105740.
291. Di Cosimo, J. I., Apesteguia, C. R., Ginés, M. J. L., et al. "Structural Requirements and Reaction Pathways in Condensation Reactions of Alcohols on Mg_yAlO_x Catalysts," *Journal of Catalysis*, V. 190, No. 2, 2000, pp. 261–75.
292. Cimino, S., Lisi, L., and Romanucci, S. "Catalysts for conversion of ethanol to butanol: Effect of acid-base and redox properties," *Catalysis Today*, V. 304, 2018, pp. 58–63.
293. Busca, G. "The surface acidity of solid oxides and its characterization by IR spectroscopic methods. An attempt at systematization," *Physical Chemistry Chemical Physics*, V. 1, No. 5, 1999, pp. 723–36.
294. Sun, Z., Vasconcelos, A. C., Bottari, G., et al. "Efficient Catalytic Conversion of Ethanol to 1-Butanol via the Guerbet Reaction over Copper- and Nickel-Doped Porous," *ACS Sustainable Chemistry & Engineering*, V. 5, No. 2, 2017, pp. 1738–46.
295. Gotoh, K., Nakamura, S., Mori, T., et al. "Supported alkali salt catalysts active for the guerbet reaction between methanol and ethanol." *Studies in Surface Science and Catalysis*, vol. 130. Elsevier, 2000. pp. 2669–74.
296. Kayanuma, M., Shinke, Y., Miyazawa, T., et al. "Theoretical study of the side reactions of the catalytic conversion of ethanol to butadiene on metal oxide catalysts," *Catalysis Communications*, V. 149, 2021, p. 106239.
297. Veibel, S., and Nielsen, J. I. "On the mechanism of the Guerbet reaction," *Tetrahedron*, V. 23, No. 4, 1967, pp. 1723–33.
298. Ogo, S., Onda, A., Iwasa, Y., et al. "1-Butanol synthesis from ethanol over strontium phosphate hydroxyapatite catalysts with various Sr/P ratios," *Journal of Catalysis*, V. 296, 2012, pp. 24–30.
299. Hathaway, P. E., and Davis, M. E. "Base catalysis by alkali modified zeolites: III. Alkylation with methanol," *Journal of Catalysis*, V. 119, No. 2, 1989, pp. 497–507.
300. Taifan, W. E., Bučko, T., and Baltrusaitis, J. "Catalytic conversion of ethanol to 1,3-butadiene on MgO: A comprehensive mechanism elucidation using DFT calculations," *Journal of Catalysis*, V. 346, 2017, pp. 78–91.
301. Pomalaza, G., Ponton, P. A., Capron, M., et al. "Ethanol-to-butadiene: the reaction and its catalysts," *Catalysis Science & Technology*, V. 10, No. 15, 2020, pp. 4860–911.
302. Chiericato, A., Velasquez Ochoa, J., Bandinelli, C., et al. "On the chemistry of ethanol on basic oxides: revising mechanisms and intermediates in the Lebedev and Guerbet reactions," *ChemSusChem*, V. 8, No. 2, 2015, pp. 377–88.
303. Bravo-Suárez, J. J., Subramaniam, B., and Chaudhari, R. V. "Ultraviolet–Visible Spectroscopy and Temperature-Programmed Techniques as Tools for Structural Characterization of Cu in CuMgAlO_x Mixed Metal Oxides," *The Journal of Physical Chemistry C*, V. 116, No. 34, 2012, pp. 18207–21.

304. Negri, C., Signorile, M., Porcaro, N. G., et al. "Dynamic CuI/Cu⁰ speciation in Cu-CHA catalysts by in situ Diffuse Reflectance UV-vis-NIR spectroscopy," *Applied Catalysis A: General*, V. 578, 2019, pp. 1–9.
305. Shimizu, K., Maeshima, H., Yoshida, H., et al. "Spectroscopic characterisation of Cu–Al₂O₃ catalysts for selective catalytic reduction of NO with propene," *Physical Chemistry Chemical Physics*, V. 2, No. 10, 2000, pp. 2435–9.
306. Goetze, J., Meirer, F., Yarulina, I., et al. "Insights into the Activity and Deactivation of the Methanol-to-Olefins Process over Different Small-Pore Zeolites As Studied with Operando UV-vis Spectroscopy," *ACS Catalysis*, V. 7, No. 6, 2017, pp. 4033–46.
307. Hemelsoet, K., Qian, Q., De Meyer, T., et al. "Identification of Intermediates in Zeolite-Catalyzed Reactions by In Situ UV/Vis Microspectroscopy and a Complementary Set of Molecular Simulations," *Chemistry – A European Journal*, V. 19, No. 49, 2013, pp. 16595–606.
308. Konnov, S. V., Pavlov, V. S., Kots, P. A., et al. "Mechanism of SAPO-34 catalyst deactivation in the course of MTO conversion in a slurry reactor," *Catalysis Science & Technology*, V. 8, No. 6, 2018, pp. 1564–77.
309. López-Curiel, J. C., Hernández-Salgado, G. I., Hernández-Terán, M. E., et al. "On the Structure-Activity Relationship for NO-SCR with NH₃ Catalyzed by Cu-exchanged Natural Chabazite and SSZ-13," *Journal of the Mexican Chemical Society*, V. 65, No. 1, 2021, pp. 74–83.
310. Pestryakov, A. N., Petranovskii, V. P., Kryazhov, A., et al. "Study of copper nanoparticles formation on supports of different nature by UV-Vis diffuse reflectance spectroscopy," *Chemical Physics Letters*, V. 385, No. 3, 2004, pp. 173–6.
311. Inaba, M., Murata, K., Saito, M., et al. "Ethanol conversion to aromatic hydrocarbons over several zeolite catalysts," *Reaction Kinetics and Catalysis Letters*, V. 88, No. 1, 2006, pp. 135–41.
312. Ghashghaee, M. "Heterogeneous catalysts for gas-phase conversion of ethylene to higher olefins," *Reviews in Chemical Engineering*, V. 34, No. 5, 2018, pp. 595–655.
313. Morris, J. C. "The Thermal Decomposition of Acetaldehyde," *Journal of the American Chemical Society*, V. 66, No. 4, 1944, pp. 584–9.
314. Gil-Av, E., Shabtai, J., and Steckel, F. "Thermal Aromatization of 1,3-Butadiene," *Industrial & Engineering Chemistry*, V. 52, No. 1, 1960, pp. 31–2.
315. Tsuchida, T., Yoshioka, T., Sakuma, S., et al. "Synthesis of Biogasoline from Ethanol over Hydroxyapatite Catalyst," *Industrial & Engineering Chemistry Research*, V. 47, No. 5, 2008, pp. 1443–52.
316. Toussaint, W. J., and Dunn, J. T. "Process for making diolefins." US2421361A, 1947.
317. Baylon, R. A. L., Sun, J., and Wang, Y. "Conversion of ethanol to 1,3-butadiene over Na doped Zn_xZr_yO₂ mixed metal oxides," *Catalysis Today*, V. 259, 2016, pp. 446–52.
318. Kourtakis, K., D'Amore, M. B., and Manzer, L. E. "Catalytic conversion of ethanol to a 1-butanol-containing reaction product using a thermally decomposed hydrotalcite catalyst." US20090054705A1, 2009.
319. Baloyi, J., Ntho, T., and Moma, J. "Synthesis and application of pillared clay heterogeneous catalysts for wastewater treatment: a review," *RSC Advances*, V. 8, No. 10, 2018, pp. 5197–211.