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New catalytic processes for the upgrading of furfural and 5-hydroxymethylfurfural to chemicals and fuels

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Abstract

The demand of energy, fuels and chemicals is increasing due to the strong growth of some countries in the developing world and the development of the world economy. Unfortunately, the general picture derived sparked an exponential increase in crude oil prices with a consequent increase of the chemical, by-products and energy, depleting the global market. Nowadays biomass are the most promising alternative to fossil fuels for the production of chemicals and fuels.

In this work, the development of three different catalytic processes for the valorization of biomass-derived has been investigated.

5-hydroxymethylfurfural oxidation was studied under mild reaction condition using gold and gold/copper based catalysts synthetized from pre-formed nanoparticles and supported onto TiO_2 and CeO_2.

The analysis conducted on catalysts showed the formation of alloys gold/copper and a strong synergistic effect between the two metals. For this reason the bimetallic catalysts supported on titania showed a higher catalytic activity respect to the monometallic catalysts.

The process for the production of 2,5-bishydroxymethyl furan (BHMF) was also optimized by means the 5-hydroxymethylfurfural hydrogenation using the Shvo complex. Complete conversion of HMF was achieved working at 90 °C and 10 bar of hydrogen. The complex was found to be re-usable for at least three catalytic cycles without suffering any type of deactivation.

Finally, the hydrogenation of furfural and HMF was carried out, developing the process of hydrogen transfer by using MgO as a catalyst and methanol as a hydrogen donor. Quantitative yields to alcohols have been achieved in a few hours working in mild condition: 160 °C and at autogenous pressure. The only by-products formed were light products such as CO, CO_2 and CH_4 (products derived from methanol transformation), easily separable from the reaction solution depressurizing the reactor.

Chapter 1

1 Aim of the work

In the XXI century the main issues related to the use of fossil fuels for the production of energy and chemicals are essentially their limited availability (non-renewable) and chemical pollution derived from their use. Currently, the greenhouse effect, increased by the massive use of these non-renewable resources (CO_2 production), is one of the most important world's problems. The demand for energy, fuels and chemicals is increasing due to the strong growth of some countries in the developing world and the development of the world economy. Unfortunately, the general picture derived sparked an exponential increase in crude oil prices with a consequent increase of the chemical by-products and energy, depleting the global market.

Nowadays biomass are the most promising alternative to fossil fuels for the production of chemicals and fuels.

The production of energy from biomass, in addition to being a renewable source, generates fewer greenhouse gas emissions compared to fossil fuels, because the CO_2 released is consumed in the process of growth of the biomass itself.

The use of biomass has sparked several controversies regarding ethical issues, for example the production of bio-ethanol used as raw materials mainly beet and sugar cane. The problems derived from the use of these feedstock are substantially two: the use of edible biomass and exploitation of arable land for the production of fuels and chemicals and the use of large amounts of water to allow a fast growth of the biomass and consequently a greater energy production.

For these reason, today, the research is moving towards the use of biomass derived from land not cultivable and inedible raw materials such as ligno-cellulosic biomass.

Ligno-cellulosic biomass is most abundantly raw material on the earth and it is composed of carbohydrates polymers (cellulose, hemicellulose) and an aromatic polymer (lignin).

Ligno-cellulosic residues from agriculture and/or sawmill can be using to produce furfural and HMF. Furfural and HMF represent a fundamental building blocks for the biorefinery, seeing as their production are environmentally sustainable and the economically feasible and they can be used as a platform molecules for the production of a large amount of chemicals, fuels and fuels additives.

Nowadays, the chemical processes used for the enhancement of these two chemicals are numerous, but very often they are economically unfavorable, for example due to the use of a large amounts of catalyst or the use of strong acid conditions, and with a high environmental impact, in fact, the use of homogeneous catalysts and large amounts of organic solvents are used in many processes.

For these reasons, the aim of my work was the development of new catalytic processes to convert HMF and furfural into chemicals through economic processes with low environmental impact.

In particular, my work has focused on:

- the 5-hydroxymethylfurfural (HMF) oxidation to 2,5-furandicarboxylic acid (FDCA) in liquid phase (water) using gold and gold/copper nanoparticles supported on TiO_2 and CeO_2. The nanoparticles synthesis was optimize by means the use of glucose and NaOH as reductant agents and PVP as stabilizer to make the process with low environmental impact.

- the HMF hydrogenation to 2,5-bishydroxymethyl furan (BHMF) alcohol using the Shvo catalyst in both homogeneous and biphasic reaction mixtures. The catalyst behavior, stoichiometric batch reactions followed by NMR, IR and ESI-MS experiments supported by DFT calculations were carried out.

- the furfural hydrogenation to furfuryl alcohol in liquid phase using magnesium oxide (derived from hydrotalcite-type precursor) as base catalyst and methanol as hydrogen donor in inert atmosphere.

Chapter 2

2 Introduction

During the second half of 20th century the consumption of petroleum has grown considerably due to the birth of new economical world powers like China, India and Brazil, the continue increase of the energy demand and mainly of the rise of the automobile industry. According to a Shell study, the number of cars on the road is expected to triple by 2050[1]. At the same time, the reserve of this non-renewable resource is declining. Several studies have demonstrated that the oil reserve will be sufficient to ensure the energy and chemical demand for only about another 40 years[2] even if today, fossil fuels such as coal, oil, and natural gas provide more than 75% of the world's energy. For all these reasons, in the recent years, the oil price has risen a lot[3].

The use of oil as energy source is also producing a large amount of CO_2 (one of the main greenhouses gas) and it has contributed to the global warming. It is necessary to reduce the CO_2 emissions to avoid serious climate change. Today, the world needs all the sustainable transport fuel options available to help meet this growing demand, with fewer CO_2 emissions. In 2011, the direct greenhouses gas emissions from facilities were 74 million tons on a CO_2-equivalent basis, a decrease of 3% from 2010. The main reasons for this slight drop were divestments in downstream business but more government actions are needed, encouraging the use of all CO_2-reducing technologies.

Biomass can represent a valid alternative to produce fuels and chemicals, moreover for our industrial society, it can be a sustainable resource of energy and organic carbon.

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[1] www.shell.com

[2] BP Statistical Review of Energy, **2006** http//www.bp.com/liveassets/bp_internet/globalbp/globalbp_uuk_English/publications/energy_reviews_2006/STAGING/local_assets/downloads/powerpoint/statistical_review_full_report_slidepack_2006.ppt;

[3] M.J. Climent, A. Corma and S. Iborra, *Green Chemistry*, **2011**, 13, 520;

Energy production from biomass produces a lower total greenhouses gas emission because, for example, CO_2 generated during oxidation processes of biofuel is utilized in the process of growth of same biomass.

Today, 85% of crude oil is used for the production of fuels, while only 10% is used for chemicals, therefore the valorization of renewable source into fuels will be a very interesting way to control all the problems caused by greenhouses gas emissions. However, from biomass, it also possible to produce numerous building blocks for the fine chemistry and the work of the chemists will be to find new pathways to convert biomass, through economic processes with low environmental impact.

For this reason, in this period, a lot of investments by chemistry departments are made for the search in the treatment and conversion of biomass. A report written by several researchers (Roadmap for Biomass Technologies) has predicted that by 2030, 20% of fuel and 25% of chemicals will be produced form biomass[4].

US Department of Energy (DOE) and the US Department of Agriculture (DA) have predicted that to achieve these targets the US should produce 1.3 billion dry tons of biomass per year[5].

2.1 Use of biomass

Biomass is the biodegradable fraction of products, waste and residues from biological origin, agriculture (including vegetal and animal substances), forestry, as well as the biodegradable fraction of industrial and municipal waste[6].

As already mentioned, biomass and fuels derived from them emit into the atmosphere, during their combustion, an amount of carbon dioxide more or less corresponding to that which is absorbed, previously, by the plants during their growth process. Other mainly environmental benefits of biomass are:

- Biodegradability;

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[4] *The Roadmap for Biomass Technologies in the U.S.*, Biomass R&D Technical Advisory Committee, US Departement of Energy, Accession No ADA 436527, **2002**;

[5] R. D. Perlack, L. L. Wright, A. Turhollow, R. L. Graham, B. Stokes, D. C. Erbach, *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*, Report No. DOE/GO-102995-2135; Oak Ridge National Laboratory, Oak Ridge, TN, **2005**;

[6] European directive 2009/28/CE;

- Absence of nitrogen and sulfur oxides and particulate in the fumes emit during their oxidation.

Unfortunately there are also many disadvantages related to biomass:

- Need large growing areas due to their low energy density;
- Need to use fertilizers;
- Logistic problems for the supply of the resource;
- Problems of environmental conditions/weather;
- Annual productions are not constant.

For these reasons, at the current state of technology, the only biofuels produced and used on a large scale are vegetable oils, when used directly as such (typically for powering agricultural machinery) or chemically transformed into a mixture of esters commonly known with the name of biodiesel, and the ethanol (or bio-ethanol) and its synthetic derivatives. In recent years also bio-methane was added to these, produced by anaerobic fermentation of livestock waste, residues and agro-industrial waste and dedicated crops (mainly corn). The latter is mainly used for powering buses used for public transport.

Biofuel include a broad and diverse range of liquids or gases can be used as alternative fuels in the transport sector and derived from biomass, thus all materials of organic origin (plant or animal) that haven’t undergone any process of fossilization.

These products are blended in increasing percentages, but overall still limited, with gasoline and diesel. In this way, there isn’t a competition between the need of the companies cars to not modify the engine or other motor vehicle components and the safety of the oil groups to introduce high quality products on the market.

Biofuels are classified as first-generation biofuels, second generation and third generation. The classification depends on the raw material used and the production process.

First-generation biofuels are considered those produced from agricultural raw materials while second-generation and third generation biofuels are considered those produced by non-food organic material whose use has no impact on the food chain (eg biofuels from lingo-cellulosic or algae). Unfortunately, today the industrial processes currently developed for the production of biofuels of second and third generation are much less than those of first.

In fact, the pursuit of biofuels has triggered a spiral of rising prices of agricultural grains, such as soybeans and corn (crops used for the production of biofuels), and it had a strong impact on access to land, to water and to income by local communities. Between the season 2004/2005 and 2008/2009, the overall global raw grains demand has increased from 979.9 million tons to 1096 (+11.85%). In this period, while the demand for food grains has remained essentially unchanged, that of non-food grains has increased from 179.2 million tons to 275.3 million (+53.62%). To get an idea of the growing influence of the application of these energy sources on the market of food, it has to consider that two-thirds of global corn production have been converted into bioethanol between 2003 and 2007[7].

In terms of prices, the cost of most food has considerably increased, registering an increase of 83% between 2006 and the beginning of 2008, resulting in an increase of people suffering from hunger by more than 100 million in 2008 alone. It is estimated that to meet today's global demand for biofuels is necessary to use more than 100 million hectares of agricultural land (about 7% of all arable land and permanent crops that occupied by the planet). Europe alone for biofuels necessary to achieve the target of 10% in the transport sector would need an area equal to two times as Belgium.

To cultivate any plant used for the production of biofuel requires arable land, and then subtract surface to other crops. In economic terms, increasing the hectares used for the production of biofuel at the expense of extending the area under cultivation for human consumption, the amount of food available in the market decreases by supporting the trend of prices.

Thus is it right to utilize agricultural raw materials to produce biofuels and chemicals?

Today, the research is moving towards the use of biomass derived from land not cultivable and inedible raw materials: ligno-cellulosic biomass.

170 billion metric tons of biomass per year are produced by nature and carbohydrates represent the 75%. Surprisingly, humans utilize only 3-4% of these compounds for food and non-food purpose[8]. Biomass carbohydrates are the most abundant renewable

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[7] www.actionaid.it

[8] Roper H., *Starch-Starke*, **2002**, 54, 89;

resources available, and they are currently viewed as a feedstock for the green chemistry of the future[9,10].

2.2 Ligno-cellulosic biomass

Ligno-cellulosic is referred to plant dry matter. It is most abundantly raw material on the earth for the production of chemicals and biofuels. Mainly it is composed of carbohydrates polymers (cellulose, hemicellulose) and an aromatic polymer (lignin). This ligno-cellulosic biomass can be grouped into four main categories: *agricultural residues* (including corn straw, sugarcane residue (bagasse), etc.), *dedicated energy crops* (poplar trees and Miscanthus giganteus), *wood residues* (including saw mill and paper mill discards) and *municipal paper waste.*

2.2.1 Cellulose

Cellulose is part of the family of polysaccharides. It is certainly the biopolymer present in greater amounts throughout the globe.

It consists of a large number of molecules of glucose (from about 7000 to 15000 units) linked together by a linear bond β (1 → 4) glycosidic[11] (Figure 1).

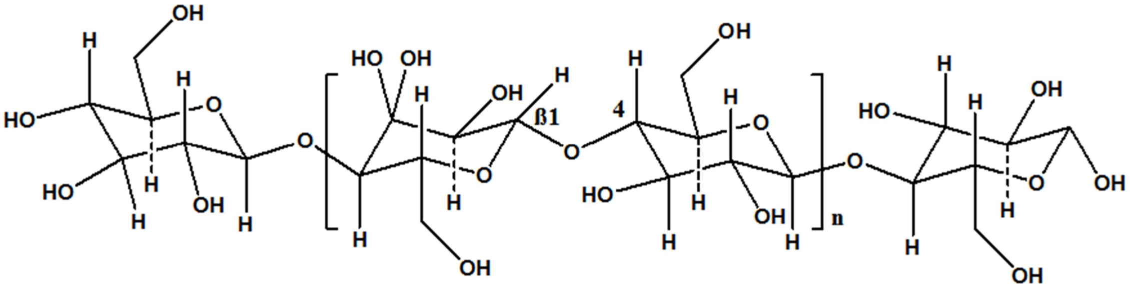

Figure 1. Cellulose

The particular bond present between the glucose units of cellulose gives some important characteristics:

- High hydrophilic character;

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[9] Lichtenthaler F. W., *Acc. Chem. Res.*, **2002**, 35, 728;

[10] Lichtenthaler F. W., *Carbohydr. Res.*, **1998**, 313, 69;

[11] Gandini A., *Green Chem.*, **2011**, 13, 1061;

- High superficial energy;
- Biodegradable;
- Low temperature resistance (degradation temperature is higher than melting point);
- High reactivity (mainly due to the presence of three hydroxyl groups in every glycosidic unit).

The main peculiarity of cellulose is represented by its ability to crystallize forming hydrogen bonds between numerous monomers.

Generally, cellulose tends to form more crystalline structure generating a fibrous matrix chemically inert.

In nature, cellulose is in the form of fibers and its main task is to provide mechanical strength to the plant structure. Often it incorporates lignin and hemicellulose giving reinforcing and compatibilizer properties.

The isolation of cellulose from lignin and hemicellulose is carried out during the traditional process of manufacturing the pulp in the paper industry and in typical processes of the integrated biorefinery.

2.2.2 Starch

Similar to cellulose, starch is a biopolymer and it also is part of family of polysaccharides.

The only difference that distinguishes starch from cellulose it is the non-linearity of the bond β (1 → 4) glycosidic11 (Figure 2).

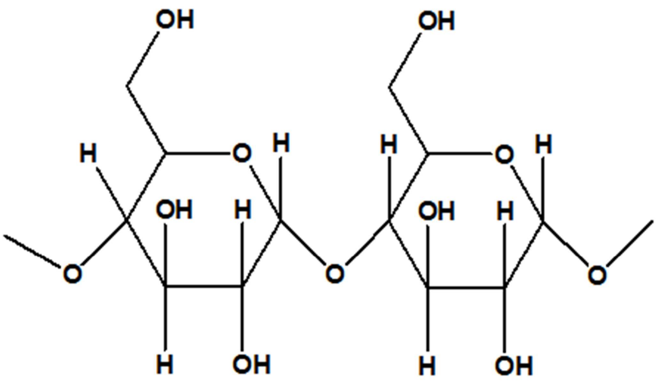

Figure 2. Starch

This polysaccharide is produced by all green plants as an energy store. It is the most common carbohydrate in the human diet and is contained in large amounts in such staple foods as potatoes, wheat, maize (corn), rice, and cassava.

Starch molecules arrange themselves in the plant in semi-crystalline granules. Each plant species has a unique starch granular size: rice starch is relatively small (about 2μm) while potato starches have larger granules (up to 100μm).

Starch becomes soluble in water when heated. The granules swell and burst, the semi-crystalline structure is lost and the smaller amylose molecules start leaching out of the granule, forming a network that holds water and increasing the mixture's viscosity. This process is called starch gelatinization.

Starch consists of two polymers: amylose (which constitutes about 20%) and amylopectin (about 80%). In both cases, these are polymers of glucose, which differ from one another in the structure. Amylose is a linear polymer that tends to wind helically, in which the glucose units are linked together by glycosidic bonds α (1 → 4)[12]. The helix is composed of 6 molecules of glucose per turn, stabilized by hydrogen bonds as in the DNA. Amylopectin is a branched polymer instead that presents basic chains of similar structure to amylose which are arranged to form a branched structure; every 24-30 glucose units are grafted side chains through bonds α (1 → 6) [13].

One molecule of amylose can contain up to 1000 glucose residues. The amylose binds together the expanded structure of amylopectin.

2.2.3 Lignin

Lignin is a heavy and complex organic polymer consists mainly of phenolic compounds. It is found mainly in the cell wall of certain plant cells. The amount for the second lignin are synthesized biopolymers on earth after cellulose. The biomass formed between cellulose and lignin represents about 70% of the total biomass.

It is composed of a polymeric structure of phenyl-propane units. So, similar to cellulose, the lignin also is a polymer very complex and with three-dimensional structure formed

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[12] Smith, Alison M., Biomacromolecule, 2001, 335, 41;

[13] Ball, Steven G., Morell M.K., *Annual Review of Plant Biology*, **2003**, 54, 207;

by a single phenyl-propane unit. The three fundamental lignin monomer precursors are coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 3)[14,15].

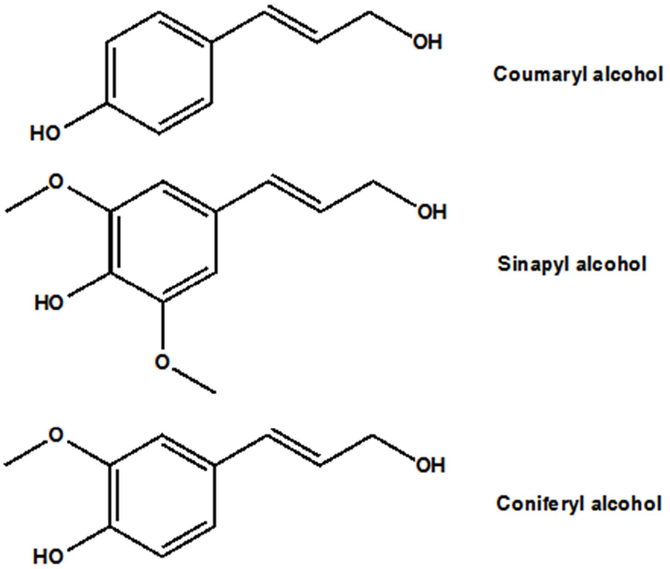

Figure 3. Lignin monomer precursor

In all plants it plays the function of binding and cementing together the fibers to give and to enhance the resistance of the vegetable.

Lignin is also known as encrusting material, because it covers the fibers. Therefore, processes for extraction of cellulose from a vegetable require an attack of lignin to break these molecules.

The lignin belongs to the class known as phenyl-propane compounds, it has no character of carbohydrate, but it falls within the class of aromatic compounds.

After the polysaccharides lignin is the most abundant organic polymer in the plant world.

This component allows to realize many functions essential to the life of plants, for example it has a very important function in the internal transport of water, nutrients and metabolites. It provides rigidity to the cell walls and it makes the connection between the various cells of the wood, creating a material highly resistant to impact, compression and bending.

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[14] Ralph J., Lundquist K., Brunow G., Lu F., Kim H., Shatz P.F., Marita M., Christensen J.H., *Phytochem Rev.*, **2004**, 3, 29;

[15] Gellersted G., Henriksson G., *Lignin: Major Source, Structure and Properties*, in Ref 3, Chapter 9, 201;

2.2.4 Hemicellulose

Hemicellulose is a polysaccharide with a low molecular weight (500 – 3000 sugar units) of irregular composition. It is closely associated with the cellulose, from which can be extracted[16].

In contrast to cellulose, whose linear molecule is formed by units of glucose alone, hemicelluloses are composed of different sugars (glucose, galactose, mannose, xylose e arabinose)[11] (Figure 4)and it also have a branched structure and not fibrous[17]. The main feature of hemicellulose is its hydrophilic property.

It also is responsible for numerous properties of the fibers, properties deriving from the chemical structure. In nature, hemicellulose is amorphous and it possesses adhesive properties.

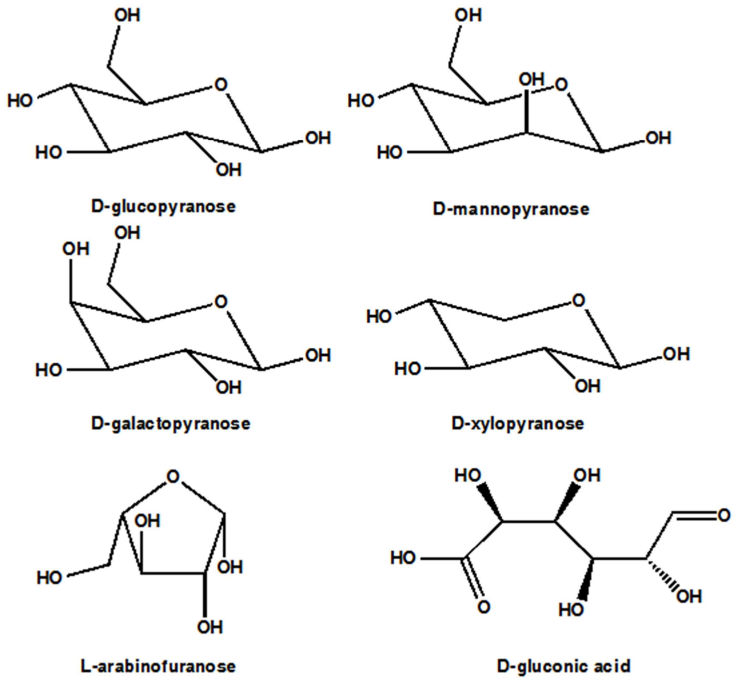

Figure 4. The main monomers of hemicellulose

The main problem in the use of ligno-cellulosic biomass in chemistry remains their high cost of processing; today, these processes have to be optimized from the economic point

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[16] Burton R.A., Gidley M.J., Fincher G.B., *Nat. Chem. Biol.*, **2010**, 6, 724;

[17] Spiridon I., Popa V.I., *Hemicellulose: Major Sources, Properties and Application*, in Ref 3, Chapter 13, 289;

of view. Obviously, the costs of processing affect the cost of final products and they make them less competitive compared to synthetic products derived from fossil fuels.

For these reasons, the organ arranged for the transformation and the development of new processes for the valorization of biomass is the biorefinery.

2.3 Biorefinery

The term biorefinery indicates a series of environmentally sustainable processes that permit the use of an organic source for the production of biomolecules, chemical compounds, or biofuels[18] (Figure 5).

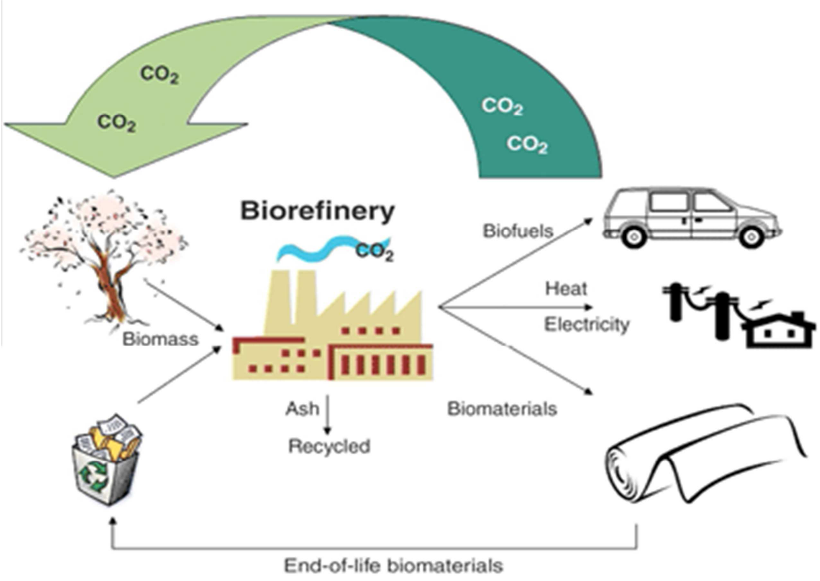

Figure 5. Biorefinery scheme

Biorefinery was born with two important objectives: an energetic objective, where the biorefinery tries to dislocate the imported petroleum preferring the domestic biodegradable raw materials, and an economic objective, building a solid biobased industry.

Nowadays unfortunately, the economy of the biorefinery is based on the production of biofuels, mainly bioethanol, biodiesel and biobutanol. But despite its high volume, fuel is a low value product.

High financial investments are needed for the development of processes for the production of biofuels, but the economic return derived from the sale of fuels is not

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[18] Chieda J.N., Huber G.W., Dumesic J.A., *Angew. Chem. Int. Ed.*, **2007**, 46, 7164;

enough to cover the initial outlay. Biofuels derived from algae are a prime example. The costs for investment in plants are blocking this promising process[19].

Financial investments are used to work with unfamiliar building blocks derived from renewable carbon, to develop the processes to convert these building blocks to final products, and to take the technology to commercial scale[20].

The only products that can satisfy the economic demands of investors are chemicals, with their high value and lower volume.

In US, the production of chemicals represents only the 7-8% of overall oil import[21,22,23], but their integration in the biorefinery economy allows to obtain a positive balance between income and expenditure, reaching energetic and economic objectives simultaneously[24,25].

As already mentioned, from the economic point of view, the addition of chemicals to the integrated biorefinery looks promising, but from processing point of view there are numerous and critical problems.

Today, the knowledge of the processes for the conversion of biomass is much lower respect to the conversion processes available for the non-renewable compounds[26], but the main problem is the identification of primary chemicals and secondary intermediates analogous to those used by petrochemical industry.

2.4 Conversion of biomass

Substantial difference between biomass and oil is the functionality of their molecules. Very few functional groups (e.g. OH, CO, COOH) are presented in petroleum therefore it is possible to use the fuels after few steps (e.g. catalytic cracking, isomerization, addition of additives), while to produce chemicals it is necessary to do more

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[19] Chisti Y., *Biotechnol. Adv.*, **2007**, 25, 294;

[20] Bozell J.J., Petersen G.R., *Green Chem.*, **2010**, 12, 539;

[21] Donaldson T.L., Culberson O.L., *Energy*, **1984**, 9, 693;

[22] Kaiser J.P., Hanselmann K.W., *Experientia*, **1982**, 38, 167;

[23] Lipinsky E.S., *Science*, **1981**, 212, 1465;

[24] Bozell J.J., *Clean: Soil, Air, Water*, **2008**, 36, 641;

[25] Bozell J.J., Holladay J.E., Johnson D., White J.F., *Top ValueAdded Chemicals from Biomass*, Volume II, **2007**;

[26] Weissermel K., Arpe H-J., *Industrial Organic Chemistry, 4thedition, Wiley-VCH,Weinheim*, **2003**;

complicated steps. The molecules need of different functionalities and the refinery is be able to add these functional groups in selectively way.

On the contrary, biomass have numerous functionalities and the task of the biorefinery to produce chemicals and biofuels is to control the functionality in the final products.

2.4.1 Fermentation

First process developed in biorefinery was the alcoholic fermentation for the production of bioethanol. Nowadays bioethanol is the biofuel mainly produced in the world, especially in South America.

Several plants in the world produce first generation bioethanol (from corn) even though biorefinery is developing new processes for the production of second generation bioethanol starting from polysaccharides.

Fermentation is a form of energy metabolism which occurs in some yeasts in the absence of oxygen.

The fermentation takes place in two phases: in the first the yeast cleavages the glycosidic bonds in complex sugars (Reaction 1),

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Reaction 1. Formation of sugar units

while in the second step is there is the formation of ethanol starting from simple sugars (e.g. fructose or glucose) (Reaction 2).

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

Reaction 2. Production of ethanol

In the second step (real fermentation), anaerobic glycolysis occurs in the cytoplasm of the organism, as already mentioned staring from simple sugars.

Sugar molecule is divided in two molecules of pyruvic acid, after the loss of two molecules of ATP. The absence of oxygen prevents the normal Krebs cycle.

The yeast deprives a molecule of carbon dioxide (eliminated in the extra-cellular) from pyruvic acid, reducing a-COOH group to form acetic aldehyde as intermediate product, extremely poisonous compound. Aldehyde is further reduced with two hydrogen ions, with formation, as a by-product, ethanol.

2.4.2 Thermal treatments (BtL)

Thermal treatments are processes that allow to directly obtain biofuels or bio-oils with high heat value in a non-selective way. The final products obtained are more handling and their transportation and storage are more easy due to the greater energy densities than raw biomass[27,28]. The properties of the obtained products change depending to the nature of the initial raw materials.

The two main processes are pyrolysis and liquefaction[29].

Pyrolysis is a thermochemical decomposition of organic dry material at elevated temperatures, in absence of oxygen. It involves the simultaneous change of chemical composition and physical phase, and it is irreversible. There are three types of pyrolysis:

- Conventional (slow heating rate and long residence time)
- Fast (heating rate 10-200 ks^{-1} and residence time 0.5-10 s)
- Flash heating rate 1000 ks^{-1} and residence time 0.5 s)

The formation of liquid products (bio-oils) is favored utilizing the fast pyrolysis, even if the process and the products are very difficult to control, due to the critical reaction conditions. The yield of the reaction is often high (65% liquid products) and the only by-products are char and gas. Unfortunately, the final bio-oils have yet a high oxygen content (35-40%)[30] and they are not miscible with organic solvents. For this reason they can’t directly blend with the common diesel but they need other treatments[31,32].

A lot of research groups are working to develop new strategies to upgrade bio-oils such as cracking, hydrotreating and decarboxylation[33].

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[27] Badger P.C., Fransham P., *Biomass Bioenergy*, **2006**, 30, 321;

[28] Rogers J.G., Brammer J.G., *Biomass Bioenergy*, **2009**, 33, 1367;

[29] Huber G.W., Iborra S., Corma A., Chem. Rev., 2006, 106, 4044;

[30] Perego C., Ricci M., *Catal. Sci. Technol.*, **2012**, 2, 1776;

[31] Shihadeh A., Hochgreb S., *Energy Fuels*, **2000**, 14, 260;

[32] Zhanga Q., Changa J., Wanga T., Xua Y., *Energy Convers. Manage.*, **2007**, 48, 87;

[33] Stocker M., *Angew. Chem. Int. Ed.*, **2008**, 47, 9200;

On the contrary liquefaction allows to obtain hydrophobic bio-oils from wet biomass, working at 300°C and *ca* 180 bar with a long residence time (10-90 min)[34], using an aqueous phase, most often provided by the constituent water of the raw biomass.

The composition of bio-oils is very complex containing for example alcohols, acids, lignin derived phenols, ketones, etc., because many reactions occur during the thermal treatment (depolymerization, decarboxylation, isomerization, aromatization, etc.).

To produce fuels from biomass, it is possible to use another thermal treatment. This process is called gasification and it is carried out in presence of air at high temperature (800-1000°C), under low to moderate pressure[30,35].

Generally, the gasification process leads to the formation of bio-syngas, that is a gas stream of H_2 and CO. When the gasification is carried out using biomass the final product is a gaseous mixture of H_2, CO, CO_2 and water.

The syngas can be burned directly in internal combustion engines, used to produce methanol or hydrogen, or converted via Fischer-Tropsch reaction (Reaction 3) in synthetic fuel (BtL).

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O}$$

Reaction 3. Fischer-Tropsch reaction

Unfortunately, to avoid the deactivation of the Fischer-Tropsch catalyst, the bio-gas must be clean, principally desulfurization treatment, because biomass often contains a large amount of nitrogen, sulphur and chlorine[30].

The thermal treatments to produce biofuels from ligno-cellulosic biomass look very promising even if still there are some doubts like upgrading processes, biomass availability, plant capacity, etc.

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[34] Peterson A.A., Vogel F., Lachance R.P., Froling M., Antal M.J., Tester J.W., *Energy Environ. Sci.*, **2008**, 1, 32;

[35] West R.M., Kunkes E.L., Simonetti D.A., Dumesic J.A., *Catal. Today*, **2009**, 147, 115;

2.4.3 Hydrolysis

In the biorefinery, hydrolysis is one of the most important processes used to treat the ligno-cellulosic biomass.

Hydrolysis is a reaction, basic, acidic or enzymatic catalyzed, to be able to break glycosidic bond between two sugar units (Figure 6).

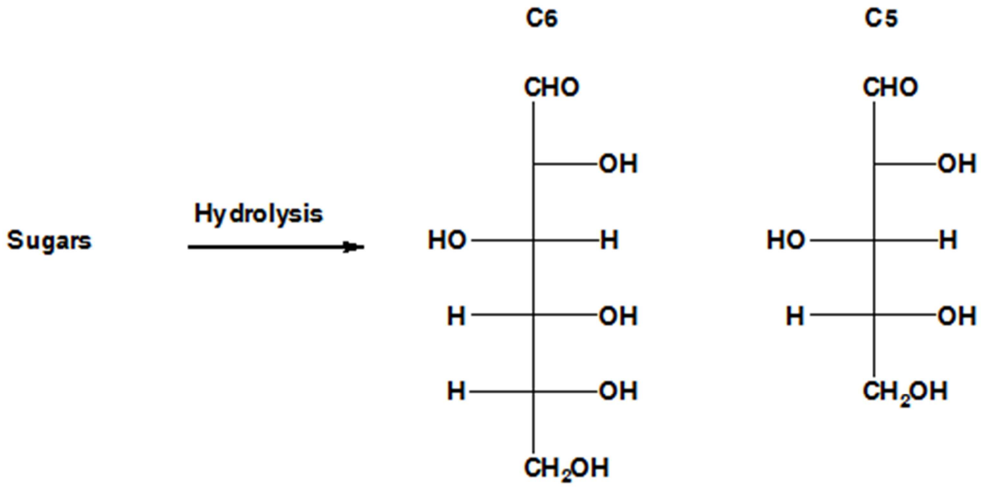

Figure 6. Hydrolysis reaction

The reaction conditions change depending to the final products desired. Typically, the hydrolysis is carried out in acidic condition (100-300°C), even if the enzymatic catalysis can lead to the total conversion of cellulose and 100% yield in glucose[36].

The main problems derived from the use of enzymatic catalysts is the non-constant catalytic activity and the difficult control of the chemical process (T, p).

In acidic conditions, hydrolysis allows to achieve up to 60-70% yield in glucose, starting from cellulose as substrate. As already mentioned, cellulose is not very reactive, due to its high degree of crystallization. It possible to use milder conditions (70-150°C) using hemicellulose and soluble starch, achieving quantitative yield in sugars[37,38].

Basic conditions are less selective, leading to the formation of condensation and/or oligomerization products[39], even if often, working with acid catalysts, degradation of sugars may occur. The degradation of sugar with five or six carbon atoms leads to the

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[36] Huber G.W., Iborra S., Corma A., *Chem. Rev.*, **2006**, 106, 4044;

[37] Moreau C., Durand R., Duhamet J., Rivalier P., *J. Carbohydr.Chem.*, **1997**, 16, 709;

[38] Nagamori M., Funazukuri T., *J. Chem. Technol. Biotechnol.*, **2004**, 79, 229;

[39] Bobleter O.,*Polysaccharides*, 2nd edition, **2005**, 893;

formation of furfural and/or 5-hydroxymethylfurfural (HMF), compounds that may be undesirable[18].

2.4.4 Dehydration

Furan compounds (e.g. HMF, furfural, furfuryl alcohol, etc.) represent a large group of chemicals very important for the economy of the biorefinery. The process that leads to their production involves the dehydration of carbohydrates and of carbohydrates derived. Various side reactions compete with the main process[40,41,42].

To avoid the low selectivity of this reaction, several studies have shown the possibility to carry out the process in various solvents (water, super-critical water, ionic liquids, organic), and in a range of temperature included between 100-300°C.

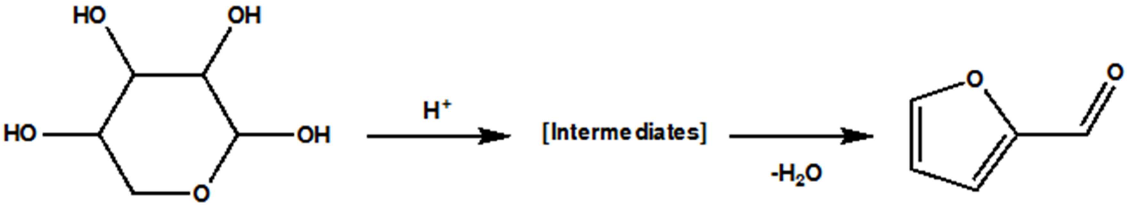

Figure 7. Carbohydrates dehydration

The main parameter to control the production of final compounds is the catalyst. Organocatalysts, salts, mineral and organic acids, solid acid catalysts (ion-exchange resin, zeolite) have been studied.

However, the process is hardly feasible on large scale, due to the high cost for the plant, derived from corrosive problems (use of water and salts)[43].

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[40] Moreau C., Durand R., Razigade S., Duhamet J., Faugeras P., Rivalier P., Ros P., Avignon G., *Appl. Catal. A*, **1996**, 145, 211;

[41] Antal M.J., Mok W.S.L., Richards G.N., *Carbohydr. Res.*, **1990**, 199, 91;

[42] Antal M.J., Mok W.S.L., Richards G.N., *Carbohydr. Res.*, **1990**, 199, 111;

[43] Ott L., Bicker M., Vogel H., *Green Chem.*, **2006**, 8, 214;

2.4.5 Isomerization

Similar to petrochemical refinery, isomerization is an important based reaction. It is used primarily to produce fructose from glucose as intermediate to HMF production.

Generally, the catalyst used for the isomerization is a base (magnesium-aluminum hydrotalcite[44]) at mild temperatures (40-80°C).

The conversion of glucose in the reaction is very low because only the sugar in the open-chain form undergoes the isomerization. The glucose in solution is present as open-chain[45], but, for example in DMSO, only the 3% of overall is acyclic and in water is only the 0.8%. The temperature can increase the acyclic form, but drastic conditions lead to a side reactions[46,47].

The isomerization reaction involves formation of intermediate enolate species through open-chain forms to transform aldohexoses to ketohexoses (Figure 8).

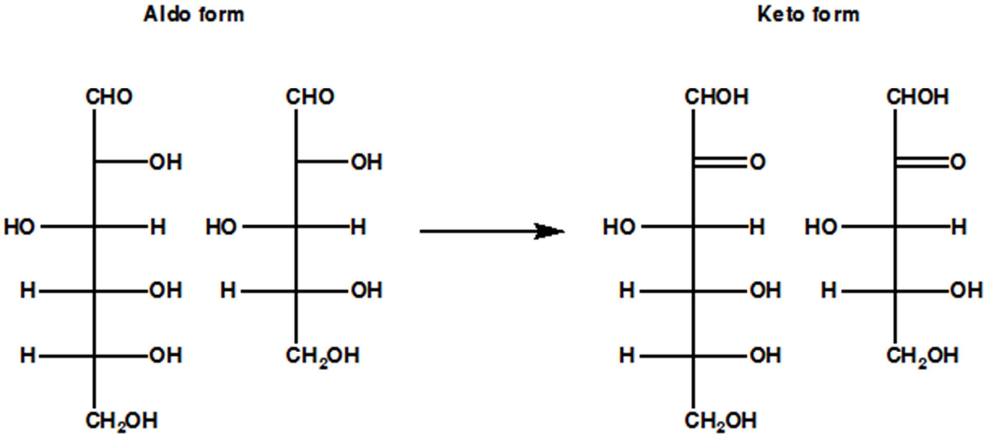

Figure 8. Isomerization reaction

2.4.6 Reforming reactions

Reforming reaction could be considered a thermal treatment of biomass, even if the temperature of the reaction doesn't exceed 200°C.

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[44] Lecomte J., Finiels A., Moreau C., *Starch/Staerke*, **2002**, 54, 75;

[45] Collins P., Ferrier R., *Monosaccharides*, Wiley, **1995**;

[46] Bicker M., Kaiser D., Ott L., Vogel H., *J. Supercrit. Fluids, 2005*, 36, 118;

[47] Dais P., *Carbohydr. Res.*, **1987**, 169, 159;

The products obtained from carbohydrates and water are H_2 (used for synthesis of ammonia, fuel cells, etc.) and CO_2, essential for the biorefinery economy[48].

This process is called aqueous-phase reforming (APR).

Catalyst support, feed concentration, pH and temperature can change the selectivity in H_2 or in CO_2. Catalysts tried are monometallic platinum and a metal alloy nickel-tin supported on different metal oxides[49,50].

Unfortunately the selectivity in hydrogen are yet low (1.05-1.41 mmol per gram of carbohydrates). The main by-products are choal and light organic chains[51].

APR process is also used in biorefinery to produce light alkenes in a reaction that involves sorbitol and platinum supported on alumina like catalyst.

It is a very promising reaction but still it need a lot of improvements.

2.4.7 Aldol condensation

Aldol condensation is a fundamental biorefinery reaction using for creating a C-C bond. The reaction permits to obtain a large molecules (C_7-C_{15}) that can subsequently be converted in components of diesel fuel[52].

Two molecules (aldehyde or ketone) with at least one hydrogen atom in position α to the carbonyl group (C=O) are combined with each other to form a β-hydroxyaldehyde or a β-hydroxyketone.

Moreover, the product formed, commonly called aldol, can dehydrate, due to its instability. It can lose a molecule of water and then it is converted into the corresponding unsaturated compound conjugate, α-β unsaturated aldehyde or an α-β unsaturated ketone. It is also possible to carry out a cross-aldol condensation between two different aldehydes or ketones.

Typically, the reaction is carried out using a basic catalyst at mild temperatures (30-100°C).

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[48] Cortright R.D., Davda R.R., Dumesic J.A., *Nature*, **2002**, 418, 964;

[49] Huber G.W., Shabaker J.W., Dumesic J.A., *Science*, **2003**, 300, 2075;

[50] Shabaker J.W., Huber G.W., Davda R.R., Cortright R.D., Dumesic J.A., *Catal. Lett.*, **2003**, 88, 1;

[51] Valenzuela M.B., Jones C.W., Agrawal P.K., *Energy Fuels*, **2006**, 20, 1744;

[52] Huber G.W., Chheda J.N., Barrett C.J., Dumesic J.A., *Science*, **2005**, 308, 1446;

Factors such as reaction temperature, solvent, reactant molar ratio, structure of reactant molecules, and the nature of the catalyst determine the selectivity of the process towards heavier compounds[53].

2.4.8 Catalytic Oxidation

Gluconic acid is a very important biodegradable product for the pharmaceutical and food industry (100000 tons per year). Nowadays, this acid is produced using a microbiological oxidation starting from D-glucose.

Catalytic oxidation of ligno-cellulosic biomass derived is a promising alternative to produce a large variety of compounds. This process can easily be integrated into pre-existing carbohydrate technologies in biorefinery.

Recently studies have demonstrated that noble metal catalysts (Pt, Pd, Au, and bi or tri metallic system)[54,55,56] supported on various mixed oxides are be able to oxidize carbohydrates in aqueous solution under oxygen or air pressure, forming chemicals may be a useful alternative to those derived from petrochemical sources.

Today, the aim of researchers is to find catalysts with high activity and selectivity, and long-term stability. An advantage of numerous noble metal catalysts with respect to biological systems is the possibility to work from alkaline to acidic conditions even if the most promising alternative is to work in absence of base using bimetallic metals (e.g. Au-Pd) like catalyst.

2.4.9 Hydrogenation

Sorbitol, mannitol and xylitol are the more representatives of the sugar alcohol industry. Overall are produced *ca* 700000 tons per year of this compounds and they represent an important economic resource for the biorefinery.

Starting from polysaccharides, a single step hydrogenation is carried out using bi-functional catalysts with acidic and metal sites.

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[53] Barrett C.J., Chheda J.N., Huber G.W., Dumesic J.A., *Appl. Catal. B*, **2006**, 66, 111;

[54] M. Besson M., Lahmer F., Gallezot P., Fuertes P., Fleche G., *J. Catal.*, **1995**, 152, 116;

[55] Karski S., Witonska I., *Chem. Environ. Res.*, **2001**, 10, 283;

[56] Abad A., Concepcion P., Corma A., Garcia H., *Angew. Chem. Int. Ed.*, **2005**, 44, 4066;

In some biorefinery processes, the production of sorbitol from starch was carried out in a batch reactor in aqueous phase using Ru supported on a zeolite (Figure 9)[57]. Unfortunately, the reaction condition need to obtain high conversion and high selectivity are quite drastic (more than 50 bar of hydrogen).

Acid sites and different metals as Ru, Ni, W permit to obtain quantitative conversion of the substrate and high selectivity in the product desired, even if the control of the acidity is fundamental for the process and for the selectivity.

For instance, using W supported on activated carbon like catalyst, in aqueous phase at high temperature (250°C), cellulose can be completely converted, producing a lot of compounds including ethylene glycol[58].

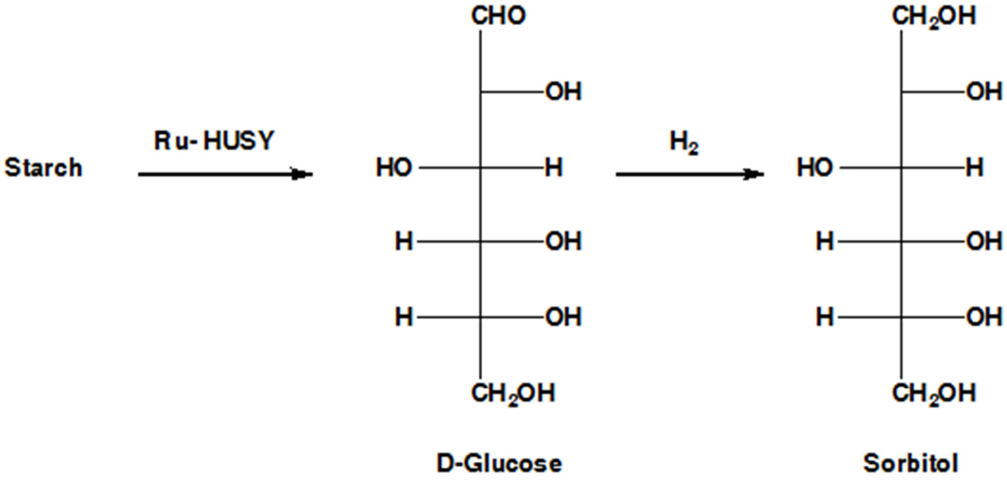

Figure 9. Hydrogenation of starch to sorbitol

2.5 Building blocks of biorefinery

Recently studies have identified some chemicals with high added value produced from carbohydrates and syngas in biorefinery processes[20]. This chemicals were selected through the evaluation of strict parameters. Compounds chosen will be the subject of present and future studies and they should lead to the development of processes used for the production of other substances, similar to what happens in the petroleum industry. This compounds will be an important platform molecules, building blocks for the

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[57] Jacobs P., Hinnekens H., Eur Pat.EP, 329923, **1988**;

[58] Zhang N.Ji.T, Zheng M.Y., Wang A.Q., Wang H., Wang X.D., Chen G.G., *Angew. Chem. Int. Ed.*, **2008**, 47, 8510;

biorefinery, with the aim to synthetize many other products in massive quantities from these.

2.5.1 Ethanol

The US Department of energy excluded ethanol from the list of the potential platform chemicals of the future because it is considered a supercommodity due to its production volume.

Nowadays, the ethanol chemistry is based on the production of ethylene, acetic acid and ethyl acetate even though, until today, the cheap oil has focused the production of ethylene on processes of petrochemical industry

On the contrary the low cost of sugarcane in Brazil and the new technologies developed to obtain ethanol from ligno-cellulosic biomass have increased the importance of this chemicals in the biorefinery concept.

Activated alumina is be able to dehydrate ethanol at 400°C in a fluidized bed reactor, allowing to obtain 99.9 % of selectivity to ethylene[59].

Catalysts based on gold nanoparticles supported on different mixed oxides permit to oxidize ethanol in acetic acid or ethyl acetate in high yield, giving nearly 95% selectivity[60,61].

2.5.2 Glycerol

The high production of first generation biodiesel and of green fuel were allowed to have a large amount of glycerol at low cost.

Until today, glycerol was burned to recover energy in the process of biodiesel production and to make the process economically feasible.

Since several studies have established that the cost could reach at 0.11 $ per Kg, glycerol has become a fundamental building block for the biorefinery to produce a huge quantities of chemicals. Today, glycerol is considered a mini sugar in the biorefinery concept.

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[59] Morschbacker A., *Polym. Rev.*, **2009**, 49, 79;

[60] Christensen C.H., Jorgensen B., Rass-Hansen J., Egeblad K., Madsen R., Klitgaard S.K., Hansen S.M., Hansen M.R., Andersen H.C., Riisager A., *Angew. Chem. Int. Ed.*, **2006**, 45, 4648;

[61] Jorgensen B., Christiansen S.E., Thomsen M.L.D., Christensen C.H., *J. Catal.*, **2007**, 251, 332;

Glycerol reduction

Propylene glycol, lactic acid, acetol and ethylene glycol are produce by hydrogenolysis reaction of glycerol (Figure 10).

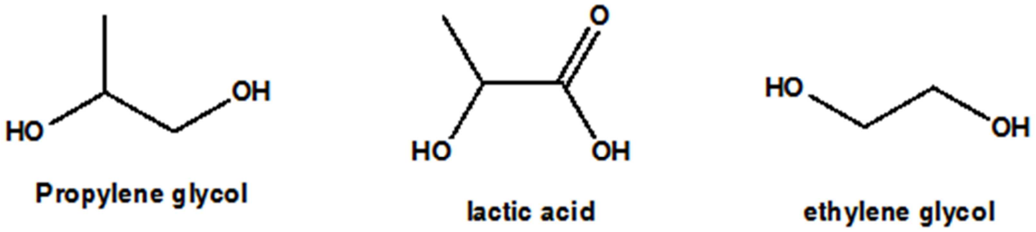

Figure 10. Chemicals from glycerol hydrogenolysis

The most important product, propylene glycol, has properties similar to those of ethylene glycol and industrially the latter is replaced with propylene glycol when more safely is needed. Propylene glycol is used for a lot of applications: as a solvent in many pharmaceutical preparations, specifically for diazepam, as a food additive, to produce polyesters, etc, and its production is over 450 million of kilograms per year[62].

Catalysts, such as copper chromite or supported ruthenium, can reduce glycerol to propylene glycol with high selectivity and about 65% of conversion, carrying out the reaction at 200 psi and 200°C. Acetol can be the intermediate in the reduction of glycerol in the production of propylene glycol. Acetol is usually prepared by the reaction between bromoacetone and sodium or potassium formate followed by hydrolysis of the ester with methanol. Also the direct oxidation of acetone with Baeyer Villiger’s acetone peroxide reagent furnishes acetol but together with the formation of pyruvic acid.

Hydrogenolysis of glycerol is the reaction that permits the higher selectivity in acetol (90%), eliminating hydrogen and using a reactive distillation[63].

Treatment of glycerol with hydrogen in the presence of Ru/C or Pt/C leads to mixtures of ethylene and propylene glycol. Carrying out the reduction in the presence of hydroxide bases induces formation of lactic acid as the major product[64].

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[62] Dasari M.A., Kiatsimkul P.P., Sutterlin W.R., Suppes G.J., *Appl. Catal. A*, **2005**, 281, 225;

[63] Chiu C.W., Dasari M.A., Suppes G.J., Sutterlin W.R., *AIChE J.*, **2006**, 52, 3543;

[64] Maris E.P., Ketchie W.C., Murayama M., Davis R.J., *J. Catal.*, **2007**, 251, 281;

Glycerol dehydration

Possible chemicals derived from glycerol dehydration are hydroxypropionaldehyde and acrolein (loss of primary hydroxyl group), and hydroxyacetone (loss of secondary hydroxyl group). Changing the reaction condition employed, it is possible to modify the selectivity in these final products.

Dehydration of glycerol can produce acrolein in 86% selectivity at 70% conversion, employing hot water for 8 s under supercritical conditions, using H_2SO_4 or $Zn(SO_4)_2$ promoters[65]. Acrolein oxidation provides the acrylic acid production, a chemical with an annual production of 1.2×10^9 kilograms. For this reason, in recent years, the attention over this aldehyde has increased a lot.

Glycerol carbonate

Glycerol carbonate is used as nonvolatile solvent, as a component in coatings, as a component in gas separation membranes, polyurethane foams[66] and surfactants[67], and as a source of new hyperbranched polymers[68].

Glycerol can be converted in glycerol carbonate in high yeld, using urea at 120°C in diethylene glycol for 24 hours[69]. Another possible route to produce glycerol carbonate from glycerol is the use of ethylene or propylene carbonate in place of urea[70]. In every case the highest yield achieved is 58%.

From glycerol to epichlorohydrine

Epichlorohydrine is an organochlorine compound and an epoxide. It is moderately soluble in water, but miscible with the most polar organic solvents. Epichlorohydrine is a highly reactive compound and it is used in the production of polymers, epoxy glues, resins and elastomers. In contact with water epichlorihydrine hydrolazes to 3-chloropropane-1,2-diol, a carcinogen found in some foods.

Nowadays, this epoxide is produced *via* propylene hydrochlorination, generating a lot of by-products and chlorinated wastes.

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[65] Watanabe M., Lida T., Aizawa Y., Aida T.M., Inomata H., *Bioresour. Technol.*, **2007**, 98, 1285;

[66] Randall D., De Vos R., *Eur. Pat. EP 419114*, **1991**;

[67] Weuthen M., Hees U., *Ger. Pat. DE 4335947*, **1995**;

[68] Rokicki G., Rakoczy P., Parzuchowski P., Sobiecki M., *Green Chem.*, **2005**, 7, 529;

[69] Okutsu M., *Japan Pat. JP 2007039347*, **2007**;

[70] Mouloungui Z., Yoo J.W., Gachen C.A., Gaset A., Vermeersch G., *Eur. Pat. EP 739888*, **1996**;

Glycerol chlorination is an alternative very promising route to produce epichlorohydrine. 1,3-dichloro-2-propanol is the intermediate in this process, produced treating glycerol with 2 equivalents of HCl in the presence of a carboxylic acid catalyst, typically HOAc. This process is not quantitative selectivity, in fact also 1,2-dichloro isomer is formed.

In the second step, this mixture is treated with base to give the epoxide (Figure 11).

By using glycerol as the starting material, the process reduces chlorinated residues eightfold and water use by 90% over conventional epichlorhydrin processes.

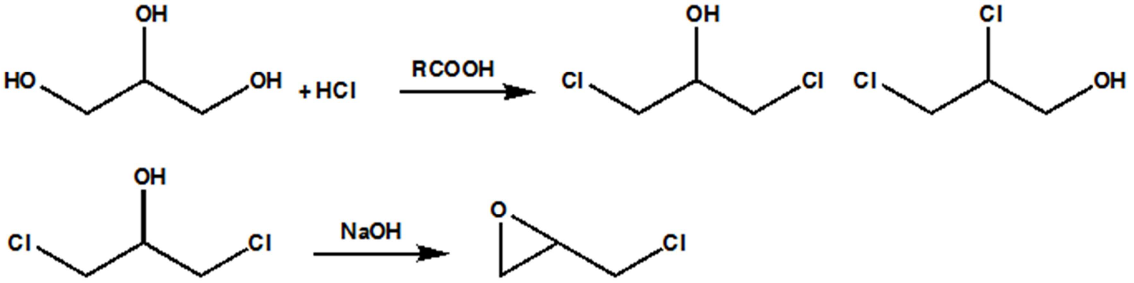

Figure 11. Epichlorohydrine production from glycerol

2.5.3 Lactic acid

As already mentioned, although it is possible to produce lactic acid *via* glycerol hydrogenolysis, the main process to obtain lactic acid in biorefinery is the fermentation of glucose using *Lactobacillus delbrueckii*[71].

Lactic acid is utilized to produce polylactic acid, a thermoplastic aliphatic polyester.

Lactic acid could directly polymerize to polylactic acid, but unfortunately, the yield of the polymer is low. So, the process provides the initial dehydration of lactic acid to form a pre-polymer with lower molecular weight, and in the second step, the latter undergoes a depolymerization, producing the monomer lactide. Lactide is easily converted using a catalytic way.in the corresponding polymer with high molecular weight[72] (PLA)(Figure 12).

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[71] Datta R., Henry M., *J. Chem. Technol. Biotechnol.*, **2006**, 81, 1119;

[72] Amgoune A., Thomas C.M., Roisnel T., Carpentier J.F., *Chem. Eur. J.*, **2006**, 12, 169;

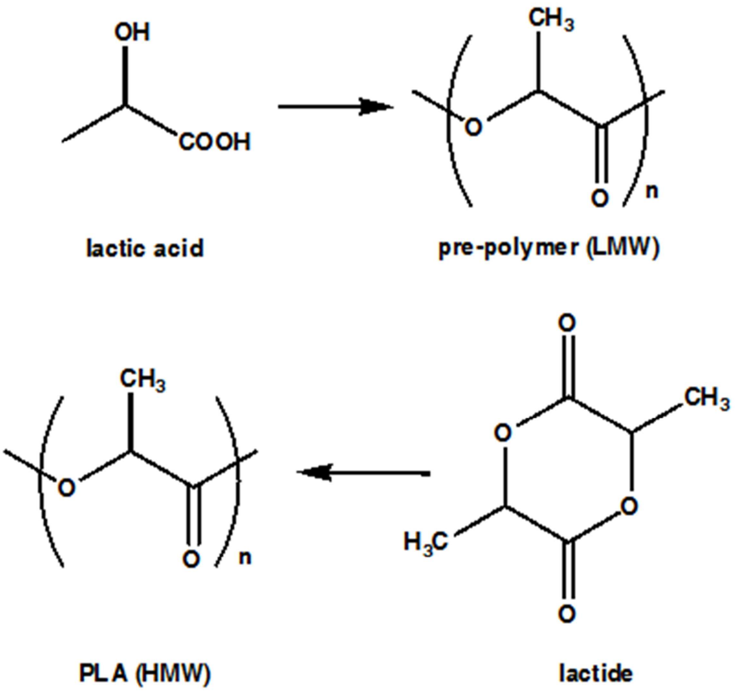

Figure 12. Production of polylactic acid

Polylactic acid is a very important polymer for the economy of the biorefinery.

PLA can be used as a compostable packaging material, either cast, injection molded, or spun. Cups and bags have been made of this material. It is useful for producing loose-fill packaging, compost bags, food packaging, and disposable tableware. In the form of fibers and non-woven textiles, PLA also has many potential uses, for example as upholstery, disposable garments, awnings, feminine hygiene products, and diapers.

PLA is also used as a medical implants in the form of screws, pins, rods, and as a mesh. Depending on the exact type used, it breaks down within the body within six months to two years.

Acrylic acid, propylene glycol and lactate esters are produced by using lactic acid as a starting material too.

2.5.4 Succinic acid

Succinic acid has a an annual production of about 30000 tons. In the biorefinery, succinic acid is produced using a various bio organisms such as: *E. coli modified, Anaerobiospirillum succiniciproducens, Mannheimia succiniciproducens,* performing a fermentation of numerous available sugars[73].

Succinic acid represents a promising platform molecule to produce some chemicals today produced in petrochemical industry.

Succinate ester, derived from esterification of succinic acid, is the intermediate compound to produce tetrahydrofuran, γ-butyrolactone and 1,4-butanediol.

For instance 1,4-butanediol is used industrially as a solvent and in the manufacture of some types of polymers, elastic fibers and polyurethanes.

For instance, world production of 1,4-butanediol is about one million metric tons per year and market price is about 2000 $ per ton.

Succinic acid is also a component of biobased polymers, such as nylon and polyesters[74][75].

Another important process regarding succinic acid is the production of unsatured dicarboxylic acid. The dehydrogenation cyclization of succinic acid leads to formation of maleic anhydride, an important intermediate to produce maleic acid and fumaric acid. Maleic anhydride was traditionally manufactured by the oxidation of benzene or other aromatic compounds. As of 2006, only a few smaller plants continue to use benzene; due to rising benzene prices, most maleic anhydride plants now use n-butane as a feedstock. For this reason, now biorefinery can develop a new promising green route to produce a maleic anhydride economically favorable respect to petrochemical industry.

2.5.5 Levulinic acid

Levulinic acid is an organic acid, with low molecular weight, classified as a keto-acid. The process utilized to produce this organic acid provides an acid treatment of ligno-cellulosic biomass at temperature above 100°C.

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[73] Bechthold I., Bretz K., Kabasci S., Kopitzky R., Springer A., *Chem. Eng. Technol.*, **2008**, 31, 647;

[74] Song H., Lee S.Y., *Enzyme Microb. Technol.*, **2006**, 39, 352;

[75] Zeikus J.G., Jain M.K., Elankovan P., *Appl. Microbiol. Biotechnol.*, **1999**, 51, 545;

Sugars with six atoms of carbon dehydrate, under acid condition, producing a molecule of 5-hydroxymethylfurfural, that undergoes an addition of water with subsequent cleavage of the furan ring and the formation of one molecule of formic acid and one of levulinic acid. The process proceeds via the intermediacy of glucose, which is isomerized to fructose and then 5-hydroxymethylfurfural. Other sugar-derivatives can be used in this process including levulose (D-fructose), inulin and starch.

The most common acid catalysts used are hydrochloric acid, sulfuric acid and Amberlyst.

Still, the mechanism that lead to the formation of levulinic acid is not entirely clear, therefore, its process continues to be investigated.

The side reactions lead to the formation of humins, organic material that do not dissolve when treated with diluted alkali solutions[76,77].

Levulinic acid is used principally for the production of lactones, pyrrolidones and levulinate esters (Figure 13)[78].

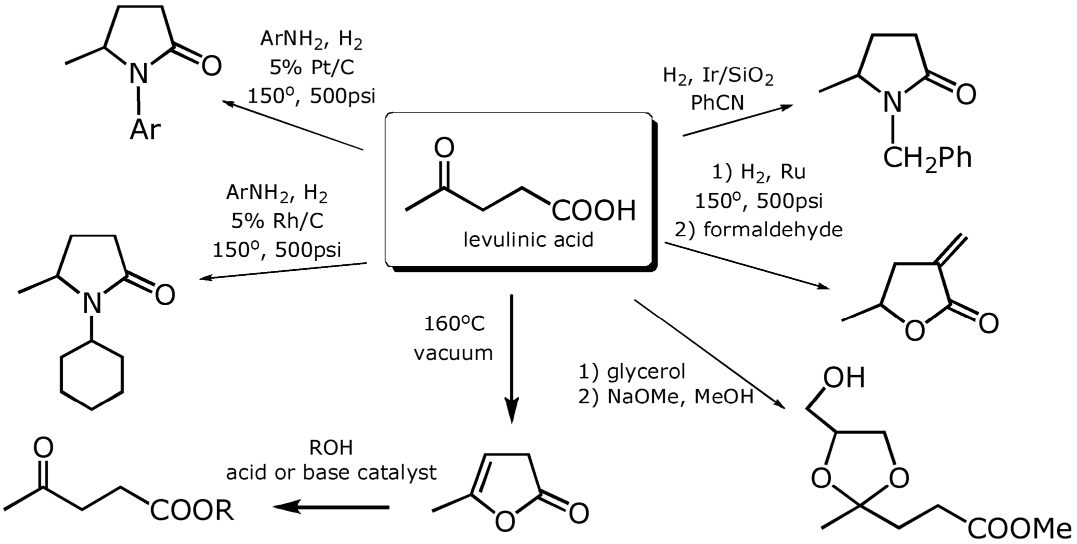

Figure 13. Levulinic as a bulk chemical

Carboxyl group can also reacts with alcohols to form esters (known more than 75), A lot of esters with a strong smell of fruit are be used subsequently as additives, while the

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[76] Girisuta B., Janssen L., Heeres H.J., *Green Chem.*, **2006**, 8, 701;

[77] Girisuta B., Janssen L., Heeres H.J., *Chem. Eng. Res. Des.*, **2006**, 84, 339;

[78] Manzer L.E., *ACS Symp. Ser.*, **2006**, 921, 40;

ethyl levulinate can be used as an additive for oxygenated fuels for diesel engine since the extent of 20%.

Several researchers are studying the possibility to convert levulinic acid using heteropoly acids in diphenolic acids, a promising green replacement for bisphenol A in the production of polycarbonates[79].

The levulinic acid chemistry is huge, so as to make this chemicals needful for the economy of the biorefinery.

2.5.6 Furan derivates

The chemistry of furans and their derivatives appears to be more interesting than the other monomers sugars and polymers (cellulose and starch), because the use of these compounds for obtaining of macromolecular materials can be planned until obtaining of synthetic strategies similar to those of petroleum derivatives.

Another relevant aspect is that using furan compounds, it is possible to obtain a huge variety of chemicals. One of the founders of this family is undoubtedly furfural, obtained by acid-catalyzed hydrolytic depolymerization of pentose sugars that are easily found from the residues from wood processing and waste products in agriculture.

The second fundamental derivative belonging to the furans family is the 5-hydroxymethylfurfural (HMF).

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[79] Guo Y.H., Li K.X., Yu X.D., Clark J.H., *Appl. Catal. B*, **2008**, 81, 182;

Chapter 3

3 Furfural and HMF

Furfural and HMF represent a fundamental building blocks for the biorefinery, seeing as their production are environmentally sustainable and the economically feasible.

Ligno-cellulosic residues from agriculture and/or sawmill can be using to produce furfural and HMF.

Furfural can be also produce as a co-product of ligno-cellulosic biofuels while HMF is produced exclusively from C6 sugars such as glucose and fructose.

3.1 Furfural Synthesis

Furfural was isolated in 1832 by the German chemist Johann Wolfgang Dobereiner, who obtained it as a byproduct of the synthesis of formic acid. At the time, the formic acid was formed by the distillation of ant bodies that probably contained a bit of plant material. In 1840, the Scottish chemist John Stenhouse found that the same chemical could be produced by distilling a wide range of cereals, such as corn, oats, wheat, bran, in an aqueous solution of sulfuric acid. Later he also determined the empirical formula ($C_5H_4O_2$) .

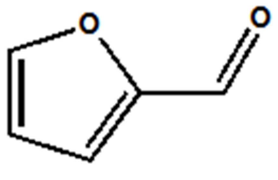

Figure 14. Furfural

Today, xylose and arabinose are the C5 sugars whence furfural is mainly produced.

Xylose is a carbohydrate with five carbons (aldo-pentose). It is commonly called wood sugar as obtained from the rich part of the xylan hemicellulose from the cell walls and the fiber of the plant. Arabinose is a monosaccharide aldo-pentose with empirical formula ($C_5H_{10}O_5$).

Unlike many other saccharides, arabinose is much more common in organisms in its configuration L (left-handed) rather than in the D (right-handed). In nature it can be found in plant tissues in the form of saponin, or as a component of biopolymers such as hemicellulose and pectin[80,81].

Generally, a plant contains a large quantity of xylan and arabinan: 10% in softwood, 20% in hardwood and up to 28% in grasses.

The content of pentose compounds in sugarcane bagasse is very interesting (up to 27% wt), mainly due to the removal of hexose sugars during the processing for production of sugar[82].

Hemicellulose is treated in aqueous stream at high temperature to produce monosaccharides such as xylose and arabinose. For this reason, industrially, furfural production is carried out in aqueous solution.

Processes of xylose dehydration proceeds generally in acid conditions (H_2SO_4 up to 2.5% wt)[83] to accelerate the reaction rate, working in a range temperature included between 150 and 220°C[84].

Nowadays, the highest furfural yield obtained doesn’t exceed 60-70%, due to several side reactions that occur in these industrial condition.

Numerous by-products are produced, in particular mainly degradation products to humins, compounds of fragmentation (C_{1-4}, aldehydes and ketones) and products of aldol condensation of the furfural.

Although to work in an aqueous media could simplify the processes of separation and purification of furfural, the low yields make the process industrially disadvantaged.

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[80] Carvalheiro F., Garrote G., Paraj J.C., Pereira H., *Biotechnol. Prog.*, **2005**, 21, 233;

[81] Kootstra A.M.J., Mosier N.S., Scott E.L., Beeftink H.H., Sanders J.P.M., *Biochem. Eng. J.*, **2009**, 43, 92;

[82] Alves E.F., Bose S.K., Francis R.C., Colodette J.L., Iakovlev M., Van Heiningen A., *Carbohydr. Polym.*, **2010**, 82, 1097;

[83] Montan D., Salvad J., Torras C., Farriol X., *Biomass Bioenergy*, **2002**, 22, 295;

[84] Zeitsch K.J., “*The Chemistry and Technology of Furfural and its many By-Products*”, Amsterdam, **2000**;

For this reasons, the possibility to work whit organic solvents has been investigated by several researchers.

By using cellulose and hemicellulose, dimethylsulfoxide (DMSO) allows to obtain higher furfural yield, even if the process is infeasible, due to the high costs derived from the solvent extraction[85].

Non aqueous media such as a mixture of organic/ionic solvents can be a promising solution to convert xylose/xylan in high furfural yield, but the feasibility of the process depends on the cost for the recovery of the final product[86].

Biphasic solvents can be a hopeful alternative to these processes. High yields are achieved using water/toluene or water/methyl isobutyl ketone (MIBK) at high temperature (170°C)[87,88]. Some acid catalysts (acid Lewis, HMOR zeolite, etc.) are tested in these conditions, showing an improvement in furfural yield.

However, today, the best process of dehydration of ligno-cellulosic biomass proceeds using a micro-mesoporous silica functionalized with a sulfonic acid group, working in an aqueous medium, and giving high furfural selectivity (82%) at 91% conversion[89].

3.2 Furfural hydrogenation

Methylfuran (MF), methyltetrahydrofuran (MTHF) and dimethylfuran (DMF) are considered promising biofuel components due to their high energy density, high research octane number (e.g. RON=119 for DMF) and ideal boiling point.

Several studies have reported that furfural can undergo selectively the hydrogenolysis of its carbonyl group and of its furan ring to form MF and MTHF (Figure 15).

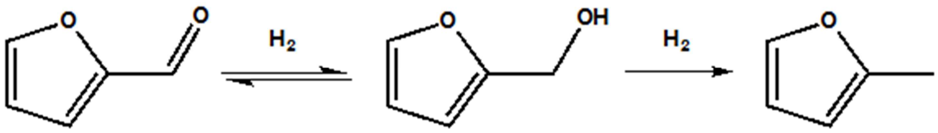

Figure 15. Furfural hydrogenation

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[85] Dias A.S., Pillinger M., Valente A.A., *J. Catal.*, **2005**, 229, 414;

[86] Binder J.B., Blank J.J., Cefali A.V., Raines R.T., *ChemSusChem*, **2010**, 3, 1268;

[87] Moreau C., Durand R., Razigade S., Duhamet J., Faugeras P., Rivalier P., Ros P., Avignon G., *Appl. Catal. A: Gen.*, **1997**, 145, 211;

[88] Moreau C., Durand R., Peyron D., Duhamet J., Rivalier P., *Ind. Crops Prod.*, **1998**, 7, 95;

[89] Dias A.S., Pillinger M., Valente A.A., *J. Catal.*, **2005**, 229, 414;

In literature some articles report processes that produce MF in gas phase, liquid phase or in reactive distillation.

The gas process of hydrogenolysis of furfural is carried out at 200-300°C and at low pressure (*ca* 1 bar of H_2) and with a H_2/furfural molar ration included between 5 and 8[90]. By using copper based catalysts (Cu/Al_2O_3, Raney-Cu and $CuCr_2O_4$) the reaction has a high MF selectivity (95%), but in the process catalysts tend to deactivate rapidly (few hours). The deactivation is attributable to the formation of coke and the deposition of furfuryl alcohol oligomers on the active sites of the catalysts. Furfuryl alcohol is the hydrogenated intermediate in furfural hydrogenolysis to MF and MTHF production.

It is possible to regenerate the catalyst oxidizing the system at high temperature (400°C), even if this operation makes the process economically not economically feasible.

For these reasons, the process carried out in liquid phase can be used to avoid the rapid deactivation of the catalysts.

Several articles describe the hydrogenolysis reaction using palladium supported catalysts at milder temperature (20-50°C) than gas phase. In this case, the main problem is the selectivity in MF, typically due to ring hydrogenation of furfural, furfuryl alcohol and/or MF. The addition of an acid co-catalyst or the use of a bi-functional catalyst could decrease the formation of by-products and they could inhibit the side reactions.

Reaction conditions affect the conversion and the selectivity of the process, in particular the use of polar solvents such as methanol and ethanol allow to obtain 100% MF yield in 1 hour at 18°C using a polymer supported palladium[91].

MF has a low boiling point (65°C) that permits to work under stripping conditions, with its continuous removal (reactive distillation). Unfortunately, it isn't possible carrying out the reaction at mild reaction condition to achieve good results, in fact the distillation requires higher temperatures (100-150°C) and an acid co-catalyst such as H_2SO_4 to improve the activity of palladium supported catalysts[92].

MF and DMF can undergo the ring hydrogenation, to obtain fuel components with a higher energy density with respect to aromatic compounds. The most widely used

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[90] Bremner J.G.M., Keeys R.K.F., *J. Chem. Soc.*, **1947**, 1068;

[91] Sun Q., Liu S., Yao X., Su Y., Zhang Z., *Hecheng Huaxue*, **1996**, 4, 146;

[92] Lange J.P., Van Buijtenen J., *WO-2009/156439*, **2009**;

catalyst for the ring hydrogenation is nickel-based catalyst at quite low temperature (130°C)[93].

As already mentioned, furfural derived compounds are very interesting as biofuels additives. One of the most important diesel fuel component is the 6-butylundecane.

The process to produce this chemical provides the furfural hydrogenation to form MF that undergoes a trimerization reaction in an aqueous acid medium at 60°C. The product formed is hydrogenated with Pt on carbon and Pt on titania as catalysts at 50 bar of hydrogen and high temperature (200-350°C) (Figure 16)[94].

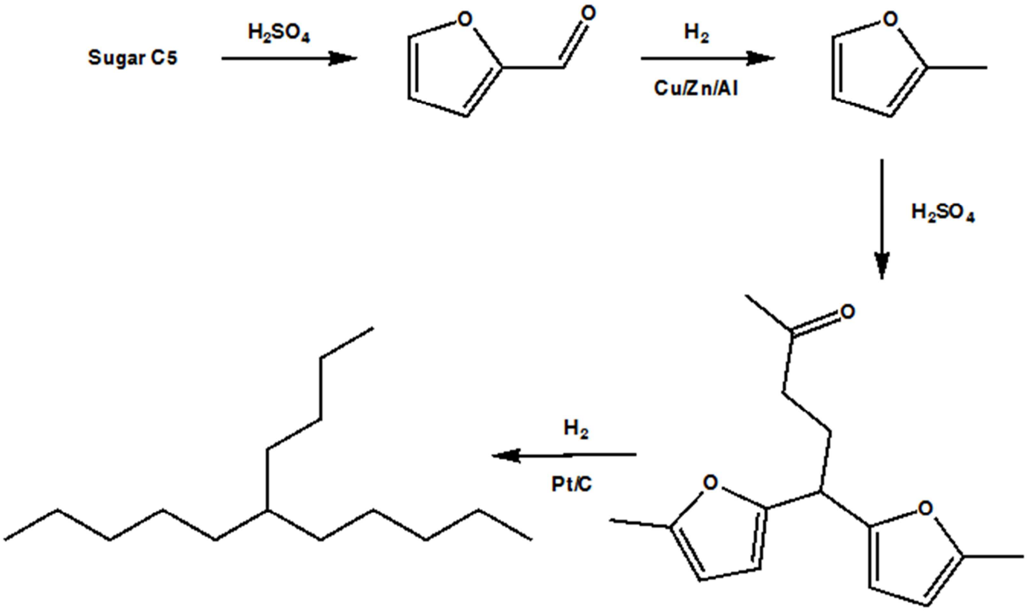

Figure 16. 6-butylundecane production

3.3 Upgrading to oxygenated biofuel components

Levulinate ethyl ester is an important platform chemical which can be further converted to pentenoate, valerate and polybutene biofuels[95][96].

The intermediate of this reaction is furfuryl alcohol which is subsequently esterificated with ethanol using a strong acids catalyst (Figure 17).

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[93] Ahmed I., *WO-2002/34697*, **2002**;

[94] Corma A., de la Torre O., Renz M., Villandier N., *Angew. Chem. Int. Ed.*, **2011**, 50, 2375;

[95] Lange J.P., Price R., Ayoub P.M., Louis J., Petrus L., Clarke L., Gosselink J., *Angew. Chem.*, **2010**, 122, 4581;

[96] Bond J.Q., Alonso D.M., Wang D., West R.M., Dumesic J.A., *Science*, **2010**, 327, 1110;

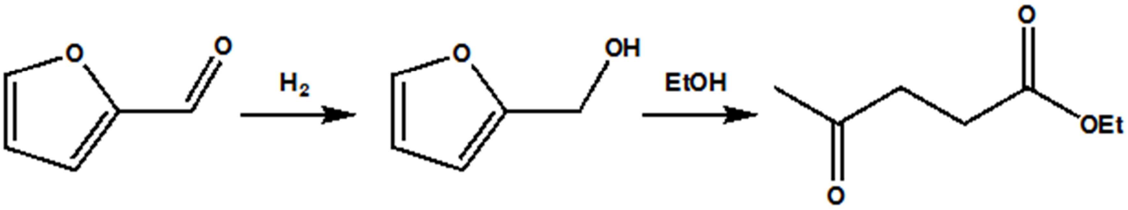

Figure 17. Ethyl levulinate production

HCl and H_2SO_4 are excellent acid homogeneous catalyst to conduct the esterification reaction, even if their use makes the industrial process not feasible. The main problems is the need to use equipment resistance to strong acid but above all the recovery of these acid catalysts is very difficult, raising the price of the final product.

For these reasons the use of heterogeneous catalysts is preferred. Acid catalysts such as zeolite, acidic ion-exchange or macroreticular sulfonated ion-exchange resins (Amberlyst 46) are very active even if the highest yield obtained is 80% in levulinate ester[97]. The only by-product formed in the esterification process is diethyl ether.

Similar to ethyl levulinate ester, also ethyl furfuryl ether is a very interesting oxygenated gasoline component.

This process proceeds by furfuryl alcohol etherification using a mild acid catalyst and ethanol as co-reagent. Zeolite is the catalyst that allows to achieved the highest yield in ethyl furfuryl ether (50%)[98]. By-product more formed is ethyl levulinate ester. Tests carried out with homogeneous catalysts such as sulfuric acid lead to maximum 30% of selectivity and low furfural conversion.

3.4 Furfural decarbonylation

Tetrahydrofuran is a fundamental biofuel component for blending into gasoline and it is mainly used as an aprotic solvent of moderate polarity. Tetarhydrofuran can be produced catalytically from furan hydrogenation.

Furfural can be decarbonylated at high temperatures (300-800°C) using different heterogeneous catalysts based on Zn, Mg, Cr, Fe, etc. Unfortunately, the selectivity and the yield of the reaction are very low, due to mainly the formation of heavy compounds

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[97] Lange J.P., Van de Graaf W.D., Haan R.J., *ChemSusChem*, **2009**, 2, 437;

[98] Haan R.J., Lange J.P., *WO-2009/77606*, **2009**;

and furan decomposition. In these conditions the catalysts undergo a rapidly deactivation making the process economically not feasible.

To increase the selectivity of the process, catalysts based on noble metals are employed at much milder condition.

Pd/Al_2O_3 is an excellent catalyst for decarboxylation working in a range of temperature between 250-400 °C in a stream of hydrogen. Unfortunately, even this catalyst undergoes rapid deactivation in a few days, although it is easily re-generable, oxidizing the coke formed on the catalyst surface using a stream of oxygen at high temperature[99,100].

Also catalysts based on Pt for example offer high yields in furan even if the selectivity of the process remains low, because products such as propane and propene, or methyl furan or products of ring opening products are produced[101]. The production of propane and propene is intriguing and warrants further investigation. In contrast to literature reports, the catalyst appeared to deactivate severely and had a half-life of approximately two days[102].

3.5 HMF synthesis

Generally, raw materials used for the HMF production are cellulose, hemicellulose and sucrose.

Sucrose is the organic compound commonly known as sugar. It is extracted from beets in European countries and from sugar cane in the rest of the world.

It is a disaccharide with a bond between the anomeric carbon of glucose and fructose (reducing ends) in α 1 and 2, so as to form a non-reducing sugar.

The fundamental steps for the HMF synthesis are the depolymerization of polysaccharides, which generally occurs under basic catalysis, and the dehydration of the C6-sugar with loss of three molecules of water (acid catalysis).

A considerable problem is the extraction and purification of HMF from the aqueous medium, due to the high affinity of this product with water[103]. For this reason have been

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[99] Gardos G., Pechy L., Csaszar E., Redey A., *Hung. J. Ind. Chem.*, **1976**, 4, 125;

[100] Gardos G., Pechy L., Csaszar E., Szigeti B., *Hung. J. Ind. Chem.*, **1975**, 3, 589;

[101] Wambach L., Irgang M., Fischer M., *US-4,780,552*, **1988**;

[102] Lange J.P., van der Heide E., van Buijtenen J., Price R., *ChemSusChem*, **2012**, 5, 150;

[103] Cukalovic A., Stevens C.V., *Green Chem.*, **2010**, 12, 1201;

used various organic solvents such as dichloromethane, ethyl acetate and tetrahydrofuran , to realize the extraction process.

The use of two different catalysts and the addition of co-solvent to extract the final product are the main problems of this process, that raise the final price of the product.

The dehydration process of fructose is favored compared to that of glucose, due primarily to its higher prevalence of being in the acyclic conformation, thus to its highest reactivity (Figure 18).

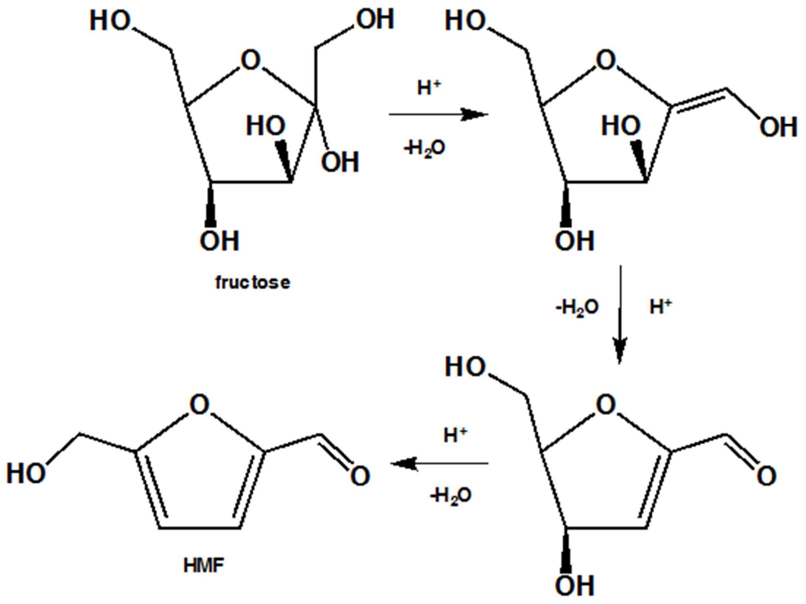

Figure 18. HMF production

Glucose is not very active also because its limiting step is the process of enolization of the aldehydic group, giving low conversion and low selectivity (Figure 18).

For these reason, as already mentioned, one of the most important process presents in biorefinery is the isomerization of glucose to fructose.

In literature some articles show the dehydration of hexoses using different acid catalysts such as organic acid (oxalic and maleic), inorganic acid (HCl and H_2SO_4)[104], ion-exchange resins[105], zeolite[106], organic and inorganic salts[107] and $VOPO_4$[108].

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[104] Asghari F.S., Yoshida H., *Ind. Eng. Chem. Res.*, **2006**, 45, 263;

[105] Mercadier D., Rigal L., Gaset A., Gorrichon J.P., *J. Chem. Technol. Biotechnol.*, **1981**, 31, 489;

[106] Moreau C., Durand R., Pourcheron C., Razigade S., *Ind. Crops Prod.*, **1994**, 3, 85;

[107] Fayet C., Gelas J., *Carbohydr. Res.*, **1983**, 122, 59;

[108] Carlini C., Patrono P., Galletti R., Maria A., Sbrana G., *Appl. Catal. A*, **2004**, 275, 111;

Unfortunately, the selectivity and the conversion of the dehydration process are very low due to the formation of numerous by-products.

The main side reactions in this process are consecutive reactions to the formation of HMF: furan ring cleavage and oligomerization/polymerization of HMF.

The furan ring opening proceeds by the addition of two molecules of water to HMF with subsequent dehydration of the hydroxyl group in position five and as the last step there is the furan cleavage with formation of one molecule of formic acid and one of levulinic acid[109].

Another parallel reaction that can occur during the synthesis of HMF is the auto-condensation to form polymers of high molecular weight.

The highest HMF selectivity (80%) is obtained using a niobium based catalyst and vanadium phosphate in water, even if with a low fructose conversion (25-50%)[110].

Also DMSO[111] and N-methylpyrrolidone[112] are used as a high-boiling organic solvents, with good results (conversion 70-90%) using an acid resin as catalyst. The selectivity is high because the organic solvent such as DMSO prevents the formation of by-products such as humic acids and levulinic acid. The disadvantage is the difficulty of separation of HMF and the formation of toxic by-products based on sulfur.

In recent years new catalytic systems have been developed such as the synthesis of HMF in aqueous solution under supercritical conditions at 240°C in the presence of zirconium phosphate; the catalyst was stable and the only products obtained were soluble polymers.

Industrially, technical-economic studies have been performed to examine the possibility to carry out a scale-up of the process of production of HMF and try to assess the possible costs of production.

The price of production of HMF is directly correlated with the cost derived from the raw materials and in particular from the cost of fructose.

In order to use the HMF as a platform chemical in the biorefinery of the future and then get the chemicals competitive in the market, the price of HMF should be around 1$/Kg.

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[109] Horvat J., Klaic B., Metelko B., Sunjic V., *Tetrahedron Letters*, **1985**, 26, 2111;

[110] Carlini C., Giuttari M., Galletti A.M.R., Sbrana G., Armaroli T., Busca G., *Appl. Catal. A*, **1999**, 183, 295;

[111] Musau R.M., Munavu R.M., *Biomass*, **1987**, 13, 67;

[112] Sanborn A., *World Pat. WO 2006/063220*, **2006**;

Numerous designs of pilot plants have been carried out by developing catalytic processes through the use of heterogeneous catalysts. Even today, in the literature it is hardly possible to find news complete on the ideal catalyst for the production of HMF, such as the life time, the regeneration after deactivation, the solvent needed for the extraction and purification of the final product.

The table shows some of the prices for the production of HMF from fructose.

Table 1. Cost of HMF production

Process	Design capacity	Fructose price	HMF price
Low boiling solvent: acetone[113]	Production of HMF: 7000 ton per year	0.5 $/Kg	2 €/Kg
Two solvent: MIBK and 2-butanol[114]		0.55 $/Kg	2.16 €/Kg
Two solvent: water and THF[114]		0.55 $/Kg	1.97 €/Kg
Two solvent: MIBK and water/2-butanol[114]		0.55 $/Kg	2.43 €/Kg

The lowest price relative to HMF production found in the literature concerns the study of a pilot plant for the co-production of DMF, a derivative of HMF used as fuel or as an additive for fuel. The process provides the combined production of these two chemicals through the use of a reaction biphasic system composed of water saturated with NaCl and 1-butanol (Figure 19). The flow sheet proposed takes into consideration the recycling of the solvent and of the unreacted substrate, the processes of purification of the products and the isolation of the by-products with high added value such as levulinic acid, important for as bulk chemical in the biorefinery. The final price of HMF, as already said, is strongly influenced by the cost of the raw material, even if the cost of the catalyst and the possibility to sell the by-products can significantly impact the cost

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[113] Bicker M., Hirth J., Vogel H., *Green Chem.*, **2003**, 5, 280;

[114] Torres A. I., Daoutidis P., Tsapatsis M., *Energy Environ. Sci.*, **2010**, 3, 1560;

of the process. Feeding a current of 300 tons per day of fructose with an approximate cost of 0.3 $/Kg the final price of HMF would be 1.08 $/Kg.

To arrive at such a low price, the lowest production of HMF must be at least 100 Kton per year. Unfortunately, all possible products derived from HMF will not enter in the market as a new and innovative products, but as products that will replace the chemicals that are being produced on a large scale in the oil industry

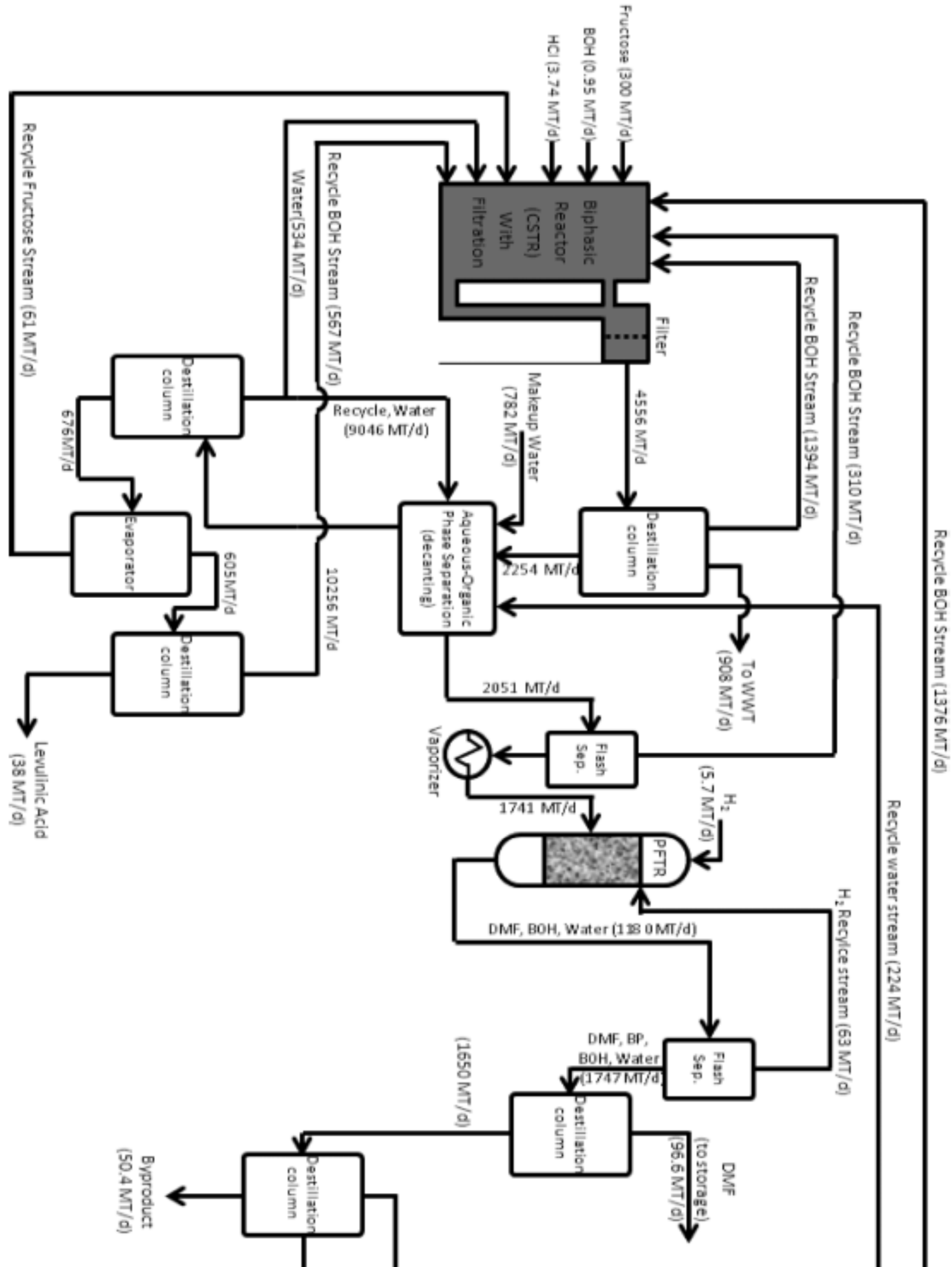

Figure 19. Flow sheet of DMF and HMF production[115]

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[115] Van Putten R-J., Van der Waal J.C., De Jong E., Rasrendra C.B., Heeres H.J., De Vries J.G., *Chemical Reviews*, dx.doi.org/10.1021/cr300182k, **2012**;

The main lines of study on HMF are two: the first is the technical and economic studies on the feasibility of production and the scale-up of pilot plants, the second is the development of catalytic processes for the production of chemicals, polymers and fuels from HMF.

In fact, the HMF can be converted into highly attractive products for the chemical industry (Figure 20).

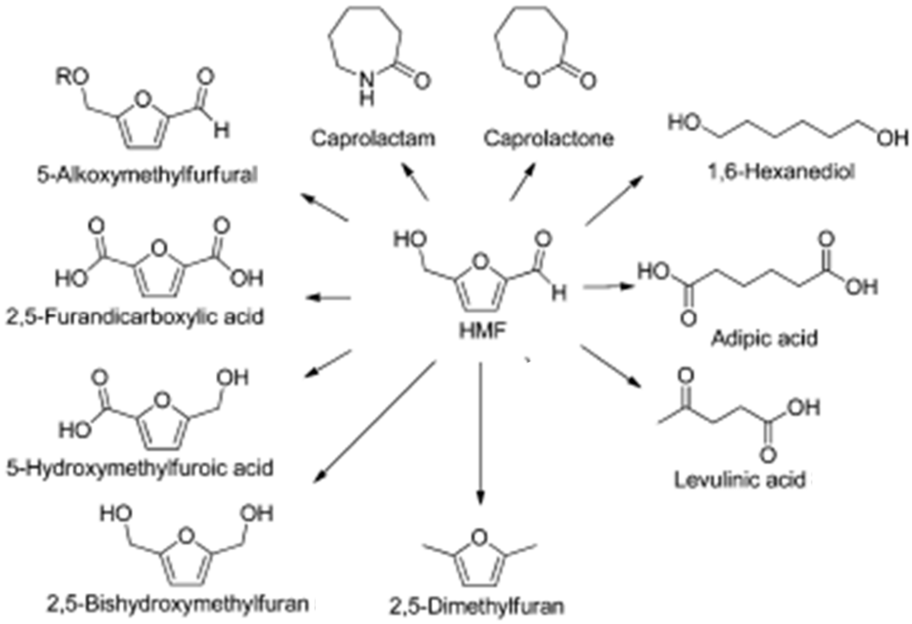

Figure 20. Chemicals derived from HMF[115]

3.6 HMF hydrogenation

As already mentioned for the hydrogenation of furfural, the most important compound derived from the hydrogenation of the HMF is the DMF, used as biofuel. It is immiscible with water and it is easier to blend with gasoline than ethanol.

Hydrogenolysis of HMF is carried out in aqueous media and using a heterogeneous catalyst under hydrogen pressure.

Pd/C allows to obtain 36% yield in DMF at 60°C in a polar solvent such as propanol. Good results are also obtained using an hydrogen transfer reaction. In this case, the hydrogen donor is cyclohexene and the addition of an acid co-catalyst such as $AlCl_3$ or another Lewis acid improves the DMF yield (90%).

HMF hydrogenolysis proceeds by formation of an intermediate: 2,5-bishydroxymethyl-furan (BHMF) (Figure 21).

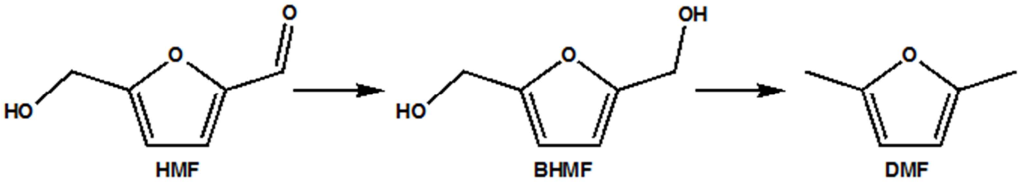

Figure 21. DMF production

BHMF is an important molecule for the production of polymers and polyurethane foams[116]. The reduction of HMF can occur with sodium boron hydride[117], but also with NaOH[118] aqueous and with catalysts such as nickel, copper chromite, cobalt oxide and molybdenum oxide.

Complete HMF conversion and BHMF selectivity are obtained using Pt/C, PtO_2 or $2CuO+Cr_2O_3$ working at 140°C and 70 bar of hydrogen, while the presence of Pd/C or nickel Raney[119] catalysts allow to achieve the hydrogenation of the furan ring forming the 2,5-bishydroxymethyl-tetrahydrofuran.

3.7 Transformations of the formyl group

The aldehydic group of the HMF can undergo numerous reaction, including the formation of hemiacetals and acetals. In particular, the hemiacetalization is an equilibrium reaction shifted toward the aldehyde and it takes place under basic or acidic conditions and in a polar solvent, typically an alcohol.

On the contrary, the formation of acetals is catalyzed by only acid catalysts such as zeoliote, ytterbium sulfate supported on Amberlyst or Lewis acids (e.g. $TiCl_4$).

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[116] Moreau C., Belgacem M.N., Gandini A., *Top. Catal.*, **2004**, 7, 11;

[117] Timko J.M., Cram D.J., *J. Am. Chem. Soc.*, **1974**, 96, 7159;

[118] Turner J.H., Rebers P.A., Barrick P.L., Cotton R.H., *Anal. Chem.*, **1954**, 26, 898;

[119] Schiavo V., Descotes G., Mentech J., *Bull. Soc. Chim. Fr.*, **1991**, 704;

One of the most important acetal is the 5-hydroxymethyl-2-furfuraldehyde bis-5-formylfurfuryl acetal (Figure 22), a chemical used for the production of flavor-improving agents[120].

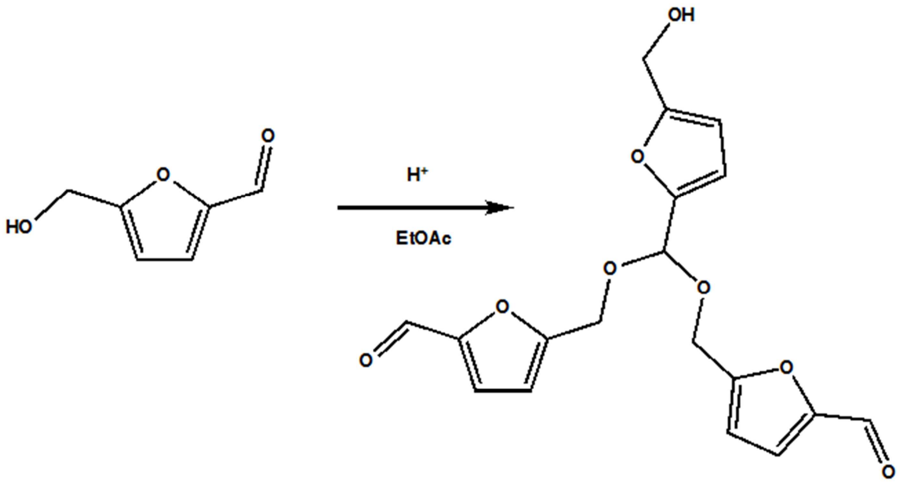

Figure 22. Reaction for flavor improving agent production

Furthermore, it is possible to produce cyclic acetals, used as chemical intermediate, carrying out a reaction between HMF and levogalactosan, or another glycol, at 100°C[121].

Another interesting transformation of the formyl group is the aldol condensation, a reaction very important for the production of biologically active compounds, components for bio fuels and liquid alkanes.

In fact, several studies claim the possibility to produce liquid alkanes performing a crossed aldol condensation with acetone and subsequent deep hydrogenation[30].

Changing the acetone equivalents in the reaction it is possible to modify the selectivity in the final products (C_9 - C_{15} alkanes).

Finally, HMF carbonyl group can also undergo a reductive amination in the presence of hydrogen gas or liquid NH_3 using a nickel Raney[122] to form a large variety of chemicals

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[120] Terada I., Takeda T., Kobayashi T., Hiramoto T., Tsuyoshi K., *US2010029786-A1 WO2008044784-A1*, **2008**;

[121] Urashima T., Suyama K., Adachi S., *Carbohydr. Res.*, **1985**, 135, 324;

[122] Elming N., Clausonkaas N., *Acta Chem. Scand.*, **1956**, 10, 1603;

or using iodine in aqueous ammonia it is possible to convert the aldehyde function into nitrile in good yield at room temperature[123].

3.8 HMF oxidation

The transformation of HMF formyl group can be carried out through the selectively oxidation on the aldehyde group or on the hydroxyl group to obtain respectively the acid 5-hydroxymethyl-2-furancarboxylic (HMFCA) and 2,5-diformylfuran (DFF). It also can be performed on both functional groups: in this case there is the formation of the acid 2,5-furandicarboxylic (FDCA).

The first oxidation reaction (HMF to HMFCA) can be carried out with different catalysts such as Ag_2O or Ag_2O-CuO under basic conditions, and H_2O_2 and CPO an enzyme active in the presence of hydrogen peroxide. The reaction is performed using air or oxygen as oxidant at mild temperatures[124].

HMFCA is a very interesting acid, and also the enzymatic oxidation is studied. 97% conversion of HMF is achieved using a whole cells of *Acetobacter rancens* or *Serratia liquefaciens*[125].

HMF oxidation to DFF is more difficult due to low selectivity of the process.

DFF is an important platform chemical, used to produce various polymers and fine chemicals such as polypinacols and polyvinyls. Industrially, it is also a starting material for the production of ligands, pharmaceutical and antifugal agents.

Several studies report the reaction catalyzed mainly by homogeneous catalyst such as pyridinium chlorochromate (PCC)[126] and DMSO–potassium dichromate oxidative complex at 100°C[127].

One of the best heterogeneous catalysts used for the oxidation to DFF is the vanadium oxide (V_2O_5) bulk or supported.

Numerous screening are carried out with these types of catalysts with the attempt to improve the selectivity of the process. Total selectivity in DFF is achieved by utilizing

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[123] Baliani A., Bueno G.J., Stewart M.L., Yardley V., Brun R., Barrett M.P., Gilbert I.H., *J. Med. Chem.*, **2005**, 48, 5570;

[124] Elhajj T., Masroua A., Martin J.C., Descotes G., *Bull. Soc.Chim. Fr.*, **1987**, 855;

[125] Mitsukura K., Sato Y., Yoshida T., Nagasawa T., *Biotechnol. Lett.*, **2004**, 26, 1643;

[126] McDermott P.J., Stockman R.A., *Org. Lett.*, **2005**, 7, 27;

[127] Cottier L., Descotes G., Lewkowski J., Skowronski R., *Org. Prep. Proced. Int.*, **1995**, 27, 564;

the vanadium oxide supported on titania at 90°C and 16 bar of O_2, although in this case the main problem is the excessive amount of catalyst necessary to obtain high conversions[128].

Currently, $PdCl_2/CuCl_2$ is the heterogeneous catalyst that has the best catalytic performances in terms of selectivity, even if the conversion of the HMF not exceed 70%, due to the presence of water in the reaction[129].

Quantitative DFF yield is obtained performing HMF oxidation with $(NH_4)_2[Ce(NO_3)_6]$ (CAN) in ionic liquid [EMIM][OTf] 1-ethyl-3-methyl imidazolium trifluoromethylsulfonate as a solvent[130]. The use of this complex catalytic system increase the cost of the process and for these reason the selective production of DFF is still under investigation.

Another important chemical derived from the HMF oxidation is FDCA. FDCA is considered by the DOE as a bulk chemical essential for the future of chemistry because it can be used as a starting point for products such as succinic acid, 2,5-furandicarboxylic acid dichloride, and 2,5-furandicarboxylic acid dimethyl ester. Furthermore, the FDCA is possible replacement of terephthalic acid for the production of PET and other polymers.

In literature numerous homogeneous catalysts such as N_2O_4, HNO_3, $KMnO_4$ are reported to perform the catalytic oxidation[131].

Several patents have been published using catalysts based on platinum (supported on charcoal and/or zirconia) obtaining almost quantitative yields and selectivity in basic medium under pressure of air[132,133].

Even the process directed by fructose to FDCA has been studied, although the yields of di-acid-are very low. The reaction involves the dehydration of the sugar and the subsequent oxidation to FDCA.

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[128] Martin T.S.A, *Ger. Patent DE 19615878*, **1997**;

[129] Halliday G.A., Young R.J., Grushin V.V., *Org. Lett.*, **2003**, 5, 2003;

[130] Mehdi H., Bodor A., Lantos D., Horvath I.T., De Vos D.E., Binnemans K., J. Org. Chem., 2007, 72, 517;

131 Miura, T.; Kakinuma, H.; Kawano, T.; Matsuhisa, H. (Canon Kabushiki Kaisha) U.S. Patent 7411078, 2008.

[132] B. W. Lew, U. S. Pat. 3326944, Chem. Abstr., 1968, 68, P49434n

[133] M. A. Lilga, R. T. Hallen, J. Hu, J. F. White and M. J. Gray, US2008103318-A1, 2007

The catalyst tested is Pt-Bi/C in combination with a solid acid catalyst in a water/MIBK solution. Using this type of catalytic system the yield and selectivity in FDCA are respectively 25% and 50%[134].

Best results (99% selectivity) are obtained using Co(acac)-SiO_2 as bifunctional catalyst at 160 °C and 20 bar air pressure even if the conversion is low yet[135].

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[134] Kroger M., Prusse U., Vorlog K.-E., *Top. Catal.*, **2000**, 13, 237;

[135] Ribeiro M. L., Schuchardt U., *Catal. Commun.*, **2003**, 4, 83;

Chapter 4

4 HMF Oxidation

DOE has identified FDCA as one of 12 chemicals for the green chemistry of the future. In fact, FDCA is as an important renewable building block because it can substitute for terephthalic acid (produced in petrochemical industry) in the production of polyesters[116].

As mentioned earlier, the oxidation of HMF leads to the formation of the FDCA.

FDCA is an important platform molecule for the production of polyesters and adipic acid, for this reason several companies have tried to industrialize its synthesis process. In particular, Avantium Chemicals has made the start-up of a pilot plant for the production of FDCA methyl ester using a catalyst based on Co/Mn/Br[136].

At the same time, there has been an exponential increase in recent years of publications on the oxidation of HMF using numerous catalysts (homogeneous and heterogeneous) and processes that are more green.

Lately, gold nanoparticles based catalysts have shown good results in this process.

Corma et al. have used gold-based catalysts supported on various oxides such as ceria, titania and carbon, working in mild condition (65 ° C) in an aqueous medium to obtain quantitative yields in FDCA in 8h reaction in an oxidizing atmosphere (O_2)[137].

TiO_2, CeO_2, Fe_2O_3 and activated charcoal were used as support to catalyze this reaction oxidation reaction, using gold nanoparticle as the active phase.

The catalysts supported on TiO_2 and CeO_2 were the best catalysts because they allow to obtain a yield in FDCA of 100%, while working with nanoparticle ceria it was possible to halve the reaction time achieving the 97% FDCA yield. This fact showed the

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[136] Mun-oz de Diego C. Schammel W.P., Dam, M.A., Gruter, G.J.M., *Int. Patent WO 2011043660*, **2011**;

[137] Casanova O., Iborra S., Corma A., *ChemSusChem*, **2009**, 2, 1138

presence of a synergistic effect between the active phase (gold nanoparticles) and the support (nano ceria).

Unfortunately, one of the major problems of this reaction using gold based catalysts was the need to use a co-oxidant such as sodium hydroxide, which makes the process less environmentally sustainable.

Christensen et al. have studied the influence of the base on the yield of di-acid. Their work has shown that a quantity of less than 4 equivalents of NaOH with respect to HMF significantly slows the reaction rate, while an amount exceeding 5 equivalents does not affect particularly on the final yields[138].

Also other articles showed a decrease of the diacid yield and a higher yield in the first intermediate HMFCA for reactions carried out in the presence of a lower pressure of oxygen or of low concentrations of base. This means that in the presence of an insufficient amount of oxygen the aldehyde group is more easily oxidized compared to the group -CH_2OH[139] while the absence of base in the reaction does not allow to obtain high conversions of the substrate, which suggests a possible deactivation of the gold based catalyst by acids initially formed.

Probably, in the absence of base, desorption of FDCA from the catalyst is significantly disadvantaged.

In the HMF oxidation process another common problem is the phenomenon of leaching of gold in optimal reaction conditions. This problem leads to a decrease of the catalytic activity of the catalyst, occurring with a lower yield in the desired product during subsequent catalytic cycles. But using a very active catalyst for the oxidation, the formation of by-products is very low.

The formation of by-products is also mainly due to the rapid deactivation of the catalysts due to the active phase being blocked by competitive adsorption.

In this work, bimetallic nanoparticles Au/Cu based catalysts have been synthesized and tested in the reaction of oxidation of HMF to FDCA with the aim to develop a catalytic process using a highly active and stable catalyst.

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[138] Gorbanev Y.Y., Klitgaard S.K., Woodley J.M., Christensen C.H., Riisager A., *ChemSusChem*, **2009**, 2, 672;

[139] Jorgensen B., Christiansen S.E., Thomsen M.L.D., Christensen C.H., *ChemSusChem*, **2008**, 251, 332;

4.1 Experimental section

This work describes the synthesis and characterization of colloidal suspensions of nanoparticles mono and bimetallic gold and copper, with different metal loading and different nanoparticles composition, the preparation and characterization of catalysts supported on TiO_2 and CeO_2 prepared using the sols synthetized and the activity of these catalytic systems in the reaction of oxidation of 5-hydroxymethylfurfural (HMF) in liquid phase.

The synthesis of nanoparticles has been developed in an aqueous medium, by reduction of metal precursors with glucose in the presence of NaOH and polyvinylpyrrolidone (PVP) as a stabilizer, while the catalysts were prepared by incipient wetness impregnation of sols of TiO_2 and CeO_2.

The techniques used for the characterization of the suspensions and catalysts were the following:

- DLS (Dynamic Light Scattering) for measuring the hydrodynamic diameter of the particles in suspension;
- XRD (X-Ray Diffraction), both on the suspension that on the catalyst, for the evaluation of the type of phases formed and the average diameter of the crystallites metal;
- XRF (X-Ray Fluorescence) for the evaluation of the reaction yield in the synthesis of nanoparticles;
- measurement of the surface area of the catalysts by BET theory;
- TGA (Thermogravimetric analysis) and DTA (Differential Thermal Analysis) for estimating the amount of organic material present on the catalyst at the end of the preparation; such organic residue derived from the synthesis of sols;
- TEM (Transmission Electron Microscopy) for estimating the average size of nanoparticles and for the evaluation of the type of phases present;
- Oxidation in programmed temperature (TPO) to evaluate the behavior of redox support;
- X-ray photoelectron spectroscopy (XPS) measurements.

The catalysts prepared were used for the study of the oxidation reaction in the liquid phase of the 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA).

4.1.1 Materials

The following reagents and products were used for the work: 5-hydroxymethyl-2-furfural (Sigma-Aldrich), 2,5-furandicarboxylic acid (Toronto Research Chemicals), 5-hydroxymethyl-2-furan carboxylic acid (Toronto Research Chemicals), $HAuCl_4$ analytic grade (Sigma‑Aldrich), $CuSO_4 \cdot 5H_2O$ analytic grade (Sigma‑Aldrich), ß-D-glucose (Sigma‑Aldrich), Polyvinylpyrrolidone PVP (Sigma‑Aldrich), TiO_2 Anatase (DT51 Millennium Chemicals), CeO2 (Ceria 90 Evonik).

4.1.2 Synthesis of nanoparticles

To perform the synthesis of the suspensions of nanoparticles of gold and gold-copper, it has been used a procedure already optimized in previous tests[140,141], varying the heating system and the mode of addition of the reagents.

The procedure used involved the preparation of an aqueous solution containing sodium hydroxide and the stabilizing agent, polyvinylpyrrolidone (PVP), followed by heating the system up to the reaction temperature (90°C).

At the right temperature, glucose (reducing agent) and metal precursor solution were added to the system, obtaining the rapid nucleation of nanoparticles (the time of reaction is only 2.5 minutes).

The formation of the metallic phase took place by means of reduction by glucose.

Despite the β-D-glucose is a reducing sugar, it was necessary the presence of NaOH to increase the reaction rate of the reduction. In the following reaction (Figure 23) sugar is represented in an open form, although in aqueous solution it is in cyclic form.

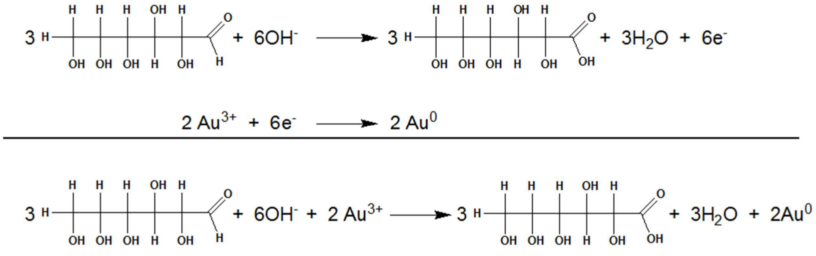

Figure 23. Metal reduction by glucose/NaOH

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[140] Pasini T., Piccinini M., Blosi M., Bonelli R., Albonetti S., Dimitratos N., Lopez-Sanchez J. A., Sankar M., He Q., Kiely C.J., Hutchings G. Cavani F., *Green Chem.*, **2011**, 13, 2091;

[141] Blosi M., Albonetti S., Dondi M., Baldi G., Barzanti A., *PCT/EP2010/052534*, **2010**;

Concentration of metal ($5*10^{-3}$ M) was always kept constant in every nanoparticles synthesis.

The molar ratios used for the synthesis of nanoparticles monometallic gold and monometallic copper were the following: [PVP] / [Au^{3+}] = 2.75; [NaOH] / [Au^{3+}] = 8; [glucose] / [Au^{3+}] = 2 ; [PVP] / [Cu^{2+}] = 15; [NaOH] / [Cu^{2+}] = 18; [glucose] / [Cu^{2+}] = 12. On the contrary, optimized values were used for the synthesis of bimetallic suspensions, that are reported in Table 2.

Table 2. Amount of reducing and stabilizing agent for suspension

Suspension	% mol Au	% mol Cu	mol PVP/ mol metal	mol NaOH/ mol metal	mol glucose/ mol metal
Au	100	/	2.75	8.00	2.00
Au_3Cu_1	75	25	5.81	10.50	4.50
Au_1Cu_1	50	50	8.88	13.00	7.00
Au_1Cu_3	25	75	11.94	15.50	9.50
Au_1Cu_6	14	86	13.25	16.57	10.57
Cu	/	100	15.00	18.00	12.00

The reaction was carried out with two different systems:

- in a microwave reactor with an heating velocity of 30°C min^{-1} able to drawing the desired temperature profile using a software that dynamically adjust the microwave power to only deliver what is need during the reaction to reach the desired temperature.
- in a three-necked flask, equipped with thermometer, refrigerant (traditional heating system);

Typically, nanoparticles synthesis was carried out mixing PVP, glucose and NaOH in a round bottom flask with 180mL of water. This solution was heated at 90°C and atmosphere pressure using the microwave oven. The last step involves the precursors addition and the agitation of the mixture for 2.5 minutes at constant temperature.

Regarding the traditional system, the only difference concerns the addition of glucose at high temperature (90°C), just before of the metals precursors. This procedure is need to avoid the degradation of glucose due to the longtime of heating (30 min).

4.1.3 Characterization of nanoparticles

The suspension of metal nanoparticles were characterized by the use of three techniques such as DLS, XRD and XRF. The operation performed for the characterization of the suspensions synthesized are summed in a schematic way (Figure 24).

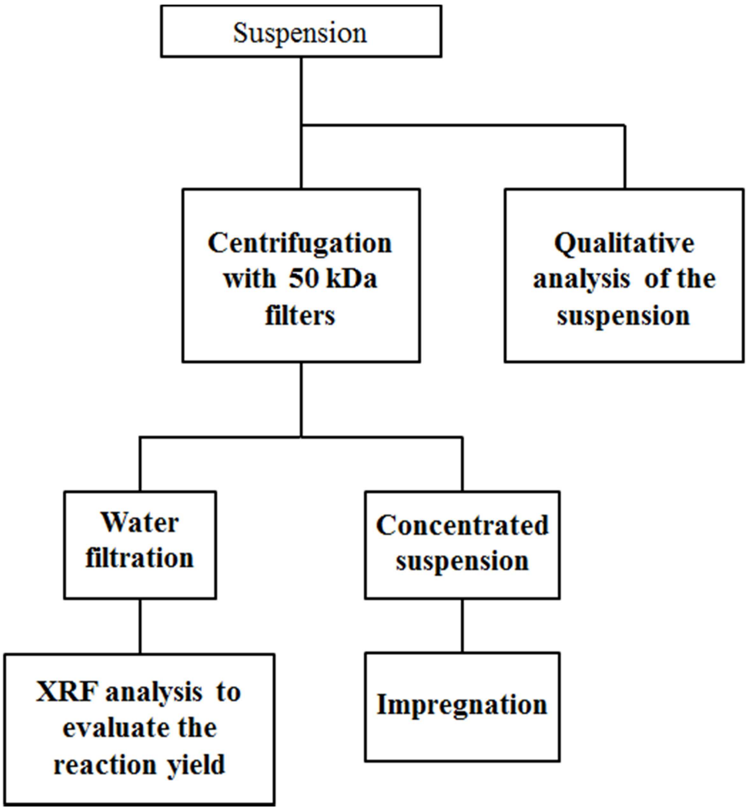

Figure 24. Work-up of suspensions synthetized

DLS (Dynamic light scattering)

The measurement of the average size of the particles in suspension has been carried out, through the technique DLS (Dynamic Light Scattering), using the instrument Nanoseries Zetasizer (Malvern Instruments).

The technique is based on the DLS scattering suffered by a laser beam that invests a colloidal suspension, in which the size of the particles are sub-micrometer (the detectability of the instrument is between 0.6 nm to 6 m).

The DLS technique is non-invasive, it is founded on the assumption that each particle (subject to random motion of Brownian type) produces the phenomenon of scattering. The speed of particles is related to their size: particles that possess a fast motion will have smaller dimensions than other that move more slowly. The intensity of the scattered light has a frequency of fluctuation dependent on the rate of diffusion of the particles, related to their size: the size of the particles can be extrapolated from the analysis of the fluctuations of the intensity of scattered light.

The instrument measures the hydrodynamic diameter of the nanoparticles, that is the diameter of the unit kinetic movement, comprising the coordination sphere and any adsorbed species on the surface (for example polymers or surfactants).

The concentrations of solid advisable to have a reliable measurement depend on the size of the particles in suspension: for smaller diameters of 10 nm it is contemplated only a lower limit of solid ([conc.] > 0.5 g/L), while for particles with diameter between 10 and 100 nm in the range of optimum concentration is between 0.1 mg/L and 5% in weight (for density of 1 g/cm^3), in order to avoid phenomena of particle-particle interaction that alter the size estimation, by changing the diffusion rate.

The instrument allows to obtain a statistical distribution of sizes, based on the intensity of scattering. Furthermore, from the results obtained, it is possible to obtain two different types of distributions calculated: the first provides the distribution with respect to the volume occupied by the particles while the second compared to the number.

From measurement, various data are obtained: a curve of particle size distribution, a value of average diameter, and an index that provides information about the degree of polydispersity (PDI) of the suspension.

PDI index is between 0 and 1, more it is close to 0, more the suspension is mono-disperse, while for an index equal to 1 the suspensions are considered totally poly-disperse. In general, a mono-disperse suspension may be considered for values of PDI ≤ 0.2, average poly-disperse for 0.2 ≤ PDI ≤ 0.5 and poly-disperse for values greater than 0.6.

XRD (X-Ray Diffraction)

The X-ray diffraction (XRD) is a technique widely used for the study of a solid. This technique allows to determine:

- the crystallinity of a solid or of a phase present in a solid;

- the estimate of the size of the microcrystals present;
- the type of phases present;
- the dimensions of the unit cell and the type of atoms that compose it.

To calculate the crystallites size Scherrer equation can be used:

$$d = K\, d / b \cos\theta$$

where b is the width at half height of reflection, θ is the angle of incidence, λ is the wavelength of the incident X-ray and K ~ 0.9 - 1.

The analyzes were carried out at room temperature with a diffractometer Bragg/Brentano X'pertPro PANalytical, using as a source of X-rays to an anode copper (Kα, $\lambda = 1.5418$ Å).

All samples were analyzed from 30 to 80 °2θ, acquiring 2s each 0.1 °2θ. Furthermore, to evaluate the size of the crystals of gold, a second acquisition of 10s every 0.1 °2θ from 34 to 46 °2θ was performed.

XRF (X-Ray Fluorescence)

The XRF analysis is used to determine the chemical composition of a sample, evaluating the elements present.

XRF analysis were carried out using a Panalytical Axios Advanced equipped with a Rh-target X-ray tube (4kW power) at 298 K.

Powder analysis were recorded in vacuum (10^{-5} bar) while liquid tests were carried out using Helium at atmospheric pressure.

This analytical technique was used to verify the yield of reaction in the synthesis of the nanoparticles, and to verify that precursors have been reduced and that cations do not remain in solution.

To perform the XRF analysis, aliquot of nanoparticle suspension was concentrated by centrifugation at 1500 rpm/min using Millipore filters. These filters consist of a membrane of regenerated cellulose having a variable mass, it able to retain the suspension of metal, eliminating the excess PVP and other reagents present dissolved in water.

4.1.4 Catalysts synthesis

Different catalysts were prepared using the nanoparticle suspensions obtained, through incipient wetness impregnation method, using titanium oxide (TiO_2) and cerium oxide (CeO_2) as supports.

The preparation of a supported catalyst by impregnation comprises a step of contact between the support and the suspension containing the metals, up to occupy with the liquid the entire volume of the pores of the support, followed by a drying step, to remove the solvent. At the end, the catalyst is dried in an oven at 120 °C overnight.

Some catalysts were prepared by keeping constant the molar ratio between Au and Cu by varying the metal loading (Table 3).

Table 3. Au and Au_1Cu_1 catalysts synthetized with different metal loading

Catalyst	Metal loading (%wt)	Au (% wt)	Cu (% wt)
0.5Au-Ti	0.5	0.5	/
1.0Au-Ti	1.0	1.0	/
1.5Au-Ti	1.5	1.5	/
2.0Au-Ti	2.0	2.0	/
0.5Au_1Cu_1-Ti	0.5	0.38	0.12
1.0Au_1Cu_1-Ti	1.0	0.76	0.24
1.5Au_1Cu_1-Ti	1.5	1.14	0.36
2.0Au_1Cu_1-Ti	2.0	1.52	0.48

Others catalysts were prepared by changing the nature of the active phase while keeping constant the metal loading (1.5%) on the support (Table 4).

Table 4. Bimetallic catalysts synthetized with different Au/Cu molar ratio

Catalyst	Support	Metal loading (% wt)	Au (% wt)	Cu (% wt)
1.5Au-Ti	TiO_2	1.5	1.5	/
1.5Au_3Cu_1-Ti			1.34	0.16
1.5Au_1Cu_1-Ti			1.14	0.36
1.5Au_1Cu_3-Ti			0.76	0.74
1.5Au-Ce	CeO_2	1.5	1.5	/
1.5Au_3Cu_1-Ce			1.34	0.16
1.5Au_1Cu_1-Ce			1.14	0.36
1.5Au_1Cu_3-Ce			0.76	0.74

The cerium oxide used as support also contains Ce^{3+}, in addition to Ce^{4+} species; the ceria is in fact an oxide which tends easily to be reduced under mild conditions. The presence of reduced species on the support has been verified by performing an oxidation at programmed temperature (TPO) with a ramp of 10 °C/min from 60 °C up to 650 °C and an isotherm at this temperature for 30 minutes. The instrument used was a ThermoQuest TPRDO 1100.

4.1.5 Catalyst characterization

The catalysts obtained were characterized by the following analytical techniques: measurement of the surface area (BET), XRD (X-Ray Diffraction), XPS (X-ray photoelectron spectroscopy), TGA (Thermogravimetric analysis) and DTA (differential thermal analysis). Analysis by TEM (Transmission Electron Microscopy) was also carried out for samples Au-TiO_2 and TiO_2-Au_1Cu_1.

Surface area

The measurement of the surface area of a catalyst, expressed as m^2/g, is one of the main parameters that characterize a material. The instrument used for the determination of the surface area was a BET Fisons Sorpty 1750 CE.

This technique uses the theory of BET (method developed by Brunauer, Emmett and Teller), and the area is measured by determining the quantity of gas that is adsorbed as a monolayer. The conditions are more favorable for the adsorption of gases on the surface of the solid occur at liquid nitrogen temperature (77 K); the measurement of the specific surface therefore takes place immediately after the cooling of the sample with liquid nitrogen. The analysis was conducted after a drying treatment of the sample at 120 °C.

XRD (X-Ray Diffraction)

XRD analysis is performed on the powder of the catalyst to be able to observe the different crystalline phases present and to verify the formation of the alloy in the bimetallic species. The analysis were carried out at room temperature with a diffractometer Bragg/Brentano X'pertPro PANalytical equipped with a X'Celerator detector, using as a source of X-rays to an anode copper (Kα, λ = 1.5418 Å). For samples supported on titania, analysis were carried out from 10 to 80 °2θ, with acquisitions of 20s every 0.05 °2θ. Furthermore, to evaluate the size of the crystallites of gold, a second acquisition of 1500s was performed every 0.08 °2θ from 40 to 47 °2θ. The coherence length of the Au crystalline domains was evaluated through single line profile fitting of the reflection at 44.3 °2θ, since at this particular angle no overlap with the anatase pattern of the support was observed. For samples supported on ceria, analyses were carried out from 20 to 85 °2θ, with acquisitions of 20s every 0.05 °2θ. Furthermore, to evaluate the size of the crystals of gold, a second acquisition of 400s was performed every 0.03 °2θ from 36 to 46 °2θ.

TGA and DTA

The methods of thermal analysis are based on the study of the effects of heat on the sample and consist in monitoring the variation of a property of the test sample as a function of temperature. The thermogravimetric analysis (TGA) is used to study the variation of mass in function of temperature, the differential thermal analysis (DTA) instead studies the effects endothermic and exothermic expressed as the difference in temperature between the sample and the inert sample.

The instrument used to perform the analysis is Rheometric Scientific STA1500; analyses were performed in air with a ramp of 10 °C/min from 25 °C up to 600 °C.

Transmission Electron Microscopy (TEM)

The transmission electron microscopy (TEM) is a technique where an electron beam is transmitted through a sample very thin (5 to 500 nm).

The transmission electron microscope works under vacuum in the absence of vibration and magnetic fields and it provides images formed by the interaction of the electrons transmitted, which are projected on a screen, making them visible. The electrons of the beam are generated usually through a process known as thermionic emission from a tungsten filament. The electrons are then accelerated by an electric potential (100-300 kV) and focused by electrostatic and electromagnetic lenses onto the sample.

The samples were analyzed with a JEOL 2200FS STEM, which uses a detector HAADF (high angle annular dark field) and operates at a power of 200 kV. To study in detail the composition and the structure of individual nanoparticles, analyses XEDS (X-ray energy dispersive) were conducted using a spectrometer Thermo-Noran XEDS.

The samples for the analysis of transmission electron microscopy in scanning (STEM) were prepared by dispersing the catalyst on a carbon film supported on a grid of molybdenum from 300 mesh.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD spectrometer. Data were acquired using a monochromatic Al source, operating at 120 W. All spectra were acquired using the Kratos immersion lens system for charge compensation, and the hybrid spectroscopy mode at pass energies of 40 and 160 eV for high resolution and survey scans respectively. Data were calibrated to the C 1s line at 284.8 eV, attributable to adventitious carbon and quantified using CasaXPSTM v2.3.15, using sensitivity factors supplied by the manufacturer.

Catalytic tests

The oxidation of 5-hydroxymethylfurfural (HMF) was carried out using a Parr Instrument 4561 autoclave reactor of 300mL capacity and equipped with a mechanical stirrer (0‑1200 rpm) and provision for measurement of temperature and pressure (Figure 25).

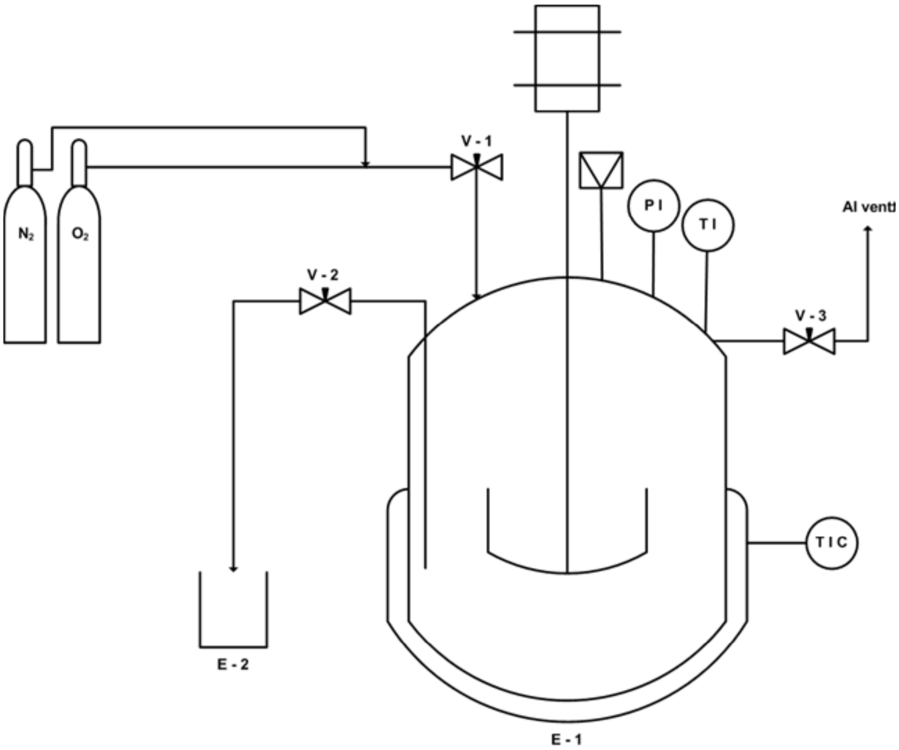

Figure 25. Autoclave reactor

The reaction was carried out in water, using sodium hydroxide as co-oxidant and the appropriate amount of catalyst.

If not differently indicated, each test was conducted for four hours with the following amounts of reagents:

- 25.5 mL of H_2O;
- 0,25g HMF;
- 4 equivalents of NaOH;
- Catalyst (HMF/total metal molar ratio 1:0.01)
- 10 bar of oxygen.

At the end of the reaction, the reaction mixture was cooled in an ice bath. The recovery of the catalyst was done by centrifugation and drying it at 120 °C.

The analysis of the reaction mixture was carried out using a HPLC (Agilent Technologies 1260 Infinity), with detector DAD UV-Vis, equipped with a Biorad AMINEX HPX 87H column (300 x 7.8 mm), ideal for the separation of organic acids.

Before carrying out the analysis it was necessary to centrifuge and filter the reaction mixture to separate the catalyst. The reaction mixture thus purified was diluted in water at a ratio 1/5 and injected by means of auto-sampler, in HPLC.
Identification of compounds was achieved by calibration using reference commercial samples.

4.2 Results and Discussion

The aim of the first part of this work was to produce monometallic gold and bimetallic nanoparticles of gold and copper by reduction of metal precursors ($HAuCl_4$ and $CuSO_4$) with glucose in aqueous solvent and in presence of NaOH and PVP (polyvinylpyrrolidone, stabilizing agent).

This procedure represents a synthesis method with low environmental impact for the production of metal nano-suspensions.

The suspensions obtained had a coloration which depends on the metallic phase; those containing only monometallic gold were dark and characterized by reflections of red color. Coloring of these nanoparticles is due to the presence of a plasmon absorption band at 525 nm. The formation of bimetallic alloys generates a variation of the electronic structure of the system: this variation causes a shift of the band of absorption with resulting change of color. The suspension bimetallic were gray, typical of Au-Cu alloy.

4.2.1 Sol characterization

DLS analysis

The suspension thus prepared were characterized by analysis DLS. In contrast to the classical analytical techniques for the determination of the size and the nature of the crystallites (XRD, TEM), DLS allows to quantify the hydrodynamic radius of the nanoparticles formed and the nature of the solvation sphere.

In Figure 26 it is possible to note an example of DLS analysis, where the intensity of the scattered light from the nanoparticles presented in solution as a function of the size of the hydrodynamic radius.

By DLS analysis and subsequent XRD analysis, the nanoparticles prepared by the use of a microwave oven or by means of a conventional heating were found to be identical, for this reason, it was subsequently decided to test only the catalysts prepared by the impregnation of sol synthesized with conventional heating.

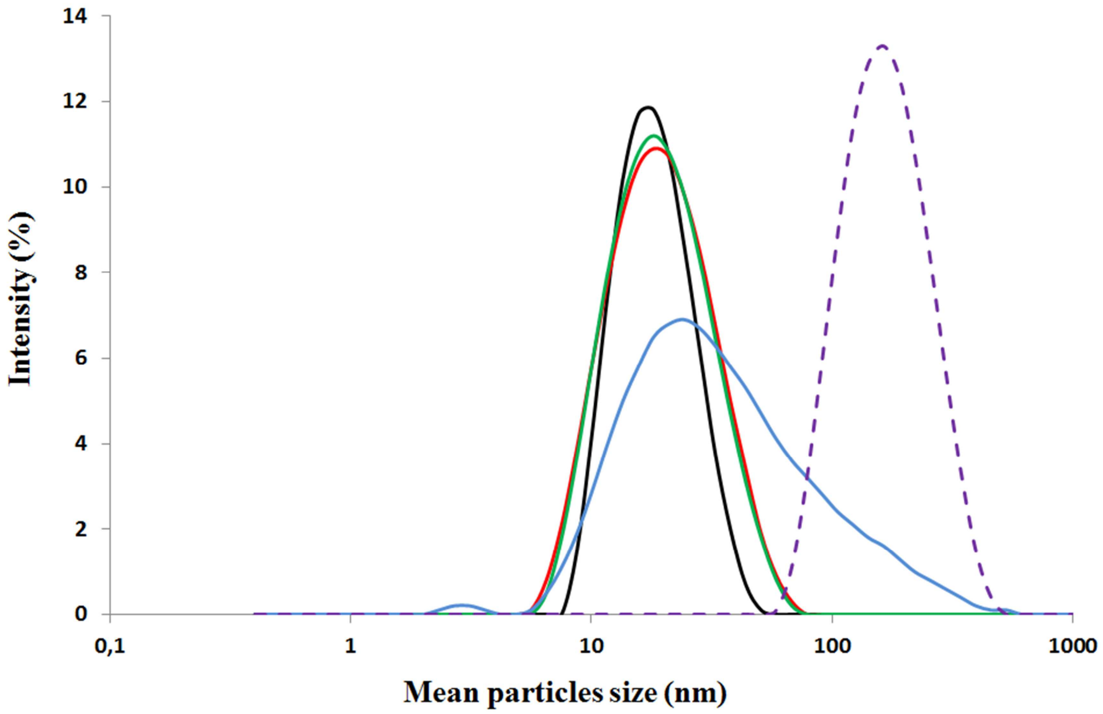

Figure 26. DLS analysis. Au (black line), Au_3Cu_1 (red line), Au_1Cu_1 (green line), Au_1Cu_3 (blue line), Au_1Cu_6 (dotted line).

The analysis carried out on monometallic suspension of gold and bimetallic suspension up to 1:1 molar ratio shows the formation of a monodispersed curve, with an average hydrodynamic diameter between 17 and 20 nm.

The tool also provides a polydispersity index (PDI), and the latter confirms that the size distribution is closely related to the average particle diameter (Table 5).

Table 5. DLS data

Suspension	Hydrodynamic diameter (nm)	PDI
Au	21	0.20
Au_3Cu_1	17	0.22
Au_1Cu_1	18	0.27
Au_1Cu_3	20	0.37
Au_1Cu_6	120	0.45

By increasing the copper content, the suspensions show a different behavior. The curves are widened (high PDI) with average diameters up to 120 nm with regard to the sample Au_1Cu_6.

This result displays that increasing the copper content nanoparticles become large, probably the formation of aggregates or nanoclusters with an inhomogeneous size and/or composition occurs.

XRD analysis

XRD analysis was performed on the suspensions synthesized to determine the type of phases present and the size of the primary crystallites, through the Scherrer equation For this purpose an analysis was made with large acquisition in the area 34-46 °2θ in which the main peak of gold is presented (38.2 ° 2θ) (Figure 27).

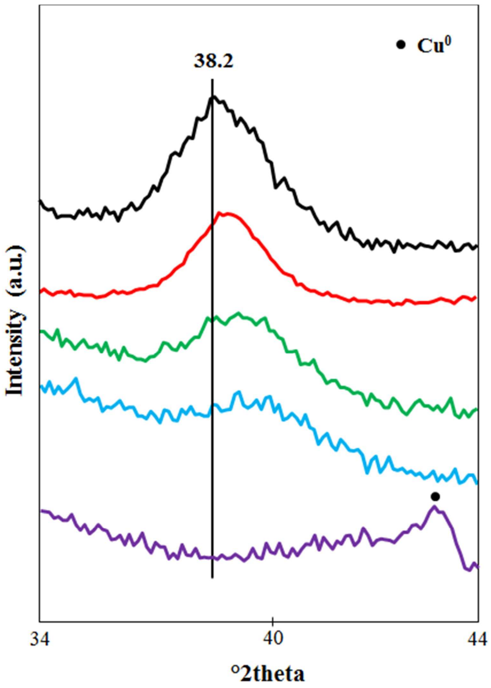

Figure 27. XRD analysis. Au (black line), Au_3Cu_1 (red line), Au_1Cu_1 (green line), Au_1Cu_3 (blue line), Au_1Cu_6 (violet line).

The peaks shown in the figure have been widened to highlight the plane 111 of the fcc structure of gold, the peak with relative intensity of 100%.

As reported in Figure 27, there is a shift of the main peak characteristic of gold, towards higher angles, increasing copper content; this supports the hypothesis of the formation of an alloy Au/Cu.

Only in the sample Au_1Cu_6 it is possible to see the peak (43.1 °2θ) relating to the formation of segregated oxides of copper (CuO_x), while in all other samples, peaks do not manifest any kind of segregation.

This technique does not allow anyway to exclude completely the presence of copper compounds, seeing the formed oxides may have amorphous form or they may be too little concentrated and very dispersed to be detected.

The size of the crystallites of the suspensions synthesized, calculated using the equation of Scherrer, are shown in Table 6.

Table 6. XRD data for the suspensions synthetized

Suspension	Size (nm)
Au	4.0
Au_3Cu_1	4.0
Au_1Cu_1	3.5
Au_1Cu_3	3.0
Au_1Cu_6	n.d

n.d. = not detectable

Increasing copper content, the bimetallic materials give broader XRD peaks, probably due to the formation of smaller crystallites respect to the monometallic sample or with low copper content.

In the sample Au_1Cu_6 the presence of the reflection characteristic of the gold or AuCu alloy was not detected, probably because it was present in low quantities.

XRF analysis

To evaluate the yield of the reaction of synthesis of the nanoparticles a quantitative analysis was carried out using a X-ray fluorescence (XRF) on the waters obtained from the concentration of the suspensions with Millipore filters. The absence of metal ions in aqueous solution confirms the complete reduction of the precursors, which means that all metals, introduced as a reagent in the form of salt, have been reduced.

It is reported in Table 7 the reaction yield for the synthesis carried out with different content of gold and copper.

Table 7. XRF analysis of the water filtered

Suspension	Au yield (%)	Cu yield (%)
Au	100	100
Au_3Cu_1	100	100
Au_1Cu_1	100	≈ 99
Au_1Cu_3	100	96
Au_1Cu_6	100	94

As seen from the data obtained, the reaction yield in gold is always total, while that of copper is quantitative for samples with a high gold content. Increasing Cu content the yield decreases slightly, confirming the greater difficulty of copper nucleation already previously highlighted.

4.2.2 Supported catalysts preparation

The catalysts were prepared by immobilization of the metal suspensions concentrated on the different oxides using the incipient wetness impregnation method. Titanium oxide (TiO_2) and cerium oxide (CeO_2) were used as supports.

Two series of bimetallic catalysts were synthesized. In one series, the molar ratio between gold and copper was kept fixed to 1, while the metal loading was varied from 0.5 to 2.0%. In the second series, the metal loading was kept constant at 1.5%, while the molar ratio between gold and copper was varied from 3:1 to 1:3.

The catalysts synthesized are shown in Table 8.

Table 8. List of catalysts synthetized

Catalyst	Support	Total metal loading (%w/w)	Au (% w/w)	Cu (% w/w)	Molar ratio (Au/Cu)
0.5Au-Ti	TiO_2	0.5	0.5	-	-
1.0Au-Ti	TiO_2	1.0	1.0	-	-
2.0Au-Ti	TiO_2	2.0	2.0	-	-
$0.5Au_1Cu_1$-Ti	TiO_2	0.5	0.38	0.12	1
$1.0Au_1Cu_1$-Ti	TiO_2	1.0	0.76	0.24	1
$2.0Au_1Cu_1$-Ti	TiO_2	2.0	1.52	0.48	1
1.5Au-Ti	TiO_2	1.5	1.5	-	-
$1.5Au_3Cu_1$-Ti	TiO_2	1.5	1.34	0.16	3
$1.5Au_1Cu_1$-Ti	TiO_2	1.5	1.14	0.36	1
$1.5Au_1Cu_3$-Ti	TiO_2	1.5	0.76	0.74	0.33
1.5Au-Ce	CeO_2	1.5	1.5	-	-
$1.5Au_3Cu_1$-Ce	CeO_2	1.5	1.34	0.16	3
$1.5Au_1Cu_1$-Ce	CeO_2	1.5	1.14	0.36	1
$1.5Au_1Cu_3$-Ce	CeO_2	1.5	0.76	0.74	0.33

4.2.3 Catalysts characterization

Catalysts supported on TiO_2

Catalysts supported on titania were characterized by surface area, XRD analysis, thermal analysis TGA/DTA and TEM analysis (1.5Au-Ti and $1.5Au_1Cu_1$-Ti samples).

BET analysis

The measures of surface area reported in the Table 9 show that the surface area is inversely proportional to the content of copper present in the catalyst. In fact, comparing the value of the support with the sample at higher copper content (Au_1Cu_3), it is possible to note that the difference in surface area is above 20 m^2/g, while as regards the monometallic catalysts, the surface area does not undergo very substantial variations respect to titanium oxide.

Table 9. measures of surface area

Catalyst	Area sup. (m^2/g)
TiO_2	83
0.5Au-Ti	78
1.0Au-Ti	74
2.0Au-Ti	73
$0.5Au_1Cu_1$-Ti	74
$1.0Au_1Cu_1$-Ti	73
$2.0Au_1Cu_1$-Ti	58
1.5Au-Ti	74
$1.5Au_3Cu_1$-Ti	72
$1.5Au_1Cu_1$-Ti	64
$1.5Au_1Cu_3$-Ti	60

Probably, the decrease of the porosity of the catalyst with increasing copper content is related to the greater quantity of organic phase present in the sol with low molar ratio of Au/Cu, as previously seen.

The catalyst $2.0Au_1Cu_1$-Ti has a low surface area, due to the large amount of suspension bimetallic deposited on the support, and accordingly to the large amount of organic content.

XRD analysis

On all catalysts synthesized, XRD analysis were carried out to identify the type of phases present and to determine the average size of the crystallites of the active phase. The diffractograms of monometallic catalysts obtained are shown in Figure 28.

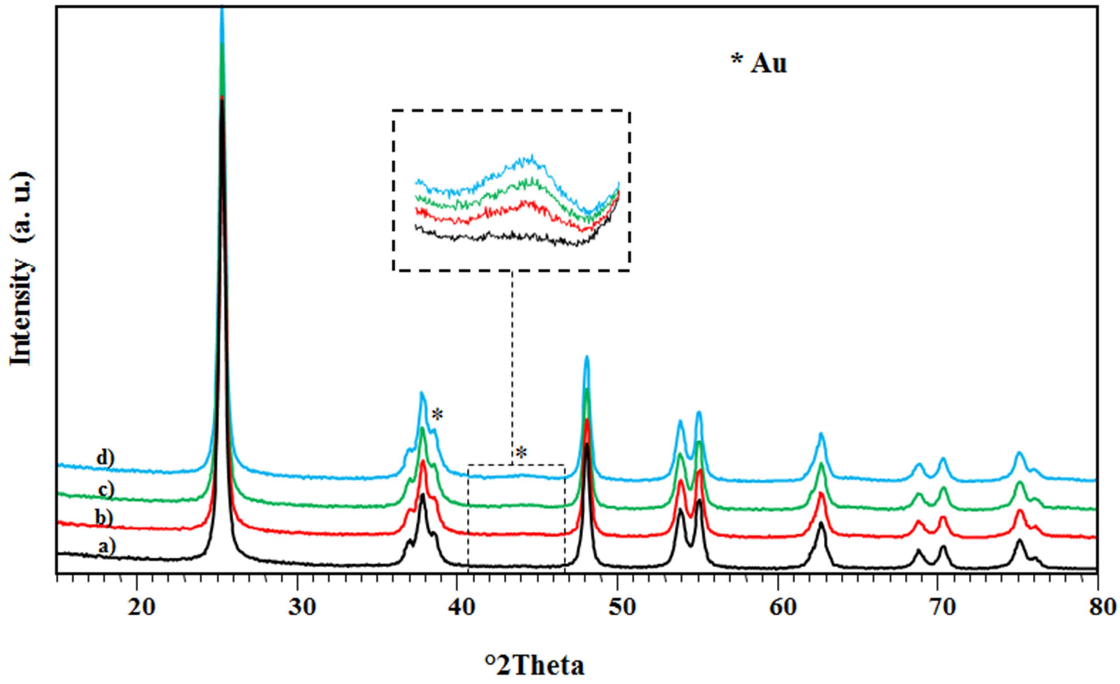

Figure 28. XRD analysis Au-Ti. a) 0.5Au-Ti, b) 1.0Au-Ti, c) 1.5Au-Ti, d) 2.0Au-Ti

From the data it is possible to identify the reflections of titania, in the form of anatase. The most intense reflections belonging to gold (38.2 ° and 44.3 °) are given respectively by the crystal planes (111) and (200) of the cell characteristic fcc gold and they have relative intensity of 100% and 50% . Unfortunately, the peak at 38.2 °2θ is covered from a titanium oxide peak, for this reason only the reflection to 44.3 °2θ was considered. For all samples this reflection is very enlarged, indicating that the metal nanoparticles are highly dispersed on the support. Through the equation of Scherrer it has been possible to estimate the size of the primary crystallites (Table 10).

Table 10. XRD data of monometallic catalysts

Catalyst	Au crystallite size (nm)
0.5Au-Ti	n.d.
1.0Au-Ti	6.0
1.5Au-Ti	6.5
2.0Au-Ti	6.5

n.d.=not detectable

Despite the size of the crystallites are very small, the data reported in table show that aggregation occurred during the impregnation phase of the sol on the support.

Also regarding the catalysts with molar ratio Au/Cu equal to 1 and different metal loading it is possible to notice a slight increase in the size of the crystallites with respect to the bimetallic suspensions, although in this case, the copper seems to perform an action of inhibition of the sintering of gold nanoparticle, with the result of obtaining smaller active phases than monometallic catalysts (Table 11,Figure 29).

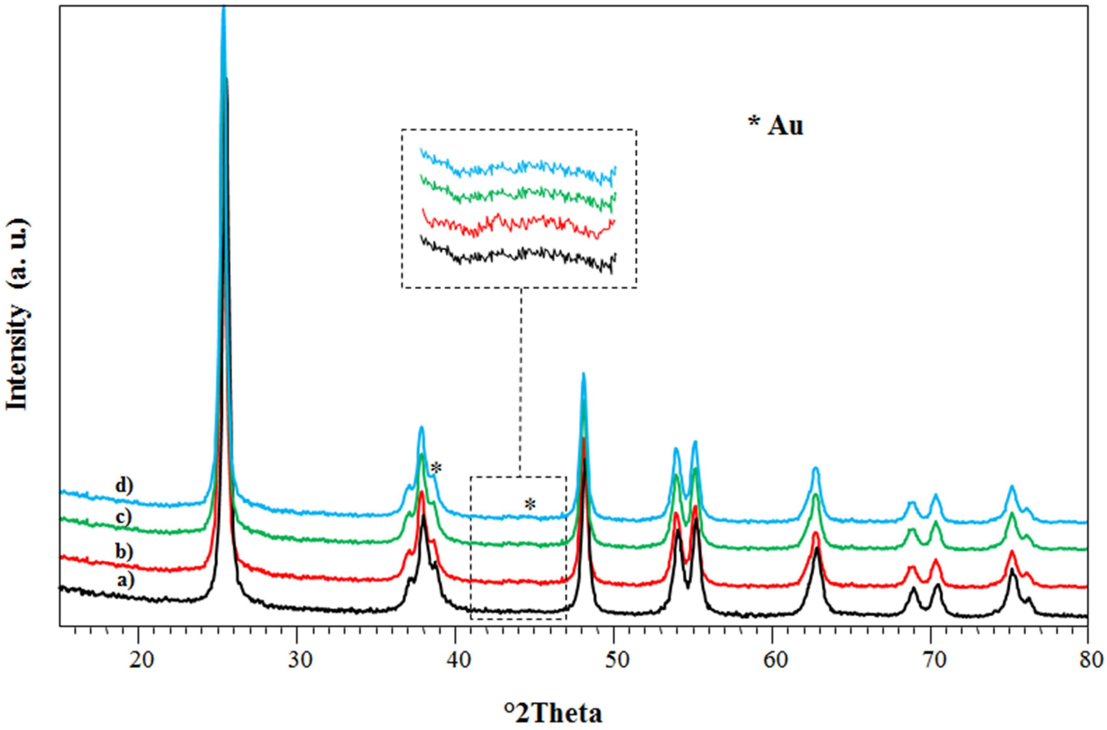

Figure 29. XRD analysis. Au_1Cu_1-Ti. a) 0.5Au_1Cu_1-Ti, b) 1.0Au_1Cu_1-Ti, c) 1.5Au_1Cu_1-Ti, d) 2.0Au_1Cu_1-Ti

Table 11. XRD data of bimetallic catalysts with molar ratio 1

Catalyst	Au crystallite size (nm)
0.5Au_1Cu_1-Ti	n.d.
1.0Au_1Cu_1-Ti	4.0
1.5Au_1Cu_1-Ti	5.0
2.0Au_1Cu_1-Ti	5.0

n.d.=not detectable

Samples with the same metal loading confirm what has already been seen; increasing the copper content in the catalyst are obtained of nanoparticles smaller than the monometallic catalysts and therefore more active phases dispersed (Table 12).

Table 12. XRD data of catalysts with metal loading of 1.5%

Catalyst	Au crystallite size (nm)
1.5Au-Ti	6.5
$1.5Au_3Cu_1$-Ti	5.0
$1.5Au_1Cu_1$-Ti	5.0
$1.5Au_1Cu_3$-Ti	5.0

XPS analysis

Monometallic and bimetallic catalysts were characterized in a region including between 83.2 – 83.8 eV corresponding to thindecese Au 4f region, where the gold is in its oxidation state 0[142,143], while the acquisition of copper peak (Cu 2p) was centered around to 932 eV.

XPS data are reported in Figure 30 (monometallic catalysts), Figure 31 (bimetallic catalysts with molar ratio 1) and Figure 32.

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[142] Zwijnenburg A., Goosens A., Sloof W.G., Graje M.W.J., Kraan A.M., Jongth L.J., Makee M., Moulijn J.A., *Journal of Physical Chemistry B*, **2002**, 106, 9853;

[143] Dimitratos N., Villa A., Bianchi C.L., Prati L., Makkee M., *Applied Catalysis A*, **2006**, 311, 185;

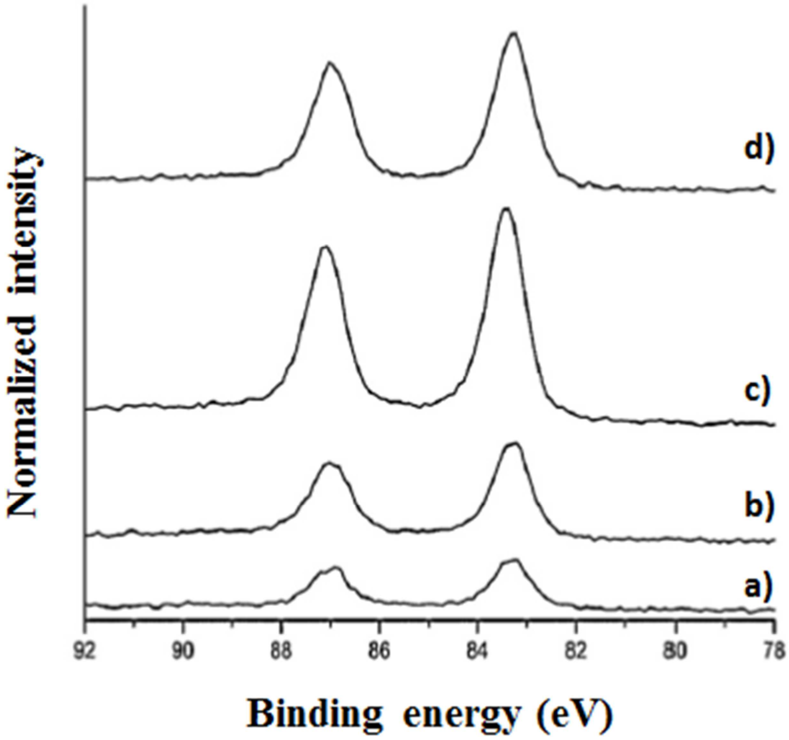

Figure 30. XPS analysis. 0.5Au-Ti, (b) 1.0Au-Ti, (c) 1.5Au-Ti, (d) 2.0Au-Ti

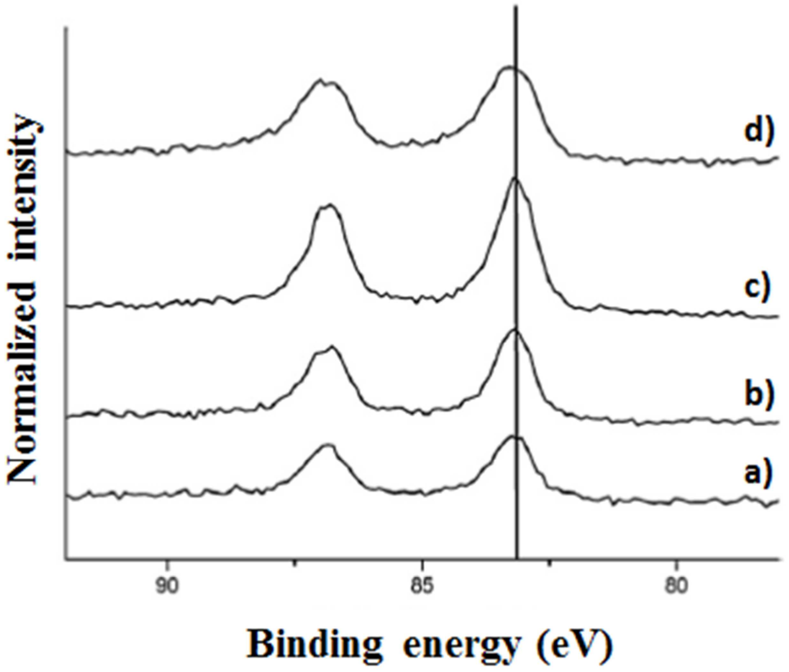

Figure 31. XPS analysis. 0.5Au$_1$Cu$_1$-Ti, (b) 1.0Au$_1$Cu$_1$-Ti, (c) 1.5Au$_1$Cu$_1$-Ti, (d) 2.0Au$_1$Cu$_1$-Ti

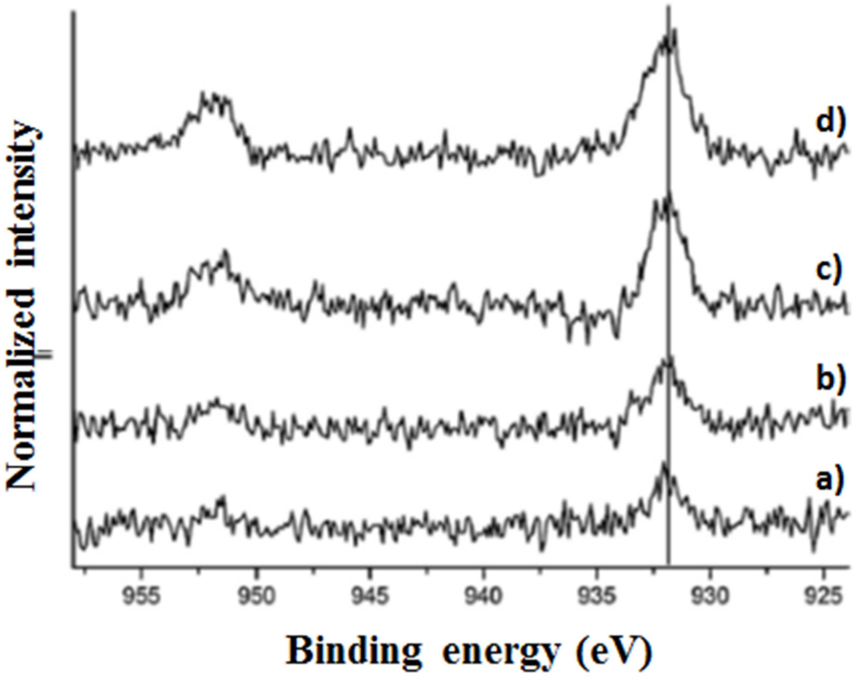

Figure 32. XPS analysis. 0.5Au$_1$Cu$_1$-Ti, (b) 1.0Au$_1$Cu$_1$-Ti, (c) 1.5Au$_1$Cu$_1$-Ti, (d) 2.0Au$_1$Cu$_1$-Ti

From the data shown in Table 13, we can see that the greater binding energy acquired is less than 84 eV, binding energy corresponding to bulk gold.

Table 13. XPS binding energies

Catalyst	B.E. Au 4f$_{7/2}$	Oxidation state	B.E. Cu 2p$_{3/2}$	Oxidation state
0.5Au-Ti	83.6	Au(0)	/	/
1.0Au-Ti	83.7	Au(0)	/	/
1.5Au-Ti	83.8	Au(0)	/	/
2.0Au-Ti	83.7	Au(0)	/	/
0.5Au$_1$Cu$_1$-Ti	83.2	Au(0)	931.9 (82), 932.6 (18)	Cu(0) Cu(δ^+)
1.0Au$_1$Cu$_1$-Ti	83.3	Au(0)	931.6 (67.2), 932.9 (32.8)	Cu(0) Cu(δ^+)
1.5Au$_1$Cu$_1$-Ti	83.6	Au(0)	931.7 (66.7), 932.4 (33.3)	Cu(0) Cu(δ^+)
2.0Au$_1$Cu$_1$-Ti	83.7	Au(0)	931.9 (67.0), 933.2 (33.0)	Cu(0) Cu(δ^+)

This means that the active phase present in our catalysts has a rounded nature, consistent with Au nanoparticles[144].

The low binding energy may be due to the small size of the nanoparticles or to a transfer of electrons from the copper to gold. The later can be explained as gold is more electronegative than copper according to Pauling’s electronegativity table therefore we could expect some electron transfer shifting of gold core levels toward lower binding energies[145].

However, the Cu 2p peak centered at ca. 932 eV is lower than the expected bulk value (932.7 eV) and that observed for smaller clusters of Cu and this contradicts the explanation of an electron transfer from copper to gold.

In view of this, we suggest that the dominant factor for the lower core level observed for Au 4f7/2 is mainly due to the smaller particle size of the Au-Cu particle. While the FWHM of the Cu 2p3/2 peak is almost twice that of, for example the corresponding O 1s, Ti 2p and Au 4f (FHWM ~ 1.1 eV), this could possibly in part be attributed to broadening of the Cu signal within the Au-Cu intermetallic[146], coupled with possible oxide formation which would present as a shoulder to the higher binding energy side, suggesting that the major component is metallic Cu within a Cu-Au alloy, whereby the shift is a result of charge transfer between the Cu and Au atoms within the alloy[147,148].

TGA and DTA

On the catalysts with metal loading corresponding to 1.5%, thermal analysis were carried out in air to have an estimate of the amount of organic waste present around the nanoparticles and on the support, because it is believed that this may lower the catalytic activity of the system, by blocking the active sites.

For all samples the first weight loss, associated with an endothermic peak around 100°C, is given by the evaporation of the water adsorbed on the catalyst. The second weight loss and the exothermic peak present at temperatures slightly above 300°C are

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[144] Radnik J., Mohr C., Claus P., *Physical Chemistry Chemical Physics*, **2003**, 5, 172;

[145] Chimentao R.J., Medina F., Fierro J.L.G., Llorca J., Sueiras J.E., Cesteros Y., Salagre P., *Journal of Molecular Catalysis A: Chemical*, **2007**, 274, 159;

[146] Cole R.J., Brooks N.J., Weightman P., *Physical Review Letters*, **1977**, 78, 3777;

[147] Kuhn M., Sham T.K., *Physical Review B*, **1994**, 49, 1647;

[148] Albonetti S., Pasini T., Lolli A., Blosi M., Piccinini M., Dimitratos N., Lopez-Sanchez J.A., Morgan D.J., Carley A.F., Hutchings G.J., Cavani F., *Catal. Today*, **2012**, 195, 120;

attributable to the organic oxidation (PVP and glucose) present on the surface of the nanoparticles and adsorbed on the support.

Comparing the results obtained for the different samples (Figure 33, Figure 34) an increase in weight loss is presented with increasing copper content; this trend is justified by the fact that in the syntheses with higher copper content, in order to stabilize the nanoparticles and monitor its growth, it has been necessary to use a larger amount of reducing agent and PVP. Furthermore, copper content increase corresponds a decrease of the temperature of the exothermic peak maximum. Samples with a high content of organic release a greater heat during the oxidation, favoring more the combustion at lower temperatures.

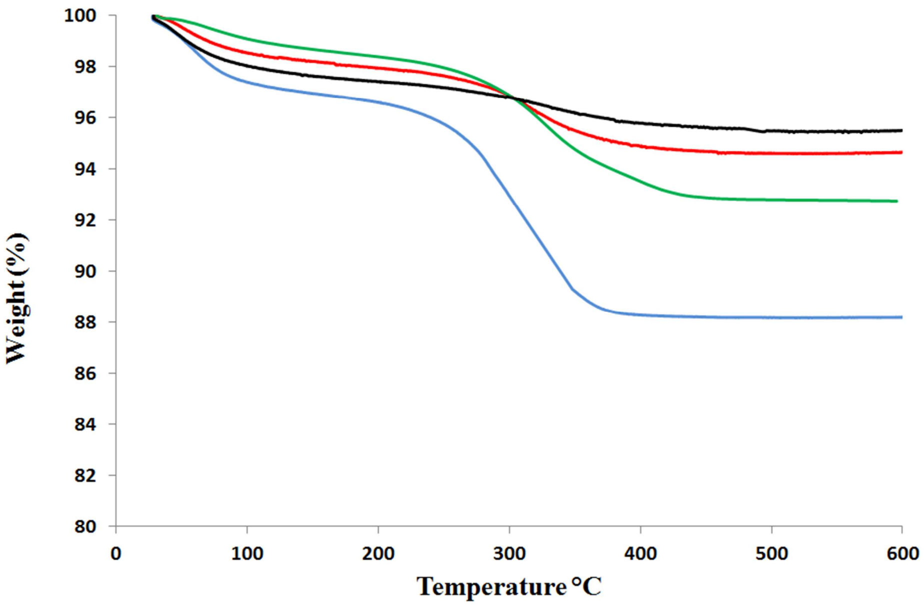

Figure 33. TGA analysis. 1.5Au-Ti (black line), 1.5Au$_3$Cu$_1$-Ti (red line), 1.5Au$_1$Cu$_1$-Ti (green line), 1.5Au$_1$Cu$_3$-Ti (blue line).

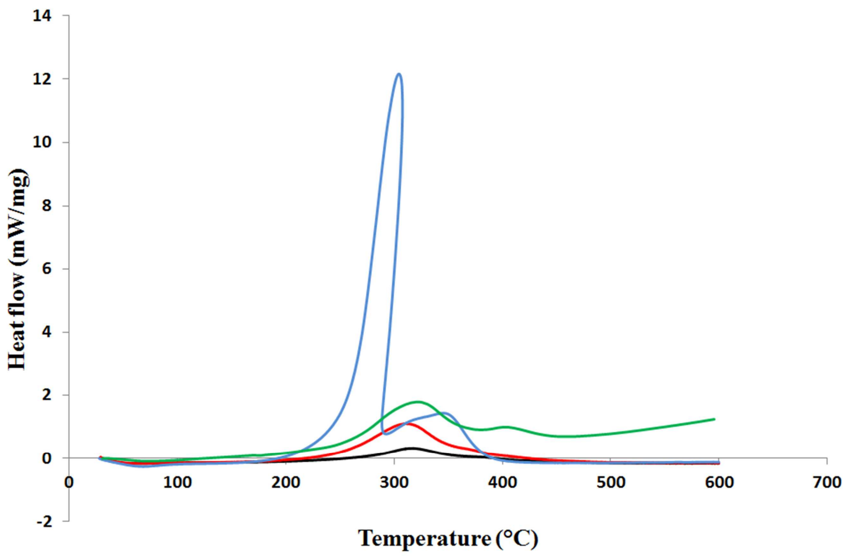

Figure 34. DTA analysis. 1.5Au-Ti (black line), 1.5Au_3Cu_1-Ti (red line), 1.5Au_1Cu_1-Ti (green line), 1.5Au_1Cu_3-Ti (blue line).

TEM analysis

The TEM analysis of the samples 1.5Au-Ti and 1.5Au_1Cu_1-Ti confirms the XRD data and XPS data in terms of size of the particles and in term of nature of the active phase; in fact, as can be seen from the graphs below the average size of the particles is about 6.6 nm for the sample containing only gold (Figure 35 B), while for the sample containing gold and copper in an equimolar ratio the dimensions are smaller, equal to about 4.4 nm (Figure 35 A).

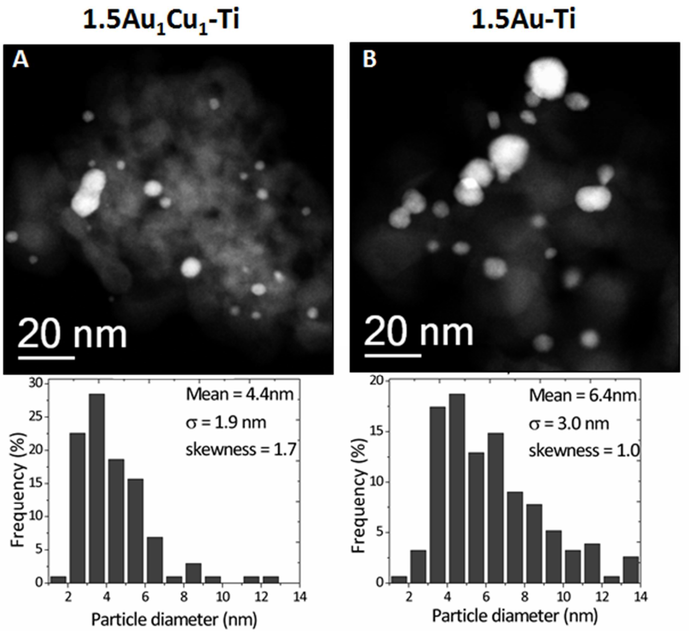

Figure 35. TEM analysis. A)1.5Au_1Cu_1-Ti, B) 1.5Au-Ti

The TEM analysis was critical to verify the presence of an alloy AuCu. In fact, in the spectrum obtained from analysis XEDS, shown in Figure 36, the copper Kα and the Lα gold are presented, indicates the presence of a homogeneous alloy AuCu 1:1. This technique does not show any effect of segregation and the ratio between the two metals in the nanoparticle is constant result in all nanoparticles analyzed, regardless of their size.

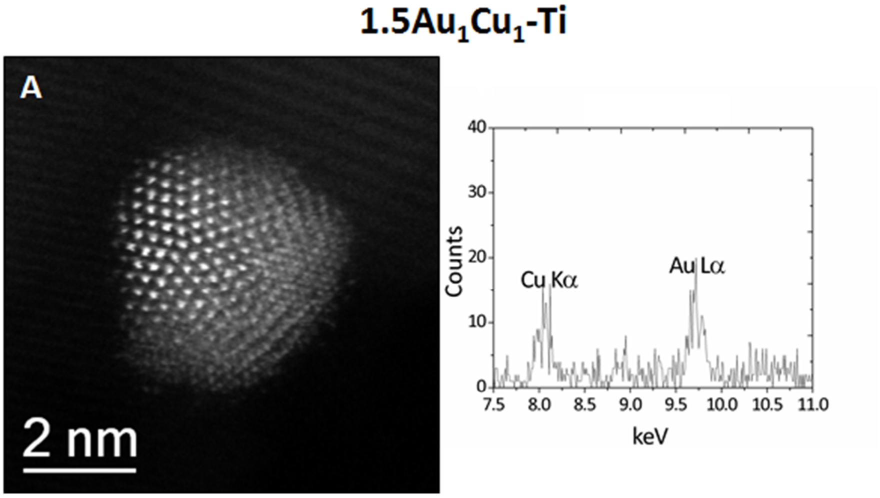

Figure 36. XDES spectrum of 1.5Au_1Cu_1-Ti nanoparticle

Catalysts supported on CeO_2

Even in this case, measure of the surface area, XRD analysis, thermogravimetry (TGA) and differential thermal analysis (DTA) were conducted to characterized all the catalysts supported on ceria.

BET analysis

The surface area of the catalyst 1.5Au-Ce is comparable with the surface area of the support (Table 14), which means that, even in this case, the deposition of the suspension of gold does not lead to a decrease of the porosity of the oxide. However, there is a decrease in surface area with the deposition of sol bimetallic. The catalyst with a lower surface area is the sample 1.5Au_1Cu_3-Ce. The decrease in surface area does not appear to be strictly attributable to an increase of the organic content (in particular of the stabilizer PVP), in fact, the sample 1.5Au_1Cu_1-Ce display a greater surface area respect to the sample with molar ratio Au/Cu equal to 3.

Table 14. Measures of surface area

Catalyst	Area sup. (m^2/g)
CeO_2	89
1.5Au-Ce	85
$1.5Au_3Cu_1$-Ce	62
$1.5Au_1Cu_1$-Ce	84
$1.5Au_1Cu_3$-Ce	49

XRD analysis

To elaborate the data relative to the size of the metal nanoparticles supported on CeO_2 it was possible to acquiring the gold peak at 38.2 °2θ relative to intensity of 100%, because in this case it was not covered by peaks of the support (Figure 37).

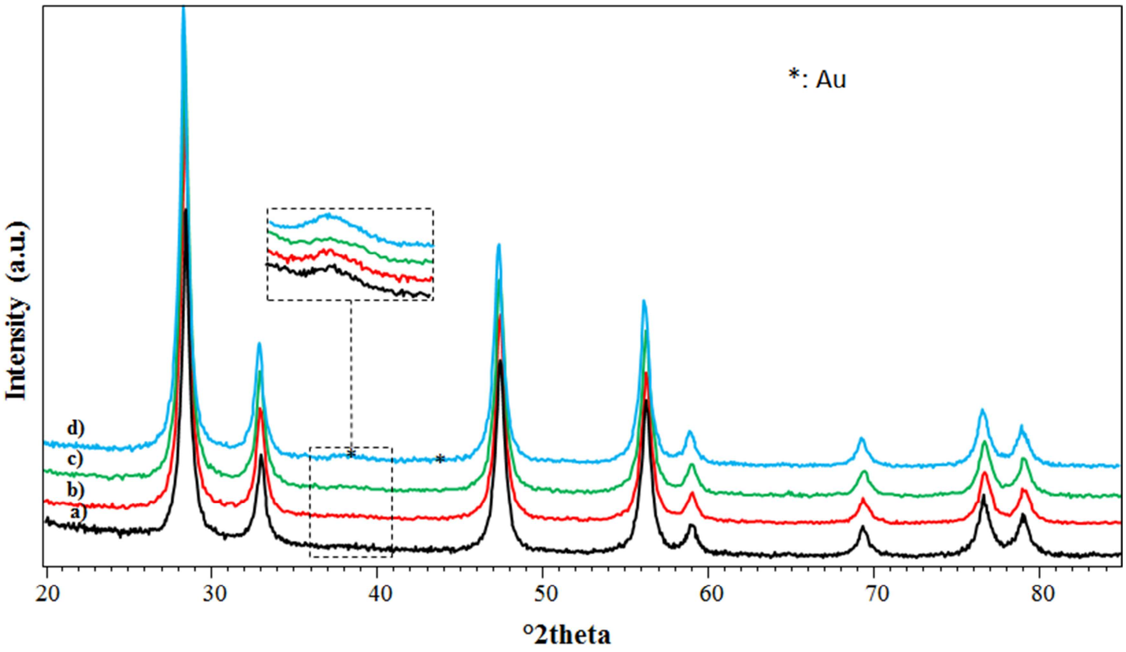

Figure 37- XRD ceria. a) $1.5Au_1Cu_3$-Ce, b) $1.5Au_1Cu_1$-Ce, c) $1.5Au_3Cu_1$-Ti, d) 1.5Au-Ce

The crystallite size of Au and Au/Cu seems slightly higher respect to the catalysts supported on titania. In effect, the calculation by the Scherrer equation reported in Table 15 shows an average size of about 5-6 nm.

Table 15. XRD data of catalysts supported on ceria

Catalyst	Au crystallite size (nm)
1.5Au-Ce	6.0
1.5Au_3Cu_1-Ce	5.0
1.5Au_1Cu_1-Ce	5.0
1.5Au_1Cu_3-Ce	<5.0

TGA and DTA

The thermal analysis carried out on catalysts supported on ceria, showed a trend almost similar to those relating to catalysts supported on titania.

Even in this case it can be seen as the first variation of the weight occurs at about 100 °C, temperature at which water adsorbed on the catalyst evaporates.

The second weight loss, the most significant one, occurs at a lower temperature compared to samples supported on titania. This phenomenon can be attributed to the higher oxidizing power of CeO_2 that catalyzes the reaction of combustion. in fact, cerium oxide is a support used to catalyze total oxidation reactions.

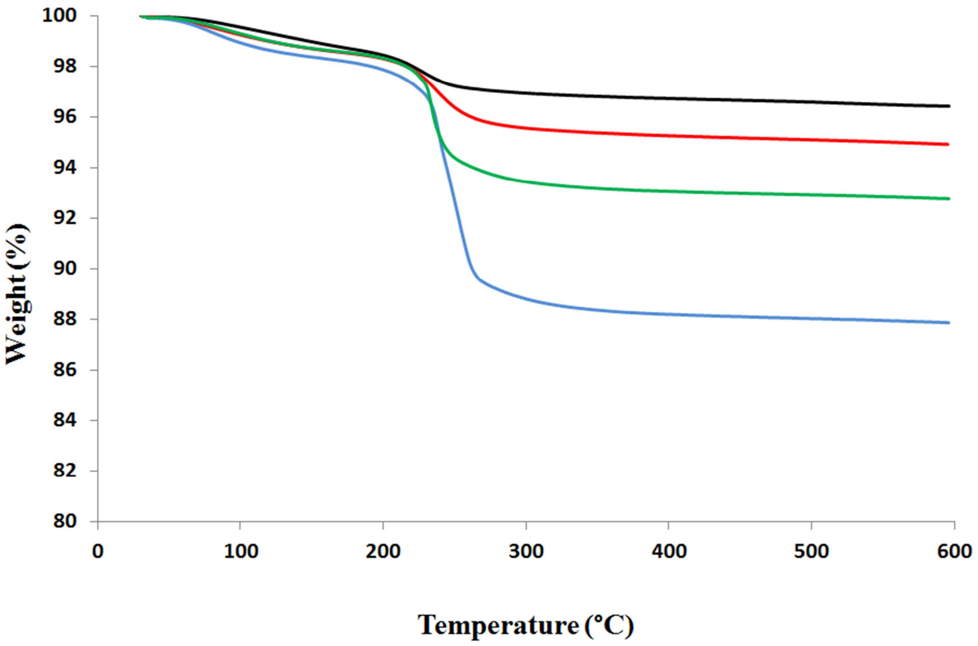

Figure 38. TGA analysis. 1.5Au-Ce (black line), 1.5Au_3Cu_1-Ce (red line), 1.5Au_1Cu_1-Ce (green line), 1.5Au_1Cu_3-Ce (blue line).

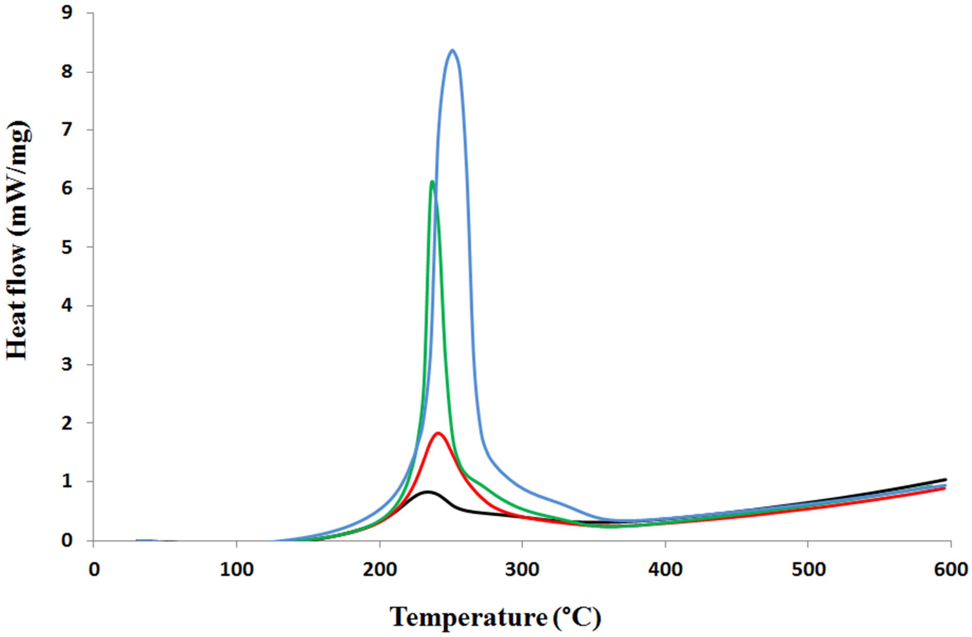

Figure 39. DTA analysis. 1.5Au-Ce (black line), 1.5Au$_3$Cu$_1$-Ce (red line), 1.5Au$_1$Cu$_1$-Ce (green line), 1.5Au$_1$Cu$_3$-Ce (blue line).

4.2.4 Catalytic test

In literature numerous articles of oxidation of HMF to FDCA are reported using gold based catalysts. In each case examined to improve the oxidation rate a co-oxidant (base) was used.

The first catalytic tests carried out have been conducted to see the stability of our reagent under the reaction conditions in the absence of catalyst. For this reason, the blank tests were carried out in an aqueous medium, in presence of a large amount of sodium hydroxide (20 equivalents) at 10 bar of oxygen. Test were conducted at 30°C and the results are reported in Figure 40.

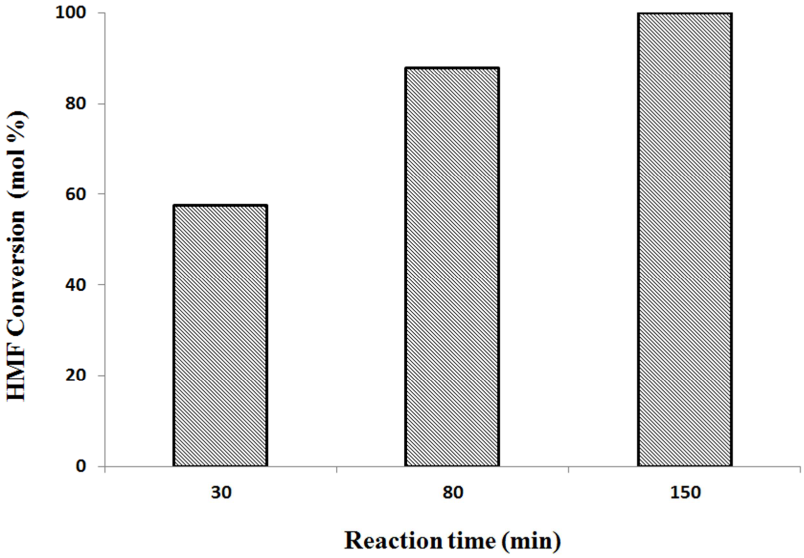

Figure 40. Blank experiment. Reaction condition:30°C, 10bar of oxygen, HMH:NaOH molar ratio 1:20

As it can be noticed, the conversion of HMF is very high in the first few minutes (60%) and it arrives at a quantitative conversion in 150 minutes of reaction.

From the first data obtained, test monitoring the influence of the base on the conversion of the substrate were conducted.

The results shown in

Figure 41 display that the HMF is a very reactive substrate in our operating conditions. In the absence of base, working at 60 °C, in 30 minutes of reaction the conversion of the reagent is equal to 60%. The addition of base, even if in small quantities, triggers numerous degradation reactions and it leads to the formation of many by-products even at low temperature.

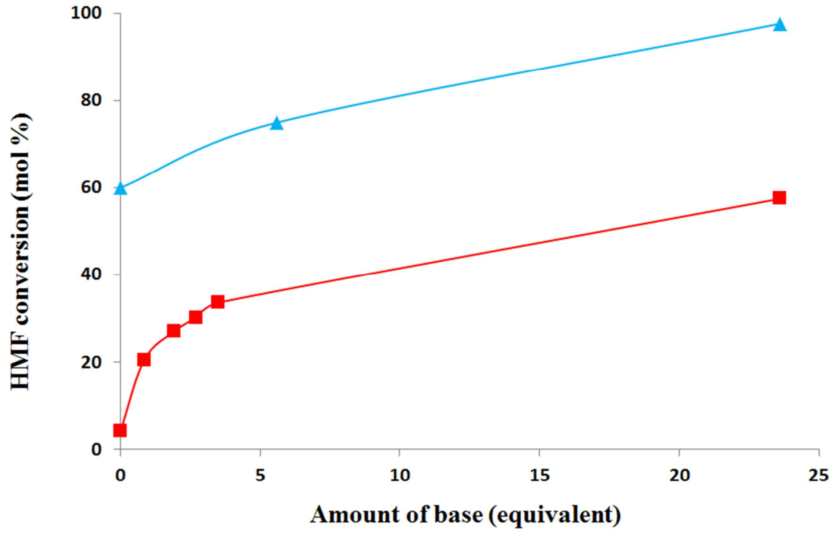

Figure 41. Blank experiments. Reaction condition: 30min, 10bar of oxygen. T:60°C (blue line), T: 30°C (red line).

The identification of by-products was found to be very complex. Surely, the products formed with a high molecular weight are formed by reactions of oligomerization/condensation of the aldehyde group present in position 5 on HMF.

To verify that the degradation reactions were accelerated by the presence of sodium hydroxide and not by the pressure of oxygen, the conversion of HMF was evaluated in tests conducted in the absence of catalyst, using 4 equivalents of soda with respect to the starting substrate at atmospheric pressure and room temperature (Figure 42).

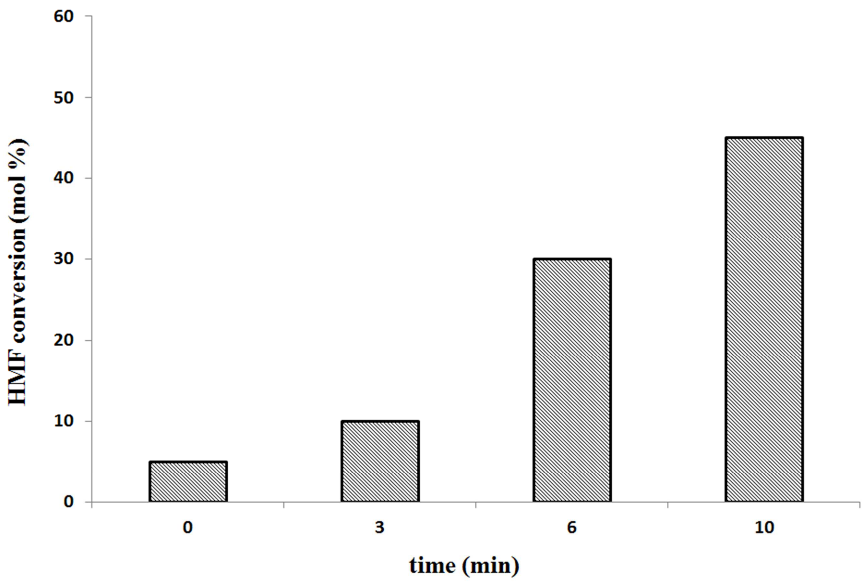

Figure 42. Blank experiment. Reaction condition. 70°C, HMF:NaOH molar ratio 1:4, 1 bar of air

Also in this case the conversion was very high in 10 minutes of reaction confirming the previous hypothesis. The same test was conducted in the absence of base, confirming further the data obtained up to now, in fact after 30 minutes of reaction the HMF was quantitatively recovered from the reaction medium.

The data so far obtained have allowed to understand that it is necessary to have in the reaction a very active catalyst for the HMF oxidation to avoid these parallel reactions of degradation of the substrate.

The oxidation of HMF to FDCA follows the pathway in Figure 43.

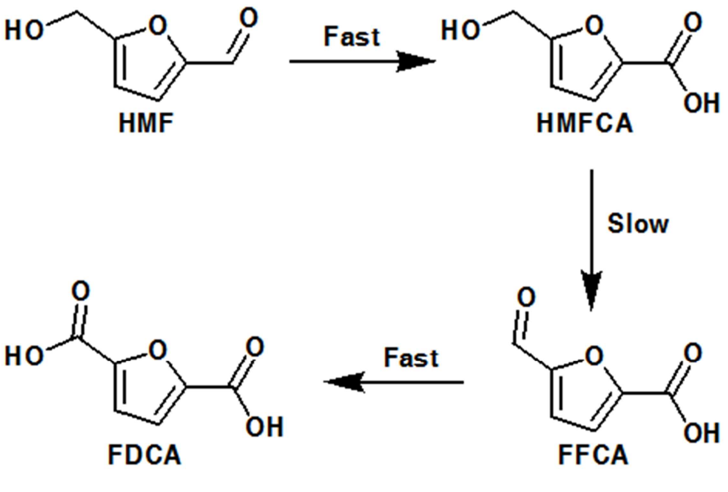

Figure 43. Reaction pathway for the HMF oxidation[140]

HMF is not oxidized directly to diacid, but it undergoes oxidation to two reaction intermediates, 5-hydroxymethyl-2.furancarboxylic acid (HMFCA) and 5-formyl-2-

furancarboxylic acid (FFCA). The first reaction is very fast leading to the formation of the monoacid already in the first minutes of reaction. The formation of the second intermediate is the limiting step of the whole system, the oxidation of the hydroxyl group of the HMFCA. The last oxidation is also very fast, leading to the formation of the desired product.

To evaluate the effective role of bimetallic nanoparticles in the oxidation reaction, a first comparison was made between the monometallic catalysts supported on titania in different metal loading and the respective bimetallic catalysts with a molar ratio gold/copper equal to 1 (Figure 44).

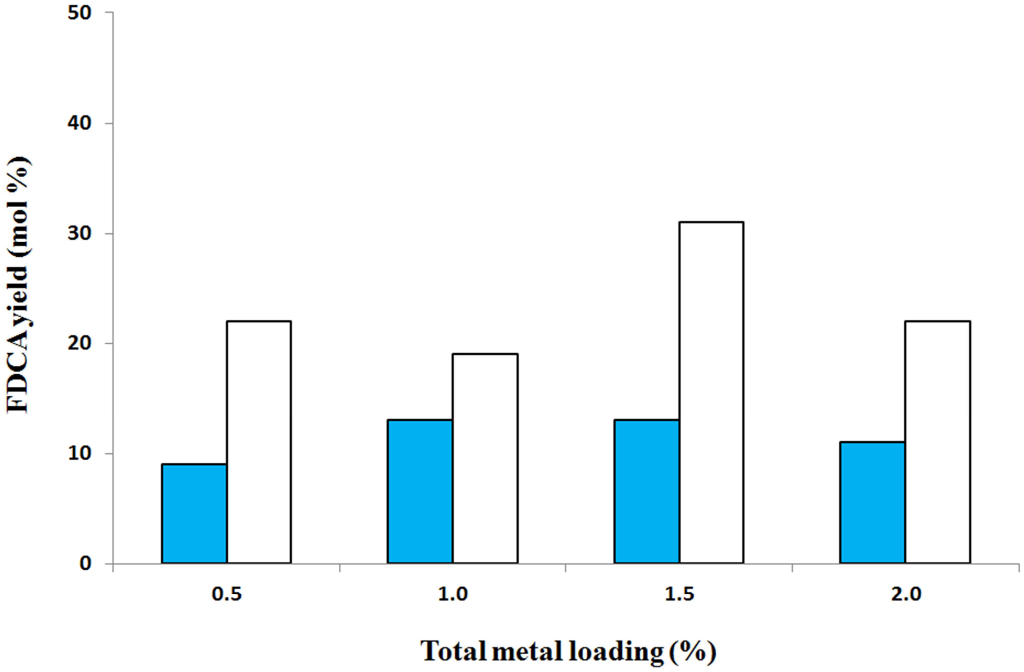

Figure 44. FDCA yield on different studied catalysts. Reaction conditions. 60°C, 240min, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. Au-Ti (blue bar), Au1Cu1-Ti (white bar).

Titanium dioxide and copper supported on titania were not active in the oxidation reaction. From the figure it is immediately clear that all of the bimetallic catalysts explained higher catalytic activity than the monometallic catalysts at constant metal loading. The best catalyst was the catalyst 1.5Au_1Cu_1-Ti.

The copper was found to be selectively inactive for the production of FDCA but it seems to favor the catalytic activity of gold.

To understand what was the role of the copper and the effectiveness of the synthesis of bimetallic nanoparticles other three catalysts were synthesized. Gold was impregnated on a support of Cu/TiO_2 using three different techniques: a) an incipient wetness impregnation of a monometallic sol stabilized by PVP, b) an immobilization of PVA stabilized gold sol or c) simple impregnation of $HAuCl_4$.

With the catalysts prepared, catalytic tests similar to those already made have been conducted and in any case the selectivity in FDCA was low or even null. HPLC analysis showed the formation of numerous by-products, comparable to those seen in the test blank. The higher activity of bimetallic 1.5Au_1Cu_1/Ti samples prepared utilizing the pre-formed Au‑Cu sol could be due to copper aiding the dispersion of the gold and/or to Cu acting as a gold promoter.

As already mentioned the catalyst which led to the best yield in the FDCA has been 1.5Au_1Cu_1-Ti, for this reason the main reaction conditions have been studied using this catalyst in comparison with the monometallic catalyst 1.5Au-Ti.

Effect of reaction conditions on catalyst performance

As the first catalytic test a time on line was performed to confirm the pathway reported in the literature for the HMF oxidation[140].

Test conducted at 95 °C using the catalyst 1.5Au_1Cu_1-Tu showed that actually the formation of the final product is the consequence of three consecutive reactions. After a few minutes reaction time almost everything HMF is converted to HMFCA. When in the reaction medium is present about 80% of the first intermediate, the formation of the diacid start. In all tests carried out, the presence of the second intermediate, FFCA, has never been noted, confirming that the last oxidation reaction is very fast and that the limiting step of the process is the oxidation of the hydroxyl group of HMFCA.

In all subsequent tests will be shown the HMF conversion was 100%, for this reason, the yield in products coincides with the selectivity.

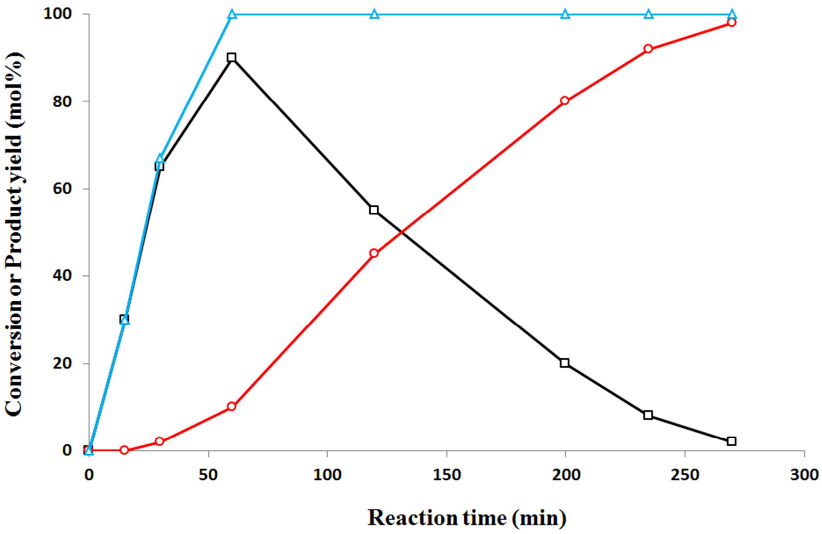

Figure 45. Products yield as a function of the time. Reaction conditions. 95°C, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. Conversion (blue line), HMFCA (black line), FDCA (red line).

The base is essential to obtain high yields in lower reaction times. In the Figure 46 the yield in FDCA as a function of equivalents of sodium hydroxide with respect to the initial substrate has been studied.

Confirming the data already present in the literature, with a quantity greater than 4 equivalents of base to yield the same operating conditions do not undergo any particular increases, while it is possible to note that using less than 4 equivalents yield the desired product remains very low[138].

Even in this case, the metal catalyst was always higher than the monometallic catalyst in terms of yield in FDCA.

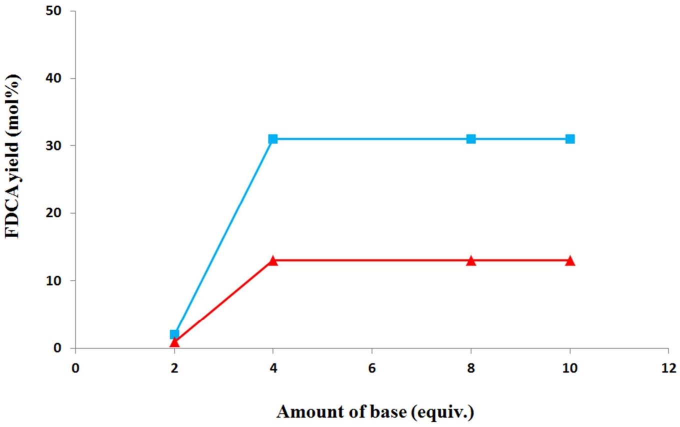

Figure 46. FDCA yield as a function of NaOH. Reaction condition. 60°C, 240 min, 10bar of oxygen, HMF:metal loading molar ratio 1:0.01. 1.5Au_1Cu_1-Ti (blue line), 1.5Au-Ti (red line).

Another fundamental parameter that has been studied is the reaction temperature.

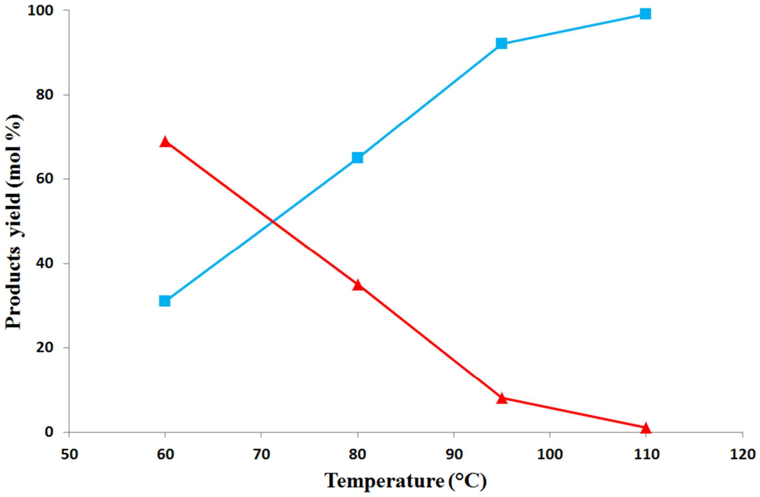

Figure 47. Products yield as a function of temperature. Reaction condition. 240 min, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. HMFCA (red line), FDCA (blue line).

The yield data obtained with increasing temperature show that this parameter is critical for this type of reaction. In fact, working at 110 ° C the quantitative FDCA yield with selectivity of 100% was achieved in 4 hours of reaction, while at 60 °C the yield slightly exceeds 30%.

Also the pressure of oxygen in the reaction medium was evaluated and as already reported in the literature also our results have shown that increasing the pressure a large increase in yield in the final product occurred.

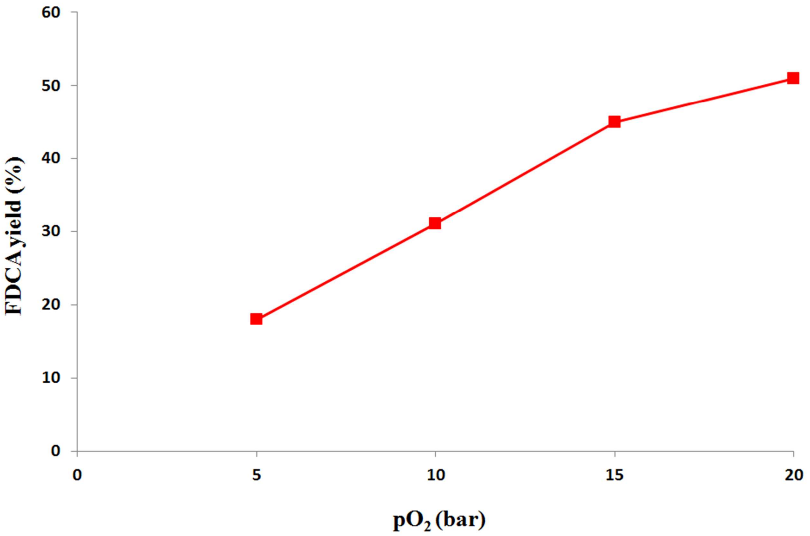

Figure 48. FDCA yield as a function of oxygen pressure. Reaction condition. 60°C, 240 min, HMF:metal loading:NaOH molar ratio 1:0.01:4.

Effect of the copper content

Seen that the bimetallic catalysts have shown very good catalytic performance the effect of copper content was studied, by performing a screening of catalysts synthesized at constant metal loading (Figure 49).

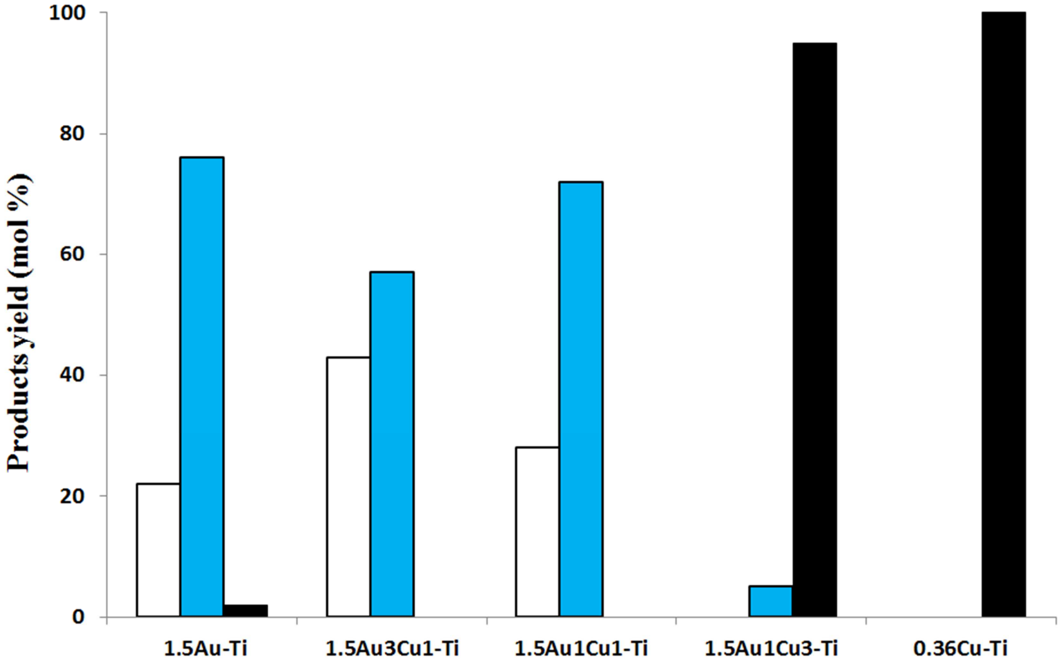

Figure 49. Effect of copper content. Reaction conditions. 70°C, 240min, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. FDCA (white bar), HMFCA (blue bar), by-products (black bar).

The addition of a small amount of copper has led to an improvement of the diacid yield compared to the catalyst containing only gold. However, with increasing copper content than the value in the equimolar system, a collapse in the FDCA yield occurred and polymer by-products were mainly obtained. From these data it can be seen, increasing the amount of copper in addition the molar ratio Au_1Cu_3, the bimetallic catalyst provides the same performance of monometallic containing only copper, which is virtually inactive for the production of FDCA.

This seems to indicate that the active phase for this oxidation reaction is gold or an alloy AuCu with high gold content, and that the copper encouraging their catalytic activity when present in a molar ratio greater than 1:1. At the moment, it is still unclear how the copper promotes the catalytic activity. The effect obtained might be to disperse the nanoparticles of gold, preventing aggregation, but also the formation of a bimetallic alloy with better performance of only gold.

From the comparison between the characterization and catalytic activity can then hypothesize that the loss of activity observed with increasing copper content, is related to the formation of CuOx on the surface of the active phase and that this phase is inactive in the reaction of interest .

The effect of reaction temperature was also studied in the bimetallic catalysts with a high gold content (Figure 50).

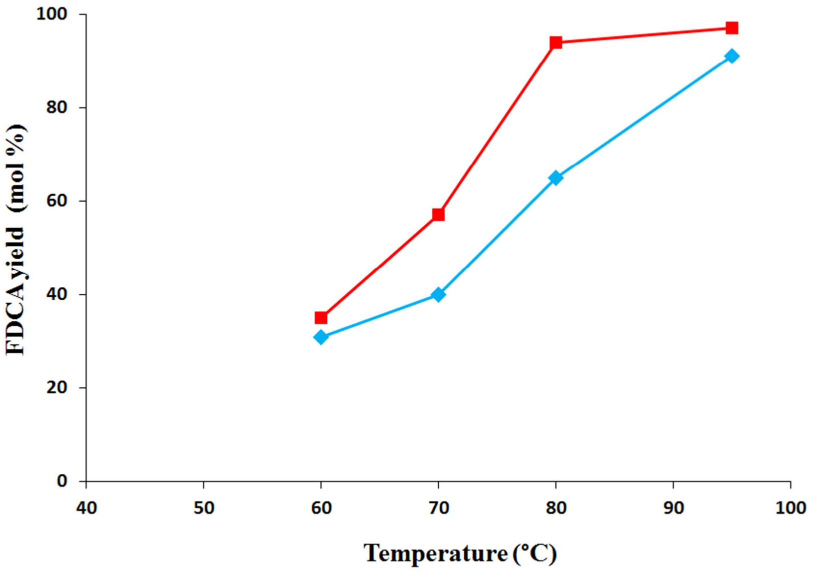

Figure 50. Products yield as a function of temperature. Reaction conditions. 240 min, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. 1.5Au_3Cu_1-Ti (red line), 1.5Au_1Cu_1-Ti (blue line)

Probably, the oxidation reaction of the aldehyde group of HMF takes place even at low temperatures, whereas oxidation of the hydroxyl group of HMFA via FFCA requires a higher temperature, above at 80 °C,to obtain good yields in lower reaction times.

Catalyst stability

Gold based catalytic systems used for this reaction undergo rapid deactivation due mainly to two reasons: a) Au leaching and b) the active phase being blocked by competitive adsorption.

The yield in FDCA as a function of catalytic cycles for the catalysts 1.5Au-Ti, 1.5Au_3Cu_1-Ti and 1.5Au_1Cu_1-Ti is shown in Figure 51.

In each experiment, the catalyst was recovered by filtration off, then it was washed and then it was loaded into a new batch with a fresh solution of HMF/NaOH.

The data obtained with the monometallic catalyst confirm the results reported in the literature[137,140]. In fact, after three catalytic cycles the catalyst 1.5Au-Ti has undergone rapid deactivation leading to the formation of a large amount of by-products. On the contrary, the presence of copper in the bimetallic catalysts has significantly improved the catalyst stability. By increasing the copper content the deactivation was in fact reduced, in particular, the catalyst $1.5Au_1Cu_1$-Ti only presented a slight decrease of FDCA yield confirming the importance of Au site isolation in the bimetallic systems due to the alloying with Cu present in this material.

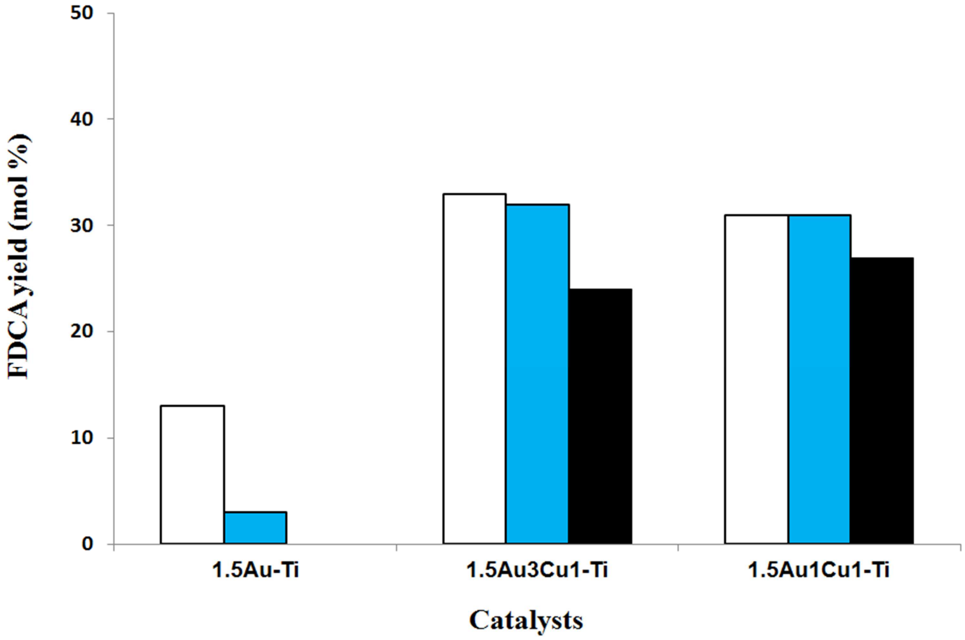

Figure 51. Catalyst re-use. Reaction condition. 60°C, 240 min, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. I use (white bar), II use (blue bar), III use (black bar).

Catalyst supported on ceria

To evaluate the effect of the support and the interaction of the support with the active phases synthesized, the same catalytic tests carried out until now have been conducted using the catalysts supported on ceria.

Catalysts were prepared by the same suspension of preformed nanoparticles, for this reason, any differences in catalytic performance should be attributable to a participation of the support in the reaction, rather than to an effect on the formation of the active phase. Molar yields of HMF and HMFCA and any by-products are shown in Figure 52 as a function of copper content for the catalysts supported on CeO_2.

The catalyst more active in the formation of FDCA was the monometallic catalyst, which showed a high yield in diacid, without the formation of by-products.

In this case, the yield obtained with the catalyst 1.5Au-Ce was approximately twice that obtained with the sample 1.5Au_3Cu_1-Ce and significantly greater than those obtained with the best systems supported on TiO_2.

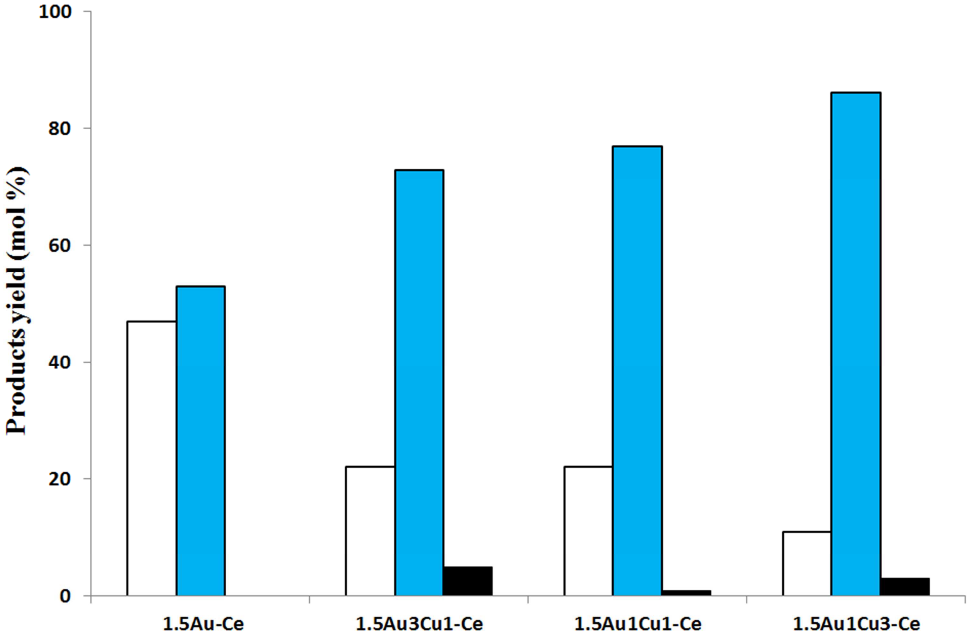

Figure 52. Effect of copper content in the catalysts supported on ceria. Reaction conditions. 70°C, 240 min, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. FDCA (white bar), HMFCA (blue bar), by-products (black bar).

These data appear to suggest an evident action of CeO_2 support in the oxidation reaction. This oxide, known for its property of oxygen donor bulk, is in fact very often used in catalysts for total oxidation reactions and used as an additive to improve the ability of resistance to coking.

Using bimetallic systems, the catalytic performances of the systems supported on CeO_2 decreased, contrary to what was observed for systems supported on TiO_2, wherein the best catalyst was that prepared by the sol Au_3Cu_1.

The largest differences between the two supports are present for the Cu content less than 0.3% wt. while high ratio Cu/Au catalytic activity decreases drastically for both systems, confirming the importance of gold which active species and / or an effect of deactivation due to the presence of a high content of residual organic in the samples. In fact, by comparing the yields obtained with the losses in weight provided by thermal analysis, the most active catalysts are also those with a smaller amount of organic adsorbed. The organic substances present on the surface of the catalyst may partially block the active sites, causing a decrease of the catalytic activity.

The difference observed for low Cu content may, on the contrary, be imputed to the different properties of the support. In particular, it is known that the properties of reducibility of CeO_2 are strongly influenced by the presence of nanoparticles of Au. In the case, the predominant effect on the catalytic activity seems to be due to the ability of the substrate to release oxygen in reaction medium. This property is greater in the presence of Au rather than Au/Cu. On the contrary, in the case of titania, the type of active phase appears to affect predominantly the reactivity.

Catalyst stability

The stability of systems supported on CeO_2 in subsequent reactions was verified by tests of reuse at 70 °C, as in the case of catalysts supported on TiO_2. In particular, tests were performed to reuse the catalysts 1.5Au-Ce (Figure 53) and $1.5Au_3Cu_1$-Ce (Figure 54).

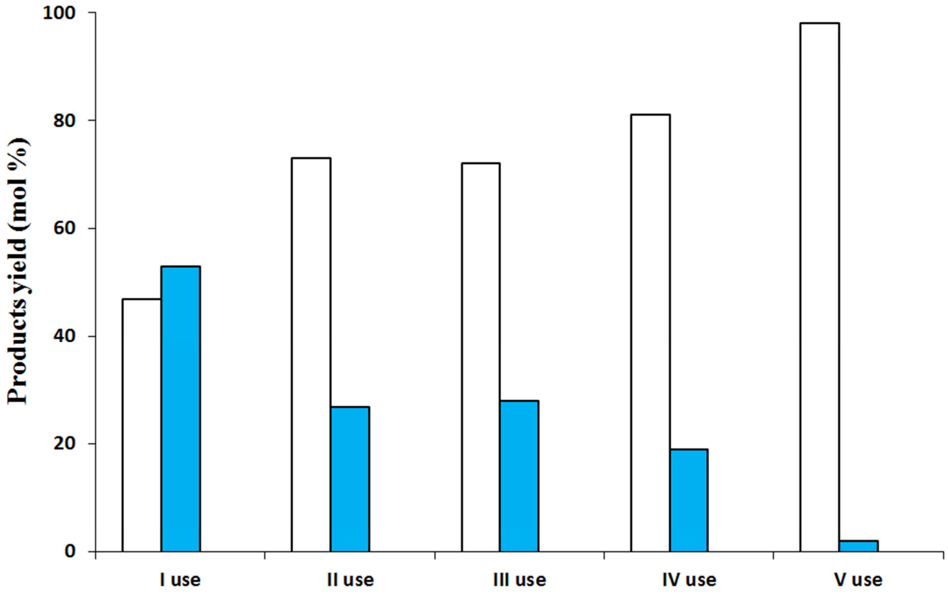

Figure 53. Monometallic catalyst reuse. Reaction condition. 70°C, 240 min, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. FDCA (white bar), HMFCA (blue bar)

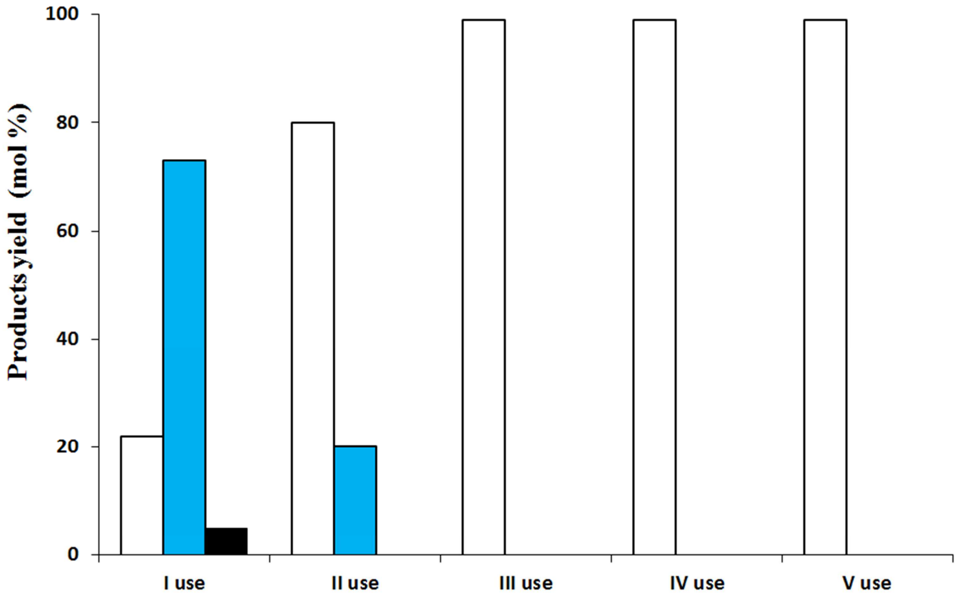

Figure 54. Bimetallic catalyst reuse. Reaction condition. 70°C, 240 min, 10 bar of oxygen, HMF:metal loading:NaOH molar ratio 1:0.01:4. FDCA (white bar), HMFCA (blue bar), by-products (black bar)

Surprisingly, the monometallic catalyst and the bimetallic AuCu with molar ratio 3:1 showed an increase in FDCA yield proportional to the number of the catalyst use. The catalysts appear to undergo an activation after the first use. This behavior can be explained assuming that the conditions of reaction and/or the treatment of recovery of the catalyst can modify the active phase. In particular, these conditions may promote the oxidation of the substrate and consequently to facilitate the oxygen mobility from the CeO2 surface, or probably may help the release of the organic substances adsorbed on the solid. To test these hypotheses, a catalyst 1.5Au-Ce was pretreated under the reaction conditions without HMF and once recovered by means the standard procedure it was used for an oxidation reaction. The results obtained showed a significant increase of the catalytic activity, with a yield of FDCA that passes from 47% to 92%.

The increase of the catalytic activity observed for the sample prepared under the reaction conditions may be due to a cleaning effect of the catalyst from the species adsorbed organic.

4.2.5 Conclusion

In this work, the synthesis of monometallic gold and bimetallic gold/copper nanoparticles at different molar ratio has been optimized. The synthesized nanoparticles were characterized by XRD and DLS analysis. The analysis showed that our synthesis has generated bimetallic nanoparticles in the range of 3-4 nm. The active phases were supported on titanium oxides and cerium oxides by incipient wetness impregnation and subsequently they were tested in the reaction of oxidation of HMF to FDCA. The catalysts supported on TiO_2 showed a catalytic activity superior respect to the all monometallic catalysts (except the catalyst with a high copper content $1.5Au_1Cu_3$) and they are also more stable and more resistant to poisoning than the monometallic ones.

The catalyst $1.5Au_3Cu_1$ presented the best catalytic activity, which allowed a fast oxidation of the limiting step of the reaction, thus the oxidation of HMFCA to FDCA. The analysis conducted on catalysts showed the formation of alloys gold/copper and a strong synergistic effect between the two metals.

The same synergistic effect was not observed in the catalysts supported on CeO_2. In fact, the monometallic catalyst showed the best catalytic activity in the oxidation of HMF to FDCA. Even in terms of stability, Au and Au/Cu catalysts have had very similar behaviors, activating in each catalytic cycle.

The different behavior obtained during the reusability test using the catalyst supported on ceria and titania is probably attributable to the nature of the supports. In fact, the reducibility of cerium is known to be favored by the presence of nanoparticles of Au, with a consequent release of bulk oxygen in the reaction medium.

Chapter 5

5 HMF hydrogenation

The production of diols from HMF is a very interesting process for the chemical industry, because these chemicals may be used, having six carbon atoms, or as chemical intermediates or directly for the production of polymers. In particular the 2,5-bishydroxymethyl furan (BHMF) turns out to be a chemical very versatile because it can be used for the production of polyurethane foams[116], but also as an intermediate for the production of adipic acid, alkyldiols, or hexamethylenediamine[149,150,151].

The BHMF is also used as an intermediate for the production of 2,5-dimethyl furan (DMF), in fact it can undergo hydrogenolysis under conditions very strong (high hydrogen pressures) and through the use of catalysts based on Ni, Ru and Pt.

As already mentioned, nowadays the DMF is a very interesting product because its chemical characteristics (high octane, high energy density and low boiling point) make it a perfect chemical compound for fuel.

The main problem of the reduction of HMF to BHMF is the low selectivity of the process. In fact, using catalysts for hydrogenation processes in liquid phase, the conversion of the starting substrate is very high, but the selectivity in the diol is quite low due to the necessary drastic conditions of reaction. For example the hydrogenation conducted with copper chromite at 150 °C and 35 bar of hydrogen leads to the formation of BHMF, but also of 2,5-bishydroxymethyl tetrahydrofuran, 1,2,6-hexanetriol, 1,2-hexanediol and 1,6-hexanediol[152].

Thus, the reaction conditions of the process become fundamental in order to obtain the high selectivity, but also the catalyst plays a very important role.

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[152] Utne T., Garber, J.D., Jones R.E., *U.S. Patent 3083236*, **1963**;

In fact the use of Ra-Ni or Ra-Cu based catalysts led to nonselective reactions also in mild conditions, due to the of over reduction of HMF with formation of 2,5-bishydroxymethyl tetrahydrofuran, while the use of Ru supported onto alumina or bimetallic catalyst Ni-Cu supported onto zirconia show good selectivity in BHMF.

The reduction of HMF can occur with sodium boron hydride[117], but also with NaOH[118] aqueous and with catalysts such as nickel, cobalt oxide and molybdenum oxide.

Complete HMF conversion and BHMF selectivity are obtained using Pt/C, PtO_2 or $2CuO+Cr_2O_3$ working at 140°C and 70 bar of hydrogen, while the presence of Pd/C or nickel Raney[119] catalysts allow to achieve the hydrogenation of the furan ring forming the 2,5-bishydroxymethyl-tetrahydrofuran.

A process proposed by Dumesic involves the use of catalysts based on Ru, Pd or Pt supported in a monophasic or biphasic reactor. The purpose of his work was to determine the effect of the metal present on the catalyst, the acidity of the system, the effect of the support and of the solvent, to see how these could influence the selectivity in BHMF. The optimal process conditions developed by the research group of Dumesic have led to a maximum yield of 90% in BHMF[153].

Homogeneous catalysis, which in principle might improve selectivity and require milder reaction conditions, has been scarcely investigated in this field. Example include hydrogenation of HMF accomplished by using formic acid as a hydrogen donor in the presence of iridium or ruthenium complexes[154]. On the light of these considerations we decide to employ a ruthenium based homogeneous hydrogenation catalyst, well known as the Shvo catalyst [Ph4(η5-C4CO)2H(CO)4Ru2](μ-H)[155] in the selective reduction of HMF to BHMF. The di-nuclear complex is stable to air, moisture and acidic conditions and selectively reduces polar double bonds leaving unaltered the aromatic ones[156,157].

At temperature higher than 90°C it dissociates into two monomeric forms: an oxidant specie (**B**) and a reducing form (**A**) (Figure 55).

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[154] Thananatthanachon T., Rauchfuss T.H., *ChemSusChem*, **2010**, 3, 1139;

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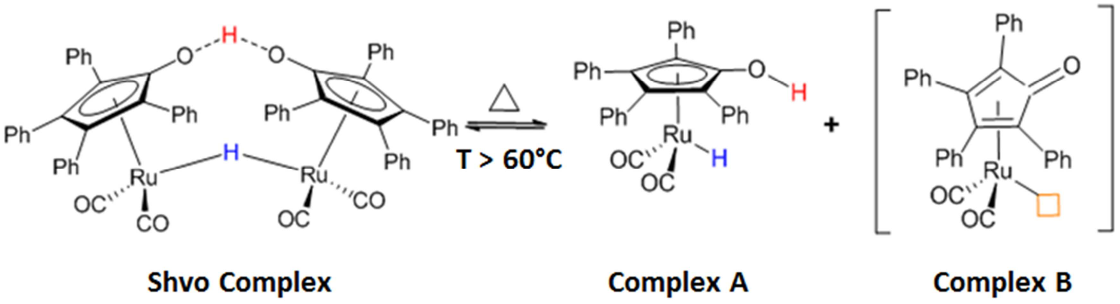

Figure 55. Dissociation of Shvo catalyst

The complex A having 18 electrons is the true catalyst for the hydrogenation reaction by performing an hydrogen transfer (hydride coordinated to ruthenium and hydrogen of the hydroxyl group) to a carbonyl group. At the same time the reduction, the complex A is transformed into B complex having 16 electrons, so unstable. In the presence of molecular hydrogen, the B complex is able to break the bond between two atoms of hydrogen and reconstitute the complex A. This catalytic cycle stops when all the carbonyl groups present in solution have been processed in the respective alcohol.

The upgrading of bio-oil from white poplar have recently demonstrated using Shvo catalyst by means of the quantitative hydrogenation of the polar double bonds under mild reaction conditions[158]. Shvo catalyst has been object of several mechanistic studies developed by Shvo and more recently by Casey and Backvall[159,160,161], the catalytic cycle involved in the case of hydrogenation of aldehydes, an example of metal-ligand bi-functional catalysis.

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[158] Busetto L., Fabbri D., Mazzoni R., Salmi M., Torri C., Zanotti V., *Fuel*, **2011**, 90, 1197;

[159] Casey C.P., Beetner S.E., Johnson J.B., *J. Am. Chem. Soc.*, **2008**, 130, 2285;

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[161] Casey C.P., Johnson J.B., Singer S.W., Cui Q., *J. Am. Chem. Soc.*, **2005**, 127, 3100;

5.1 Experimental section

In this work, a detailed investigation on the catalytic activity of the Shvo catalyst is reported in the selective hydrogenation of HMF to BMHF in both homogeneous and biphasic reaction mixtures. The catalyst behavior showed to be influenced by the product BHMF. Stoichiometric batch reactions followed by NMR, IR and ESI-MS experiments supported by DFT calculations allowed us to propose some mechanistic hypotheses, which will be also presented and discussed.

5.1.1 Materials

The following reagents and products were used for the work: methanol (Sigma-Aldrich), toluene (Sigma-Aldrich), $CDCl_3$ (Sigma-Aldrich), toluene-d8 (Sigma Aldrich), tetraphenyl-cyclopentadienone (Sigma Aldrich), triruthenium-dodecacarbonyl ($Ru_3(CO)_{12}$) (Strem), 5-hydroxymethylfurfural (Sigma-Aldrich), 2,5-dihydroxymethylfuran (Toronto Research Chemical).

5.1.2 Catalyst preparation

The procedure reported in the literature stat is followed for the production of the complex of Shvo $\{[2,3,4,5\text{-}Ph_4(\eta_5\text{-}C_4CO)]_2H\}Ru_2(CO)_4(\mu\text{-}H)$ (1). 3 equivalents of cyclopentanedione together to 1 equivalent of $Ru_3(CO)_{12}$ were reacted in methanol for 40 hours[162].

Subsequently, the complex has been purified by precipitation and characterized by means of IR, ^{1}H-NMR, ^{13}C-NMR and ESI-MS.

5.1.3 Catalytic test

The hydrogenation of 5-hydroxymethylfurfural (HMF) was carried out using a Parr Instrument 4561 autoclave reactor of 300mL capacity and equipped with a mechanical stirrer (0‑1200 rpm) and provision for measurement of temperature and pressure (Figure 25). The reaction was carried out in toluene or in a solution of toluene/water, using the appropriate amount of catalyst.

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[162] Johnson J.B., Backvall J.E., *J. Org. Chem.*, **2003**, 68, 7681;

If not differently indicated, each test was conducted for one hour at 90°C with the following amounts of reagents:

- 30 mL of toluene or 30mL of a solution toluene/water (in variable ratio);
- 0.200g HMF;
- Catalyst (HMF/total metal molar ratio 1:0.001);
- 10 bar of hydrogen

The autoclave reactor was purged 3 times with N_2 (40 bar) and then pressurized at 10 bar (H_2). The temperature was increased to 90 °C and the reaction mixture was stirred at ca. 1000 rpm for the time requested.

At the end of reaction, the reaction mixture was cooled in an ice bath and the final product BHMF was separated from 1 and analyzed using HPLC (Agilent Technologies 1260 Infinity), equipped with a C-18 core shell column 50x4.6mm employing a solution of 80% of 0.01 M H_3PO_4 and 20% acetonitrile as mobile phase.

Identification of compounds was achieved by calibration using reference commercial samples.

5.1.4 Analytic methods

The complex was characterized using a Perkin Elmer Spectrum 2000 FT-IR spectrophotometer. The analysis were carried out at 25 °C and atmosphere pressure.

ESI-MS spectra were recorded using Waters Micromass ZQ 4000 with samples dissolved in CH_3CN. The instrument used for the NMR analysis is a Varian Mercury Plus VX 400 instrument (^{1}H, 399.9; ^{13}C, 100.6 MHz).

5.1.5 XRF analysis

The XRF analysis is used to determine the chemical composition of a sample, evaluating the elements present.

XRF analysis were carried out using a Panalytical Axios Advanced equipped with a Rh-target X-ray tube (4kW power) at 298 K.

Powder analysis were recorded in vacuum (10^{-5} bar) while liquid tests were carried out using Helium at atmospheric pressure.

5.2 Result and Discussion

5.2.1 Effect of the reaction conditions

Initially a screening of the main operating conditions of the process has been carried out. As already mentioned previously, the real hydrogenation catalyst is the complex A while the complex of Shvo is only its precursor. The rupture of the complex di-nuclear occurs at high temperature while it is stable at room temperature[159]. This theory is confirmed by the data shown in the figure. The figure shows the trend of the yield in BHMF as a function of temperature. In fact it is possible to note that the yield in BHMF is greater with increasing temperature, while there is no catalytic activity at 30 °C

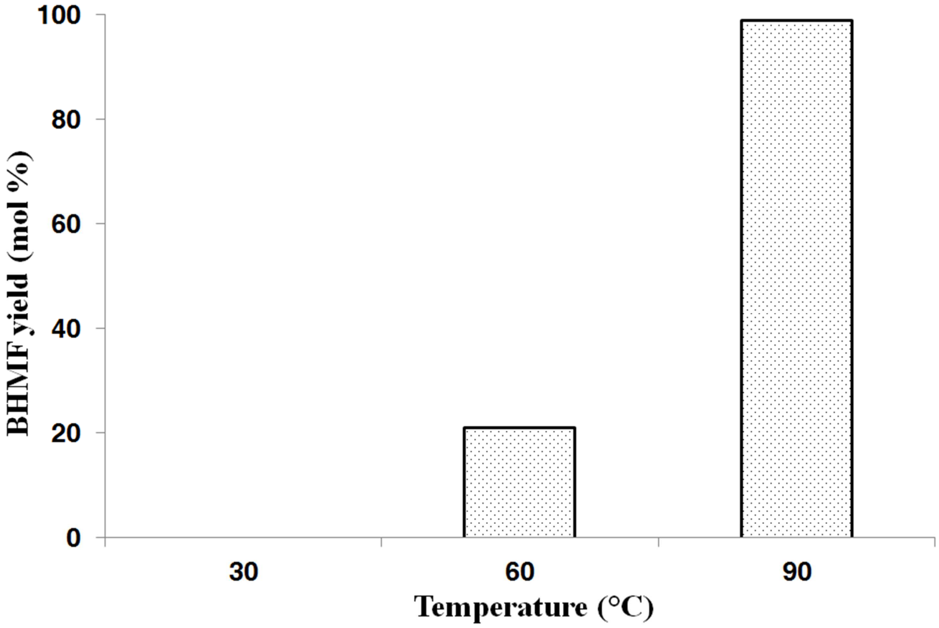

Figure 56. BHMF yield as a function of temperature. Reaction condition. 60min, 10 bar of hydrogen, HMF:complex molar ratio 1:0.001

Working at 90 °C the conversion of HMF was quantitative and selective of 100% in BHMF. Important to note that in 1 hour of reaction over reducing products or by-products were not formed.

The yield and the selectivity of the reaction was investigated by varying the pressure of hydrogen too.

The yield in the desired product is greatly influenced by the amount of hydrogen present in solution. In fact, by varying the pressure from 3 bar to 10 bar in the same reaction time yield in BHMF rises of 30%.

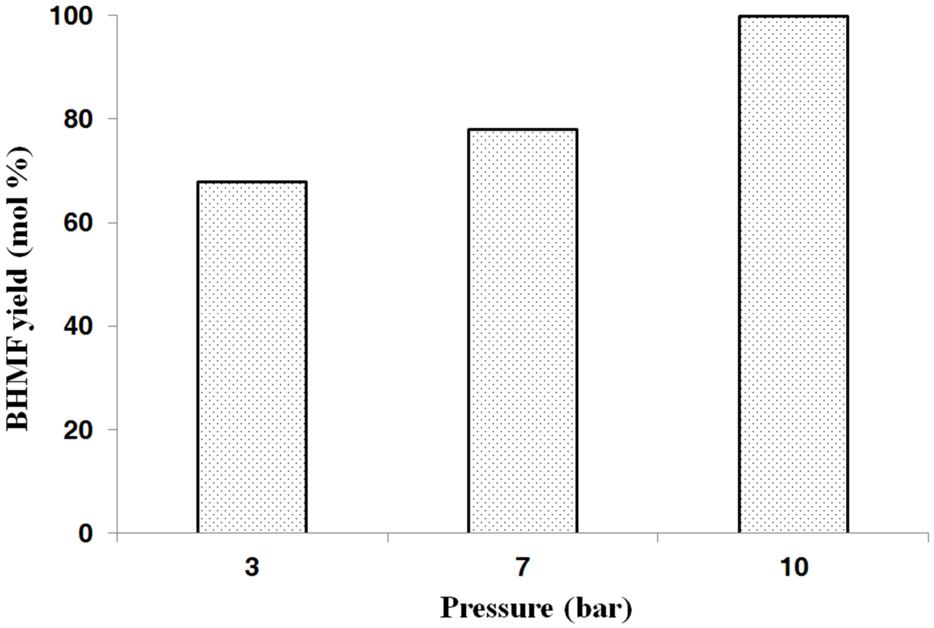

Figure 57. BHMF yield as a function of hydrogen pressure. Reaction condition. 60min, 90°C, HMF:complex molar ratio 1:0.001

The high pressure of hydrogen promotes the formation of the complex A from the complex B and thus to build up the catalyst.

Last, the kinetics of the hydrogenation reaction has been studied. The kinetics of hydrogenation of BHMF was compared with that of benzaldehyde in the same reaction conditions. From the data obtained in the Figure 58 it is possible to note that the yield of benzyl alcohol follows the trend of a classical kinetic, while the curve corresponding to the yield in BHMF presents a flexed between 30 and 60 minutes of reaction.

Probably the kinetics of hydrogenation reaction of HMF is influenced by interaction between the catalyst and the product formed BHMF, that unlike the benzyl alcohol has two hydroxyl groups instead of one.

The interaction between the catalyst and the product will then be investigated by DFT calculations

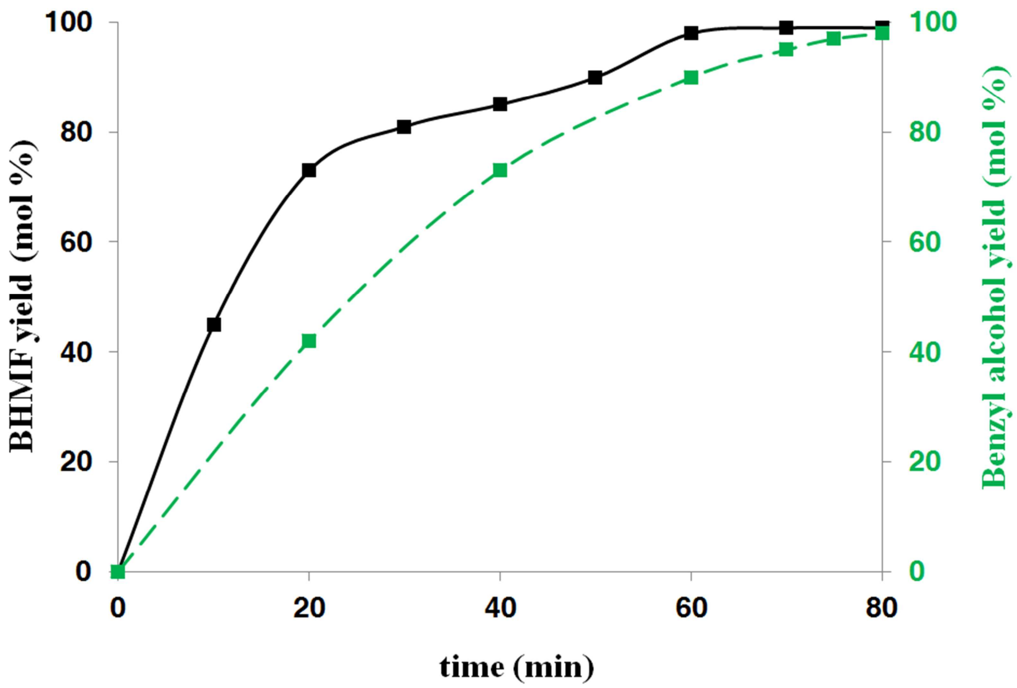

Figure 58. Kinetic studies. Reaction condition. 90°C, 10 bar of hydrogen, HMF:complex molar ratio 1:0.001

5.2.2 Catalyst stability and recyclability

Despite being a homogeneous catalyst, the importance of carrying out the re-use of the catalyst was evaluated. In particular different work up of the final reaction mixture have been developed in order to use the catalyst for more catalytic cycles.

The complex of Shvo is completely insoluble in water while HMF and BHMF have a great affinity for this solvent. For this reason, an extraction in water was made at the end of reaction, the reagent and the product were recovered in the aqueous phase and the catalyst in the organic phase. After three catalytic cycles the yield in BHMF was halved (55%) due mainly to a deactivation of the catalyst (Figure 59, black bar on the right). The deactivation was confirmed by XRF analysis of the aqueous phase extraction which showed the presence of ruthenium metal, confirming a partial degradation of the catalyst during the extraction step.

To avoid the degradation of the catalyst, three catalytic cycles were conducted without removing the product at the end of reaction and adding a quantity of fresh HMF after each cycle. At the end of the three cycles, also in this case, a small catalyst deactivation is observed (90% yield) compared to the first cycle (Figure 59, bar with dots on the left and on the right). This behavior confirms the possible interaction of the catalyst with the product formed, which slows down the reaction kinetics.

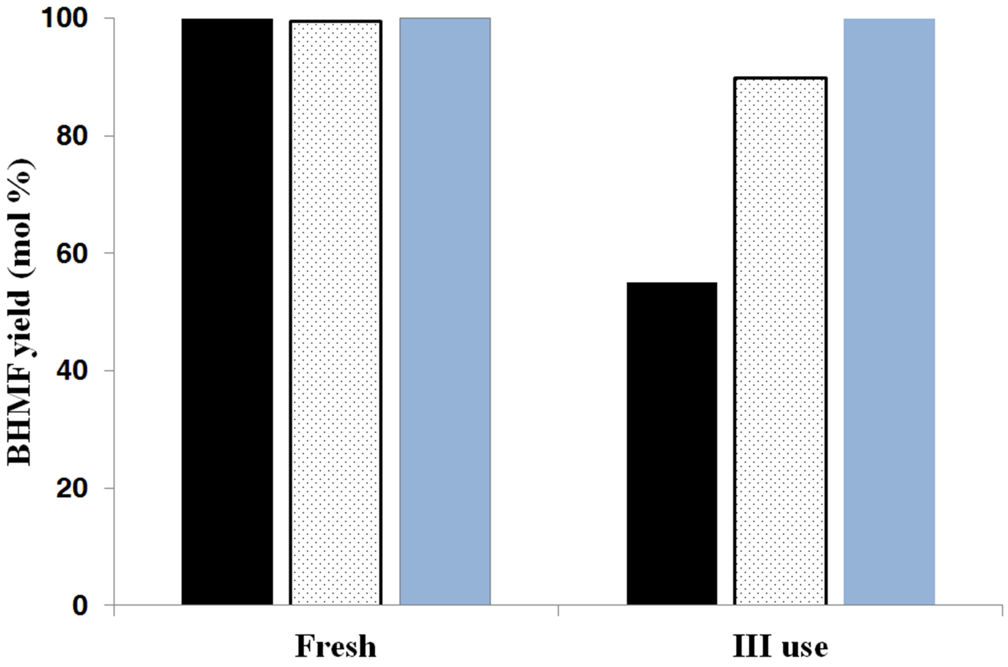

Figure 59. Re-use test. Reaction conditions. 60 min, 90°C, 10 bar of hydrogen, HMF:complex molar ratio 1:0.001. Extraction with water (black bar), no workup (bar with dots), BHMF precipitation (blue bar)

Surprisingly, it was discovered that cooling very quickly the final reaction mixture, the product crystallizes, precipitating and separating from the solvent. On the light of these considerations, as the last test, three catalytic cycles were carried out by removing the product by precipitation. As can be seen from the Figure 59 (blue bars), after the three tests, the yield of BHMF was always quantitative. This demonstrates that the catalyst is usable for more catalytic cycles, not undergoing deactivation, and that, in this particular process, it can be easily separated from the organic compounds.

5.2.3 Solvent effect

Industrially, a process which provides a very fast cooling process for the recovery of the product is economically unfavorable. For this reason, the possibility of carrying out the reaction in a biphasic solution was investigated. The use of water may facilitate the separation of the catalyst from the organic compounds without further processes

In particular, tests were conducted in a mixture water/toluene trying to optimize the ratio between the two solvents and to avoid the deactivation of the catalyst in contact with the water.

In Table 16 results obtained from the tests carried out at 90°C are reported.

Table 16. Biphasic hydrogenation at different toluene/water ratio

Reaction	**toluene/water (v/v)**	**time**	**BHMF yield (mol %)**
1	0.1	30	11
2	9	30	34
3	29	30	66
4	29	60	90
5	29	80	99
6	toluene	30	80

As already noted, the data reported display a high deactivation of the catalyst when the reaction mixture is composed of a large quantity of water (Reaction 1) respect to the organic solvent (Reaction 6).

Increasing the quantity of organic and decreasing the water, the yield in BHMF increases to reach a quantitative yield in 80 minutes of reaction (Reaction 5), compared to 60 minutes used in homogeneous phase.

The really interesting thing is that using water as co-solvent, the BHMF once formed enters into aqueous solution and it does not interact with the catalyst. In fact, as can be seen in the Figure 60, the kinetic curve derived from the data obtained in biphasic conditions no longer shows the point of inflection obtained in toluene solution alone. This behavior confirms the hypothesis of an interaction of the catalyst with the product as opposed to other substrates such as for example the benzyl alcohol

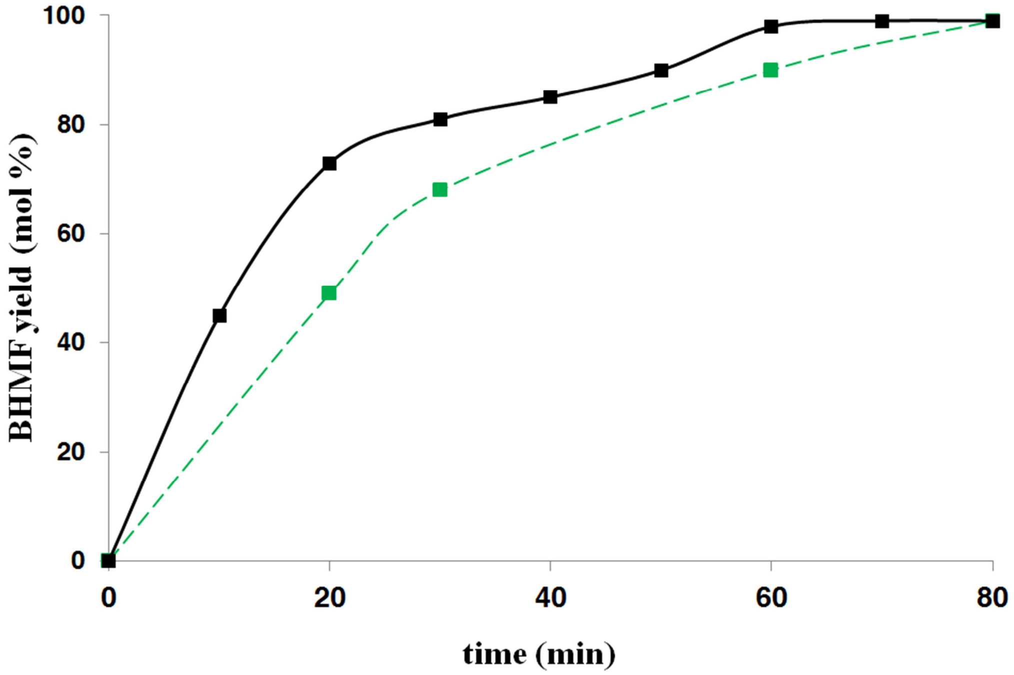

Figure 60. Time on line of biphasic reaction. Reaction conditions. 90°C, 10 bar of hydrogen, HMF:complex molar ratio 1:0.001. Biphasic reaction (green line), monophasic reaction (black line)

5.2.4 Hypothesis of mechanism

The test previously carried out have shown that the catalyst may undergo a deactivation on the part of the final product, in this case BHMF. The catalytic cycle of hydrogenation is shown in Figure 61. As already said, the complex A is the catalyst that makes the hydrogen transfer, producing the product BHMF, and at the same time it forms the B complex, which breaks the bond to a hydrogen molecule to form again the complex A.

Several mechanisms may be considered to explain the deactivation of the catalyst in our process. For example, in contrast to the benzyl alcohol, the BHMF has two hydroxyl groups and it presents the oxygen on the aromatic ring of the furan. Precisely the oxygen present on the ring of furan could interact with the hydroxyl group of the catalyst, preventing to a molecule of HMF, in particular of its aldehyde group, to coordinate (Figure 62) (complex D).

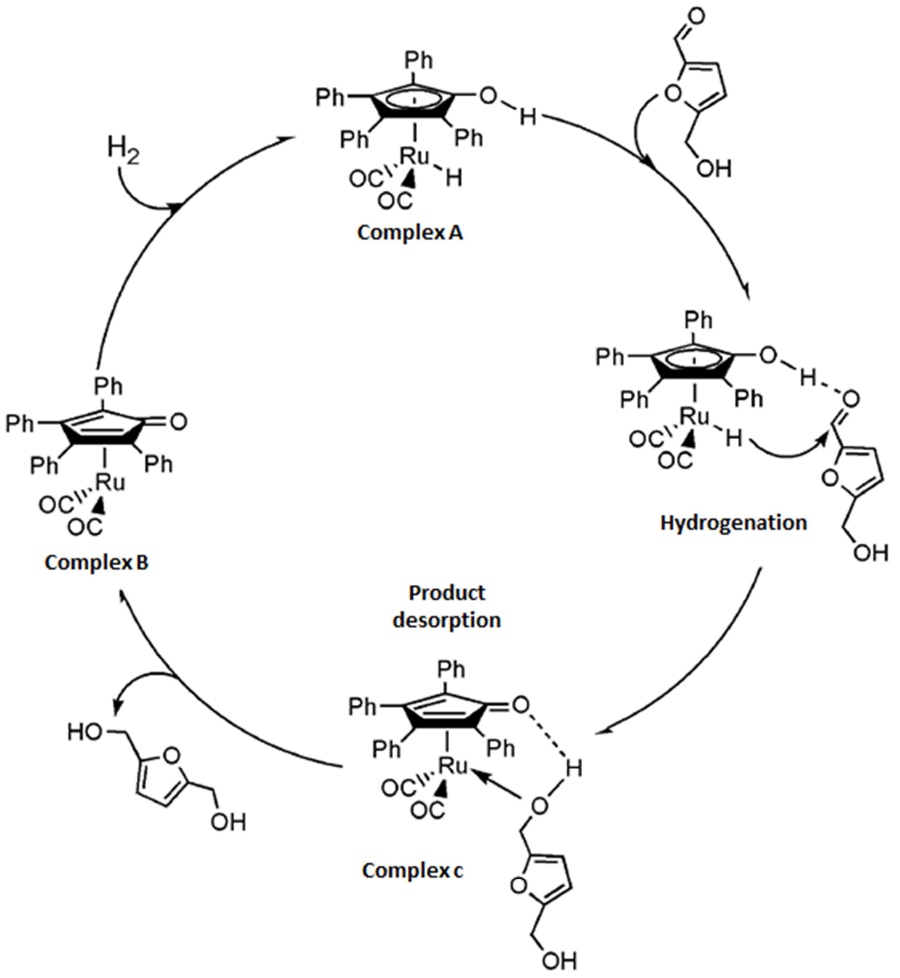

Figure 61. Catalytic cycle of HMF hydrogenation

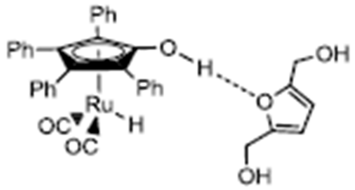

Figure 62. Interaction between catalyst and the furan oxygen

Another possible deactivation may be caused by the formation of a complex between the B complex having 16 electrons and BHMF (Figure 63). In particular, an interaction between the hydroxyl group of BHMF and the cyclopentadienone with a resulting interaction between the oxygen of the furan ring and the vacant coordination of ruthenium (complex E), or even stronger interaction can be established between the two hydroxyl groups of the BHMF and the oxygen of the ketone on the cyclopentadienone (complex F).

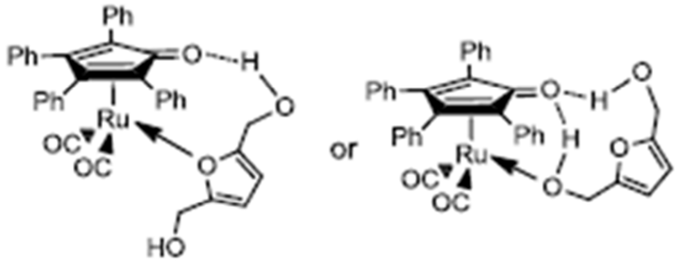

Figure 63. Interaction between complex B and BHMF

5.2.5 DFT calculation

DFT calculations were performed to determine if any of the proposed intermediates correspond to energy minima, and to evaluate their relative stability. Calculations were done using B3LYP[163,164] and the LANL2DZ basis set on all atoms[165]. Given the known X-ray data and calculations[166] available for this type of compounds, the helical disposition of the four phenyl groups was employed in all the starting geometries. All the optimized geometries of hypothesized complex did correspond to energy minima (no imaginary frequencies were observed in the frequency analysis), and the optimized Ru-C bond length were very similar to that observed in the solid state for a similar compound[167]. While the relative energy of complex E is much higher, the calculated energies for complex C (Figure 61) and complex F are similar, and the lowest energy structure depends on the kind of calculation. The F intermediate was calculated to be more stable by 0.6 kcal/mol when the internal energy is considered. If the solvent is included in the calculations (toluene, PCM method[168]) the two conformations are

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[163] Stephens P.J., Devlin F.J., Chabloski C.F., Frisch. M.J.J., *J. Phys. Chem.*, **1994**, 98, 11623;

[164] Becke A.D., *Chem. Phys.*, **1993,** 98, 5648;

[165] Hay P.J., Wadt W.R., *J. Chem. Phys.*, **1985**, 82, 299;

[166] Brydges S., McGlinchey M.J., *J. Org. Chem.*, **2002**, 67, 7688;

[167] Hollmann D., Jiao H., Spannenberg A., Bähn S., Tillack A., Parton R., Altink R., Beller M., *Organometallics*, **2009**, 28, 473;

[168] Tomasi J., Mennucci B., Cammi R., *Chem. Rev.*, **2005**, 105, 2999;

isoenergetic. If thermochemistry corrections are applied without considering the solvent, the C conformation becomes the most stable by 1.4 kcal/mol.

Given the presence of two hydroxyl groups in BHMF, an alternative hypothesis could be the interaction of a second molecule of the 16-electron B with the free hydroxyl of complex C to yield a bis-ruthenium complex (D2-BHMF) (Figure 64).

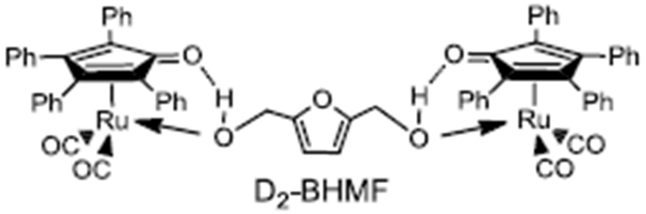

Figure 64. Bis-ruthenium complex (D2-BHMF)

A reliable calculation of the stabilization energy of D2-BHMF with respect to the C complex is not straightforward because of the known effect of basis set superimposition error (BSSE)[169]. The optimization of the 2:1 complex at the B3LYP/LANL2DZ level of theory confirmed that it did correspond to an energy minimum with global C2 symmetry. When the energy difference between the 2:1 and the 1:1 complex was calculated by the sum of the energies of the 1:1 complex C and one molecule of free D[167], the dimeric structure was favored by 21.1 kcal/mol (as internal energy without thermochemical corrections, by 9.3 kcal/mol if ZPE-corrected free energy was considered).

When the BSSE was taken into account by the counterpoise method[170], the stabilization was still 16.4 kcal/mol (4.8 with ZPE-correction). Thus, regardless the calculation method, the D2-BHMF complex appears to be stabilized with respect to the C and F complexes. If the same approach is applied to evaluate the total stabilization of D2-BHMF complex with respect to free BHMF and two molecules of B, the total energy gain increases to 35.6 kcal/mol (8.0 with thermochemistry corrections).

The availability of the dimeric complex D2-BHMF could also explain the peculiar behavior of the substrate under study versus the catalytic activity of the Shvo catalyst. On the basis of what previously described, a new catalytic cycle can be proposed for the

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[169] Boys S.F., Bernardi F., *Mol. Phys.*, **1970**, 19, 553;

[170] Turi L., Dannenberg J.J., *J. Phys. Chem.*, **1993**, 97, 2488;

HMF reduction catalyzed by Shvo catalyst in which F and D2-BHMF are involved. DFT calculations are in agreement with the experimental observation of a concomitant decrease in the reaction speed while increasing the BHMF yield.

5.3 Conclusion

In this work, the hydrogenation of HMF in BHMF was investigated using the complex of Shvo as a catalyst in mild condition. The process was optimized by studying the main reaction parameters such as temperature, hydrogen pressure and time. Complete conversion of HMF and selectivity of 100% were achieved working at 90 °C, 10 bar of hydrogen and with a molar ratio between catalyst and substrate equal to 1000. Several types of work up of the final reaction solution have been developed to make the process economically feasible. The catalyst of Shvo was found to be re-usable for at least three catalytic cycles without suffering any type of deactivation.

Unfortunately, it has been discovered that BHMF slowed the reaction rate, forming stable complexes with the catalyst. The assumptions described were subsequently proven through the use of DFT calculations. These calculations have shown the feasibility of formation of different complexes, in particular the complex of bis-ruthenium D2-BHMF was found to be the more stable.

Chapter 6

6 Furfural hydrogenation

The furfural is a renewable building block present in biorefinery used for the production of numerous chemicals and fuels. in particular one of these chemical can be the furfuryl alcohol (FFA). Nowadays, the FFA is mainly used as a modifier of phenolic and urea resins or as a solvent non-reactive for the production of epoxy resins.

Another important application of FFA is certainly its use as an intermediate for the production of vitamin C, lysine and tetrahydrofurfuryl alcohol.

Its hydroxyl group and its sufficiently high ratio C/O make this chemical a perfect candidate for the production of additives for fuel and as a lubricant, in fact several studies are investigating the application of the ethers derived from furfural in biorefinery concept.

Industrially, the production of FFA is carried out in liquid phase or in gas phase[171].

Similar to HMF hydrogenation, the control of the process parameters of hydrogenation of furfural has to be accurate as well as the use of an appropriate catalyst, to obtain high selectivity in furfuryl alcohol. In fact, decarbonylation, hydrogenolysis, hydrogenation and furan ring opening can occur.

One of the most employed catalysts is the Cu-Cr mixed oxides used in gas phase processes[172,173]. For the above reasons described Cr-free catalysts are being considered to work at mild condition and to achieve high selectivity to the desired product.

Products derived from ring opening are butanal, butanol and butane obtained using mainly undoped-silica supported Nickel[174]. On the contrary, Nickel alloy such as Ni-Cu,

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[171] Bauer K., Garbe D., *Common Fragrance and Flavor Materials*, VCH, Weinheim, **1985**;

[172] Rao R.S., Baker R.T.K., Vannice M.A., *Catal. Lett.*, **1999**, 60, 51;

[173] Seo G., Chon H., *J. Catal.*, **1981**, 67, 424;

[174] Roman-Leshkov Y., Barrett C.J., Liu Z.Y., Dumesic J.A., *Nat. Lett.*, **2007**, 447, 982;

Ni-Fe or Ni-Ce were found to be very active in furfural hydrogenation, allowing to achieve 98% selectivity to FFA[175,176].

Heterogeneous catalytic hydrogen transfer (HT) may be regarded as an alternative pathway for the production of alcohols in the presence of a carrier of hydrogen and not of molecular hydrogen.

As already mentioned earlier for example hydrogenation of HMF accomplished by using formic acid as a hydrogen donor in the presence of iridium or ruthenium complexes allowed to obtain high yield in BHMF[154].

The use of Cu-MgO catalysts was employed in the process of reduction of furfural to FFA with cyclohexanol as hydrogen donor working at 200-300°C of temperature. The process doesn't need the use of molecular hydrogen, but the maximum yield achieved is no higher than 60%[177].

Isopropanol, having a particular structure, is one of the most hydrogen donor employed in the HT process. Furfural was converted into FFA with a 99% yield using isopropanol accomplished with a Ru carbene complex and KOtBu, KOH and THF as solvents at 60°C and 24 hours of reaction time. Unfortunately, the by-product obtained from the isopropanol HT is acetone, which has to be separated from the final mixture, increasing the cost of the process[178].

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[175] Vaidya P.D., Mahajani V.V., *Ind. Eng. Chem. Res.*, **2003**, 42, 3881;

[176] Liu B.J., Lu L.H., Wang B.C., Cai T.X., Iwatani K., *Appl. Catal. A*, **1998**, 171, 117;

[177] Nagaraja B.M., Padmasri A.H., Raju B.D., Rao K.S.R., *Int. J. Hydrogen Energy*, **2011**, 36, 3417;

[178] Strassberger Z., Mooijman M., Ruijter E., Alberts A.H., de Graaff C., Orru R.V.A., Rothenberg G., *Appl. Organometal. Chem.*, **2010**, 24, 142;

6.1 Experimental section

In this work, an investigation on the catalytic activity of MgO, synthetized from hydrotalcite-type precursor, is reported in the heterogeneous catalytic hydrogen transfer using methanol as hydrogen donor in the reduction of furfural and HMF into respectively FFA and BHMF.

Methanol, employed as co-reagent and solvent, forms as by-products only gaseous compounds, i.e. CO, CO_2 and CH_4, derived from the methanol transformation during the catalytic process.

6.1.1 Materials

The following reagents and products were used for the work: magnesium nitrate hexahydrate (Sigma-Aldrich), sodium carbonate (Sigma-Aldrich), sodium hydroxide (Sigma-Aldrich), methanol (Sigma-Aldrich), furfural (Sigma-Aldrich), HMF (Sigma-Aldrich), FFA (Sigma-Aldrich), BHMF (Toronto Research Chemicals).

6.1.2 Catalyst preparation

MgO synthesized has been prepared by thermal decomposition of brucite. The brucite was synthesized following the procedure of conventional coprecipitation reported in the literature[179,180].

The salt of magnesium nitrate was co-precipitated dropwise into a solution containing sodium hydroxide 1 molar. The base solution was kept constant at temperature of 55 °C and at pH of 10.5. At the end of the precipitation, an aging treatment (1 hour) was carried out in order to increase the crystallinity of the formed phase. The obtained solid was then filtered and washed with two liters of water per gram of solid. Finally, the brucite was dried at 70 °C in static air overnight.

The precursor obtained was calcined in air at 450 °C for 5 hours.

The phase of the precursor and of the magnesium oxide were characterized by XRD technique to evaluate the yield of the synthesis. The analysis were carried out at room

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[179] Cavani F, Trifirò F., Vaccari A, *Catal. Today*, **1991**, 11, 173;

[180] Bolognini M., Cavani F., Scagliarini D., Flego C., Perego C., Saba M., *Catal. Today*, **2002**, 75, 103;

temperature with a diffractometer Bragg/Brentano X'pertPro PANalytical and they were carried out from 5 to 80 °2θ, with acquisitions of 10s every 0.1 °2θ.

The catalyst was also characterized by analysis of surface area. The measurement of the surface area of a catalyst, expressed as m^2/g, is one of the main parameters that characterize a material. The instrument used for the determination of the surface area was a BET Fisons Sorpty 1750 CE.

The analysis was conducted after a drying treatment of the sample at 120 °C.

6.1.3 Catalytic test

The hydrogenation of furfural and HMF was carried out using a Parr Instrument 4561 autoclave reactor of 300mL capacity and equipped with a mechanical stirrer (0‑1200 rpm) and provision for measurement of temperature and pressure (Figure 25).

The reaction was carried out in methanol, using the appropriate amount of catalyst.

If not differently indicated, each test was conducted for three hours at 160°C with the following amounts of reagents:

- 50 mL of methanol;
- 1.21 mmol of furfural or HMF;
- 0.25 g of MgO;
- 1 bar of nitrogen

The autoclave reactor was purged 3 times with N_2 (20 bar) and then pressurized at 1 bar (N_2). The temperature was increased to 160 °C and the reaction mixture was stirred at ca. 1000 rpm for the time requested.

At the end of reaction, the reaction mixture was cooled in an ice bath and the MgO was separated by filtration. The liquid products were analyzed using HPLC (Agilent Technologies 1260 Infinity), equipped with a C-18 core shell column 50x4.6mm employing a solution of 80% of 0.01 M H_3PO_4 and 20% acetonitrile as mobile phase.

The gas phase was collected and analyzed with an Autosystem XL (Perkin Elmer) GC equipped with an Elite Plot Q capillary column 30mmx0.32mm attached to a methanizer assembly flame ionization detector (FID)

Identification of compounds was achieved by calibration using reference commercial samples.

6.1.4 NMR analysis

NMR analysis were carried out using a 400MHz NMR instrument.

6.2 Results and Discussion

The precursor of the catalyst and magnesium oxide were characterized by means of XRD analysis. The Figure 65 shows the comparison between the brucite and the magnesium oxide. The peaks relative to the phase of the magnesium hydroxide (blue line) allow to affirm that the synthesis of the precursor was good and the subsequent oxidation has allowed us to obtain the phase of magnesium oxide in homogeneous way.

The analysis of surface area conducted on magnesium oxyde showed an area of 125m^2/g.

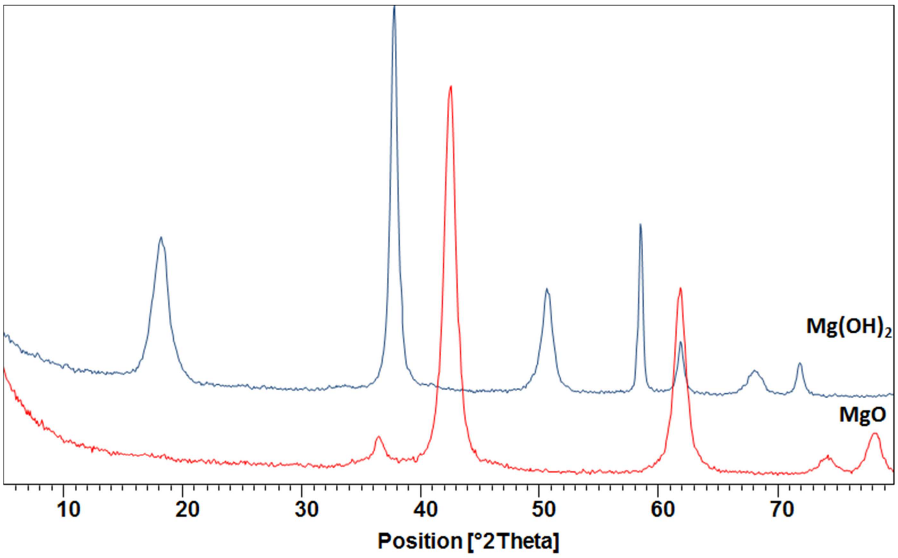

Figure 65. XRD analysis of brucite (blue line) and MgO (red line)

The first catalytic tests were carried out with the purpose to optimize the amount of catalyst in the process of hydrogenation of furfural. As shown by the graph in Figure 66 quantitative yield in FFA was obtained within 3 hours of reaction at 160 °C and with a quantity of MgO equivalent to 1 gram. Lowering the amount of catalyst selectivity in FFA remains constant at 100%, but the yield decreases to the value of 46% using a quantity of catalyst equal to 0.1 gram (10 times lower).

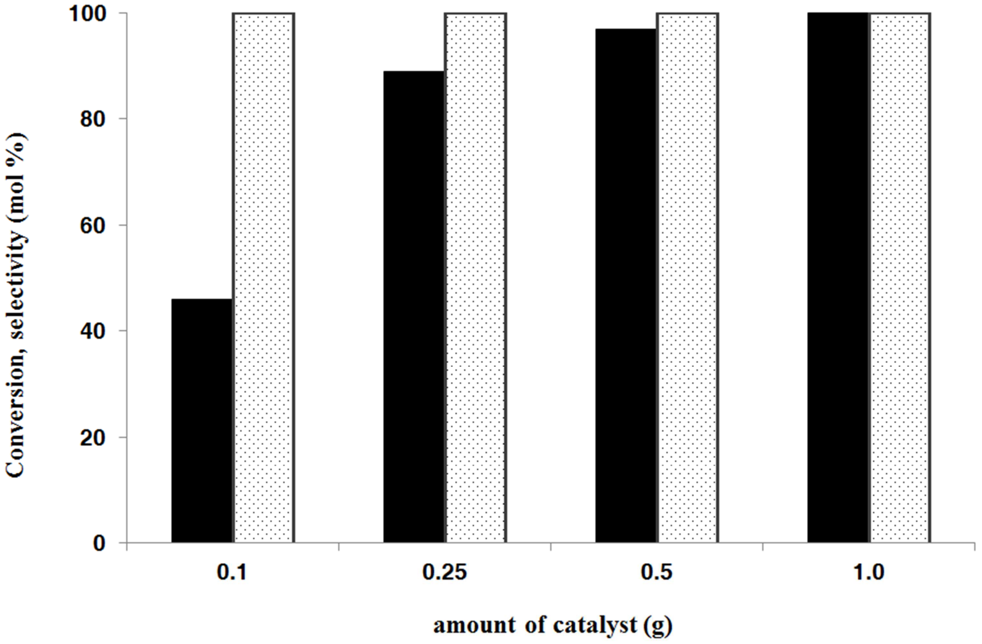

Figure 66. Conversion and selectivity as a function of grams of catalyst. Reaction condition. 180 min, 160°C, 1.21 mmol Fu, 1 bar of nitrogen. Conversion:black bar; Selectivity: bar with dots.

Changing the reaction conditions, especially temperature and concentration of substrate, the yield in FFA undergoes some changes.

Table 17. Effect of reaction temperature and concentration of furfural in FFA yield

Entry	Temperature (°C)	time (min)	Concentration of furfural (M)	MgO (g)	FFA yield (%)	TOF[a] (h^{-1})
1	100	180	0.024	0.5	0	0
2	130	180	0.024	0.5	55	1.2
3	160	180	0.024	0.5	97	2.2
4	210	45	0.024	0.25	51	9.1
5	230	30	0.050	0.1	43	57.8
6	160	180	0.024	0.1	46	5.2
7	160	180	0.121	0.5	61	6.8
8	160	180	0.242	1.0	55	6.2

[a] TOF= expressed as mol FFA produced per basic site/reaction time in hours; the number of basic sites is assumed to coincide with the number of moles of CO_2 adsorbed during CO_2-TPD experiments.

The data in Table 17 show that increasing the temperature it is possible to obtain quantitative yields and selectivity of 100% in a shorter reaction time and with a lower amount of catalyst (Entry 4 and 5).

In the table the value of TOF also is showed, calculated by assuming that all the surface basic sites, previously determined by means of CO_2-TPD[181,182] contribute to the reaction; this assumption clearly leads to an underestimation of the TOF value.

At low temperatures, the acetalization reaction is favored at the expense of hydrogenation of furfural, in fact working at 100 °C the only product formed is the acetal of furfural with a yield of 17%, while at 130 °C the yield of acetal is equal to 5% (Entry 1 and 2).

This behavior displays that the selective activation of methanol on MgO occurs at temperatures above 130 °C, allowing to obtain selectivity of 100% in alcohol.

Despite TOF value increases considerably with the temperature (57.8 Entry 5), it turns out to be a quite low value. This result could be derived from a partial deactivation of the catalyst by means of the CO_2 produced by the transformation of methanol (see below). In fact, the CO_2 is able to adsorb on the sites of basic catalysts, forming carbonates and deactivating partially the MgO.

The TOF value also increases with increasing concentration of the initial substrate. This results confirms the catalytic nature of the reaction and that the reaction rate is heavily influenced by the concentration of the reagent (Entry 3 and 7).

The same experiments conducted in the hydrogenation of furfural were carried out in the HMF hydrogenation.

The data obtained (Figure 67) from the tests display that also in this case, with increasing the amount of catalyst an increase of the BHMF yield was obtained and a quantitative yield was achieved using 1 gram of MgO in three hours of reaction at 160°C.

These data demonstrate that the reaction of hydrogen transfer with methanol and MgO is not affected by the type of substrate, but that the limiting step of the reaction appears to be the activation of methanol on the catalyst.

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[181] Bolognini M., Cavani F., Scagliarini D., Flego C., Perego C., Saba M., *Catal. Today*, **2002**, 75, 103;

[182] Bolognini M., Cavani F., Scagliarini D., Flego C., Perego C., Saba M., *Microp. Mesop. Mater.*, **2003**, 66, 77.

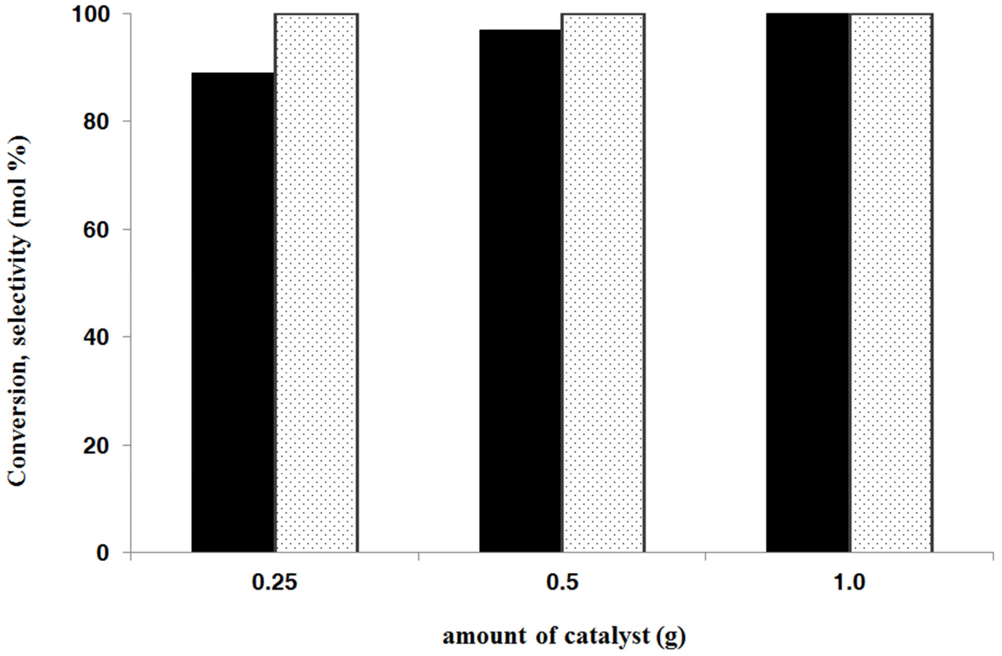
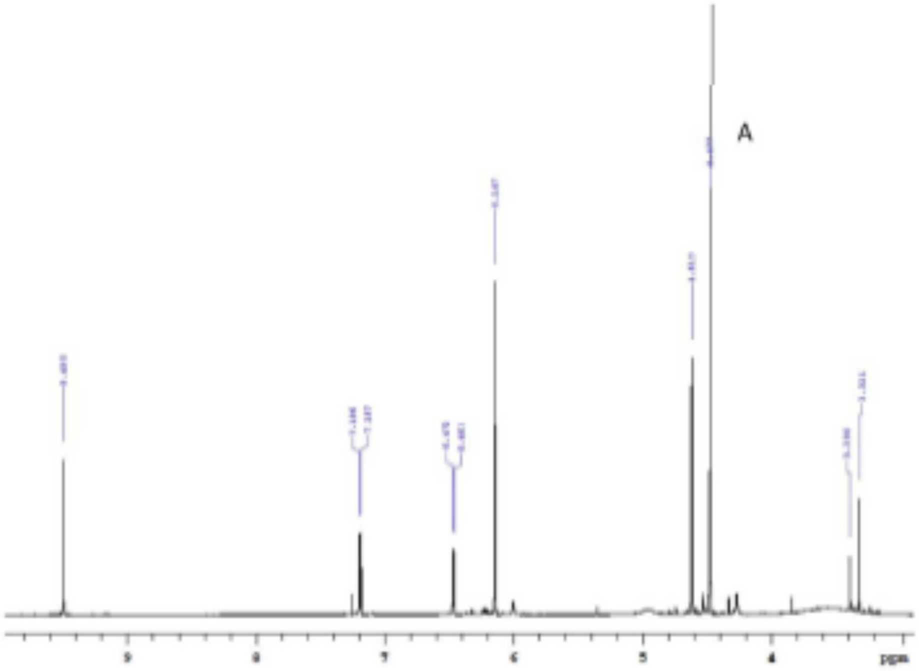


Figure 67. Conversion and selectivity as a function of grams of catalyst. Reaction condition. 180 min, 160°C, 1.21mmol HMF, 1 bar of nitrogen. Conversion:black bar; Selectivity: bar with dots.

To confirm the yields obtained by HPLC analysis and to verify the possible presence of by-products, the reaction solutions were characterized by NMR.



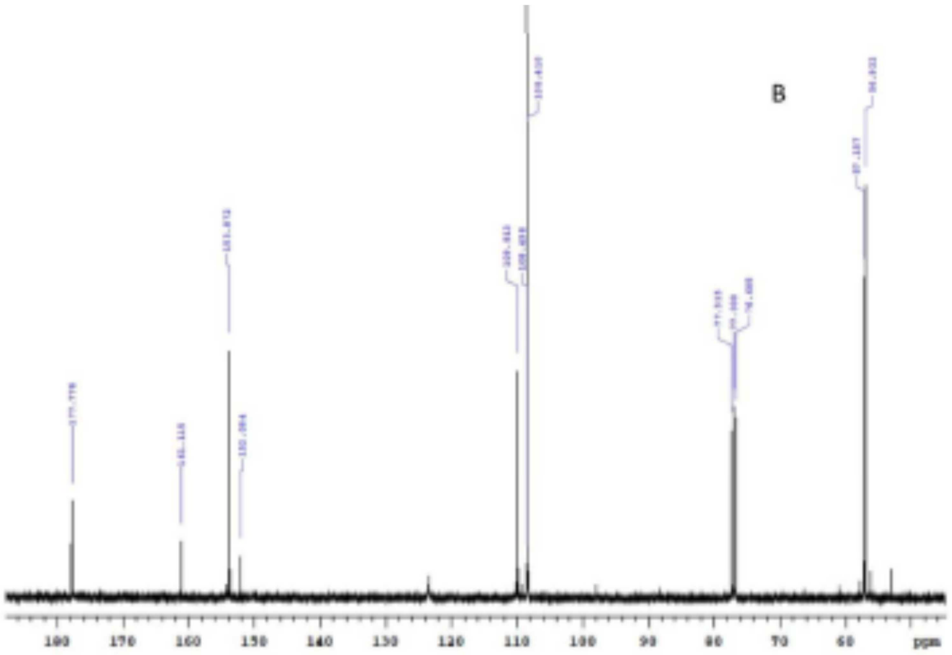


Figure 68. NMR analysis of the final reaction mixture carried out with 12.1 mmol of HMF, methanol 50 ml, reaction time 180 min, temperature 160°C. [A] ^{1}H-NMR ($CDCl_3$); [B] ^{13}C-NMR ($CDCl_3$)

NMR spectra were compared with the NMR spectra obtained from commercial compounds of HMF and BHMF. The formation of by-products was not detected in solution and are present only HMF and BHMF

As previously said, hydrogen transfer processes currently reported in the literature using alcohols such as iso-propanol or iso-butanol as hydrogen donors, forming in the environment of reaction by-products which must subsequently be separated from the products. In this case, the only by-products analyzed, derived from the transformation of methanol were CO, CO_2 and CH_4. These by-products, which are present in the head of the reactor, were easily separated from the liquid phase depressurizing the autoclave.

In the liquid phase, products of dimerization or formaldehyde were never detected. CO is the product of dehydrogenation of formaldehyde, which is formed by the dehydrogenation of methanol. The CO_2 and CH_4 are derived from the rapidly decomposition of methylformate at high temperatures, which is produced by the condensation of two molecules of formaldehyde on the catalyst (Scheme 1).

$$CH_3OH \rightarrow H_2CO + H_2$$

$$H_2CO \rightarrow CO + H_2$$

$$H_2CO + H_2CO \rightarrow HCOOCH_3$$

$$HCOOCH_3 \rightarrow CO_2 + CH_4$$

Scheme 1. Transformation of methanol over MgO

In Figure 69, a test as a function of the reaction time is reported, showing the moles of FFA produced and the moles of CO, CO_2 and CH_4 generated at the same time. The data confirm the scheme described above, in fact by GC, the moles of CO_2 and CH_4 were found to be always equimolar while the moles of CO were about double of the latter two.

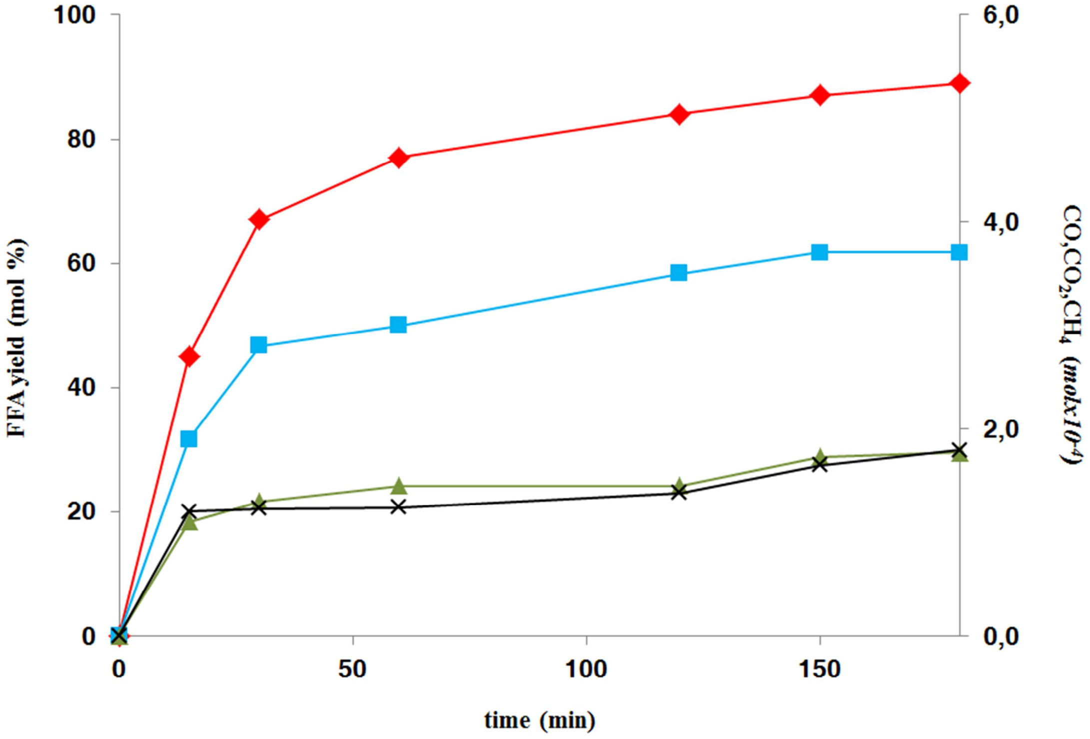


Figure 69. FFA yield (Diamonds), CO (squares), CO_2 (crosses) and CH_4 (triangles) generated as a function of reaction time. Reaction conditions. 160°C, 1.21 mmol Fu, 0.5 g MgO, 1 bar of nitrogen.

knowing the moles of by-products generated by the above scheme it is possible to calculate the total moles of hydrogen generated. Plotting the moles of hydrogen generated and the moles of FFA produced as a function of time it is possible to note that the two curves coincide at every point of the graph shown.

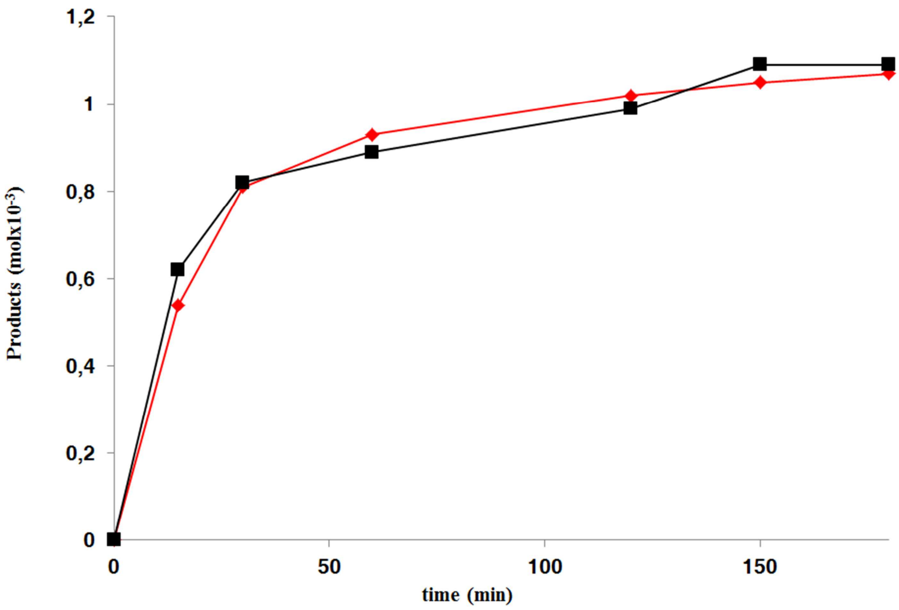


Figure 70. FFA moles (diamonds), H_2 (squares) generated as a function of reaction time. Reaction conditions. 160°C, 1.21mmol Fu, 0.5g MgO, 1 bar of nitrogen.

These data demonstrate that all the hydrogen produced by the transformation of methanol is used in the reaction of hydrogen transfer and hydrogen gas is not produced. However, the total selectivity in hydrogen is not 100% but it is 45% due to the production of methane.

Test of recycling of the catalyst were also performed and the data shown in the figure show that MgO can be used for several catalytic cycles without any loss of catalytic activity even if a thermal treatment at 450 °C for 5 hours in air is required to remove the adsorbed substances on the basic sites of the catalyst.

A simple heat treatment of drying is not sufficient to clean the catalyst, in fact, the yield obtained in a second catalytic cycle with this catalyst is lower (than the yield obtained with the fresh catalyst or re-calcined.

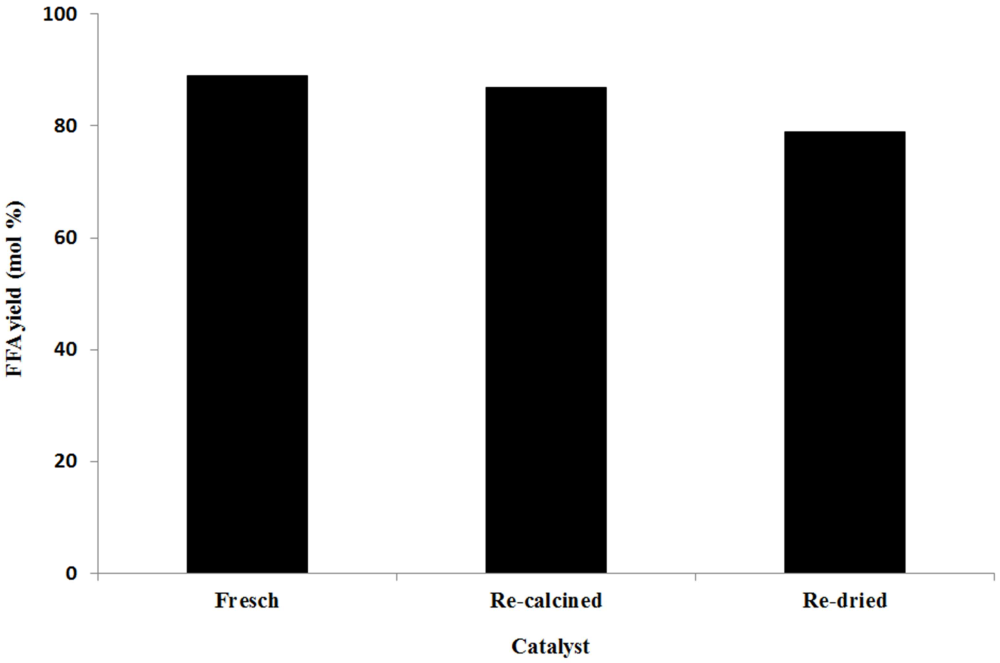


Figure 71. Reusability test. Reaction condition. 180 min, 160°C, 1 bar of nitrogen, 1.21 mmol furfural, 0.5 g of MgO.

6.2.1 Conclusion

In this work, the hydrogenation of furfural and HMF has been investigated with the aim of producing selectively the respective alcohols. The process has been optimized by using MgO as a catalyst and methanol as a co-reactant and as a solvent. Quantitative yields to alcohols have been achieved in a few hours working in mild condition: 160 °C and at autogenous pressure. The only by-products formed were light products such as CO, CO_2 and CH_4, easily separable from the reaction solution depressurizing the reactor.

The reusability of the catalyst was also evaluated and it was possible to re-use the catalyst without any loss in yield and selectivity for several catalytic cycles.

Chapter 7

7 Conclusion

In this work, development of three different catalytic processes has been optimized, in particular, the liquid phase oxidation of HMF to FDCA using gold and gold/copper based catalysts, the hydrogenation in the liquid phase of HMF to BHMF with the use of Shvo complex and the catalytic hydrogenation of furfural to furfuryl alcohol by a process of hydrogen transfer using methanol as hydrogen donor and magnesium oxide as base catalyst.

The synthesis of monometallic gold and bimetallic gold/copper nanoparticles at different molar ratio has been optimized. The synthesized nanoparticles were characterized by XRD and DLS analysis. The analysis showed that our synthesis has generated bimetallic nanoparticles in the range of 3-4 nm. The active phases were supported on titanium oxides and cerium oxides by incipient wetness impregnation and subsequently they were tested in the reaction of oxidation of HMF to FDCA. The catalysts supported on TiO_2 showed a catalytic activity superior respect to the all monometallic catalysts (except the catalyst with a high copper content $1.5Au_1Cu_3$) and they are also more stable and more resistant to poisoning than the monometallic ones.

The catalyst $1.5Au_3Cu_1$-Ti presented the best catalytic activity, which allowed a fast oxidation of the limiting step of the reaction, thus the oxidation of HMFCA to FDCA. The analysis conducted on catalysts showed the formation of alloys gold/copper and a strong synergistic effect between the two metals.

The same synergistic effect was not observed in the catalysts supported on CeO_2. In fact, the monometallic catalyst (1.5Au-Ce) showed the best catalytic activity in the oxidation of HMF to FDCA. Even in terms of stability, Au and Au/Cu catalysts have had very similar behaviors, activating in each catalytic cycle.

The different behavior obtained during the reusability test using the catalyst supported on ceria and titania is probably attributable to the nature of the supports. In fact, the reducibility of cerium is known to be favored by the presence of nanoparticles of Au, with a consequent release of bulk oxygen in the reaction medium.

The hydrogenation of HMF to BHMF was investigated using the complex of Shvo as a catalyst in mild condition. The process was optimized by studying the main reaction parameters such as temperature, hydrogen pressure and time. Complete conversion of HMF and selectivity of 100% were achieved working at 90 °C, 10 bar of hydrogen and with a molar ratio between catalyst and substrate equal to 1000. Several types of work up of the final reaction solution have been developed to make the process economically feasible. The catalyst of Shvo was found to be re-usable for at least three catalytic cycles without suffering any type of deactivation.

Unfortunately, it has been discovered that BHMF slowed the reaction rate, forming stable complexes with the catalyst. The assumptions described were subsequently proven through the use of DFT calculations. These calculations have shown the feasibility of formation of different complexes, in particular the complex of bis-ruthenium D2-BHMF was found to be the more stable.

Finally, hydrogenation of furfural and HMF has been investigated with the aim of producing selectively the respective alcohols. The process of hydrogen transfer has been optimized by using MgO as a catalyst and methanol as a co-reactant and as a solvent. Quantitative yields to alcohols have been achieved in a few hours working in mild condition: 160 °C and at autogenous pressure. The only by-products formed were light products such as CO, CO_2 and CH_4 (products derived from methanol transformation), easily separable from the reaction solution depressurizing the reactor.

The reusability of the catalyst was also evaluated and it was possible to use the catalyst without any loss in yield and selectivity for several catalytic cycles.