Alma Mater Studiorum – Università di Bologna

DOTTORATO DI RICERCA IN

Chimica Industriale

Ciclo XXV

Settore Concorsuale di afferenza: 03/C2

Settore Scientifico disciplinare: CHIM 04

Catalytic processes for the transformation of ethanol into acetonitrile

Presentata da: Federico Folco

Coordinatore Dottorato	**Relatore**
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ABSTRACT

This thesis deals with the transformation of ethanol into acetonitrile. Two approaches are investigated: (a) the ammoxidation of ethanol to acetonitrile and (b) the amination of ethanol to acetonitrile. The reaction of ethanol ammoxidation to acetonitrile has been studied using several catalytic systems, such as vanadyl pyrophosphate, supported vanadium oxide, multimetal molibdates and antimonates. The main conclusions are: (I) The surface acidity must be very low, because acidity catalyzes several undesired reactions, such as the formation of ethylene, and of heavy compounds as well. (II) Supported vanadium oxide is the catalyst showing the best catalytic behaviour, but the role of the support is of crucial importance. (III) Both metal molybdates and antimonates show interesting catalytic behaviour, but are poorly active, and probably require harder conditions than those used with the V oxide-based catalysts. (IV) One key point in the reaction network is the rate of reaction between acetaldehyde (the first intermediate) and ammonia, compared to the parallel rates of acetaldehyde transformation into by-products (CO, CO_2, HCN, heavy compounds).

Concerning the non-oxidative process, two possible strategies are investigated: (a) the ethanol ammonolysis to ethylamine coupled with ethylamine dehydrogenation, and (b) the direct non-reductive amination of ethanol to acetonitrile. Despite the good results obtained in each single step, the former reaction does not lead to good results in terms of yield to acetonitrile. The direct amination can be catalyzed with good acetonitrile yield over catalyst based on supported metal oxides. Strategies aimed at limiting catalyst deactivation have also been investigated.

SUMMARY

Introduction

Nitriles: features, synthesis and uses of most common nitriles

Nitriles are important starting materials for solvents and polymers as well as for the synthesis of many pharmaceuticals and pesticides. The –CN moiety is extremely polar, which results in nitriles having a high dipole moment. This large dipole moment leads to intermolecular association; hence, nitriles have higher boiling points than would be expected from their molecular mass. Most of the lower molecular mass aliphatic nitriles are liquids at room temperature. Simple nitriles such as acetonitrile, propionitrile, glycolonitrile, and malononitrile are miscible with water; the latter two having a higher solubility because of the presence of two polar groups. Nitriles with higher molecular mass are sparingly water-soluble. Nitriles are good solvents for both polar and nonpolar solutes. Aromatic and araliphatic nitriles are liquids or crystalline solids, mostly sparingly soluble in water (some heteroaromatic cyano-compounds have a higher water solubility) with sometimes considerable thermal stability. Benzonitrile and a range of substituted benzonitriles have a characteristic odor resembling bitter almonds. Some substituted benzonitriles sublime readily [1]

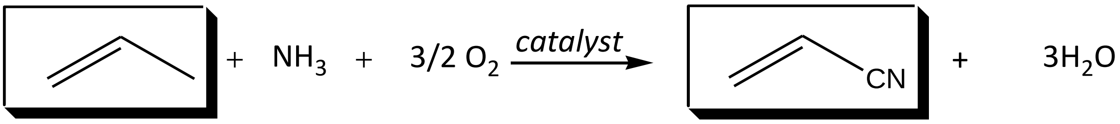
Some physical characteristics are shown in table 1.

Nitrile	***Mr***	***mp, °C***	***Bp, °C***	***d20***	n_D^{20}
Acetonitrile	41.05	-45	81.6	1.3441	0.7138
Propionitrile	55.08	-93	97.2	1.3670	0.782
Butyronitrile	69.10	-111.9	116 – 117	1.3838	0.7936
Valeronitrile	83.13	-96	141.3	1.3971	0.8008
Tetradecanonitrile	209.38	19.25	226 (10 kPa)	1.4392	0.8281
Malononitrile	66.06	30 – 31	218 – 219	1.4146	1.0494
Succinonitrile	80.09	57	265 – 267	1.4173	0.9867
Glutaronitrile	94.12	-29	286	1.4295	0.9911f
Allyl cyanide	67.09	-84	119	1.4060	0.8329
Methyleneglutaronitrile	106.12	-9.0	113 (0.66 kPa)	1.4558	0.9831

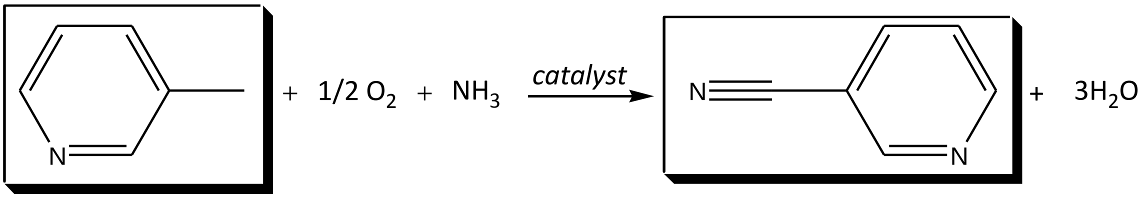
Table 1. Properties of nitriles.

The major part of both aliphatic and aromatic nitriles are mainly produced through the following four processes:

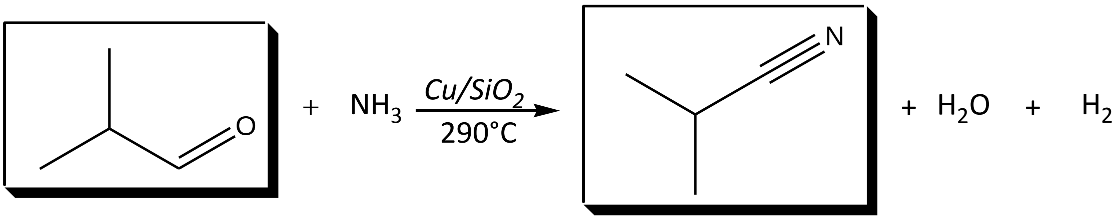
1. Reaction of nitrogen-free precursors (alkanes, olefins, alcohols, aldehydes, or acids) with ammonia. Gas phase reaction of olefins with ammonia in the presence of oxygen (ammoxidation) and oxidation catalysts (vanadium or molybdenum based catalysts) has attained the greatest industrial importance for the production of acrylonitrile from propene. Acetonitrile and hydrogen cyanide are formed as byproducts in typical quantities of 30 – 40 kg and 140 – 180 kg, respectively per 1000 kilograms of acrylonitrile [2]. Propane can also be used as feedstock (the first step being the dehydrogenation to propene) as well as acrolein [3]; recently, direct ammoxidation of propane to acrylonitrile has been studied. Similarly, the simplest aliphatic nitrile, hydrogen cyanide, can be obtained from methane, ammonia, and oxygen (Andrussow process). The ammoxidation process can also be advantageously carried out with aldehydes as starting materials, when they are readily available. This is especially the case for butyraldehyde and isobutyraldehyde which yield butyronitrile and isobutyronitrile, respectively [4]. The amination of alcohols or aldehydes can also be conducted under dehydrogenation conditions [5].



Example of ammoxidation, SOHIO process.



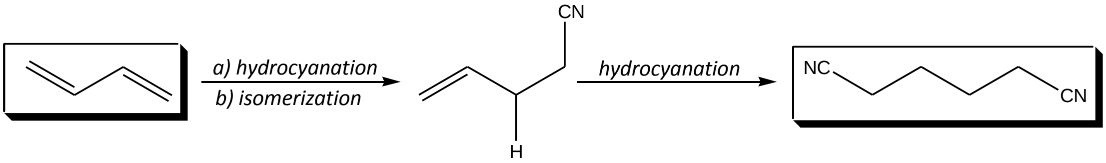
Example of ammoxidation, Lonza process.



Example of amination in dehydrogenation condition, Rurhchemie patent.

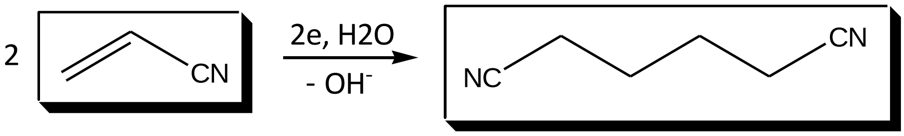
2. Formation of the cyano moiety from nitrogen-containing precursors such as amines, amides, or formamides. If an amine is employed as starting material, it is usually produced in situ from the corresponding alcohol and ammonia, the dehydrogenation step is then performed catalytically [5].

3. Reaction of HCN or cyanide ions with double bonds, carbonyl compounds, hydrogen or halogens. A typical industrial example of the hydrogen cyanide addition to double bonds is the direct hydrocyanation of butadiene to adiponitrile [6].



Example of hydrocianation, DuPont ADN process.

4. Reaction of the activated carbon in nitrile - containing precursors. The electro hydrodimerization of acrylonitrile to adiponitrile known as ‘‘EHD process’’ is also significant.



Example of electro hydrodimerization, EHD process.

From an industrial point of view the most relevant aliphatic and aromatic nitriles are listed below:

Acetonitrile is a colorless liquid miscible with water, ethanol and many organic solvents but immiscible with many saturated hydrocarbons (e.g., petroleum fractions). The physical properties are listed in Table 1. Characteristics of acetonitrile are its high dipole moment (3.84 D) and dielectric constant (38.8 at 20 C). Acetonitrile and hydrogen cyanide are the principal byproducts from the ammoxidation of propylene to acrylonitrile (Sohio process). Some acrylonitrile producers recover and purify acetonitrile, but most companies burn the byproducts as plant fuel.

Propionitrile is a colorless liquid which is miscible with water, ethanol, dimethylformamide, and diethyl ether. The physical properties are listed in Table 1. Propionitrile is obtained either by hydrogenation of acrylonitrile [7] or by the gas-phase reaction of propanal or propanol with ammonia [4]. It is also obtained as a byproduct in the electrohydrodimerization of acrylonitrile to adiponitrile (EHD process). Hydrogenation of propionitrile yields Npropylamines [8]. It is also used as an organic intermediate, for example, in the synthesis of the pharmaceuticals *flopropione* (via Houben – Hoesch reaction) [9] and *ketoprofen* [10].

Butyronitrile, is a colorless liquid slightly miscible with water, miscible with ethanol and diethyl ether. The physical properties are listed in Table 1. Butyronitrile is usually obtained by the catalytic gase-phase reaction of butanol or butyraldehyde with ammonia [3], [4]. Its major use is the manufacture of the poultry drug *amprolium* [11].

Isobutyronitrile, is a colorless liquid miscible with ethanol and diethylether, slightly miscible with water. Isobutyronitrile is usually obtained by the catalytic gas-phase reaction of isobutyraldehyde or isobutanol with ammonia [3], [4]. Its major use is the synthesis of the insecticide *diazinon* [12].

Succinonitrile, is a colorless, waxy solid slightly soluble in water and ethanol. The physical properties are listed in Table 1. Succinonitrile is obtained by addition of hydrogen cyanide to acrylonitrile [13]. Subsequent hydrogenation of succinonitrile yields 1,4-diaminobutane, which reacts with adipic acid to form the new polyamide 4,6. The polymer, developed by DSM, is marketed under the trade name *Stanyl*; the latter is reported to have excellent mechanical properties at high temperature [14].

Adiponitrile is a viscous, colourless liquid, it is an important precursor to the polymer nylon 66. The majority of adiponitrile is prepared by the nickel-catalysed hydrocyanation of butadiene, as discovered at *DuPont*. The process involves several stages, the first of which involves monohydrocyanation, affording isomers of pentenenitriles as well as 2- and 3-methylbutenenitriles. These unsaturated nitriles are subsequently isomerized to the 3-and 4-pentenenitriles. In the final stage, these pentenenitriles are subjected to a second hydrocyanation, in an anti-Markovnikov sense, to produce adiponitrile. Adiponitrile is used almost exclusively to make hexamethylene diamine (HMDA), of which 92% is used to make nylon 6,6 fibres and resins.

Methacrylonitrile is a liquid which is miscible with ethanol, diethyl ether and acetone; it is immiscible with water. Methacrylonitrile can be produced by ammoxidation of isobutene. Its copolymerization with methacrylic acid gives poly (methacrylimide), an engineering plastic commercialized under the trade name Rohacell by *Evonik*.

Tetracyanoethylene, preferred synthetic preparation of TCNE involves the debromination of the KBr complex of dibromomalononitrile. Tetracyanoethylene is a reactive compound that undergoes a variety of reactions including addition, replacement and cyclization.

Phenylacetonitrile is a colorless, oily, toxic liquid, is produced by the reaction of benzyl chloride with alkali cyanide in alcohol or aqueous solution under phase transfer catalysis with N,N-dialkylbenzylammonium chloride [15]. Phenylacetonitrile is used as an intermediate in the production of synthetic penicillins or barbiturates, in the synthesis of optical bleaches for fibers, in the production of insecticides, and for perfumes and flavors (via phenylacetic acid to ''honey-type'' ester compounds).

Other minor nitriles are:

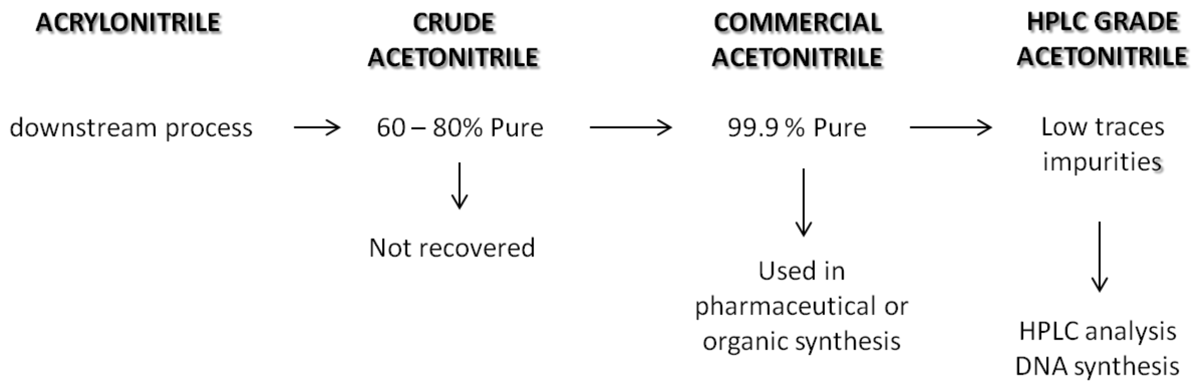
- **1,2-Phenylenediacetonitrile** used as an intermediate for the synthesis of optical brighteners [16].
- **Phenylglyoxylonitrile** used as an intermediate in the synthesis of plant protection agents [17].
- **D,L-Mandelonitrile** is used as an intermediate in the production of mandelic acid.
- **Benzothiazolyl-2-acetonitrile** is used as dye [18].
- **4-Chlorobenzonitrile** is used as pigment.

- **2,6-Dichlorobenzonitrile** is used as herbicide (*Casoron,* Solvay Pharmaceuticals) [1].
- **2,6-Difluorobenzonitrile** is used as insecticide (*Dimilin*, Shell) [1].
- **4-Hydroxybenzonitrile** is used for the production of the herbicides 3,5-dibromo- and 3,5-diiodo-4-hydroxybenzonitrile (*Bromoxynil, Ioxynil*, May & Baker) [1].

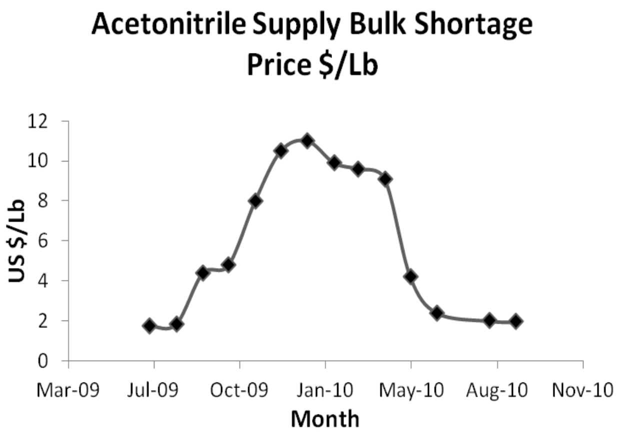
Acetonitrile: The 2008 – 2009 shortage

During the end of 2008 and throughout 2009 the chemicals industry has experienced a severe acetonitrile shortage. Acetonitrile had been a readily available commodity and users paid very little attention to its supply chain. In the first quarter, the situation had deteriorated to the point here almost any price was paid just to secure any available product.

Unique chemical properties, such as polarity, miscibility with water, low boiling point, low acidity and low UV cutoff, make acetonitrile a versatile solvent. It is used as a reactant in chemical syntheses like the production of malononitrile, pesticides like *Acetamiprid* (Aventis CropSciences) or pharmaceuticals like *Lopinavi*r (knowed also as *Kaletra*, an HIV-1 protease inhibitor), and as a solvent in the synthesis of pharmaceuticals and intermediates, oligonucleotides, and peptides. High purity acetonitrile is also a key solvent for HPLC analysis. Unlike other solvents, such as methanol, commercial acetonitrile is not the result of a direct synthesis but is a by-product of the industrial-scale production of acrylonitrile. Acrylonitrile is the primary product of the SOHIO process or ammoxidation, where propylene reacts with ammonia and air or oxygen in the vapour phase. Usually only 2-4% acetonitrile is formed, although acrylonitrile producers claim to have improved the yield by several percentage points by using co-feed processes. Acrylonitrile is purified by distillation. In most cases, the waste from this, mostly acetonitrile, is incinerated. In a few cases, the waste stream is used to isolate acetonitrile by a subsequent distillation. Depending on the waste stream and the distillation capability, different qualities are obtained. Not all acetonitrile which came to market during the recent supply bottleneck was suitable for the manufacture of pharmaceuticals. For analytical applications and some preparative HPLC, low water content and high transparency in the UV range are critical. These requirements can be met by an additional purification and drying, which is usually done by specialists in solvent distillation [19].



Demand was not affected by the global economic crisis during the 2008 – 2009. The situation was completely different in the market for acrylonitrile, which is mainly used as a monomer in plastics and fibres at about 25% in acrylonitrilebutadiene-styrene and about 30% in styrene-acetonitrile resins. Both are standard building materials for automotive parts such as bumpers, household items like telephones and luggage and in construction. Acrylonitrile is also used as starting material for acrylic fibres for carpets and textiles. These market segments were all hit hard in second half of 2008. In addition, other types of plastic made a dent in acrylonitrile volumes, as high price pressure and improved performance pushed the industry toward alternatives. This situation was further aggravated by the Beijing Olympic Games. The Chinese government forced many chemicals companies to reduce or completely shut down their production prior to and during the games to improve air quality and minimise pollution. Shipments of chemicals on land and overseas were also prohibited [20].

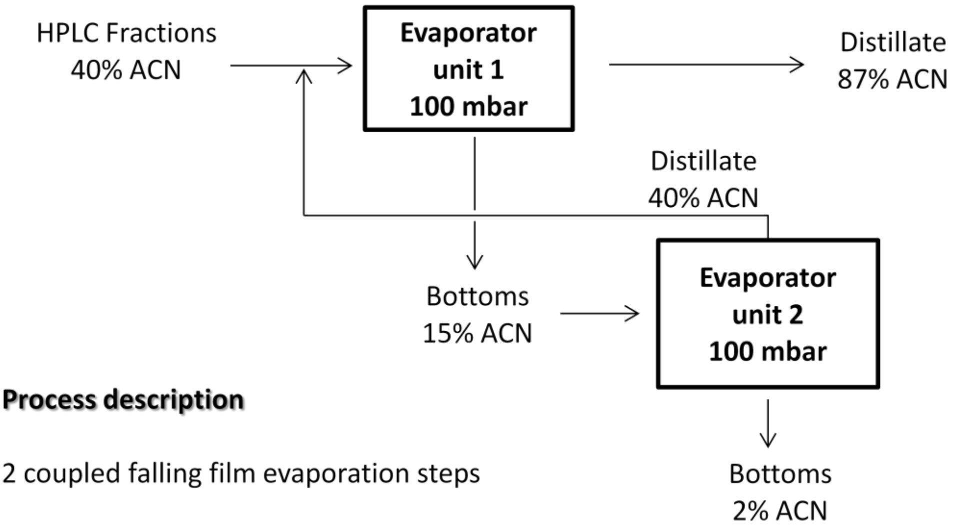


Some acetonitrile producers stopped production altogether. Finally there was Hurricane Ike, which hit the US Gulf Coast in September, causing a temporary shutdown of one of the large acetonitrile producers. The market has reacted to the crisis in several different ways, including the recycling and re-use of solvent, minimising use or outright replacement where possible. Here we report two schematic examples of new process dedicated to the recovery and recycling of acetonitrile developed in 2009 by Novasep [21].

Hypothesis:

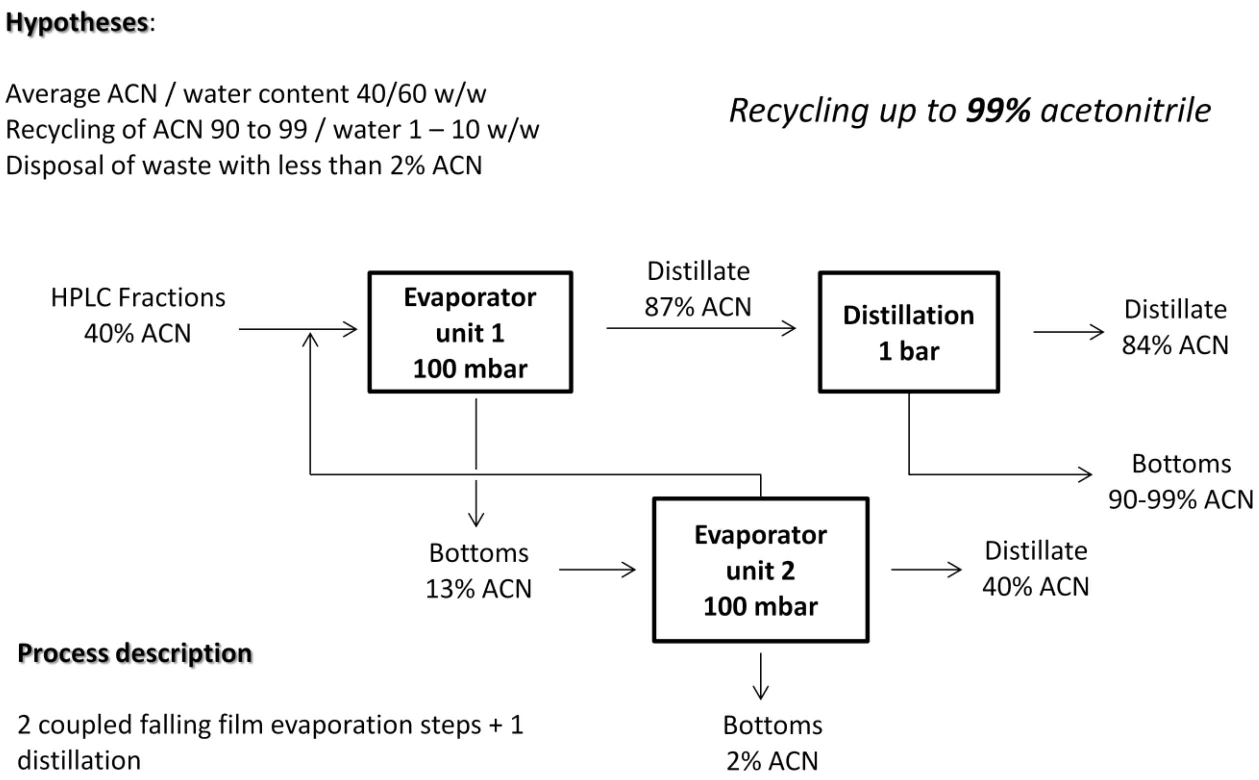
Average ACN / water content 40/60 w/w
Recycling of ACN / water 87/13 w/w
Disposal of waste with less than 2% ACN

*Recycling up to **87%** acetonitrile*



Process description

2 coupled falling film evaporation steps



Hypotheses:

Average ACN / water content 40/60 w/w
Recycling of ACN 90 to 99 / water 1 – 10 w/w
Disposal of waste with less than 2% ACN

Recycling up to ***99%*** *acetonitrile*

Process description

2 coupled falling film evaporation steps + 1 distillation

New sources of acetonitrile have also appeared. These were produced using purified acrylonitrile waste streams, with mixed results in terms of quality. The Achilles' heel of these strategies was that they still depended on an unpredictable supply chain. The main underlying problem - that the availability of acetonitrile depends on acrylonitrile, whose market dynamics are quite different - was not solved. A solution would be the direct synthesis of acetonitrile.

Alzchem, a subsidiary of Evonik, claimed in 2009 the start-up of a gas-phase ammoxidation process for the synthesis of acetonitrile (Speciality Chemicals Magazine, September 2009). Details on the technology are not available; however, based on a patent claiming the synthesis of benzonitrile from benzoic acid or benzamide, issued by the same company, it can be hypothesized that the process starts from acetic acid, and makes it react with ammonia in the gas phase, with a catalyst based on B phosphate, doped with Zn [R. Möller, M. Gomez, K. Einmayr, J. Hildebrand, H.-G. Erben, H.-P. Krimmer, US Patent 7,629,486 B2 (2009), assigned to AlzChem Trostberg]

Acetonitrile: Dedicated processes

The major amount of acetonitrile is nowadays produced as a by-product of propylene ammoxidation into acrylonitrile. However, several routes have been investigated so far for the synthesis of acetonitrile in a dedicated process. They can be summarized as follows (the list is limited to the routes which have been the object of a possible industrial implementation):

1. Reaction between CO, H_2 and NH_3

In this process two moles of carbon monoxide reacts with one mole of ammonia and two moles of molecular hydrogen to lead one mole of acetonitrile and two moles of water.

$2 CO + NH_3 + 2 H_2 \rightarrow CH_3CN + 2 H_2O$

The reaction is carried out in gas phase and typical conditions described in Monsanto's patents [22,23,24] are 350-550°C, GHSV 150-2000 h^{-1} using molybdenum or iron catalyst supported over silica, prereduced at 500°C with hydrogen; inlet composition ratios are $CO:H_2:NH_3$ 2:4,7:3. Tatsumi *et al*. [25] reproducing the same catalyst and changing slightly the reaction condition reached 50% of selectivity in acetonitrile with 16% of CO conversion at 450°C. In Kim and Lane paper [26] the best selectivity reached into acetonitrile is 28.4% with 46.5% of conversion at 425°C using a $CO:H_2:NH_3$ 6:6:6 ratios. The mechanism is not completely understood actually and different explanations are possible, for instance finding the principal intermediate is one of the most discussed issue in the literature. Tatsumi *et al*. [25] by mean of different probe molecules demonstrate that HCN plays a key role in the CH_3CN formation reacting with carbene species. HCN is formed by dehydration of formamide, witch, in turn, it's formed by the catalytic carbonilation of ammonia. Tests made changing W/F ratio (figure 1) demonstrate the kinetic relationship between hydrogen cyanide and acetonitrile.

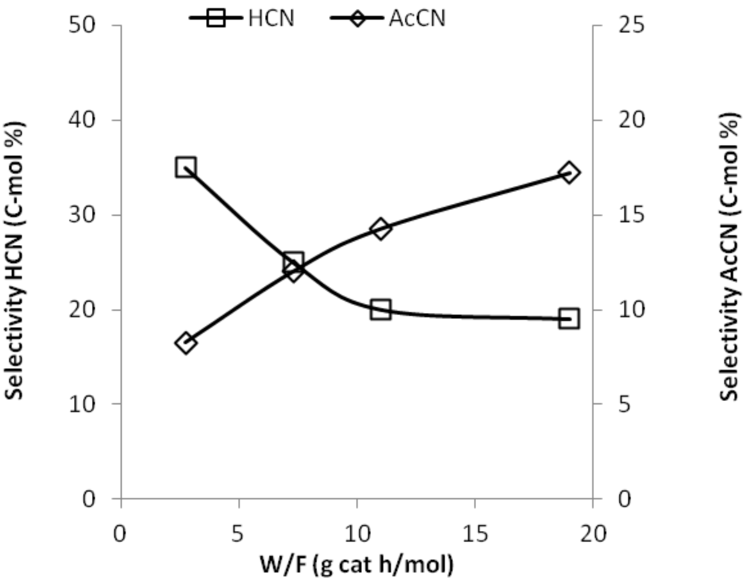


Figure 1. Kinetic relationship between HCN and acetonitrile. [25].

The reaction scheme hypotized is the following:

Catalytic carbonilation	$CO + NH_3 \rightarrow HCONH_2$
Carbene formation	$CO + H_2 \rightarrow :CH_2 + O$
Formamide dehydration	$HCONH_2 \rightarrow HCN + H_2O$
Carbene insertion on HCN	$HCN + :CH_2 \rightarrow CH_3CN$

Using molybdenum over silica catalyst Kim and Lane [26] proposed a different and more complex mechanism; in their paper in fact several tests changing feeding composition are made. Results show clearly that the chemistry of the process is a combination of Fisher-Tropsch synthesis, Water-Gas-Shift reaction and nitrile synthesis. HCN is formed only in particular condition as a minor product and does not play any role as principal intermediate. Thanks to a series of transient experiments they hypotized that the nitrile synthesis seems to occur by the initial formation of a CN intermediate which then inserts into a CH_x species. This mechanism involves an isocyanide ligand which undergoes an insertion reaction into an alkyl ligand.

In the mechanism proposed by Henrici-Olive and Olive [27] amines are formed from the ammonia-modified Fisher-Tropsch Synthesis over iron catalysts following a Schulz-Flory distribution; in particular, ammonia was hypothesized to act as a chain-transfer agent, terminating the grow of hydrocarbon molecules. Amines are then sequentially dehydrogenated to nitriles. However in this mechanism the Shulz-Flory distribution, seems not to occur (figure 2) when molybdenum-silica catalysts are used; Kim and Lane demonstrate the dramatic difference between the products distribution found in their work. Compared to the theoretical Schulz-Flory distribution is clear that acetonitrile is produced by a mechanism quite different from the Fischer-Tropsch-Synthesis and that ammonia is not a simple chain-transfer agent.

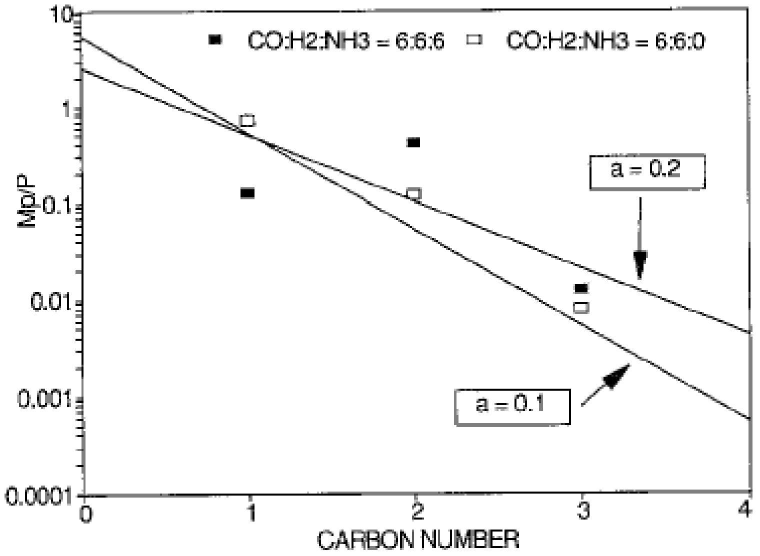


Figure 2. Shulz-Flory distribution for CO, H2, NH3 mixture (full square) and CO and H2 mixture (empty square) [27].

2. Hydrocyanation of C_1-C_2 compounds

In this process one mole of methane reacts with one mole of hydrocianidric acid to produce one mole of acetonitrile and hydrogen.

$CH_4 + HCN \rightarrow CH_3CN + H_2$

Since 1950 the Pure Oil Co. has published several patents [29-30-31] based on the hydrocyanation reaction to produce aliphatic nitriles; when the starting material are methane and hydrocyanidric acid the reaction is carried out without catalyst at high temperature (900-950°C T range), and acetonitrile and molecular hydrogen are formed in good yield. For instance, when methane and HCN are fed with ratio of 0.55 at 931°C, using gas hourly space velocity of 241 h^{-1}, 86.6% of selectivity (calculated with respect to methane) to acetonitrile is reached. Pure Oil co. disclosured also the method to prepare acetonitrile starting from methane and cyanogens; in this case HCN is co-product. When the starting materials are acetylene and HCN or cyanogen the reaction, at the same experimental conditions described above, leads to negligible amount of acetonitrile, however if a small amount of catalyst composed of refractory oxide (such as alumina, silica, pumice) containing from 0.05% to 5% wt. of group VIII nobel metal (such as platinum, palladium, rhodium, etc..) is used, good yield in acetonitrile and propionitrile are obtained. Small amount of acrylonitrile are detected also.

Monsanto Co. published a patent [32] in wich the use of catalytic amounts of free-radical generating compounds, such as acetonitrile, propionitrile, propylene, ethylether, and others is claimed for the hydrocyanation reaction. In particular, when methane and HCN are mixed at high temperature with small amount of the mentioned free-radical generating compounds, conversion and yield of methane and acetonitrile, respectively are enhanced. These catalysts are generally used in amount of 0.5 to 7 mole percent of the feed mixture, typical W/F ratio is from 0.8 s to 0.9 s and temperature range is from 800 to 900°C; methane to hydrogen cyanide mole ratio is from 1:10 to 1:100. In these conditions, without catalyst, HCN conversion is around 1.8%, whereas 4.5% mol of acetonitrile are premixed in the reaction mixture, the HCN conversion increase up to 14.5% at 800°C.

Tokyo Institute of Technology has patented [33] the preparation of catalysts for the transformation of acetylene and ammonia into acetonitrile. In this case, catalysts are made of alumina and alkali; in fact it was found that the addition of alkali metal hydroxides, or salts, or alkaline earth metal salts (chloride salts are preferred) during the synthesis of alumina starting from aluminum hydroxide gel, has a positive effect for the transformation of acetylene into acetonitrile. For instance, a typical preparation is 20% wt. sodium chloride with respect to alumina. When acetylene and ammonia are fed with ratio of 1:1,2 (a small excess of ammonia is needed to avoid the unwanted formation of pyridines) at the temperature range of 500 to 650°C, yield of 94% to acetonitrile (calculated with respect to acetylene) is reached.

3. Ethane or ethylene amination or ammoxidation

$CH_3CH_3 + NH_3 + 3/2\ O_2 \rightarrow CH_3CN + 3\ H_2O$

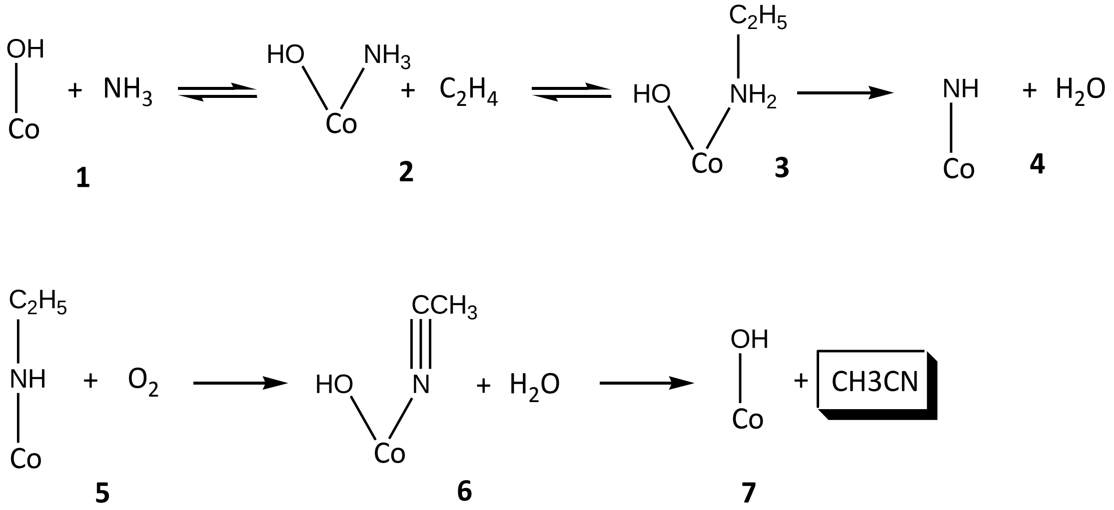
Literature on ethane ammoxidation is relatively poor; Centi and Perathoner [34] investigated ethane ammoxidation using alumina supported Nb-Sb oxide catalyst. In their work comparisons between V-Sb oxides (active and selective systems for propane ammoxidation) and Nb-Sb oxides are made, in particular they pointed out three main differences: (i) NbSbO based catalyst, differently from VSbO based one, give oxidation with carbon chain rupture and nearly equimolar formation of carbon monoxide and acetonitrile from a probable common intermediate; (ii) the order of reactivity, both regard to the increase of the carbon chain series and the difference between alkane and alkene reactivity (in the case of propane and propene) is different in the two cases, and (iii) allylic type reactivity (H abstraction and O insertion) is absent in NbSbO, differently from VSbO. In terms of catalytic performance these systems showed selectivity to acetonitrile around 50% with 30-35% of ethane converted at 500°C.

Differently Banares [35] focused on Nb-promoted Nickel oxides catalysts; it has been found that a moderate Nb doping significatively promotes Ni-Oxide catalyst in ethane ammoxidation; apparently an incipient interaction of niobium with NiO lattice would promote the system, while a well-defined niobium–nickel oxide phases is not efficient to ammoxidize ethane to acetonitrile. The best yield obtained in ethane ammoxidation with Nb-promoted Nickel oxide catalysts is close to 19% at 450°C using a mixture of $C_2H_6/O_2/NH_3$ equal to 9.8/25/8.6.

Unlike metal-alumina supported catalysts and Nb-promoted Nickel oxides above mentioned, metal exchange zeolites could be also used for ethane ammoxidation; Yueing and Armor [36] investigated deeply different Co exchange zeolites. In their work not only the reactivity of Cobalt ZSM-5, Cobalt β and Cobalt NU-87 zeolites is compared, but also the effect of different metal cations has been the subject to further investigations; in particular metal ZSM-5 zeolite catalysts, where metal stands for Cu or Ni or Ag or Pd or Rh, were tested. However an impressive 44,4% yield to acetonitrile is obtained with CoZSM-5 catalyst using a W/F ratio of 1.2 seconds and ethanol : ammonia : oxygen molar ratio of 5:10:6.5 at 450°C. Yueing and Armor are also mentioned as inventors in US 5576802 [37] patent which assignee is Air Products and Chemical Inc. The patent claims the ammoxidation process for producting acetonitrile from ethane and/or ethylene using Metal exchange zeolites catalyst.

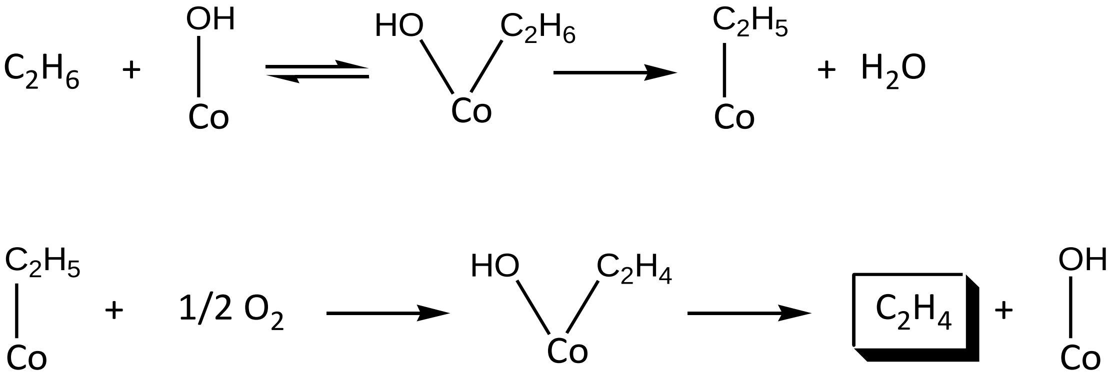
Finally ZSM-5 zeolite has been used by Pan, Lian and Jiam [38] for supporting antimony oxide; in particular, it is believed that Sb improves the ethane conversion, suppresses CO_x formation and increases total C_2 selectivity (as sum of acetonitrile plus ethylene); using 5% wt. of Sb2O3 over ZSM-5 the best result achieved is 64% ethane conversion at 550°C, with 51 % selectivity to acetonitrile and 32 % to ethylene.

Li and Armor [39]investigate the reaction pathway carrying out TPD experiments and varying ammonia, hydrocarbon and oxygen partial pressures. The elementary steps for ethene ammoxidation are proposed and described below.

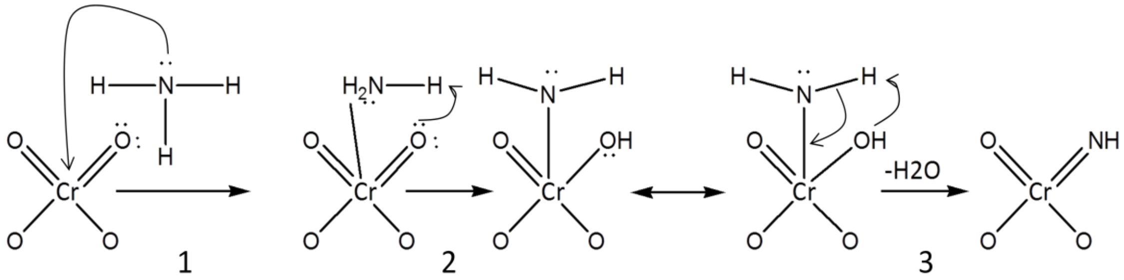


Ammonia is adsorbed on a hydroxylated Co^{2+} site (**1**). The NH_3 adsorption is a reversible process, and its equilibrium is dependent on the reaction temperature. However, its adsorption should be the strongest among all the reactants. The next step involves an addition of a gaseous C_2H_4 to the adsorbed NH_3 forming an adsorbed ethylamine molecule (**2-3**). The adsorbed amine is dehydrogenated by reacting with its neighbouring OH forming an ethylamine anion and H_2O as a by-product (**4**). This adsorbed amine anion is subsequently oxidized by a gaseous O_2 forming an adsorbed pair of C_2H_3N and OH group and H_2O as a by-product (**5-6**). Finally, C_2H_3N is desorbed (**7**).

For ethane ammoxidation, C_2H_6 needs first to be activated, and its activation is likely to be aided by O_2; in particular the first step for ethane activation would be its oxidative dehydrogenation. Li and Armor believe that ethane is activated by sequential oxidative H abstractions. The first H abstraction is accomplished by dehydration between an OH group and ethane. The adsorption of ethane on Co^{2+} is not favoured in the presence of ammonia. However, this process becomes feasible at higher temperatures at which some vacant sites are available by desorbing ammonia. This assumption is consistent with the fact that selectivity to ethene and acetonitrile increase along with the temperature, especially arise at high temperature. Assuming that each mole of acetonitrile generated requires one mole of ethene, ethane activation is only favoured at high temperatures. The mechanism presented in summarized in the following scheme:

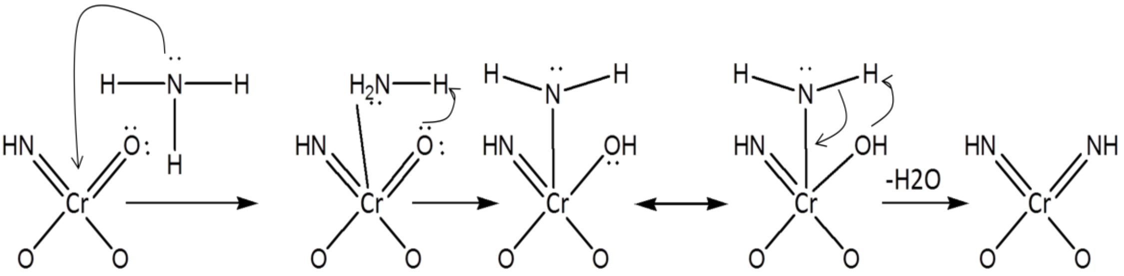


F. Ayari *et al*. [40] investigated the relationship between structure and reactivity using different CrZSM zeolite type catalysts. The work shows clearly that effect of Cr loading, considered as chromium aluminium ratio, and the difference given when chromium acetate or chloride salts are used in synthesis as sources of chromium. Summarizing chlorides are better than acetates as precursor because are able to prevent Cr2O3 agglomeration witch inhibit the accessibility of internal chromate sites to the reactants, however high metal loading (Al:Cr ratio > 1.5) are to be avoided independently from the precursor. Indeed Ayari et al. proposed a possible mechanism for the ammonia activation:



Adsorption of ammonia on chromate site (**1**), transfer of hydrogen from ammonia to an oxo group (**2**), desorption of water leaving behind the imino group, Cr(VI)O(NH)O_2 (**3**).

With respect to CoZSM-5 mechanism proposed by Li and Armor, here chromium sites are able to adsorb one more molecule of ammonia; the activation of the second ammonia molecule proceeds in the same way except that it start from CrO(NH)O_2 site and ends up with $Cr(NH)_2O_2$ site.



Consequently, available imido sites would adsorb more than one molecule of C_2H_4 which explain the improved catalytic activity of CrZSM-5 catalyst.

Detail concerning the literature of ethanol ammoxidation and amination are reported in section A and B, respectively.

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Experimental

Setting up the reaction apparatus

The simplified flow-sheet of the lab reactor assembled is shown in Figure 1.

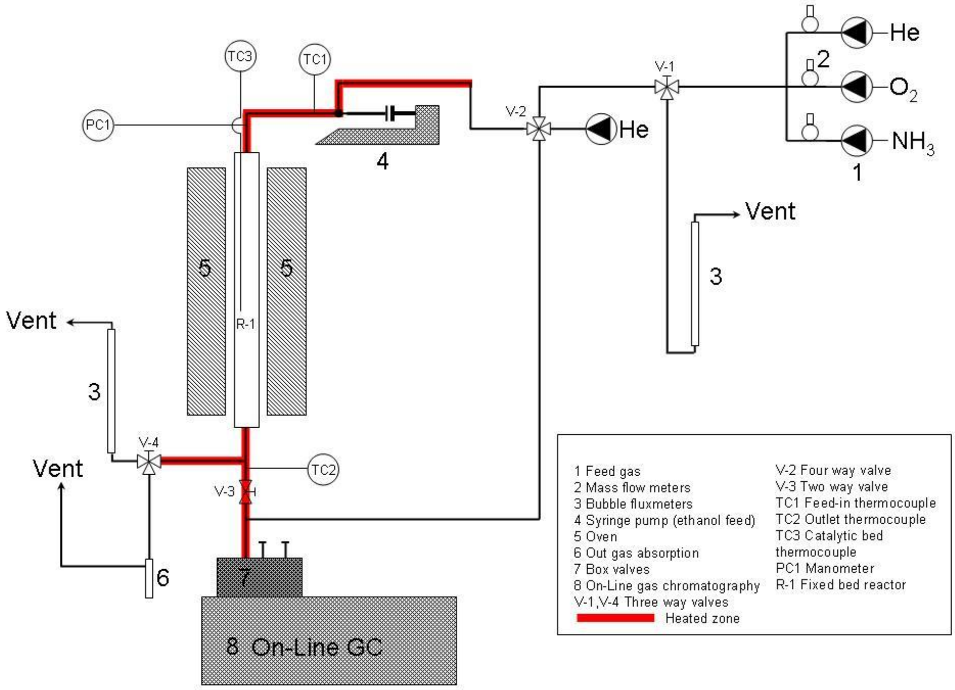


Figure 1. Simplified flow sheet of the reaction apparatus.

Main parts of the system:

1. **Feed section**, for the control of inlet flow rates of the main reaction components: helium, oxygen, ethanol (water) and ammonia. Gaseous components feeds are regulated by means of mass-flow controllers, and then mixed together. Ammonia is used as a diluted component from a 40% NH_3/He cylinder. The ballast component used is He, in place of N_2, to allow an easier detection of the N_2 eventually formed by ammonia combustion; the possible drawback is that due to the different heat-conductive properties of He and N_2, the catalyst surface temperature might be slightly different in the two cases. Concerning the liquid stream, tests have been carried out using the azeotropic mixture of ethanol (95.6 wt%) and water (4.4 wt%);

the liquid flow is regulated by means of a high-precision syringe-pump, and is then vaporized into the gaseous stream. We carried out a pre-calibration of the flow-rate of the syringe pump.

Valve V1 allows selection for feeding the gaseous stream either to the reactor or to the measure of the flow rate. Valve V2 allows selection for conveying the gaseous stream either to the reactor or to the GC for analysis; in this latter case, purge He is fed through valve V2 in order to leave a gaseous stream on the catalyst.

The complete stream (gases + vapours) is fed to the reactor through a heated line (200°C).

2. **Reaction zone**. The reactor is tubular type, quartz-made, with internal diameter of 0.8 cm and is in overall 46 cm long. The catalytic bed is positioned at about half of the height, corresponding to the isothermal zone of the furnace; in this zone, the internal diameter of the reactor is 1 cm. The catalyst is hold on a porous septum of synthered glass. A 1/16" diameter internal tube, made of stainless steel, contains a thermocouple (TC3) that allows the measurement of the temperature at the different heights inside the catalytic bed. At the exit of the reactor, the temperature is maintained at 200°C by means of a heating strip.
3. **Products collection and sampling system.** Downstream the reactor, the valve V3 allows to regulate the amount of exit stream that is sent to the sampling devices. When V3 is closed, the entire exit stream is sent either to the condensation/abatement system through valve V4, or to the flow measurement, and the sampling system is maintained under an He stream. When V3 is open, a fraction of the exit stream is sent to the sampling system, the remaining part to the abatement system and then to the vent. The abatement system contains water solvent. The sampling system is made of two valves, installed inside a furnace and maintained at the temperature of 200°C. The two 6-lines valves are equipped with two calibrated loops (volume 100 and 80 μl). The operational procedure for gas sampling is the following (Figure 2): Phase I: the gas effluent stream fill the two loops and exit to the vent; Phase II: start up of the analysis, the first valve injects into the column HP MS 5A, the second valve is still in loading position. Phase III: 4 min after the first injection, the second valve injects into the HP Plot U column. The exit stream

by-passes the two loops and goes directly to the vent. Phase IV: end of the analysis, the two valves are again in the loading position.

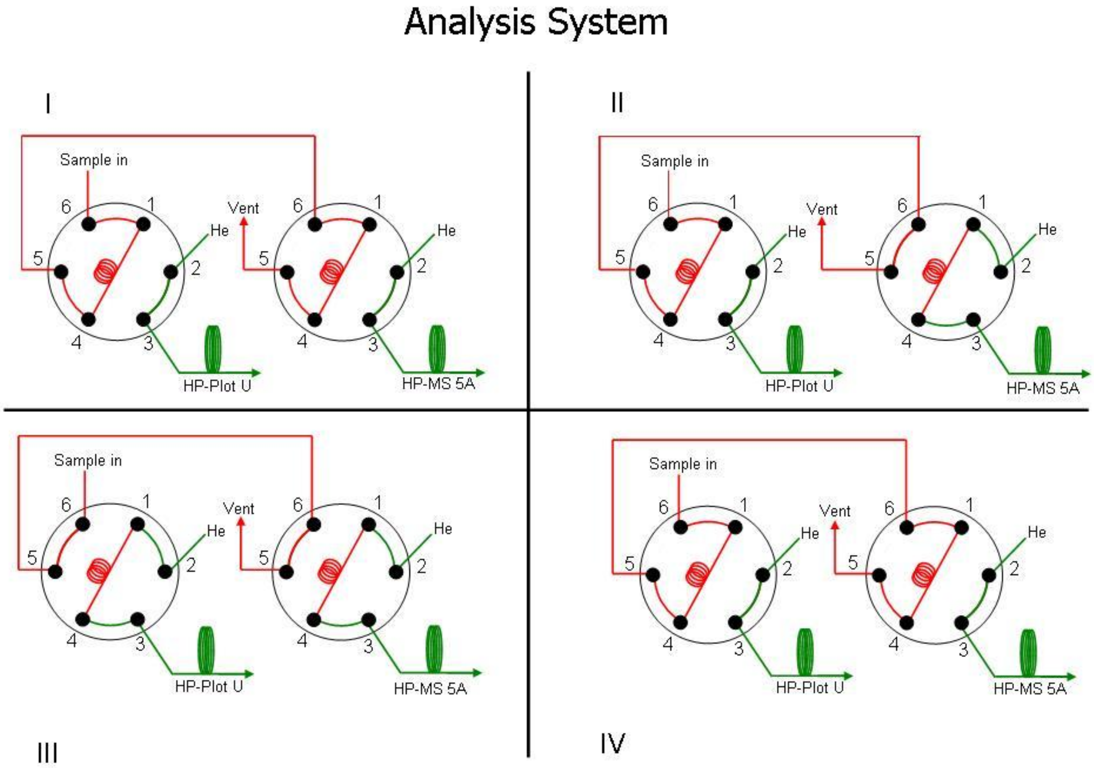


Figure 2. Sampling system and operations sequence.

4. **The analytical system**. The gas-chromatograph is an HP 5890A instrument, with two columns: (a) a semicapillary HP Plot U, 30 mt long, internal diameter 0.53 mm and fixed phase 20μm thick; the maximum T allowed is 190°C. This column is used to separate ethanol, ammonia, carbon dioxide, water, acetaldehyde, acetonitrile and other C-containing by-products (hydrocyanic acid, other nitriles,…). (b) a semicapillary HP Molesieve, 30 meter long, internal diameter 0.53 mm, maximum T allowed 300°C; this column is used to separate oxygen, nitrogen and carbon monoxide. The two columns are joined to a splitter/union (Figure 3) and then conveyed to the thermal-conductivity detector. The GC oven temperature is programmed as follows: 6.8 min at 60°C, heating rate 40°C/min up to 100°C, isothermal step for 8.5 min, heating rate 60°C/min up to 130°C, isothermal step for 5 min, final heating rate 60°C/min up to 170°C, final isothermal step 8 min.

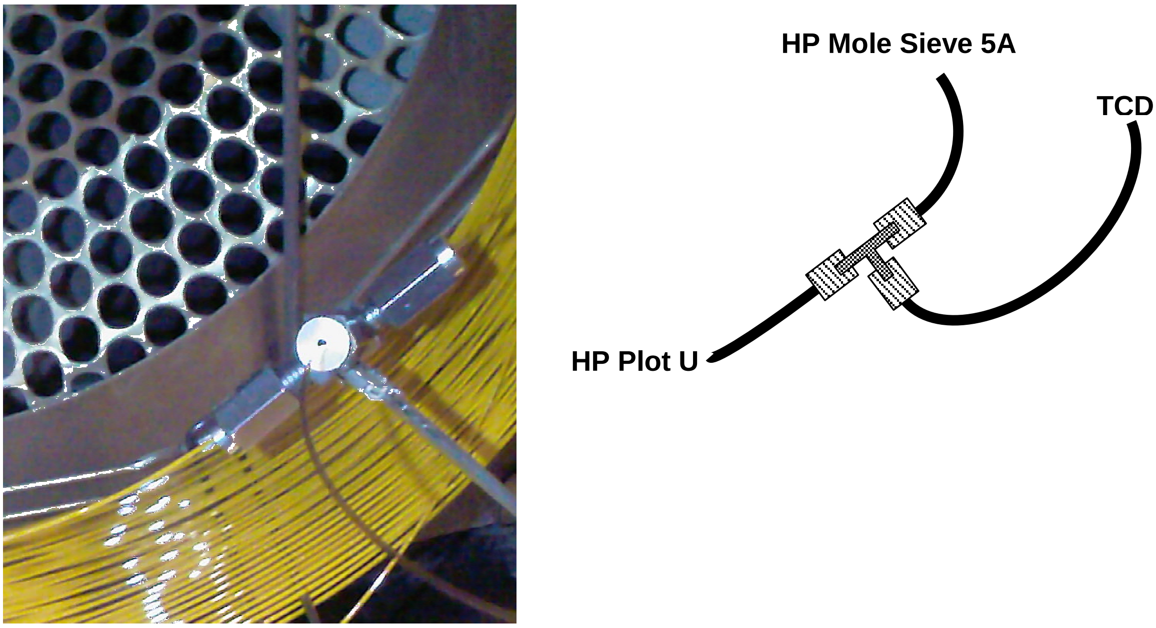


Figure 3 Columns connection.

Catalyst characterization

Specific surface area analysis (B.E.T. single point).

The specific surface area was determined by N_2 absorption at 77K (the boiling temperature of nitrogen) with Sorpty 1750 Instrument (Carlo Erba) The sample was heated 150°C, under vacuum, to eliminate water and other molecules eventually adsorbed on the surface. After this pretreatment, sample was maintained at 77K in a liquid nitrogen bath, while the instrument slowly sent gaseous N_2, which was adsorbed on the surface. By B.E.T. equation it is possible to calculate the volume of the monostrate and finally the sample surface area.

X-Ray powder diffraction analysis

The XRD measurements were carried out using Philips PW 1710 apparatus, with Cu Kα (λ = 1.5406 Å) as radiation source in the range of $5° < 2\theta < 80°$. Reflects attributions was done by Bragg law, using the d value: $2d\ sen\theta = n\lambda$.

Raman spectroscopy analysis

Raman studies were performed using Reinshaw 1000 instrument, equipped with Leica DMLM microscope, laser source Argon ion (514 nm) with power 35 mW.

XPS analysis

X-Ray Photoelectron Spectroscopy surfaces analysis were performed using Kratos AXIS Ultra spectrometer with monochromatic Al Kα radiation (hν = 1486.6 eV)

Temperature programmed oxidation analysis (TPO)

TPO analysis were carried out with TPDRO instrument ThermoQuest 1100 (Carlo Erba), using as oxidant gas mixture of 5% of oxygen diluted in helium.

A. The ammoxidation of ethanol to acetonitrile

Introduction

Ethanol ammoxidation can be carried out in the same reactor and process where propylene is ammoxidized into acrylonitrile [1]; in fact, acetonitrile is a by-product of the acrylonitrile process, and conditions aimed at the ammoxidation of ethanol are not much different from those necessary for conducting propylene ammoxidation. However, some authors have investigated the ammoxidation of primary alcohols into nitriles using dedicated catalysts and conditions. Table 1 summarizes the results reported in the literature about the gas and liquid-phase ammoxidation of primary alcohols into nitriles using oxygen as the oxidant.

Catalyst	T,°C (GP/LP)	Alcohol	Alcohol/H_2O/NH_3/O_2 (molar ratios)	Alcohol conv, RCN yield (%)	By-products	Ref
MnO_2	100, LP	Benzyl alcohol	0.5 mmol/--/0.85MPa/0.5MPa	100, 100[a]	-	2
Co_3O_4	100, LP	Benzyl alcohol	0.5 mmol/--/0.85MPa/0.5MPa	96, 94	-	2
V/P/Sb/O-Al_2O_3	400, GP	Ethanol	Ethanol/water ½ v/v; NH_3/air 2.1/1	84, 82[b]	acetaldehyde	3
SAPO	350, GP	Ethanol	1/1/5/air	100, 99[c]	-	4
VAPO	350, GP	Ethanol	1/1/5/air	100, 96.5[d]	acetaldehyde	5
$Ru(OH)_3$-Al_2O_3	120, LP	Benzyl alcohol	NH_3/alcohol 1.8/1, air 6 bar	-, 72[e]		6

[a] doping the catalyst with Au enhances the hydration of the nitrile into benzylamide, without further addition of water. Solvent: toluene.

[b] the authors hypothesize that the reactions occurs via intermediate formation of acetic acid and acetamide, which is then dehydrated into the nitrile.

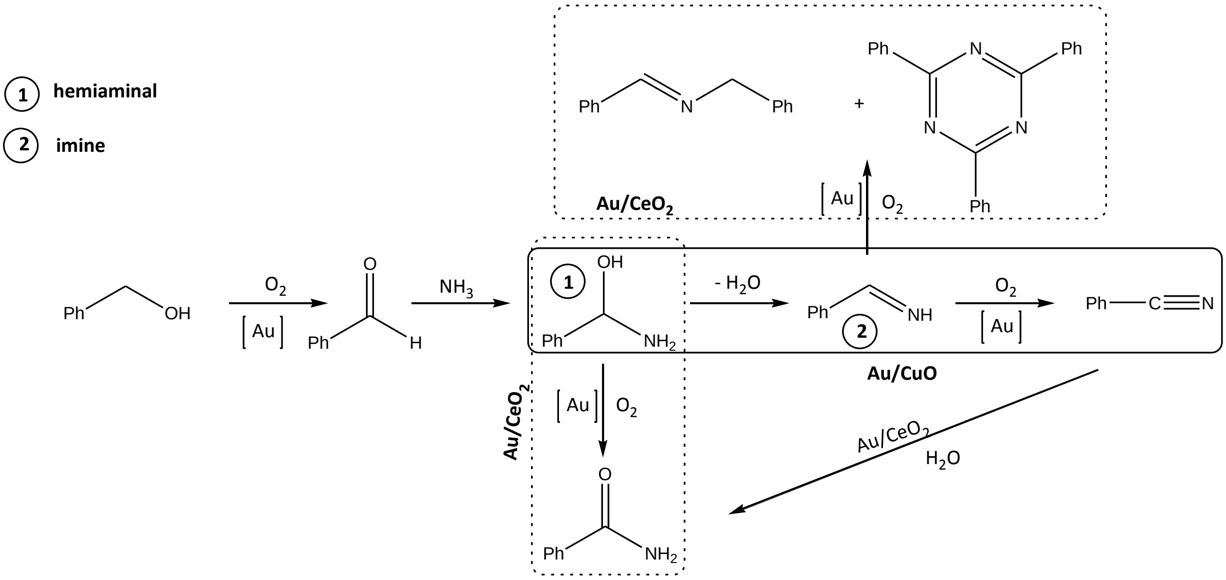
[c] the authors hypothesize a mechanism via aldehyde and imine, or a mechanism via ethylamine.

[d] the authors hypothesize a mechanism via aldehyde and imine.

[e] the mechanism is proposed to occur via acetaldehyde and imine formation. The addition of water after nitrile synthesis leads to the hydrolysis into the amide.

Mizuno et al have recently published several papers dealing with synthetic procedures for the aerobic preparation of nitriles, and for the direct synthesis of primary amides (where the latter form by consecutive hydration of the nitrile). Catalysts described are based either on $Ru(OH)_3$-alumina, but also on manganese oxide based octahedral molecular sieves (KMn_8O_{16}: OMS-2) [7a]. Manganese oxide is also a catalyst for the oxidative desulphurization of primary thioamides into the corresponding nitriles [7b], and Ru hydroxide is a catalyst for the oxidative transformation of primary azides into nitriles [7c].

Scheme 1 shows the reaction mechanism for the liquid-phase ammoxidation of benzyl alcohol, as proposed by Ishida et al [2].



Scheme 1. Reaction mechanism proposed by Ishida et al [2] for benzyl alcohol ammoxidation.

Other procedures for the ammoxidation of alcohols into nitriles (especially aryl alcohols) refer to conventional methods of the organic synthetic chemistry; see, for instance, the several methods cited in refs [8], using properly selected oxidants and reagents as N sources.

In the aerobic ammoxidation of alcohols into nitriles, there are several issues which make the reaction challenging; for example, the formation of the -C≡N moiety requires the removal of hydrogen from -CH=NH in the intermediately formed imine. Moreover, the activation of the strong N-H bond in ammonia (107 kcal/mole) may require hard reaction conditions. One key reaction intermediate, as reported in the literature, is the hemiaminal compound (1-aminoethanol in the case of ethanol ammoxidation, CH_3-CH(OH)-NH_2, see Scheme 1), obtained by addition of ammonia to the carbonyl moiety in acetaldehyde; the hemiaminal may be the precursor of either acetaldehyde imine (ethanimine, via dehydration), or of acetamide (via dehydrogenation or oxidative dehydrogenation). In regard to this, it is claimed that the presence of an acid functionality in the catalyst may be essential to accelerate the dehydration of 1-aminoethanol, during the non-reductive amination of ethanol [9].

In view of these arguments, we decided to investigate the catalytic behavior of a vanadyl pyrophosphate catalyst for the direct ammoxidation of ethanol into acetonitrile, because of the following reasons: (a) a V/P/O-based system is claimed in the literature as being one of the systems giving the best selectivity and yield to acetonitrile in ethanol ammoxidation [3]; (b) it has also been investigated as a catalyst for the direct gas-phase ammoxidation of alkylaromatics into the corresponding nitriles [10]; (c) it holds moderate acidic properties, which derive from the presence of surface phosphate groups [11].

One further aim of this study was to investigate about the key steps in ethanol ammoxidation which are essential in achieving high yield to the desired compound.

Results and Discussion

1. Ethanol ammoxidation with the vanadyl pyrophosphate (VPP) catalyst

We first carried out some reactivity experiments by feeding the reactants mixture with composition: ethanol/ammonia/oxygen mol% 13/13/6, without any catalyst, and by filling the reactor with inert material (corundum). We found that ethanol conversion ranged between 3 and 8% in the temperature interval 300-to-500°C; the main product was acetaldehyde, with minor formation of CO and CO_2. This means that the contribution of surface-catalyzed reactions and of homogeneous reactions was small, and it can be neglected during catalytic experiments.

Figure 1 shows the results of ethanol ammoxidation with the VPP catalyst, using a feed composition made of 5 mol% ethanol (azeotrope), 13 mol% oxygen, 13 mol% ammonia, remainder inert (in all experiments, typically we used He as the ballast component, because this allowed a better analysis of the N_2 produced during reaction, but using N_2 or Ar led to the same results).

Results reported in Figure 1 demonstrate that the catalyst was moderately selective to acetonitrile; total conversion of ethanol was reached at ca 440°C, for a W/F ratio of 0.80-0.85 g s mL^{-1}; ammonia and oxygen conversion both reached the maximum value of 35-40% conversion at high temperature, these reactants being fed in excess with respect to the stoichiometric amount required for acetonitrile synthesis. At low temperature the main by-product was acetaldehyde, whereas selectivity to CO+CO_2, ethylene and HCN were no higher than 10% at 350°C. However, the increase of temperature led to a progressive decline of selectivity to both acetaldehyde and acetonitrile, and to the rapid raise of selectivity to ethylene and to CO+CO_2; selectivity to HCN was not much affected by temperature. The figure also shows the selectivity to “heavy compounds”, which have been calculated taking into account the C balance; these compounds are in part eluted in the GC column (but have not been identified, being in very small amount), in part accumulate on the catalyst. Their relative amount is nevertheless low, if compared to the corresponding amount formed at higher ethanol concentration (see below). One additional important effect observed was the raise of selectivity to N_2, deriving from ammonia combustion.

Results reported demonstrate that the distribution of products is greatly affected by reaction conditions; the low selectivity to acetonitrile derives from a probable contribution of both parallel reactions, leading to ethylene, HCN and CO+CO_2, and consecutive reactions leading to carbon oxides. Therefore, an efficient transformation of acetaldehyde into acetonitrile is an important requisite in the aim of achieving a high selectivity to acetonitrile.

In order to confirm the role of acetaldehyde as the key reaction intermediate in the sequence of reactions leading to the formation of acetonitrile, we carried out experiments by changing the W/F ratio, at fixed temperature (370°C and 440°C) and feed composition (ethanol/ammonia/oxygen 5/13/13, mol%); results are shown in Figures 2 and 3.

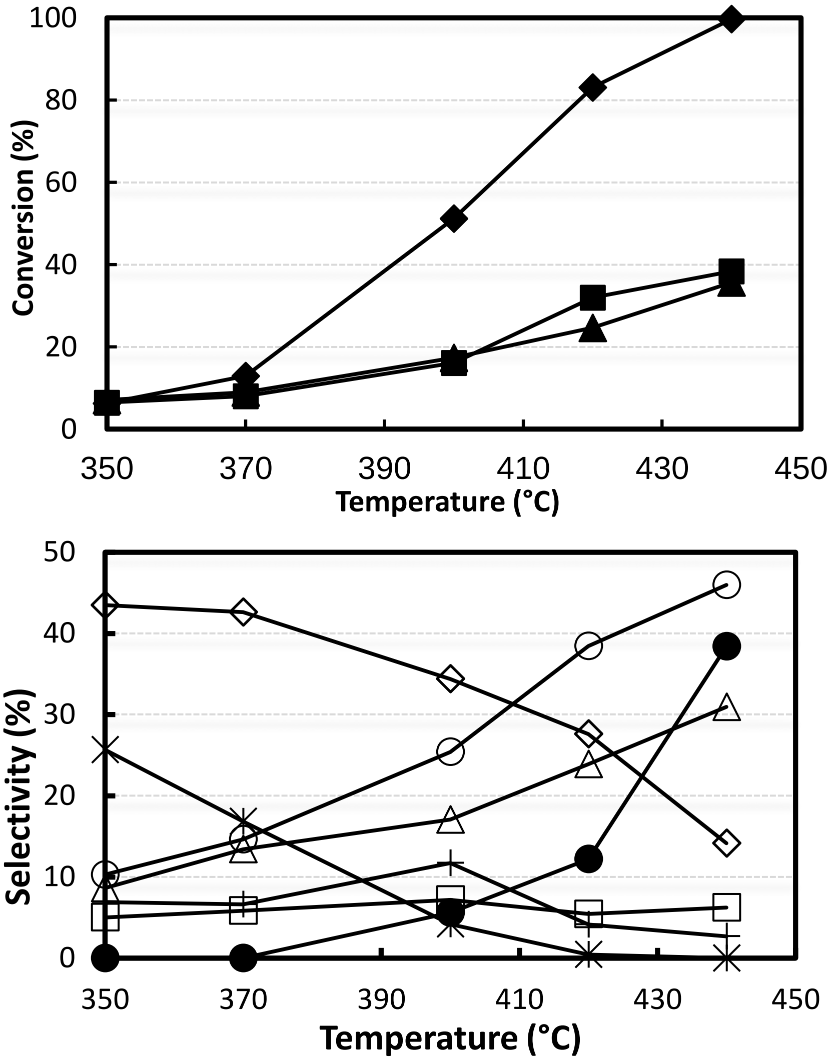
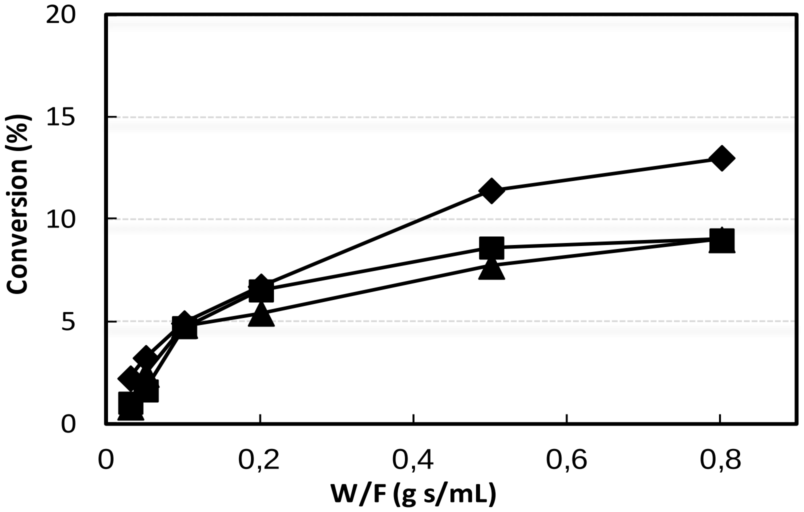


Figure 1. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope ethanol/water 95.6/4.4 wt%)/ammonia/oxygen/inert 5/13/13/69. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO+CO_2 (○), HCN (□), heavy compounds (+) and N_2 (calculated with respect to converted ammonia) (●). Catalyst VPP.



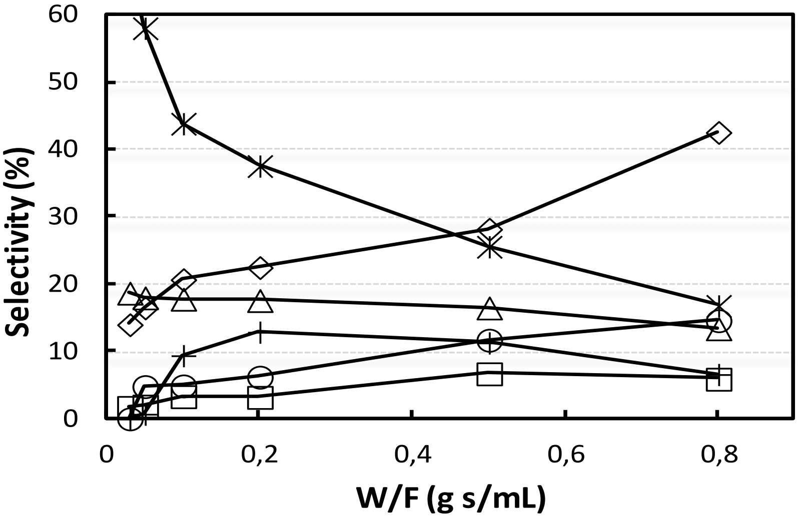
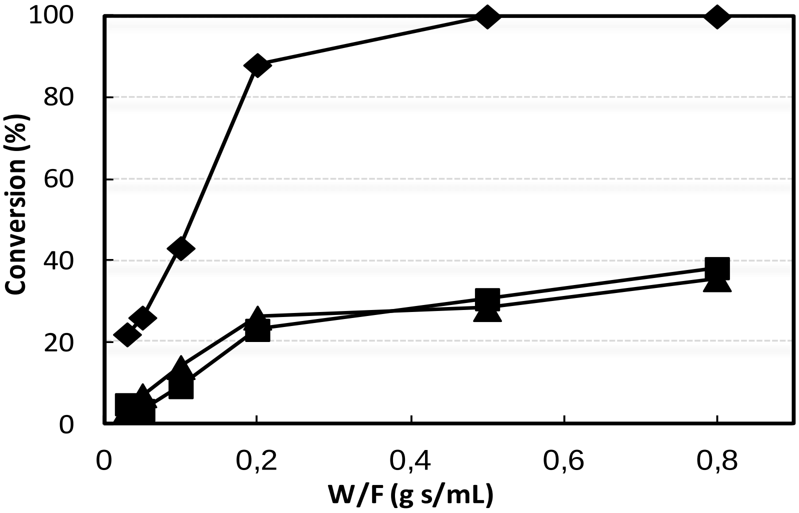


Figure 2. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: T 370°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/13/13/69. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO+CO_2 (○), HCN (□), and heavy compounds (+). Catalyst VPP.

At 370°C (Figure 2) reactants conversion was less than 15%. In regard to the distribution of products in function of W/F ratio, results indicate that the only primary products were ethylene and acetaldehyde; the selectivity to ethylene then underwent only a minor decrease when the W/F ratio was increased, whereas that to acetaldehyde rapidly declined, with a corresponding increase of selectivity to acetonitrile, $CO+CO_2$, HCN and to undetected heavier compounds as well; however, the selectivity to the latter products reached a maximum value at 0.2 g s mL^{-1} W/F ratio and then declined.



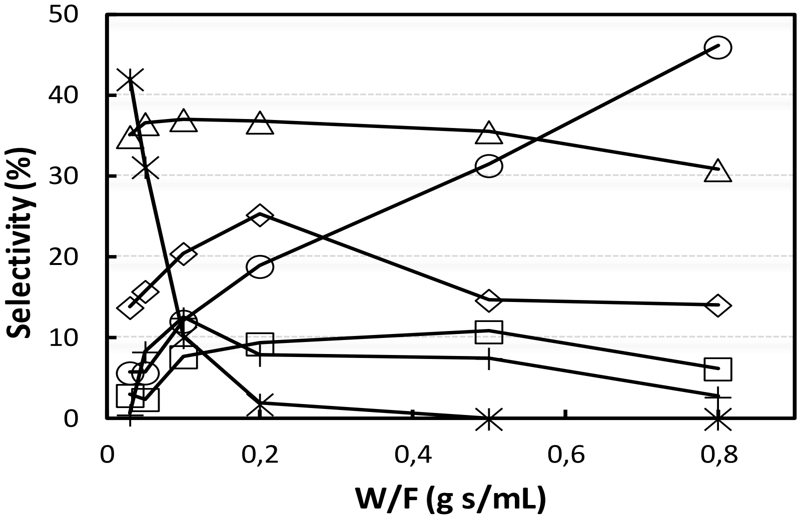


Figure 3. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: T 440°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/13/13/69. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), $CO+CO_2$ (○), HCN (□), and heavy compounds (+). Catalyst VPP.

These experiments confirm the kinetic relationship between acetaldehyde and acetonitrile, an indication that the mechanism occurs by reaction of the aldehyde with ammonia and generation of the ethanimine intermediate compound. The data also clearly highlight that the catalyst acidity is detrimental for catalytic behavior, since ethylene formation is relevant already at 370°C. The formation of N_2, deriving from ammonia combustion, was in this case negligible, because of the low temperature used.

When the experiments were carried out at 440°C (Figure 3), the same reaction network was inferred, with acetaldehyde and ethylene as the only primary products; it is worth noting that the initial selectivity to $CO+CO_2$ (that means, the selectivity extrapolated to nil conversion) was close to zero; which means that ethanol does not undergo a direct reaction of combustion even at such relatively high temperature. Once again, the rapid decline of acetaldehyde selectivity corresponds to the increase of selectivity to acetonitrile, to HCN, to $CO+CO_2$ and to heavy compounds. One major difference with respect to experiments carried out at lower temperature is that at W/F ratio above 0.1-0.2 g s mL^{-1}, the selectivity to acetonitrile and to heavy compounds both decrease. Therefore, at high temperature the acetonitrile is not a stable compound, and undergoes consecutive combustion to CO_x.

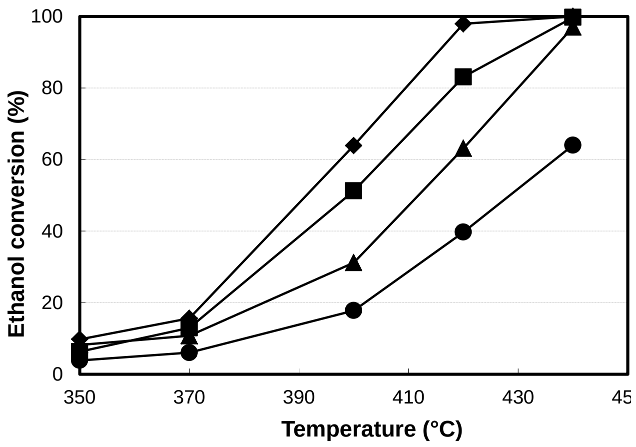
These experiments demonstrate that the relatively low selectivity obtained with the VPP catalyst is related not only to the important parallel contribution of ethanol dehydration into ethylene, but also to the fact that the key reaction intermediate undergoes consecutive transformation to both the desired compound and by-products, ie, CO, CO_2, HCN, and heavy compounds as well. Finally, even acetonitrile undergoes consecutive combustion when the reaction is conducted at high temperature.

Since the control of selectivity in partial oxidation reactions, when carried with mixed oxide catalysts (and especially with the VPP) is strictly related to the redox properties of the active metal ion, and to its average oxidation state under steady conditions, the latter being in turn affected by the gas-phase composition, we carried out a series of experiments by changing the partial pressure of ethanol, while keeping constant the inlet concentration of oxygen and ammonia; ethanol molar fractions equal to 0.02, 0.05, 0.075 and 0.13 were used. The results are summarized in Figure 4. The following effects can be noticed:

a) The conversion of ethanol, which in all cases increases over the entire range of temperature examined, shows a decreasing trend in correspondence of an increased partial pressure of ethanol in feed. This is a clear indication of a surface saturation effect; in fact, the rank related to the overall integral rate of ethanol transformation, taken at 400°C, is: 2.5% ethanol < 5% ethanol ≈ 7.5% ethanol ≈ 13% ethanol. Correspondingly, since both the oxygen and ammonia inlet partial pressures are the same in all series of experiments, and because of the saturation effect, the oxygen and ammonia conversions are less affected by ethanol concentration than ethanol conversion is. Differences observed in ammonia and oxygen conversion are due to the different distribution of products obtained (see below).

b) In all cases, the selectivity to acetonitrile shows either a maximum value at an intermediate temperature, or continuously decreasing values; the decrease in general is due to the formation of $CO+CO_2$, whereas the presence of a maximum value is due to a relatively higher formation of undetected compounds (referred to as "heavy" compounds) at lower temperature. The best selectivity is obtained with the lower concentrations of ethanol in feed; the greater difference is shown when the concentration of ethanol is increased from the 5% to 7.5%, and this is mainly due to the greater formation of heavy compounds.

c) The acetaldehyde selectivity declines when the temperature is raised; the greater selectivity to acetaldehyde is shown with tests carried out at the higher ethanol concentration. This is probably due to the fact that under conditions of surface saturation, the reactions involving acetaldehyde are slower than on a "cleaner" surface. Moreover, under these conditions acetaldehyde is less efficiently transformed into acetonitrile, and undergoes side reactions to form heavier compounds. This is due to the fact that because of the high surface coverage by the adsorbed ethanol and acetaldehyde, bimolecular reactions between adsorbed molecules are more favored.


Ethanol conversion (%)
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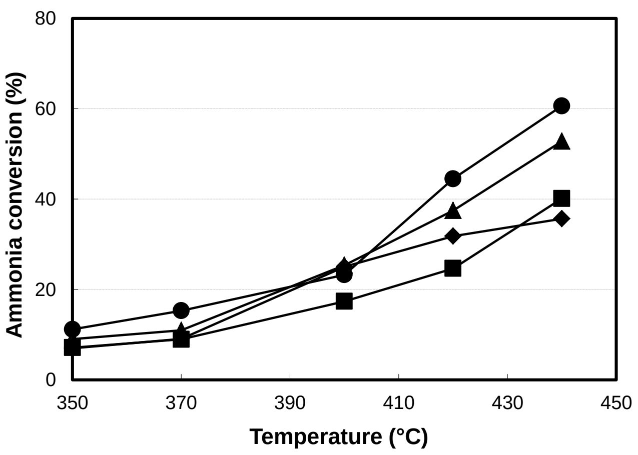
40
60
80
100
350
370
390
410
430
45
Temperature (°C)


Ammonia conversion (%)
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60
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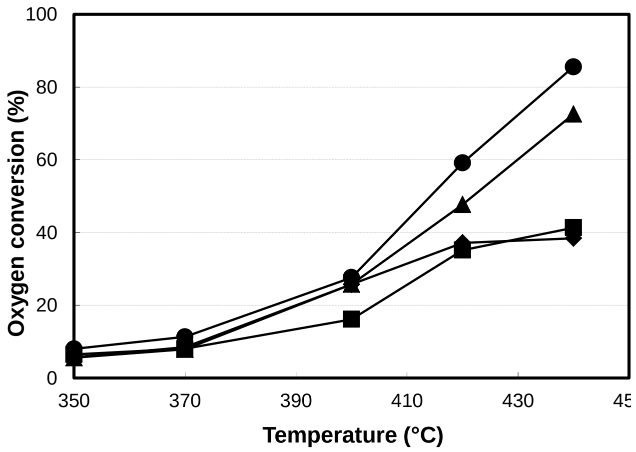
350
370
390
410
430
450
Temperature (°C)


Oxygen conversion (%)
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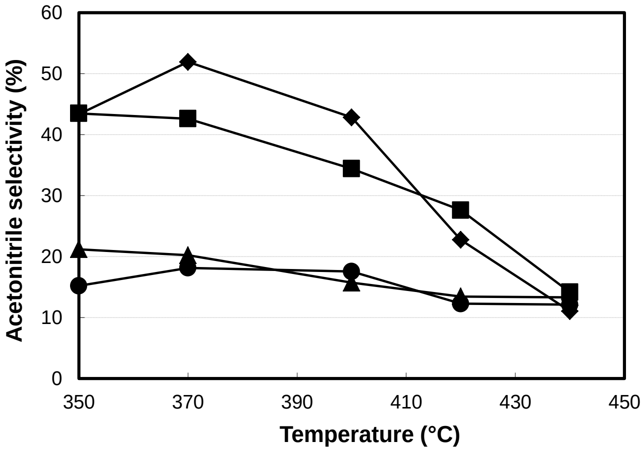
60
80
100
350
370
390
410
430
45
Temperature (°C)


Acetonitrile selectivity (%)
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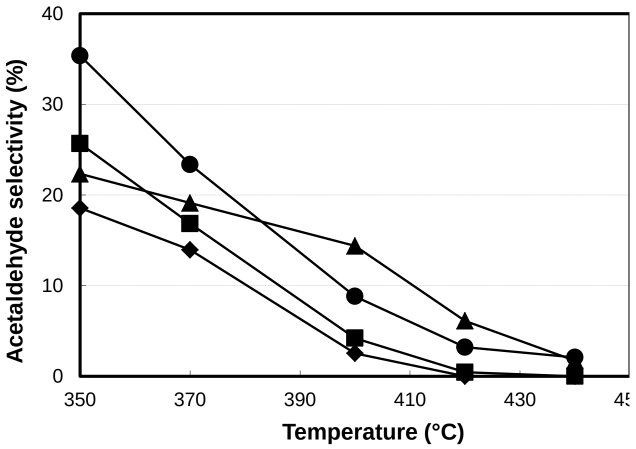
30
40
50
60
350
370
390
410
430
450
Temperature (°C)


Acetaldehyde selectivity (%)
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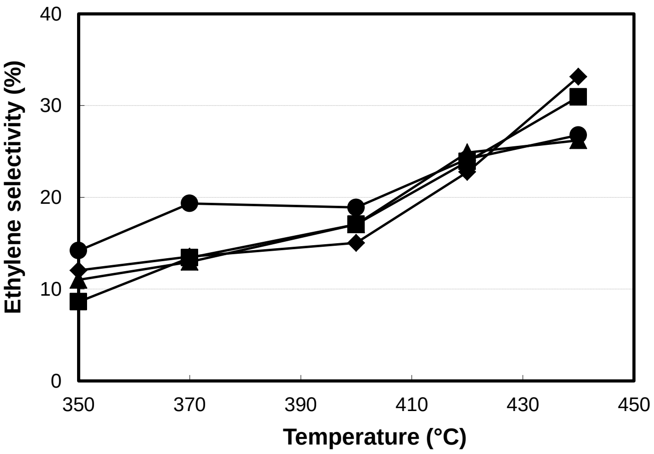
20
30
40
350
370
390
410
430
45
Temperature (°C)


Ethylene selectivity (%)
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10
20
30
40
350
370
390
410
430
450
Temperature (°C)

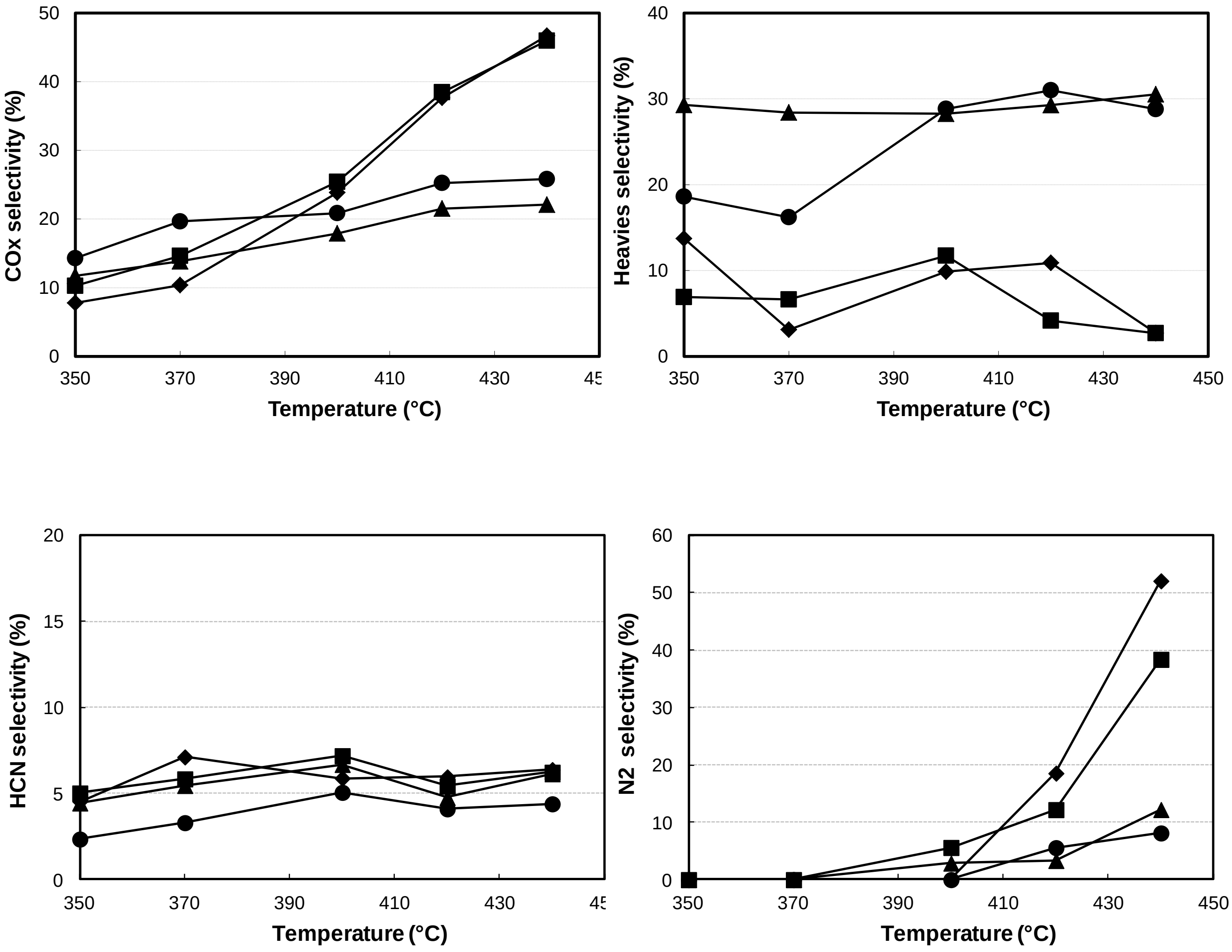


Figure 4. Conversion of ethanol, oxygen and ammonia, and selectivity to the products in function of temperature. Feed composition: ethanol 2% (◆), 5% (■), 7.5 (▲), or 13% (●), ammonia 13%, oxygen 13%, remainder He. Catalyst VPP.

d) The selectivity to ethylene is not much affected by ethanol partial pressure; this is a clear indication of the fact the ethanol dehydration to ethylene occurs on sites which are different from those responsible for ethanol (oxi)dehydrogenation into acetaldehyde. However, for these sites a saturation effect is also observed, because the overall rate of ethylene formation reaches a plateau.

e) With all series of experiments, the selectivity to CO+CO_2 increases along with the temperature raise; however, the variation shown is different in function of the partial pressure of ethanol. In fact, in experiments carried out using 2 and 5 % ethanol in feed, the selectivity to $CO+CO_2$ is relatively low at low temperature, but then the raise observed in function of temperature is very steep. Conversely, in experiments carried out using 7.5 and 13% ethanol in feed, the selectivity to $CO+CO_2$ is slightly higher at lower temperature, compared to experiments at lower ethanol concentration, but then the increase shown along with temperature raise is not so relevant. In consequence of this, at high temperature and high ethanol concentration the selectivity to $CO+CO_2$ is much lower than that observed under leaner ethanol conditions. This effect can be explained by taking into account the surface saturation due to the adsorbed C_2 molecules; a saturation implies a lower availability of oxidizing sites (in other words, it can be viewed as a surface "over-reduction"), those which are supposed to be responsible for the combustion to carbon oxides. Therefore, under these "saturated surface" conditions, the catalyst is less selective to combustion compounds, but more selective to heavier, condensation compounds.

f) The effect of ethanol concentration on selectivity to N_2 is relevant. It is shown that the greater is the ethanol concentration in feed, the lower the amount of ammonia which is unselectively oxidized into molecular nitrogen. This is attributable not only to the fact that the reaction between the intermediately formed acetaldehyde and ammonia is quicker compared to the parallel reaction of ammonia combustion when there is a greater concentration of adsorbed acetaldehyde; an important contribution may derive, once again, from the V over-reduction under surface saturation conditions, that makes the combustion of ammonia kinetically less important than under conditions at which the catalyst surface is cleaner.

Concluding, an important output of these experiments is that the best yields to acetonitrile are obtained at either 2% (27% at 400°C and 22% at 420°C) or 5% ethanol in feed (18% at 400°C and 23% at 420°C), but the best productivity to acetonitrile (calculated by multiplying the yield of acetonitrile by the inlet molar fraction of ethanol and the volumetric flow rate, and dividing the result by the molar volume and the catalyst weight) is obtained with the 5% ethanol in feed (at 420°C). Therefore, further experiments were carried out using the feed composition: 5 vol% ethanol, 13% ammonia, 13% oxygen (which are the conditions also used for experiments reported in Figures 1-3).

In regard to the nature of the so-called "heavy" products, the following compounds have been identified (using 13% ethanol in feed; in fact, under ethanol-rich conditions the formation of these compounds is more favored): fumaronitrile, pyrazine, lactonitrile, 2-ethylidenamino-propionitrile, and some olefins as well, such as 3-methyl-1-butene and 2-pentene. Those formed in greater amount are the products containing N; it is worth noting that they did not form by consecutive reaction upon acetonitrile (which is a stable compound, see experiments reported below); therefore, we can assume that they formed starting from some N-containing intermediate, such as ethanimine. It is possible that the imine intermediate, which is very reactive, under conditions of surface saturation more easily reacts either with acetaldehyde or with another adsorbed imine to generate condensation compounds, instead of being (oxi)dehydrogenated into the nitrile. It can be assumed that the relative rate between the two competitive reactions of acetaldehyde transformation (condensation *vs* oxidehydrogenation) is a function of both the surface concentration of adsorbed species and the surface availability of oxidizing V species; the latter is the lower when the catalyst surface is completely covered by the adsorbed intermediate compounds, acetaldehyde and ethanimine.

The data obtained in function of W/F ratio, at 440°C, using 7.5% ethanol in feed, that is, under conditions of surface saturation, confirm the hypothesis made. The results, shown in Figure 5, demonstrate that the consecutive reaction occurring on acetaldehyde leads not only to acetonitrile and $CO+CO_2$ (which is also what is shown in the case of experiments carried out under non-saturated surface conditions), but also to heavy compounds; in fact, the selectivity to the latter increases in concomitance with the decrease of acetaldehyde selectivity. On the other hand, the selectivity to heavy compounds shows a maximum value, probably due to consecutive combustion.

The effect of oxygen and ammonia partial pressures, at 0.8 g s mL^{-1} W/F ratio, 370°C and with 5% ethanol in feed, is shown in Figures 6 (ammonia 13%) and 7 (oxygen 13%), respectively. In regard to the effect of oxygen, it is shown that the increase of the oxygen partial pressure leads to a proportional increase of ethanol conversion; this means that oxygen has an important role in the dehydrogenation of ethanol to acetaldehyde (a primary product), and that the VPP does not catalyze the simple dehydrogenation of ethanol to the aldehyde.

Oxygen also affects considerably the distribution of products; it facilitates the transformation of acetaldehyde into CO, CO_2 and HCN, and into acetonitrile as well; this means that the formation of acetonitrile also involves the contribution of oxygen, for the oxidative dehydrogenation of ethanimine into the nitrile. On the other hand, concentrations of oxygen higher than 13% cause a decrease of the selectivity to acetonitrile, and a corresponding increase of selectivity to CO_2. Oxygen does not affect the selectivity to ethylene, which is an expected result. The selectivity to heavy compounds is below 10% over the entire range of oxygen partial pressure investigated, and it does not seem to be significantly affected by this parameter.

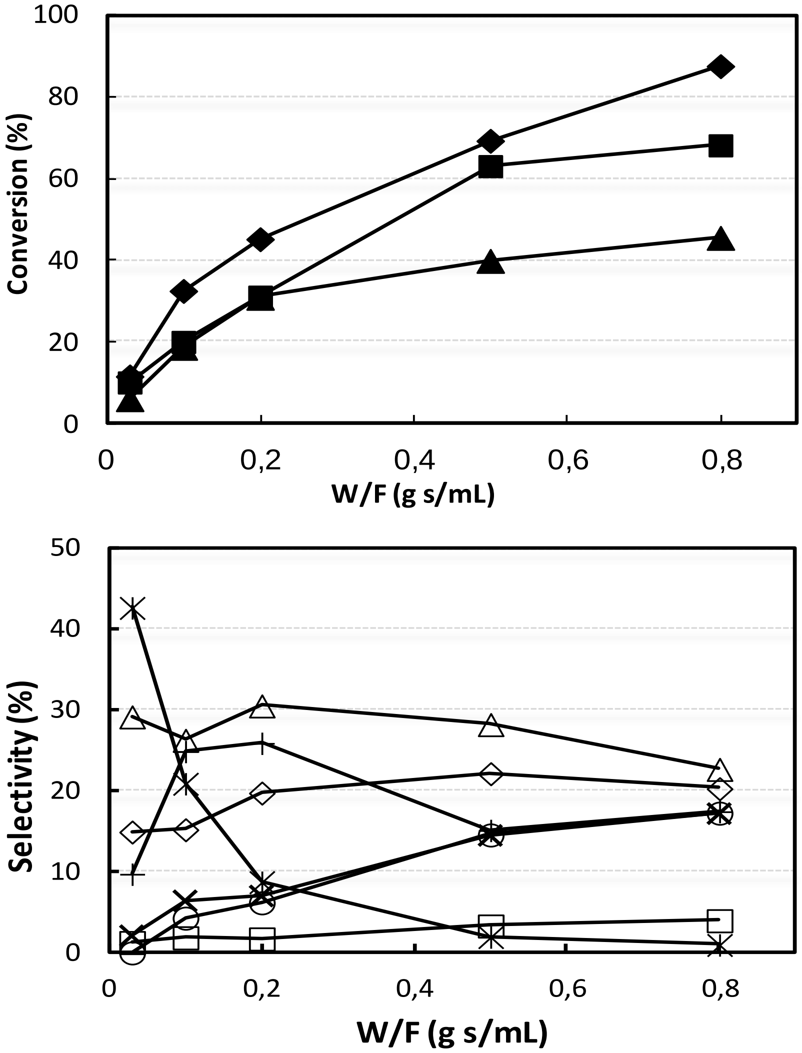
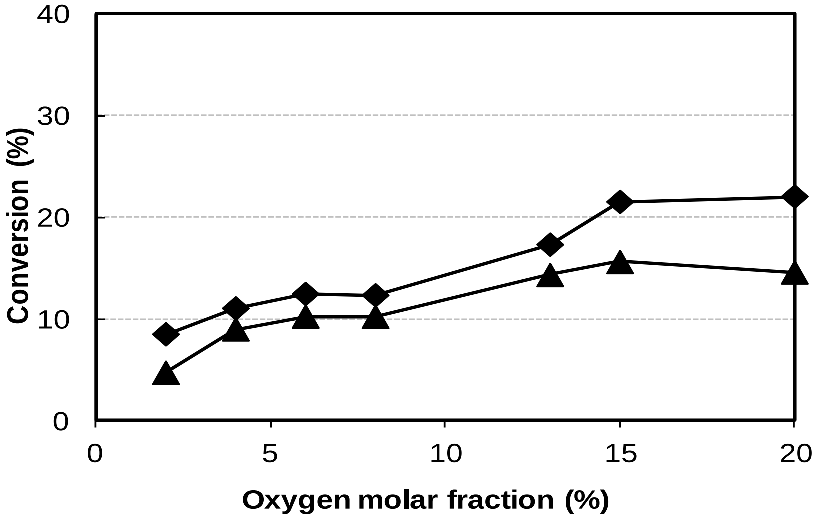


Figure 5. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: T 440°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 7.5/13/13/66.5. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO_2 (×), HCN (□), and heavy compounds (+). Catalyst VPP.



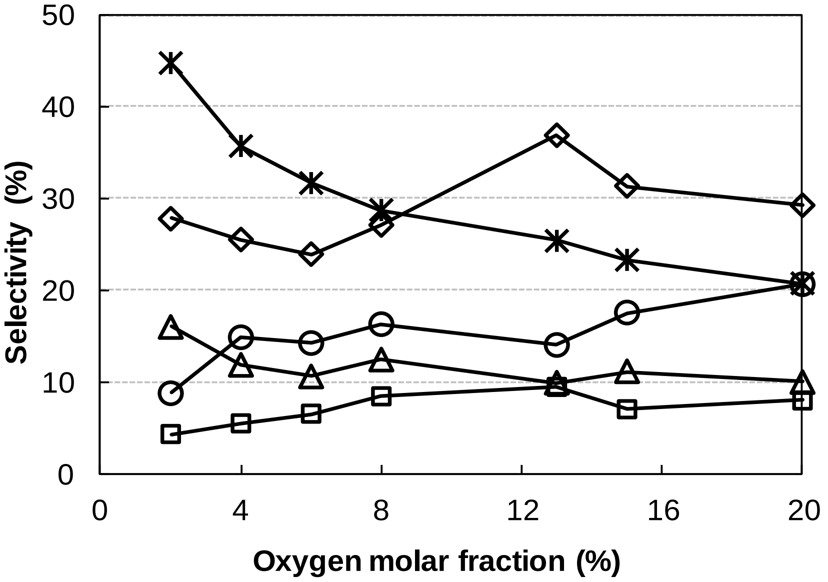


Figure 6. Effect of oxygen inlet molar fraction on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, T 370°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/13/x/82-x. Symbols: ethanol conversion (◆), and ammonia conversion (▲). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO+CO$_2$ (O), and HCN (☐). Catalyst VPP.

For what concerns the role of ammonia, Figure 7 shows that there is an inhibition effect on ethanol conversion. This decrease is due to both a decline of yield to ethylene (in fact, the selectivity to this compound is not affected by ammonia), and of the reaction pathway leading to acetaldehyde and then acetonitrile. Therefore, ammonia interacts with both types of sites, the acid one (leading to ethylene formation; this implies the existence of string acid sites, which are poisoned by ammonia at high temperature), and the redox one responsible for acetaldehyde formation.

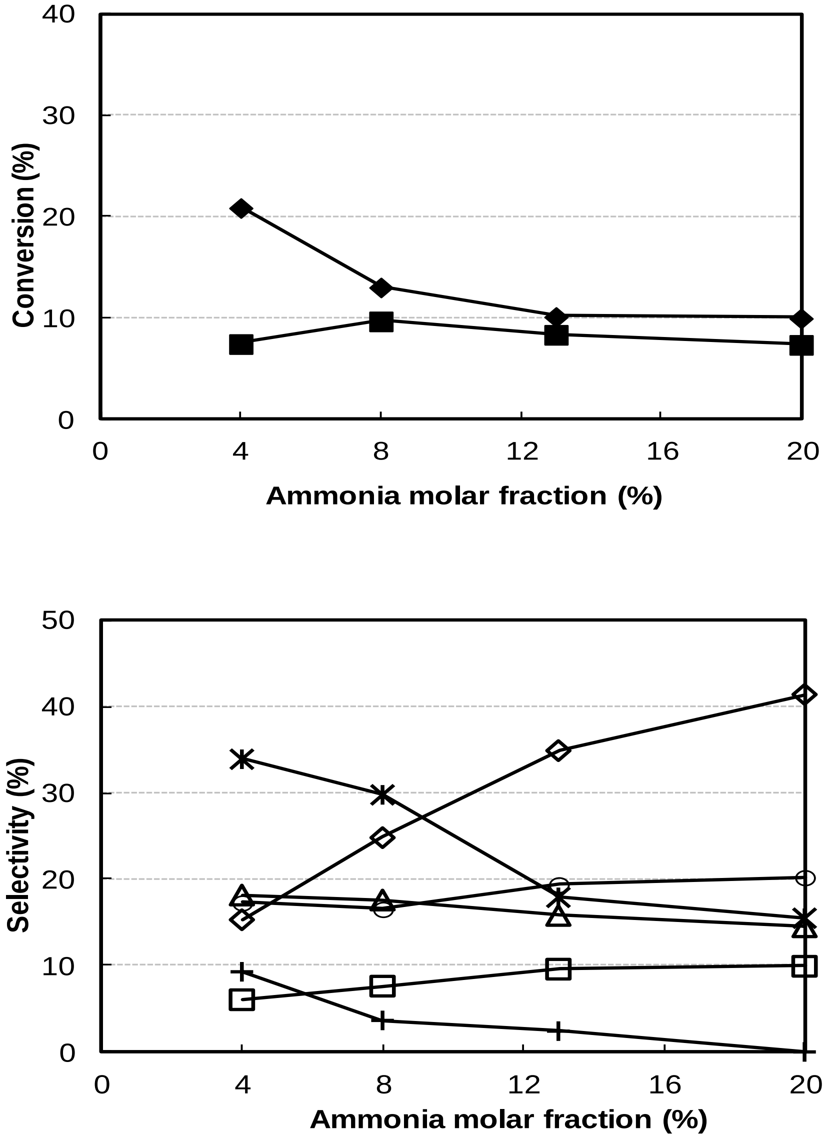


Figure 7. Effect of ammonia inlet molar fraction on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, T 370°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/x/13/82-x. Symbols: ethanol conversion (◆), and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO+CO$_2$ (O), HCN (□), heavy compounds (+). Catalyst VPP.

The data shown in Figure 7 demonstrate that a large excess of ammonia, compared to the stoichiometric amount, leads to an improvement of performance, because of a better selectivity to acetonitrile, and a lower selectivity to acetaldehyde and heavy compounds.

Therefore, we decided to carry out experiments under conditions of surface saturation, with 13% ethanol in feed, but using a large excess of ammonia, 39% molar fraction. It is worth noting that Figure 4 shows that when a feed of composition ethanol/ammonia/oxygen (molar fractions %) equal to 13/13/13 is used, the main drawback is the large formation of heavy compounds; we hoped that using a large excess of ammonia might lead to a better performance. The results obtained with the two different feed composition are shown in Figures 8 (ethanol/ammonia/oxygen 13/13/13) and 9 (13/39/13).

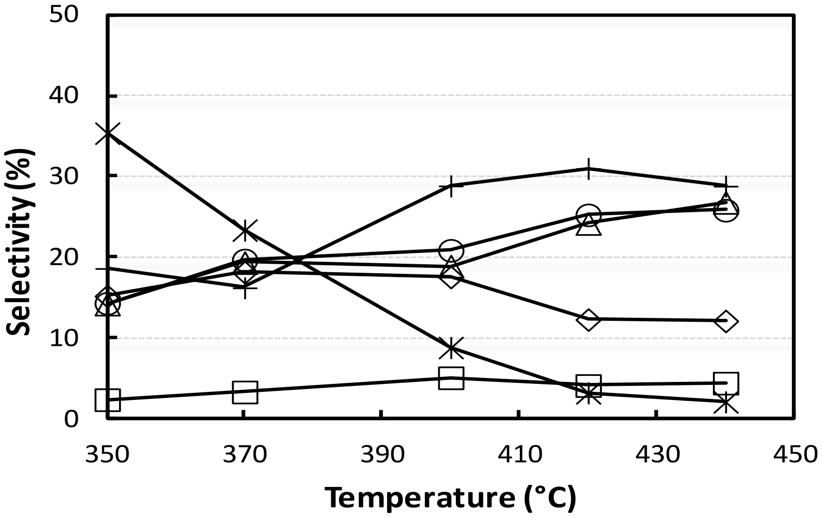


Figure 8. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 13/13/13/61. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO+CO$_2$ (O), HCN (□), and heavy compounds (+). Catalyst VPP.

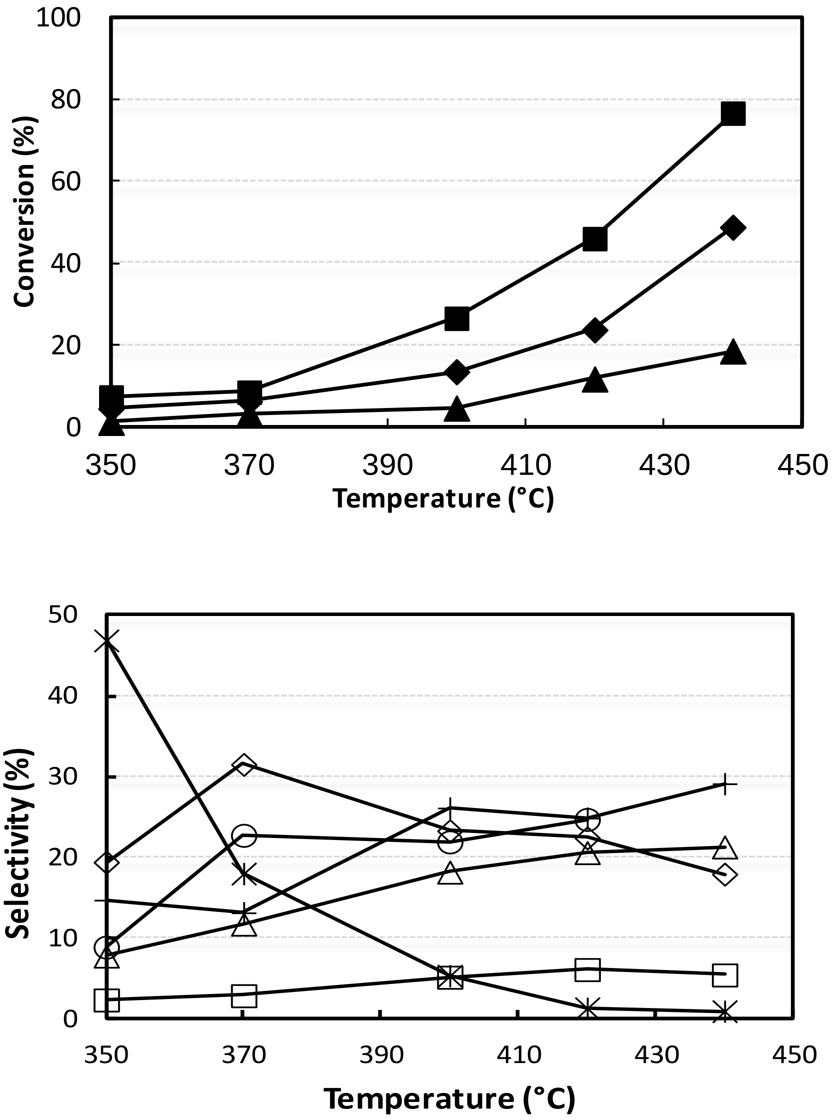


Figure 9. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 13/13/39/35. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO+CO$_2$ (○), HCN (□), and heavy compounds (+). Catalyst VPP.

For what concerns the selectivity to the various products, an increase of ammonia partial pressure accelerates the consecutive transformation of the aldehyde into the nitrile. Another interesting effect is the decrease of selectivity to heavy compounds; this confirms that acetaldehyde is directly involved in the formation of these products, and that the acceleration of the reaction pathway leading to acetonitrile (due to the high ammonia concentration) occurs at the expense of the competitive route of heavy compounds formation.

Comparing the results reported in Figures 8 and 9, it is shown that indeed a better acetonitrile selectivity is obtained at very high ammonia partial pressure, because of both the lower selectivity to ethylene, and the slightly lower selectivity to heavy compounds, and to a steeper decrease of selectivity to acetaldehyde. However, in overall the effect observed is not remarkable, and still the formation of heavy compounds remains predominant. Concluding, the best feed composition is that one with 5% ethanol in feed, and both ammonia and oxygen molar fraction equal to 13%.

In regard to the possible contribution of homogeneous reactions, we compared experiments carried out with the composition ethanol/ammonia/oxygen mol% 7.5/13/13 and the usual reactor configuration (no inert filling the hot, void space of the reactor before the catalytic bed), with experiments done filling the reactor with steatite before the catalytic bed. It is worth noting that preliminary experiments carried out by filling the entire reactor (without catalyst) with inert material highlighted a negligible contribution of the "inert" surface on reactivity. Figure 10 shows the results obtained with the new reactor configuration, that should be compared with those reported in Figure 4, for the same feed composition.

There are some differences between the two set of experiments; specifically, using the new reactor configuration (with the inert material) we observed:

a) Reactants conversions similar to those obtained with the usual reactor configuration;

b) A higher selectivity to acetonitrile (about 10% more over the entire range of temperature), and a slightly lower selectivity to acetaldehyde (about 5% less).

c) A higher selectivity to $CO+CO_2$; selectivity to ethylene is lower, especially at high temperature. The heavy compounds selectivity is also slightly less (around 25%, whereas it is close to 30% with the usual reactor configuration).

In overall, the conversion of reactants is not so much affected, but there are some differences concerning the products distribution.

Concluding, experiments carried out clearly highlight that one problem of the VPP catalyst is its intrinsic acidity, which facilitates the dehydration of ethanol into ethylene. Therefore, we finally carried out experiments using a K-doped catalyst. The catalyst was prepared as follows: 0,0066 g KNO_3 were dissolved in 50 ml H_2O; then, 10 ml of the solution were used to impregnate 1 g of the VPP catalyst by means of the wet impregnation technique. The excess solvent was evaporated under vacuum, and the solid recovered was finally dried and then thermally treated in N_2 flow at 550°C. The final V/K atomic ratio was equal to 500.

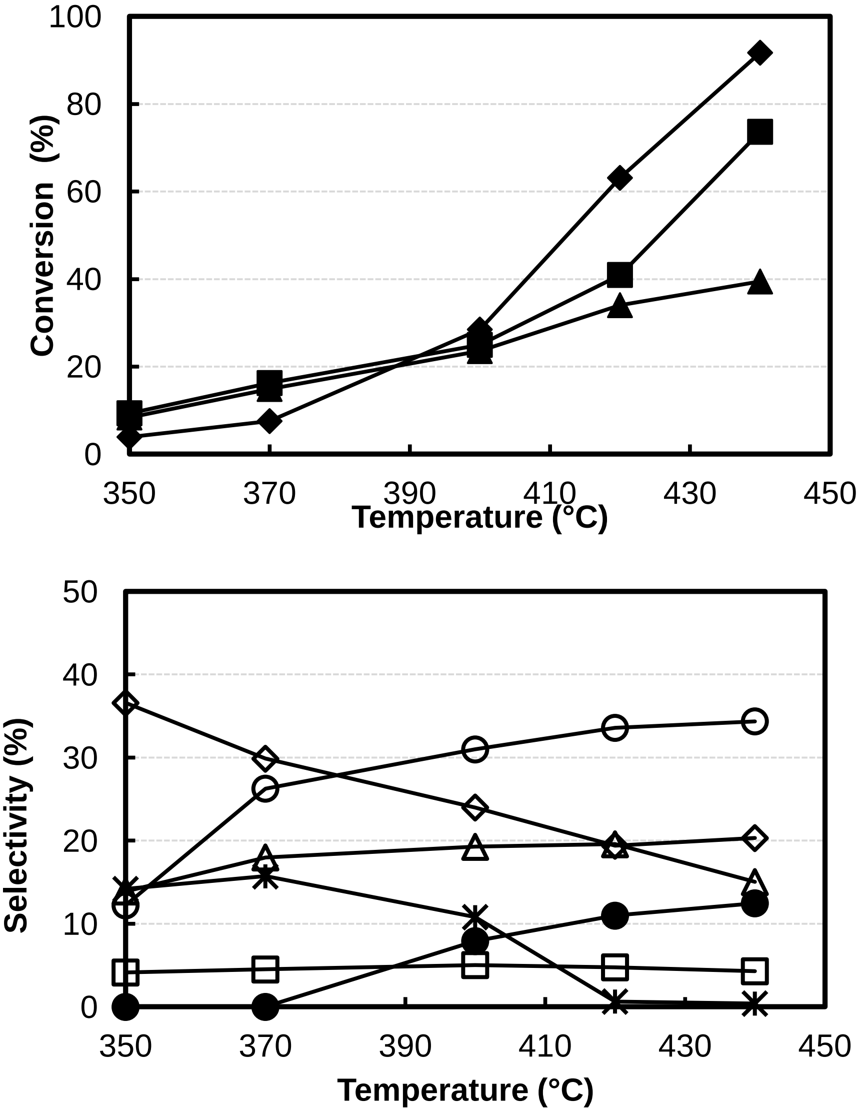


Figure 10. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1} (void section of the reactor filled with steatite), feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 7.5/13/13/65.5. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO+CO_2 (○), HCN (□), heavy compounds (+) and N_2 (calculated with respect to converted ammonia) (●). Catalyst VPP.

The results of experiments carried out using the feed ethanol/ammonia/oxygen/inert 7.5/13/13/65.5 (and the usual reactor configuration), with the K-doped VPP catalyst, are shown in Figure 11; they have to be compared with those reported in Figure 4, for the same feed composition. It is shown that the results obtained were almost identical, for both the undoped and the K-doped VPP catalysts; noticeably, the selectivity to ethylene was not affected at all. This indicates that the procedure adopting for the neutralization of the catalyst acid sites was not effective.

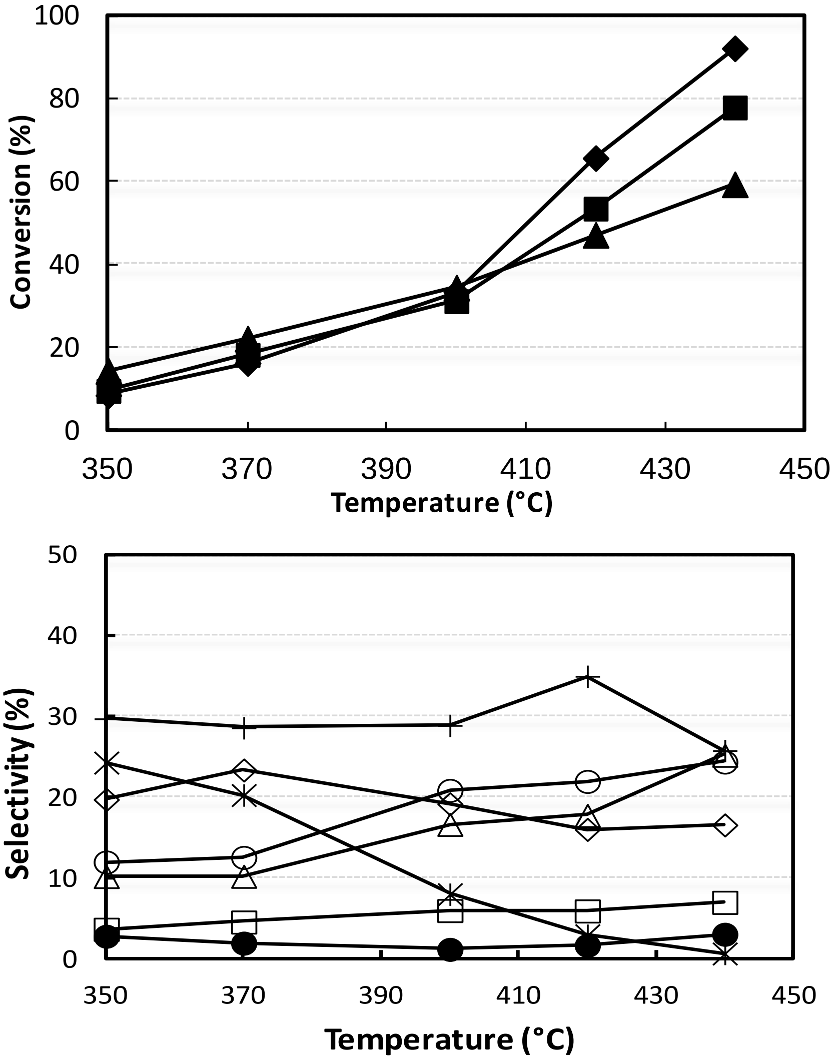


Figure 11. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 7.5/13/13/65.5. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO+CO$_2$ (○), HCN (□), heavy compounds (+) and N$_2$ (calculated with respect to converted ammonia) (●). Catalyst: K-doped VPP.

In the aim of confirming the reaction mechanism proposed, we carried out experiments by feeding the possible reaction intermediates, acetaldehyde and ethylamine. In fact, even though the experiments clearly highlight the existence of a kinetic relationship between acetaldehyde and acetonitrile, we cannot exclude the possible existence of a side-reaction pathway, with a direct exchange between –OH and $-NH_2$ (see the Chapter on amination of alcohols); the amine might then yield acetonitrile by oxidehydrogenation.

$CH_3CH_2OH + NH_3 \leftrightarrows CH_3CH_2NH_2 + H_2O$

$CH_3CH_2NH_2 + O_2 \rightarrow CH_3CN + 2\ H_2O$

We first carried out experiments by feeding acetaldehyde, using the feed: acetaldehyde/ammonia/oxygen mol% 0.5/13/13; acetaldehyde was fed by means of vaporization of the pure compound, in the same way as we did with ethanol. We checked both the effect of temperature (W/F ratio 0.8 g s mL^{-1}) and of W/F ratio (T 350°C); results are shown in Figures 12 and 13, respectively. In regard to the effect of temperature, we notice the following:

a) The C balance is very good, with no formation of heavy compounds; this is likely due to the low inlet concentration of acetaldehyde used.

b) Acetaldehyde is very reactive; total conversion is shown already at 400°C.

c) The aldehyde is mainly converted into acetonitrile and HCN, which form with similar selectivity (however, since selectivity is referred to the number of C atoms, the number of HCN moles produced is greater than that of acetonitrile).

d) The $CO+CO_2$ selectivity trend is similar to that shown by HCN; however, the number of moles produced remains always lower than that of HCN.

In overall, the behavior shown has analogies but also differences compared to that one observed from ethanol; the main difference concerns the large amount of HCN, which instead forms with low selectivity from ethanol, even at low ethanol concentration. Indeed, we would have expected a much more efficient transformation of acetaldehyde into acetonitrile, especially because of the very large amount of ammonia fed.

In order to interpret this difference, we carried out the experiments in function of W/F ratio, at 350°C. Results reported in Figure 13 show that the main primary product of acetaldehyde transformation is acetonitrile, which however undergoes consecutive transformation into both $CO+CO_2$ and, at a major extent, of HCN. After 0.8 g s mL^{-1} W/F ratio (which is the same used for experiments reported in Figure 12) both acetonitrile and HCN undergo a consecutive transformation into CO_2 and N_2.

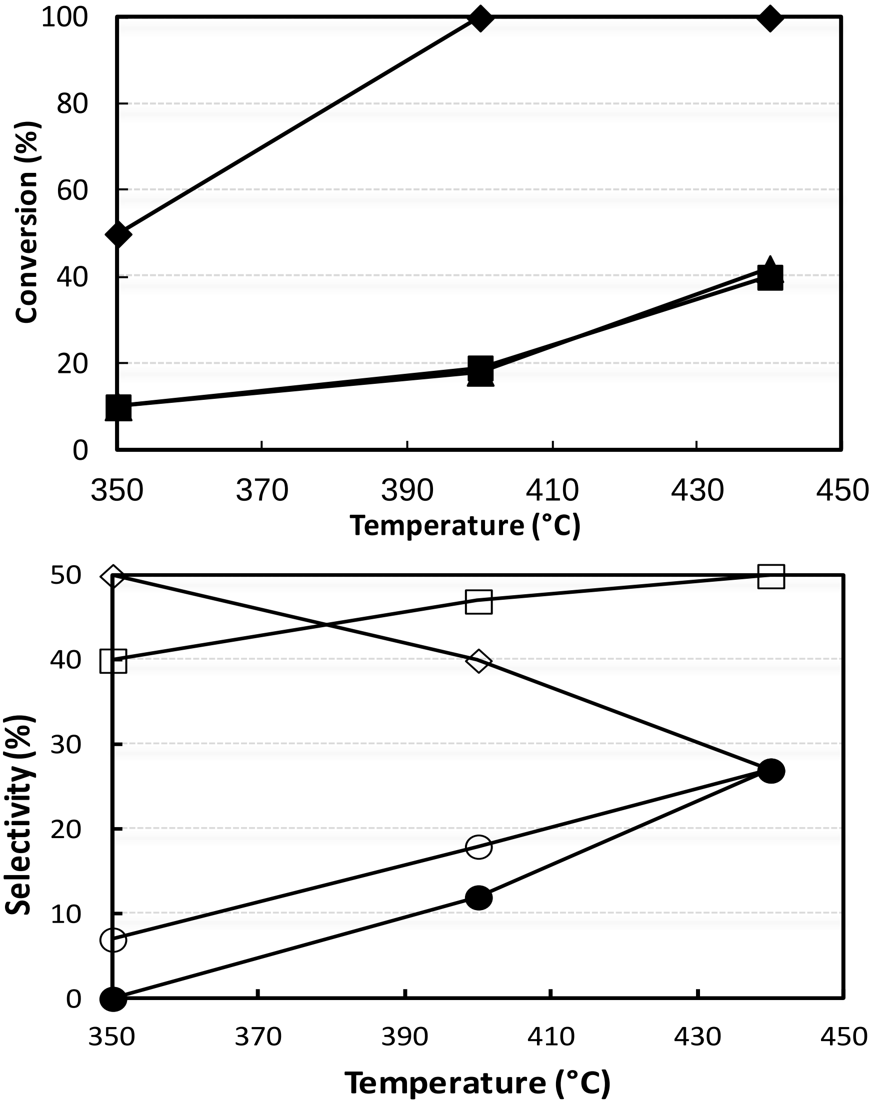
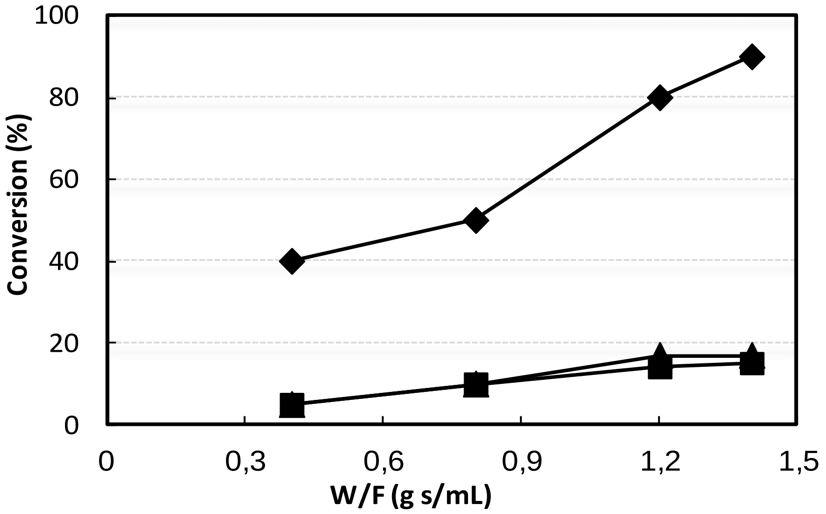


Figure 12. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): acetaldehyde/ammonia/oxygen/inert 0.5/13/13/73.5. Symbols: acetaldehyde conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), $CO+CO_2$ (O), HCN (□), and N_2 (calculated with respect to converted ammonia) (●). Catalyst VPP.

Therefore, these experiments allow two important conclusions:

a) The scheme of the ethanol-to-acetonitrile reaction also includes the reactions of consecutive transformation of acetonitrile into HCN and of both compounds into CO_2.

b) Since in experiments carried out with ethanol, at 370°C (Figure 2), any consecutive reaction on acetonitrile and HCN give minimal contribution, we can say that the occurrence of these reactions is relevant only under conditions of low surface saturation. In other words, a non-saturated surface (because of the low concentration of acetaldehyde fed during these experiments) is more active in the consecutive oxidative degradation of both acetonitrile (into HCN and $CO+CO_2$), and HCN (into CO_2 and N_2).



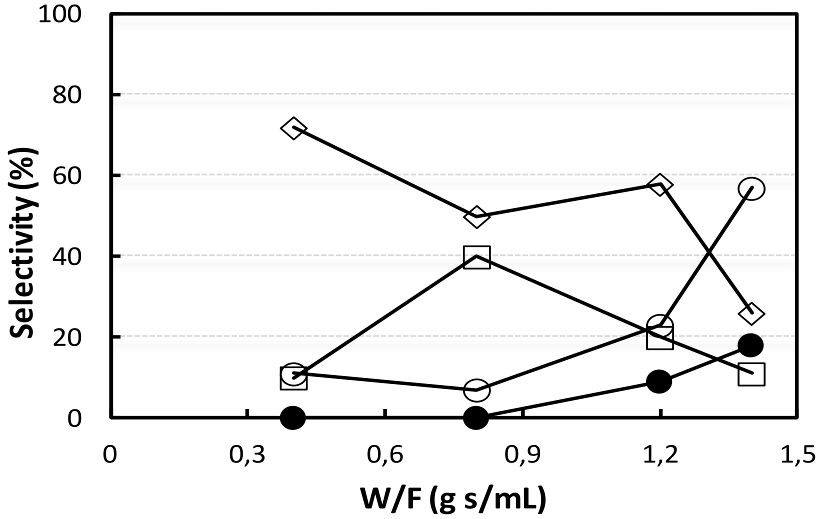


Figure 13. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: temperature 350°C, feed composition (molar %): acetaldehyde/ammonia/oxygen/inert 0.5/13/13/73.5. Symbols: acetaldehyde conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), CO+CO_2 (O), HCN (□),and N_2 (calculated with respect to converted ammonia) (●). Catalyst VPP.

The presence of a non-saturated surface under the conditions used for these experiments is also demonstrated by the fact that there is practically no formation of heavy compounds. In order to confirm this hypothesis, we carried out some experiments by feeding 1.5% acetaldehyde (with 13% oxygen and 13% ammonia); because of the huge problems met with these experiments (formation of polymeric compounds, with blockage of the reactor lines), we cannot report the values of conversion and selectivity obtained. However, one important result is that we noticed the formation of large amounts of heavy compounds, which were exactly the same, also formed in experiments with ethanol under surface saturation conditions: 2-ethylidene-amino-propionitrile, 1-butene-3 methyl, fumaronitrile etc. The only product formed, which instead was not observed from ethanol, is acetic acid; however, it forms in significant amount at 350°C, but in negligible quantity at 400°C.

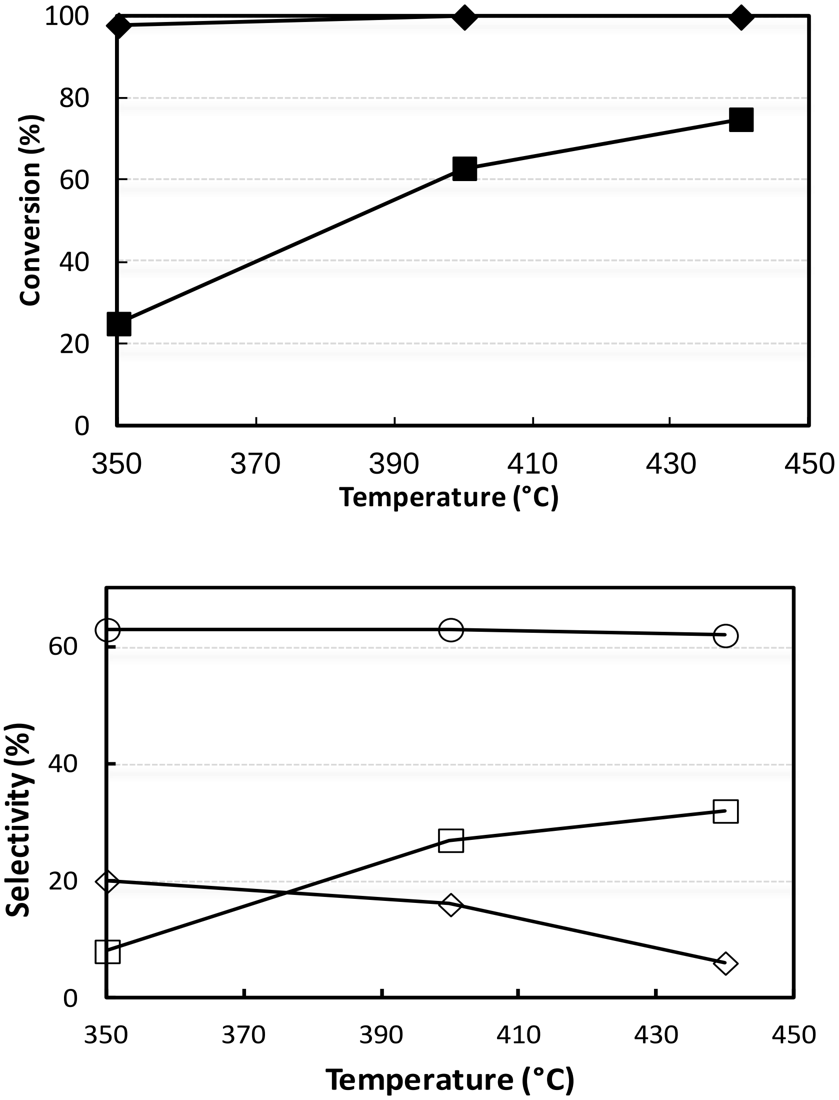


Figure 14. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethylamine/oxygen/inert 0.9/13/86.1. Symbols: ethylamine conversion (◆), and oxygen conversion (■). Selectivity to: acetonitrile (◇), CO+CO$_2$ (○), and HCN (□). Catalyst VPP.

In regard to the reactivity of ethylamine, results of experiments carried out by feeding 0.9 mol% ethylamine and 13% oxygen are illustrated in Figure 14; the experiments were carried out without ammonia in feed. The amine is very reactive; almost total conversion is shown already at 350°C. Predominant products are carbon oxides, the selectivity of which is not affected by temperature (even though the ratio CO/CO_2 decreases, as also shown by the considerable increase of oxygen conversion observed along with the temperature raise). The selectivity to acetonitrile is 20% at 350°C, but then it shows a decline, with a corresponding raise of selectivity to HCN. At low temperature, we also noticed the formation of small amounts of $CH_3CH_2N=C=O$. It is evident that the low selectivity to ethylamine allows us to disregard the reaction mechanism of acetonitrile formation via intermediate ethylamine formation.

Ethylene is one of the major by-products of the reaction, and in all experiments carried out in function of W/F ratio, its selectivity was not affected by this latter parameter, implying that it is a very stable product. This was confirmed by experiments carried out by feeding ethylene, using the feed composition: ethylene/ammonia/oxygen mol% 7.5/13/13. Results demonstrate that ethylene is poorly reactive, as shown by its modest conversion in function of temperature (Figure 15). Minor products are HCN and COx, whereas the major product is tentatively attributed to toluene. This indicates that the VPP catalyst is able to transform olefin into aromatics, a property typically shown by acid catalysts.

The last point investigated was the stability of acetonitrile under reaction conditions. In fact, experiments carried out in function of W/F ratio highlighted that acetonitrile is a stable product; however, under specific reaction conditions it may undergo consecutive reactions of oxidative degradation. We carried out first an experiment by feeding acetonitrile and oxygen, without catalyst, in the temperature range 350-440°C; at 440°C, acetonitrile conversion was 8% only. This indicates that there is no homogeneous oxidative degradation of the product. Other experiments were carried out by feeding acetonitrile and oxygen over the VPP catalyst, using two different feed compositions (Figures 16 and 17).

The results obtained with the two series of experiments are not much different; with both acetonitrile-lean and –rich inlet feed, acetonitrile conversion is moderate, and the products observed are HCN and $CO+CO_2$ (the former one prevailing at high temperature, the latter at low temperature). In the first series of experiments, with high acetonitrile concentration in feed, we experimented serious blockage of the lines because of polymers formation, and also the C balance was poor over the entire range of temperature examined. Heavy compounds formed in lesser quantity during experiments carried out with low acetonitrile concentration in feed.

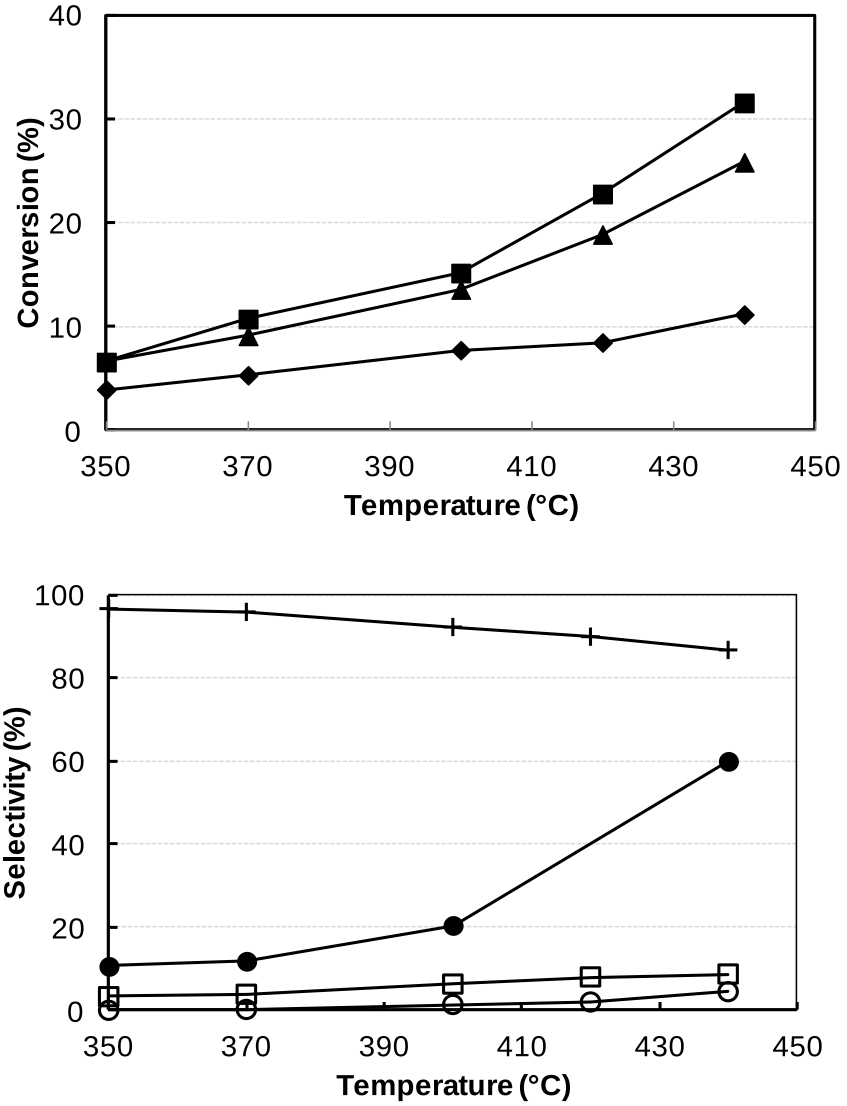


Figure 15. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethylene/ammonia/oxygen/inert 7.5/13/13/66.5. Symbols: ethylene conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: $CO+CO_2$ (○), HCN (□), unknown compound (possibly toluene, +) and N_2 (calculated with respect to converted ammonia) (●). Catalyst VPP.

We carried out some characterization of the VPP catalyst, in order to gather more information concerning the type and the strength of acid sites on the VPP surface (TPD analysis) and check whether the catalyst undergoes surface changing after reaction (Raman spectroscopy); Figure 18 shows the ammonia-TPD profile of the VPP catalyst; the desorption profile shows that there are medium-strength acid sites (ammonia desorption between 150 and 300°C) and very strong sites (desorption at above 450°C). Therefore, at reaction condition in ethanol ammoxidation the stronger acid sites are neutralized by ammonia, however the medium-strength acid sites are not occupied by ammonia, and hence they may act as sites for ethanol dehydration. Figure 19 shows the Raman spectra of both fresh and used VPP catalyst; In the case of fresh VPP catalyst (black line) is possible to see Raman shift at 936 cm-1, 1200 cm-1 and 977 cm-1 belongs to the P – O asymmetric stretching of phase, while Raman shift at 1135 cm-1 belongs to the $(VO)_2P_2O_7$ phase [16]. The catalyst used (red and blue lines), with respect to the fresh one, does not show significant differences, in fact, the δ-$VOPO_4$ Raman shift continue to be present, this indicates that the catalyst is stable in the reaction conditions throughout the temperature range studied thus the surface do not undergo any transformation. However, it is easily noticeable a strong drift signal that typically indicates the formation of organic substances, tars, which are deposited over time on the surface of the catalyst, this is consistent with by-products analyzed during the reaction.

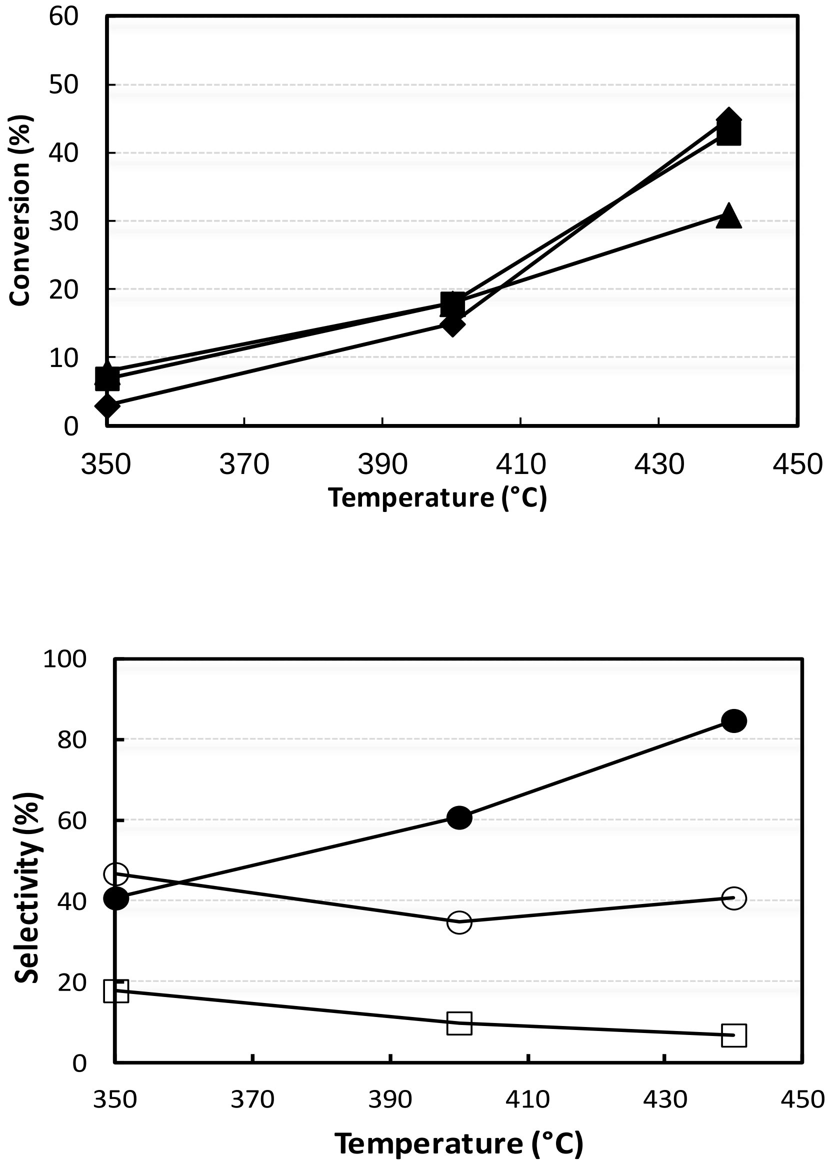
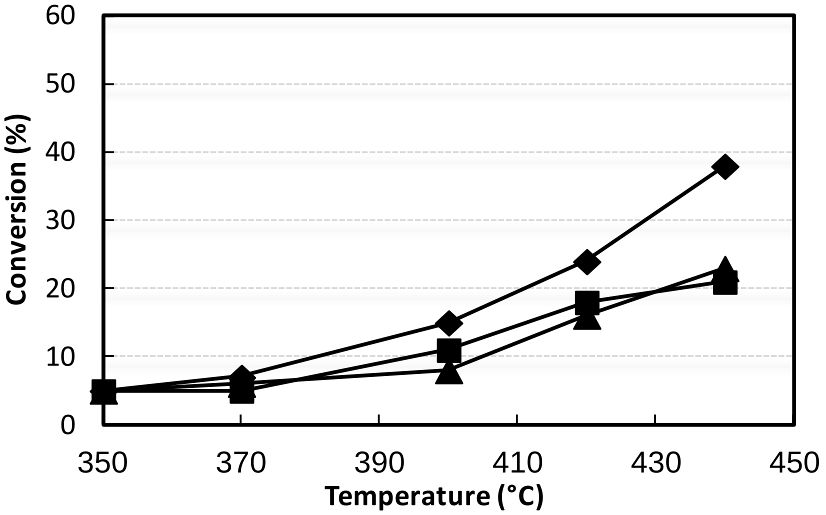


Figure 16. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL-1, feed composition (molar %): acetonitrile/ammonia/oxygen/inert 7.5/13/13/66.5. Symbols: acetonitrile conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: $CO+CO_2$ (○), HCN (□),and N_2 (calculated with respect to converted ammonia) (●).



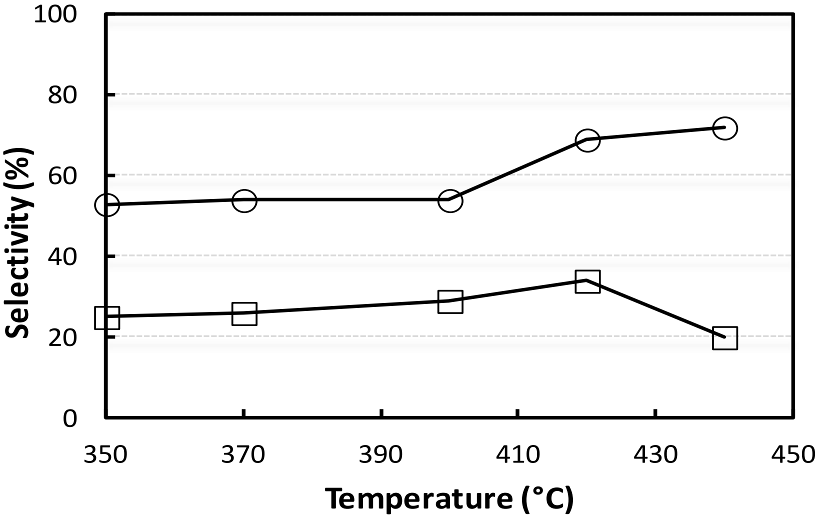


Figure 17. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL-1, feed composition (molar %): acetonitrile/ammonia/oxygen/inert 1/13/13/66.5. Symbols: acetonitrile conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: CO+CO_2 (○), and HCN (☐).

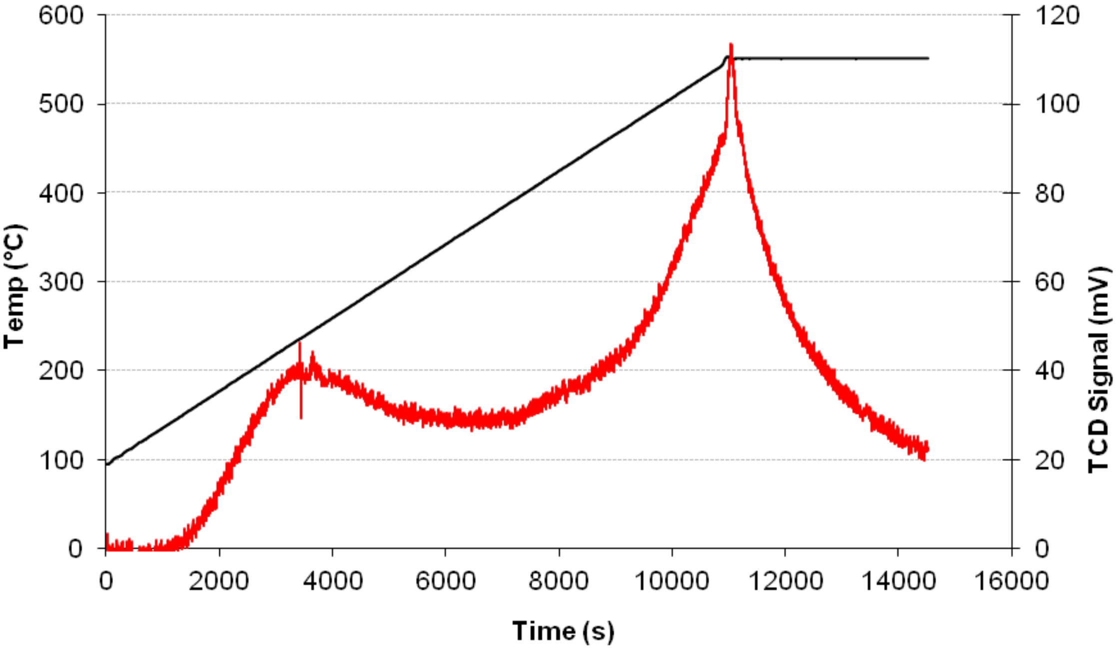


Figure 18. Characterization of the surface acidity of the V/P/O; TPD tests after ammonia adsorption at 100°C

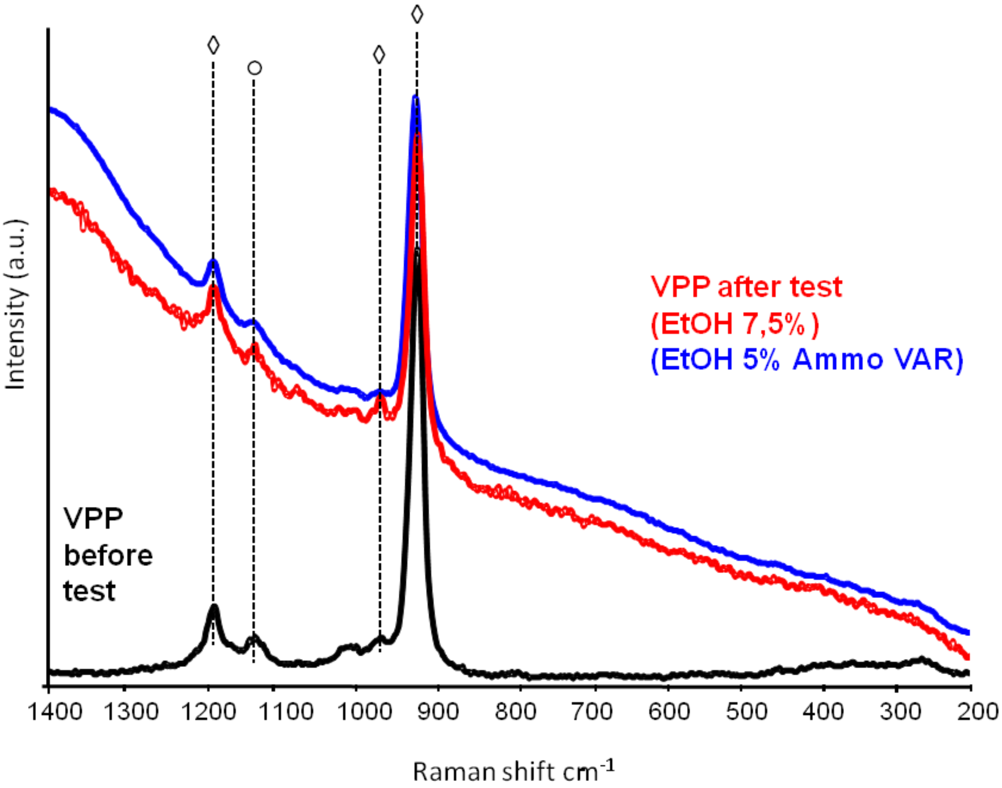
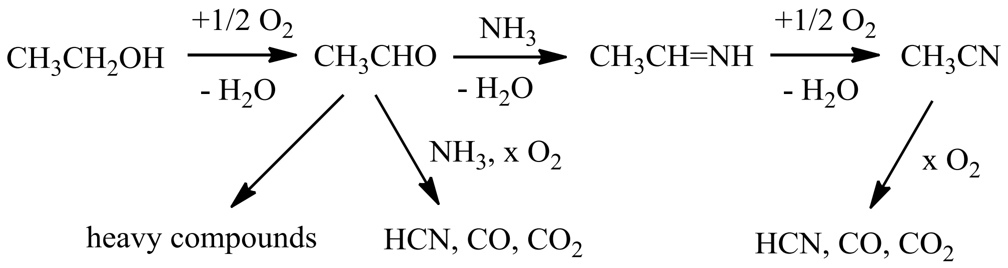


Figure 19. Characterization by Raman spectroscopy; spectra collected before catalytic tests (black line), after 7,5% mol ethanol feeding test (red line) and after ammonia varying test (blue line). ◊ = δ $VOPO_4$, ○ = $(VO)_2P_2O_7$.

Concluding, the best acetonitrile yield achieved with the VPP catalyst is 27% only; this is due to several concomitant factors, such as (i) the intrinsic acidity, which leads to the formation of ethylene, especially at the higher temperatures; (ii) the formation of heavy compounds, especially under conditions of surface saturation, also likely due to the surface acidity; (iii) the consecutive transformation of acetaldehyde, which not only gives the formation of acetonitrile, but also of carbon oxides, and (iv) under specific conditions, the consecutive degradation of acetonitrile itself. These conclusions also allow drawing a picture on the main features that a catalyst for the ammoxidation of ethanol should have; it should not hold acid sites, and should be very effective in the transformation of acetaldehyde into acetonitrile.

The reaction network, as inferred from the reactivity experiments, is summarized in Scheme 1.



Scheme 1. General reaction network for ethanol ammoxidation to acetonitrile catalyzed by VPP.

2. Ethanol ammoxidation with supported vanadium oxide catalyst

Because of the medium-strength acidity of the VPP, which is one reason for the low yield to acetonitrile shown by this catalyst, we decided to investigate the reactivity of catalysts made of supported vanadium oxide; titania (anatase) with surface area 22.5 m^2/g (from Millenium) was the support chosen. In fact, literature papers report about the use of V/Ti/O catalysts for the ammoxidation of alkylaromatics into the corresponding nitriles [10,12]; moreover, supported vanadium oxide is known to be active in alcohols oxidehydrogenation. The catalysts were prepared by means of the wet impregnation method; details about the procedure of preparation are reported in ref [13]. The experimental conditions chosen are those giving the best performance with the VPP catalyst: inlet feed ethanol/ammonia/oxygen mol% 5/13/13, W/F ratio 0.8 g s mL^{-1}.

We first checked the effect of vanadium oxide loading on catalytic behavior; Figures 1-3 show the results obtained with catalysts having 0, 2 and 7 wt% V_2O_5 on anatase (V0/Ti/O, V2/Ti/O and V7/Ti/O codes, respectively). Surprisingly, it is shown that the titania alone (sample V0/Ti/O), even though less active than the vanadium oxide-containing catalysts (the conversion at 350°C is only 20%, whereas with V2/Ti/O and V7/Ti/O it is 100% at the same temperature), displays a catalytic behavior which is similar to that of the latter catalysts. It is also shown that the behavior of V2/Ti/O and V7/Ti/O is very similar, with a maximum acetonitrile yield of ca 46-47%, at 320°C.

The main features shown by these catalysts are:

a) At low ethanol conversion, i.e., at low temperature (250-300°C for V2/Ti/O and V7/Ti/O, 350-400°C for V0/Ti/O) acetaldehyde is an important product; however, its selectivity declines along with temperature, until it becomes nil. In the same temperature range, products whose selectivity increases are acetonitrile, CO (whereas the selectivity to CO_2 is not much affected by temperature) and HCN. This suggests again a kinetic relationship between these compounds; experiments carried out with variation of W/F ratio will confirm this hypothesis.

b) At the temperature at which ethanol conversion is complete, several phenomena strat to take place: (i) ammonia combustion becomes an important side-reaction, as shown by the impressive increase of the selectivity to N_2; (ii) the selectivity to acetonitrile starts to decline, as it also does that to HCN; (iii) at the same time, the selectivity to CO+CO_2 and that to ethylene start to raise.

In overall, this catalyst type shows a much better behavior than that displayed by the VPP, provided temperatures higher than those at which ethanol converts completely are not used. Also, the V/Ti/O system is clearly more active than the VPP, for the same catalyst weight charged in the reactor. Another advantage is that the C balances are always very good, which implies that no heavy compounds form; this is likely a consequence of the absence of acid sites.

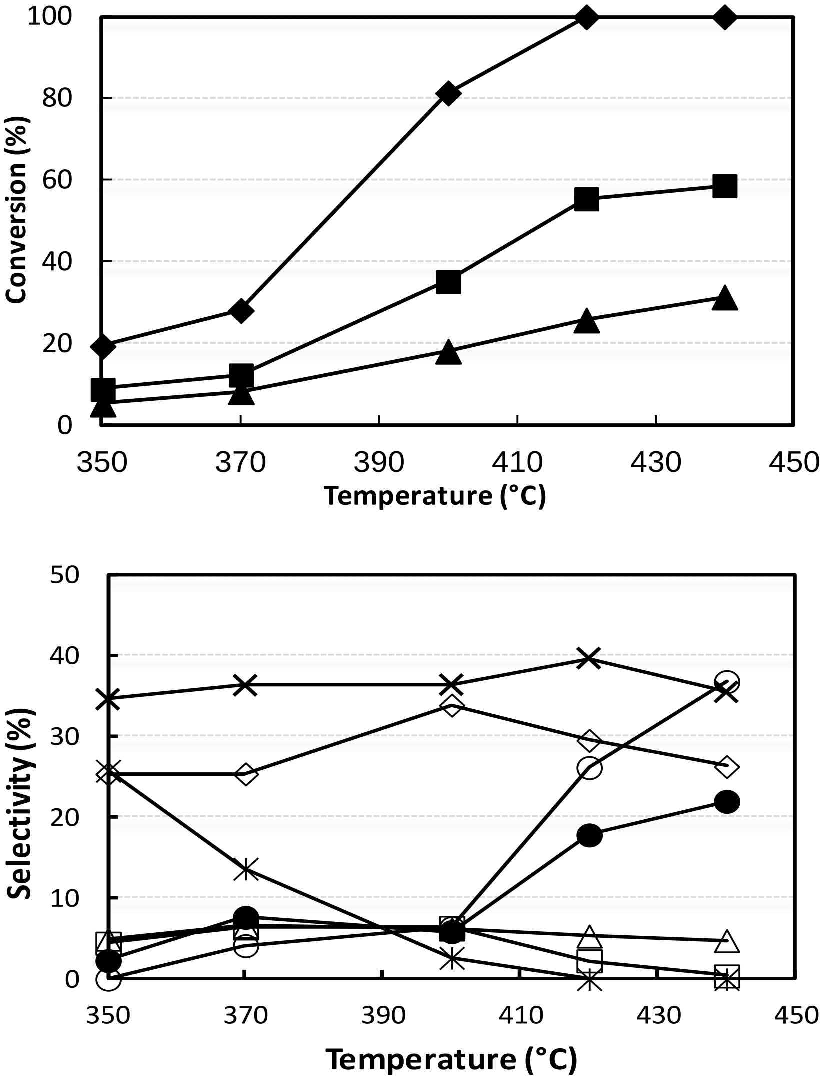


Figure 1. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/13/13/69. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO_2 (×), HCN (□), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V0/Ti/O.

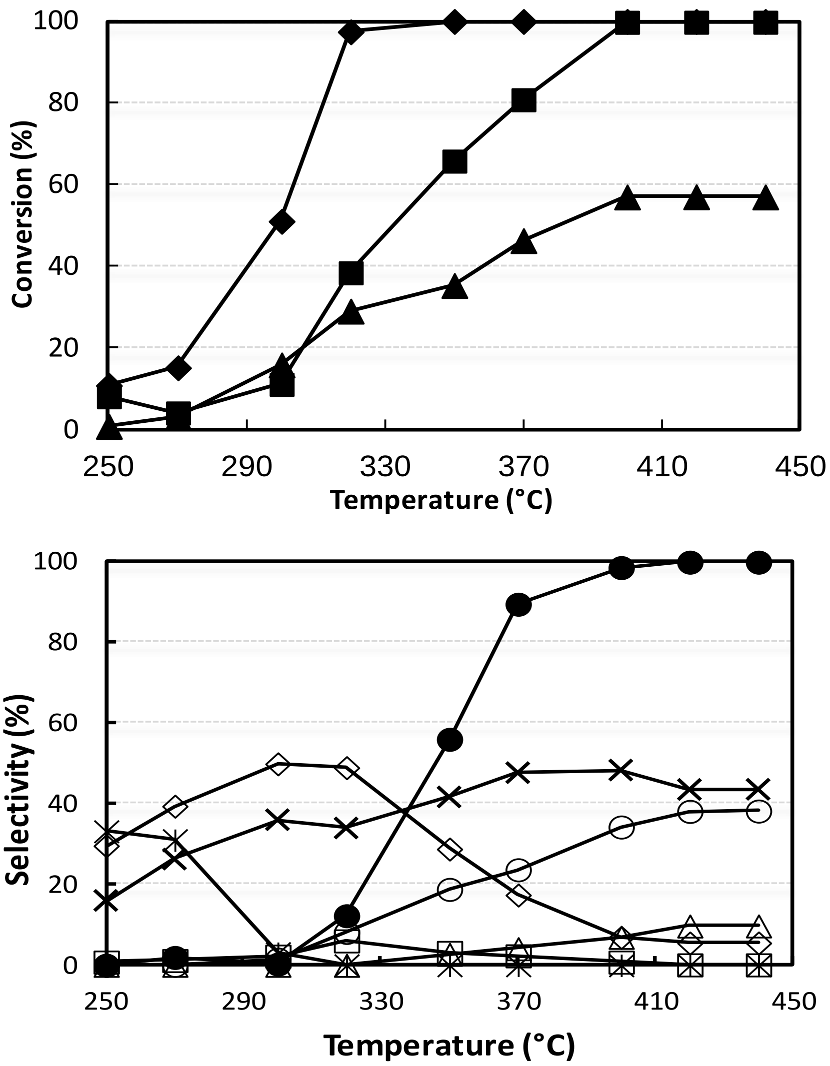


Figure 2. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/13/13/69. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO$_2$ (×), HCN (☐), and N$_2$ (calculated with respect to converted ammonia) (●). Catalyst V2/Ti/O.

An important result is the unexpected catalytic behavior shown by the bare titania (V0/Ti/O sample). Even though we cannot exclude a role played by contaminants in the anatase, however, the catalytic behavior suggests that the role of vanadium oxide is not that one of generating active sites, but rather that of increasing the intrinsic activity of the Ti-O sites. The redox couple Ti^{4+}/Ti^{3+} might play a role in the oxidative process, and the formation of Ti-O-V linkages might enhance the redox properties, by promoting the electrons exchange between the reactants and the catalyst; moreover the O^{2-} anion involved might that one bridging the two metal ions, as also proposed in the literature for other oxidative reactions [14].

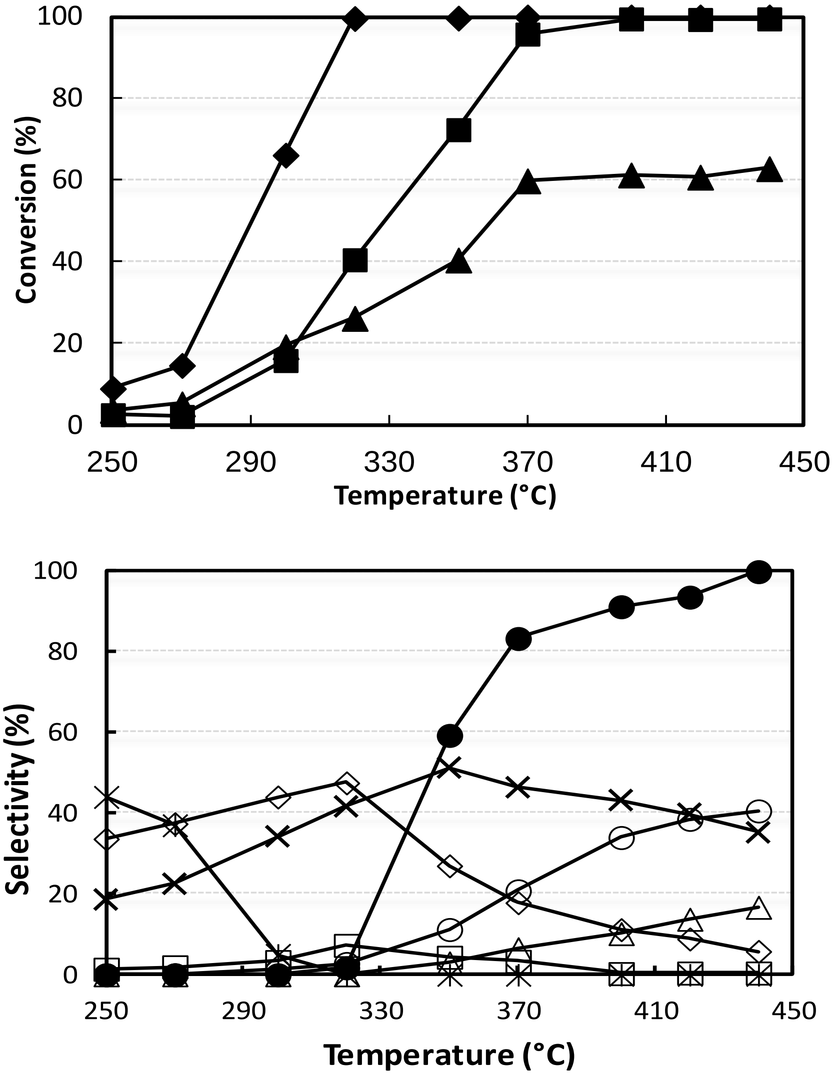
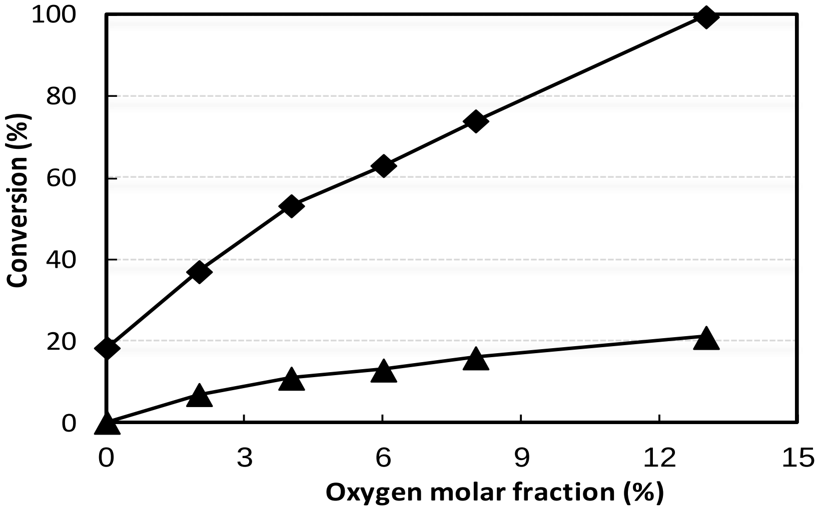


Figure 3. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen/inert 5/13/13/69. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO_2 (×), HCN (□), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V7/Ti/O.

The effect of oxygen on catalytic behavior, shown in Figure 4, is also surprising; the inlet composition (except for oxygen) and the W/F ratio are the same as for tests reported in Figures 1-3 (5% ethanol, 13% ammonia), temperature is 320°C, at which the best yield to acetonitrile is obtained; the catalyst used is the V7/Ti/O sample.



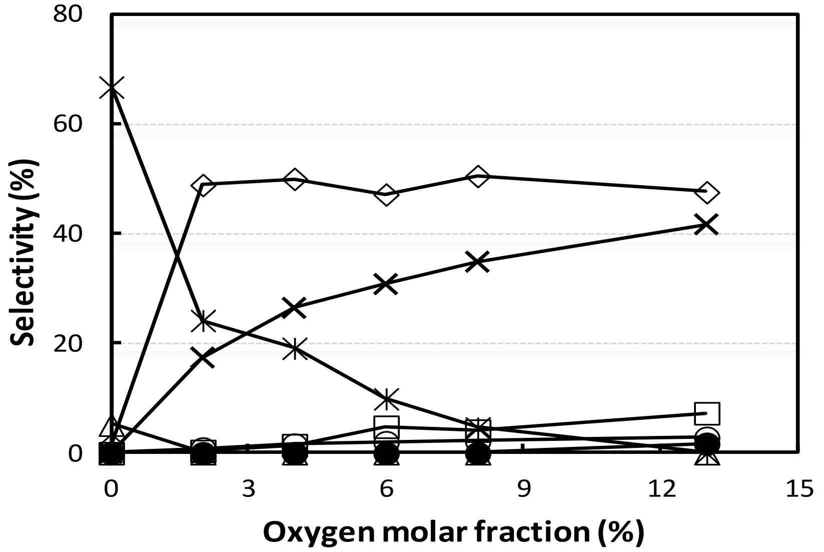


Figure 4. Effect of oxygen partial pressure on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: temperature 320°C, W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/variable. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO_2 (✕), HCN (□), heavy compounds (+), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V7/Ti/O.

It is shown that ethanol converts even in the absence of oxygen, giving the formation of acetaldehyde, and of other unknown by-products (the C balance is about 75%). Adding oxygen, leads to a progressive decline of acetaldehyde, and to a corresponding increase of CO_2 (conversely, yield to CO remains always very low). The selectivity to acetonitrile shows a steep raise for the addition of 2% oxygen in feed, but then remains unaffected during further addition of oxygen. One interpretation for this behavior is that in the absence of oxygen, the catalyst dehydrogenates ethanol into acetaldehyde, which reacts with the large excess of ammonia present, yielding ethanimine; this compound needs oxygen in order to be transformed into acetonitrile by means of oxidehydrogenation, and because of the absence of oxygen it reacts to yield condensation compounds. Therefore, the addition of oxygen has several effects: (i) it accelerates the transformation of ethanol into acetaldehyde, via oxidehydrogenation; (ii) it catalyzes the combustion of acetaldehyde into CO_2, and the rate of CO_2 formation is almost directly proportional to the oxygen content in the inlet feed; (iii) it accelerates the transformation of the imine into the nitrile, by means of oxidehydrogenation; this also causes the decrease of the rate of imine condensation to heavier by-products.

The effect of W/F ratio was first investigated with the V2/Ti/O catalyst, at 320°C, using the feed composition ethanol/ammonia/oxygen 5/13/7 (Figure 5); a lower amount of oxygen was used (corresponding to the almost stoichiometric amount) compared to experiments shown in Figures 1-3, because results plotted in Figure 4 demonstrate that excess oxygen favors the transformation of acetaldehyde into CO_2, and to acetonitrile as well.

The peculiarity of results shown in Figure 5 is that for W/F ratio between 0.03 and 0.08 s, during which the conversion of ethanol increases from 10 to 20%, the selectivity to acetaldehyde and acetonitrile both display a trend which is not that typically shown for a consecutive reaction; in other words, the two compounds seem to form by parallel, kinetically independent reactions. However, a further increase of W/F ratio leads to a jump of conversion, which causes a fall of acetaldehyde selectivity and a concomitant increase of selectivity to both CO_x and acetonitrile. Then, for a further increase of the W/F ratio, there is no further change in the products distribution. The sudden jump of conversion might be the consequence of a remarkable increase of the catalyst surface temperature, the latter in turn being due to the large amount of heat generated and not efficiently dispersed by this catalyst type. Therefore, we may expect that by using much lower concentration of reactants we should limit this phenomenon.

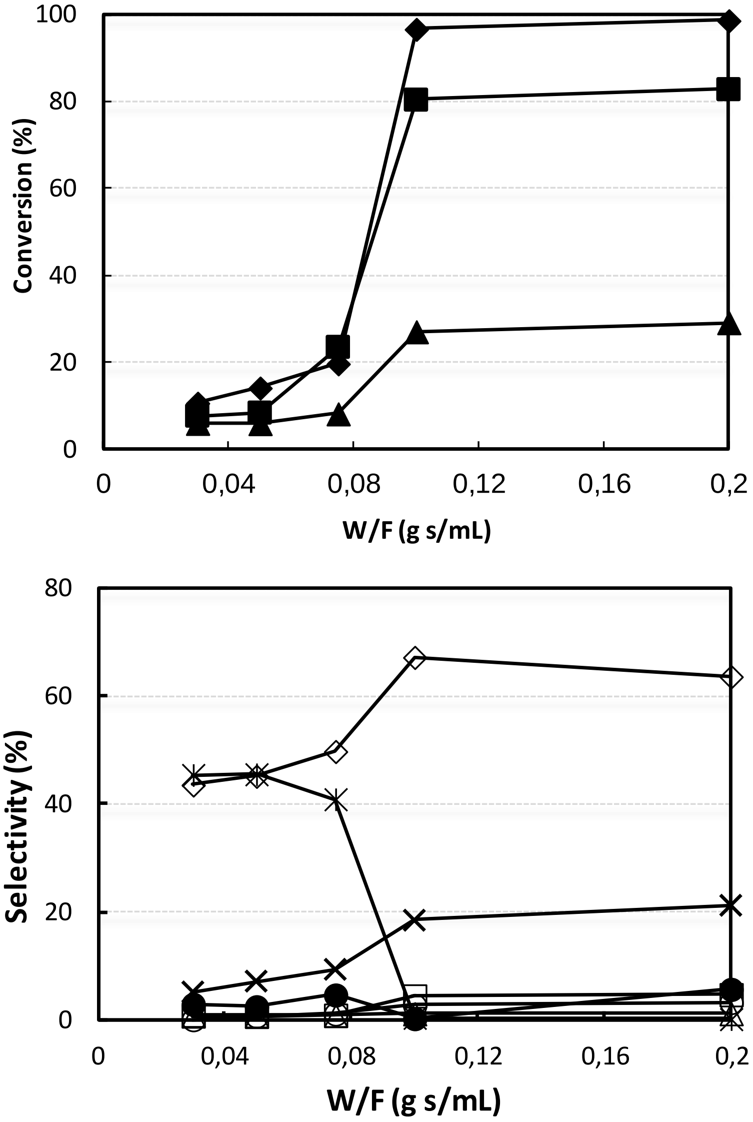


Figure 5. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: temperature 320°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/7. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO_2 (✕), HCN (☐), heavy compounds (+), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V2/Ti/O.

In fact, with the feed composition ethanol/ammonia/oxygen (mol%) 1.4/3.6/1.7 (T 320°C, catalyst V2/Ti/O) (Figure 6), the behavior shown is the expected one: a progressive increase of ethanol conversion leads to both a decline of selectivity to acetaldehyde, and a corresponding raise of selectivity to acetonitrile and CO_x. Despite this, still the initial selectivity to acetonitrile, extrapolated to nil conversion, seems to be higher than zero, which might suggest the existence of another direct route from ethanol to acetonitrile (besides that with ethanimine as the intermediate), which does not include acetaldehyde as the reaction intermediate. Therefore, still we cannot exclude that with the V/Ti/O catalyst the reaction network is more complex than with the VPP catalyst.

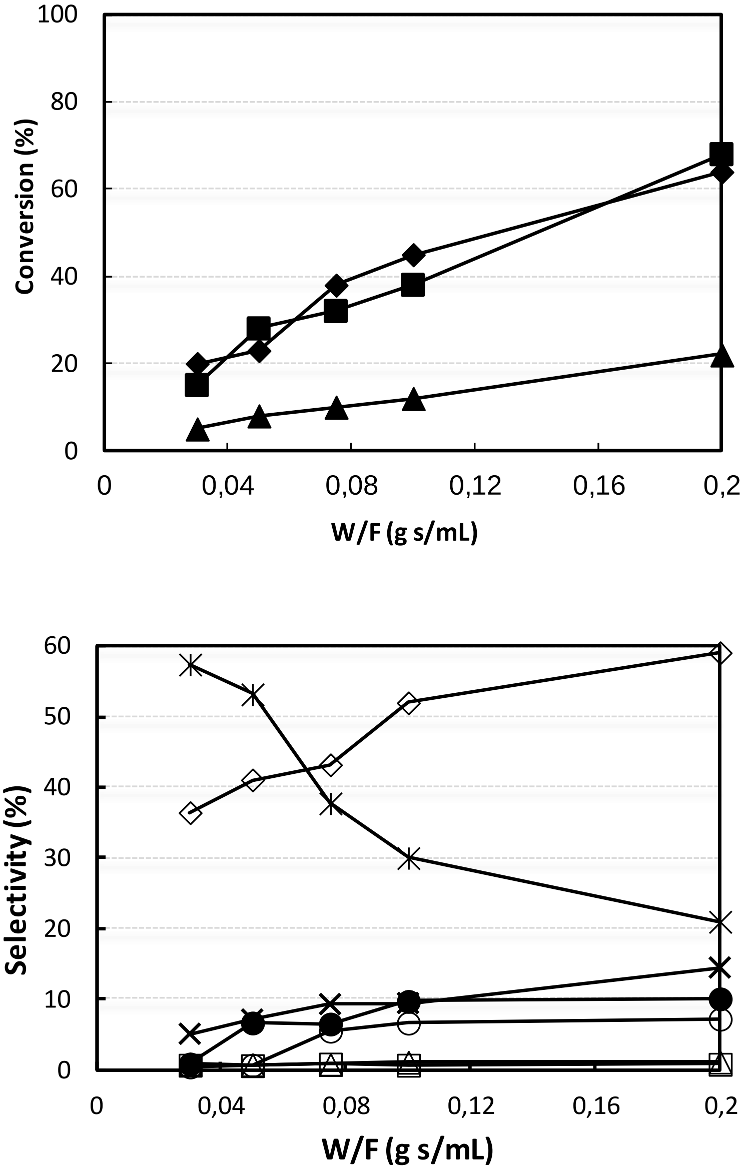


Figure 6. Effect of W/F ratio on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: temperature 320°C, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 1.4/3.6/1.7. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO_2 (✕), HCN (□), heavy compounds (+), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V2/Ti/O.

It is also important to note that in the experiments carried out in function of the W/F ratio, but with high ethanol concentration (5%, Figure 5), at 0.1 g s mL^{-1} W/F ratio the selectivity to acetonitrile is 68-69%, with very high ethanol conversion. This excellent result may be due either to the fact that the W/F ratio is low (in fact, in Figure 2, at 320°C and 0.8 g s mL^{-1} W/F ratio, the selectivity is 46% only, with total ethanol conversion), or that the oxygen concentration is low (7% *vs* 13%, for the experiment shown in Figure 2). In order to discriminate between the two hypothesis, we carried out a study of the effect of oxygen concentration at low W/F ratio (indeed, results shown in Figure 4 demonstrate that likely the effect shown is mainly due to the low W/F ratio used, because selectivity to acetonitrile is not so much affected by oxygen partial pressure); results are shown in Figure 7. The experiments were carried out at 320°C, with 5% ethanol and 13% ammonia in feed, and 0.1 g s mL^{-1} W/F ratio.

We can see the same phenomenon already observed in Figure 5: the sudden increase of conversion, which in this case is due to an increase of oxygen concentration; this confirms that with this catalyst and at relatively high ethanol concentration, phenomena of heat-transfer limitation can affect the catalytic behavior. It is also shown that for oxygen concentration comprised in the range 4-5 mol%, the selectivity to acetaldehyde and that to acetonitrile are similar, and not affected by oxygen variations. Beyond the 5% oxygen, the rapid raise of conversion corresponds to a fall of selectivity to acetaldehyde and to an increase of selectivity to acetonitrile, with also a minor increase of CO_x formation. Apparently, a slight maximum of acetonitrile selectivity is reached at 7% oxygen in feed: 68-69% selectivity, corresponding to a 66-67% yield (which is the same result obtained under the same reaction conditions in Figure 5). Concluding, it can be said that by combining a low W/F ratio with an oxygen concentration close to the stoichiometric value, it is possible to obtain a remarkable 67% acetonitrile yield; the positive effect of W/F ratio is however predominant over that of oxygen.

Some final experiments were aimed at the determination of the by-products formed in the reaction under specific conditions (for instance, in the absence of oxygen), in order to gain further information on the reaction mechanism. Specifically, we carried out experiments by feeding acetaldehyde (0.5 or 1 mol%) and ammonia (13%), with (6%) and without oxygen, at 320°C with the V2/Ti/O catalyst, and W/F ratio of 0.1 and 0.4 g s mL^{-1}.

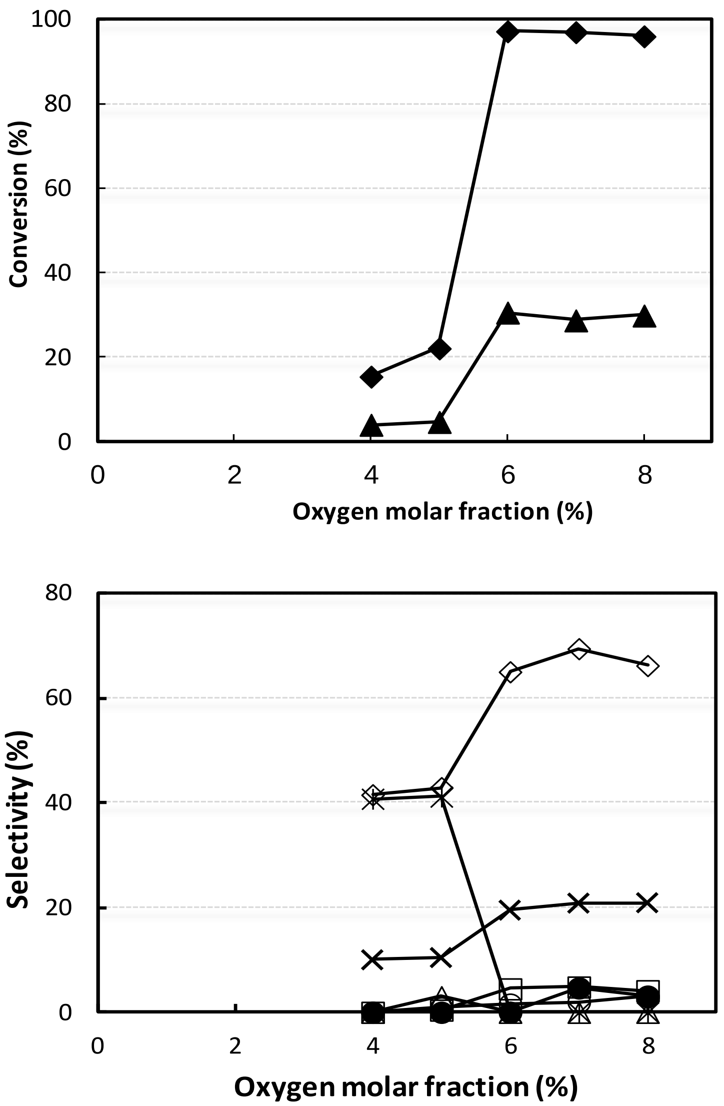


Figure 7. Effect of oxygen partial pressure on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: temperature 320°C, W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/variable. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO_2 (✕), HCN (□), heavy compounds (+), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V2/Ti/O.

Three sets of experiments were carried out, as shown in Figures 8-10. It is possible to comment as follows:

a) Under the conditions used for tests in Figure 8, in the presence of oxygen the selectivity to acetonitrile is good, as expected, with low formation of both HCN and CO_x; however, after removal of oxygen the conversion of acetaldehyde becomes 5% only, and the main products are heavy compounds, with 5% selectivity to acetonitrile. Heavy by-products identified are ethanimine, butyrraldehyde, butyrronitrile, and other N-containing compounds; an important product is dihydrofuran. These data confirm that the transformation of acetaldehyde into acetonitrile is greatly accelerated in the presence of oxygen, but it may occur even in its absence; this means that the mechanism involves, as proposed above, the formation of the imine, which in the presence of oxygen is quickly transformed into the nitrile, otherwise it is also transformed to other condensation compound

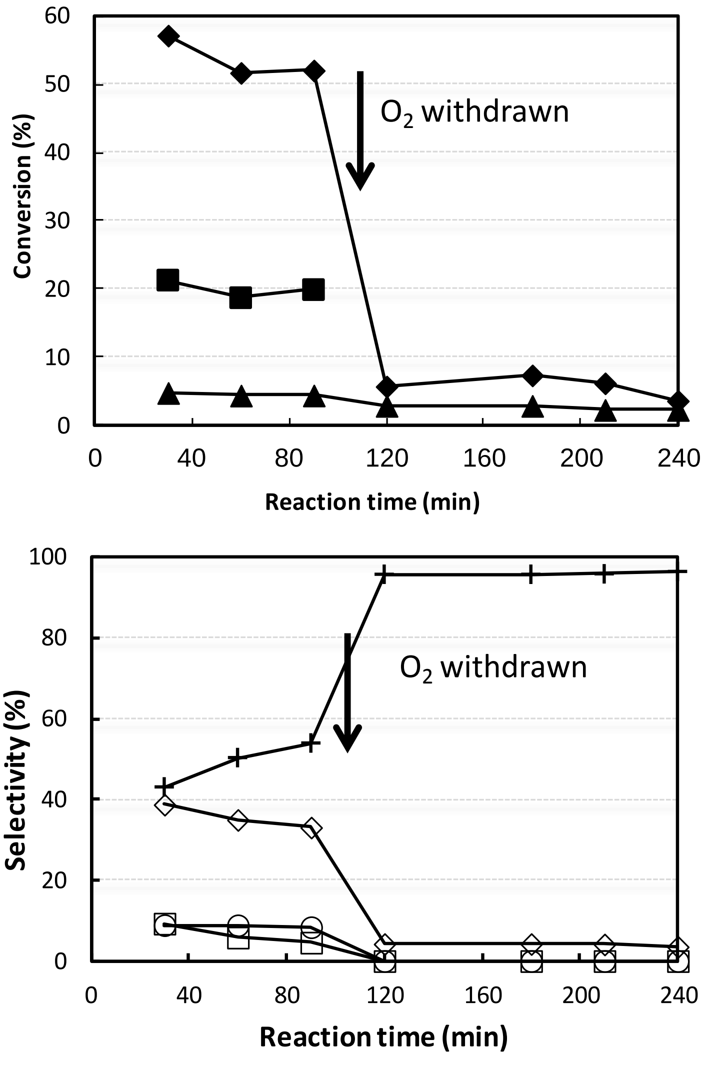


Figure 8. Effect of reaction time on reactants conversion (top Figure) and selectivity to products (bottom Figure). Reaction conditions: temperature 320°C, W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): acetaldehyde/ammonia/oxygen 0.5/13/6. Symbols: acetaldehyde conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), $CO+CO_2$ (O), HCN (□), and heavy compounds (+). Catalyst V2/Ti/O.

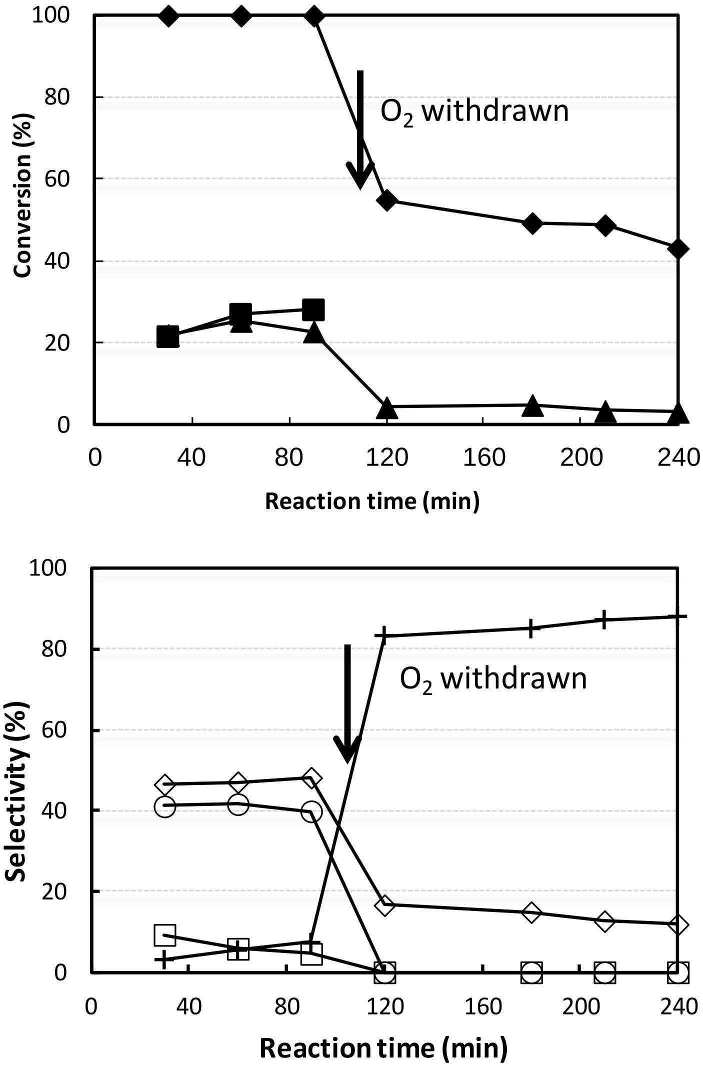


Figure 9. Effect of reaction time on reactants conversion (top Figure) and selectivity to products (bottom Figure). Reaction conditions: temperature 320°C, W/F ratio 0.4 g s mL^{-1}, feed composition (molar %): acetaldehyde/ammonia/oxygen 0.5/13/6. Symbols: acetaldehyde conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), $CO+CO_2$ (○), HCN (□), and heavy compounds (+). Catalyst V2/Ti/O.

b) Under the conditions used for experiments in Figure 9, in the presence of oxygen the selectivity to acetonitrile is lower than that observed in the previous case (Figure 8), because of the higher W/F ratio used. Also in this case, the removal of oxygen causes a decline of conversion, which however still remains high (around 40%). As in the previous case, CO_x and HCN disappear; in practice, the main reason for the decrease of acetaldehyde conversion is the fact that the oxidative degradation reactions do not occur anymore. However, the C balance is low, because of the formation of the heavy compounds, which are the same as those observed previously.

c) Finally, under the conditions of experiments shown in Figure 10, all the phenomena are the same as those previously shown; due to the higher concentration of acetaldehyde used, the formation of condensation compounds in the absence of oxygen is even more favored than it was before.

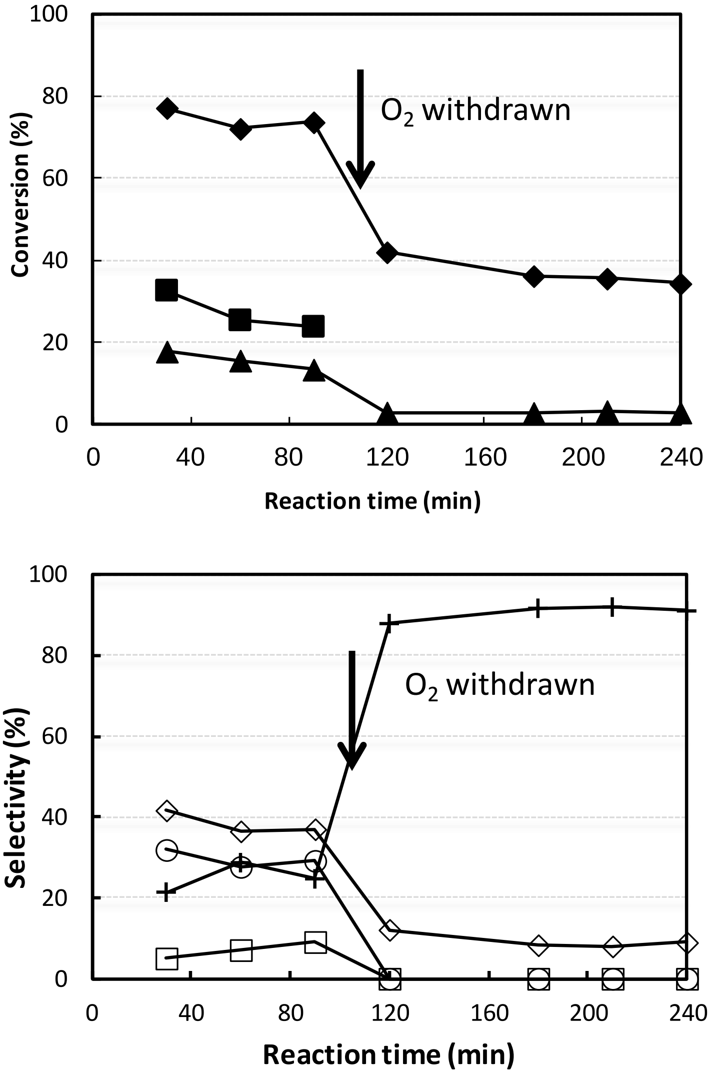


Figure 10. Effect of reaction time on reactants conversion (top Figure) and selectivity to products (bottom Figure). Reaction conditions: temperature 320°C, W/F ratio 0.4 g s mL^{-1}, feed composition (molar %): acetaldehyde/ammonia/oxygen 1/13/6. Symbols: acetaldehyde conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), CO+CO_2 (○), HCN (□), and heavy compounds (+). Catalyst V2/Ti/O.

These experiments confirm that in the transformation of acetaldehyde into acetonitrile the main role of oxygen is that of accelerating the oxidehydrogenation of the intermediate imine into the nitrile, so limiting the formation of condensation compounds. On the other hand, it also plays a negative role, because it favors the formation of COx and HCN. The role of oxygen is also that of accelerating the transformation of ethanol into acetaldehyde.

We also carried out some experiments with a catalyst containing 7 wt% vanadium oxide and 0.5 wt% Cs_2O as dopant; in fact, this element is considered a promoter of selectivity not only because of the neutralization of acid sites, but also because it affects the redox properties of V oxide, and its presence considerably decreases the combustion during o-xylene oxidation to phthalic anhydride [13]. Results are shown in Figure 11; the feed composition was ethanol/ammonia/oxygen 5/13/13; W/F ratio was 0.8 g s mL^{-1}. It is shown that doping with Cs leads to a catalyst more selective to acetaldehyde and less to $CO+CO_2$, but finally acetonitrile yield is similar to that obtained with the undoped catalyst; however, acetonitrile seems to be more stable at high T, since it undergoes less combustion. It is possible that the presence of the basic dopant may favor the desorption of the nitrile, so limiting its overoxidation at the adsorbed state.

Concluding, the catalyst made of titania-supported vanadium oxide shows a catalytic behavior which is greatly enhanced compared with that of the vanadyl pyrophosphate. Its main drawback is the remarkable degree of ammonia combustion shown, but this occurs only at temperatures higher than those of complete ethanol conversion. The best acetonitrile yield (around 67%) is obtained at 0.1 g s mL^{-1} W/F ratio, temperature 320°C, and feed composition (mol%) ethanol/ammonia/oxygen 5/13/7.

Since the role of support is known to be of enormous influence on the catalytic behavior of vanadium oxide-based catalyst [14b], we also prepared a catalyst made of vanadium oxide supported over zirconia (surface area 30 m^2/g), containing 7 wt.% of V_2O_5 [14c, 14d]. Figure 12 reports the results obtained with this V/Zr/O catalyst, using the feed ethanol/ammonia/oxygen (mol%) 5/13/6, and W/F ratio 0.4 g s mL^{-1}. The behavior shown has some analogies with that one of the V/Ti/O catalyst, but also some important differences:

a) The selectivity to acetaldehyde shown at low temperature is much better than that observed with the V/Ti/O catalyst, with a corresponding lower selectivity to acetonitrile but also to CO_2. This however can be attributed to the lower W/F ratio used with the V/Zr/O catalyst.

b) When the temperature is increased, the selectivity to acetaldehyde declines, with a concomitant increase of selectivity to both CO_2 and acetonitrile. However, the selectivity to acetonitrile keeps on increasing up to 370°C (at which complete conversion of ethanol is reached), whereas with the V/Ti/O catalyst the selectivity starts to decline already at 320°C. This important difference is mainly due to the negligible ammonia combustion to N_2 shown by the V/Zr/O catalyst (in the next figures, the selectivity to N_2 will be no longer reported, since its always lower than 10%).

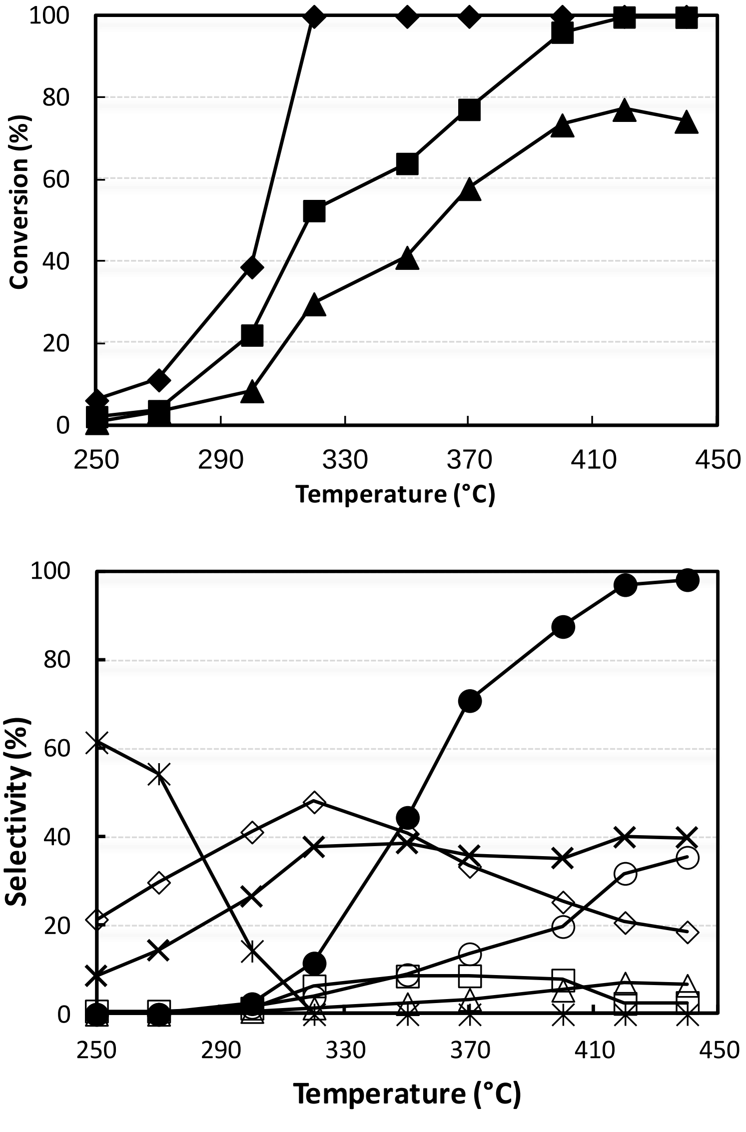
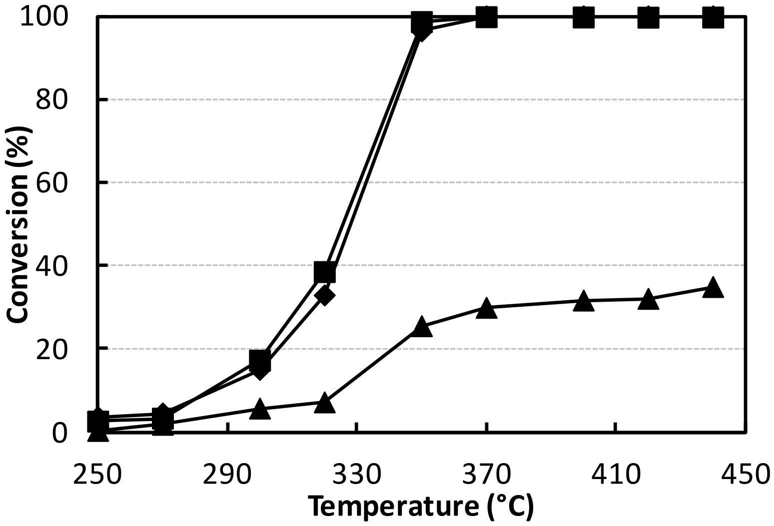


Figure 11. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.8 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/13. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO_2 (✕), HCN (□), and N_2 (calculated with respect to converted ammonia) (●). Catalyst Cs-doped V7/Ti/O.

c) With the V/Ti/O catalyst, the decline of selectivity to acetonitrile takes place with a concomitant raise of selectivity to CO and, at a minor extent, to CO_2. With the V/Zr/O catalyst, the overall amount of CO+CO_2 produced remains substantially constant at above 330°C.

d) The highest yield to acetonitrile obtained with the V/Zr/O catalyst is 70%.



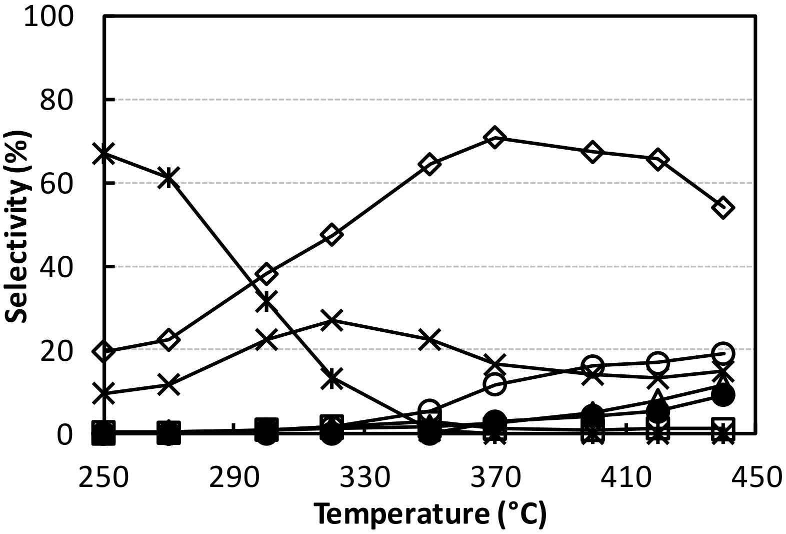


Figure 12. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.4 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/6. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO_2 (✕), HCN (□), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V/Zr/O.

Figure 13 displays the effect of temperature at W/F ratio 0.1 g s mL^{-1}. It is shown that the behavior is very similar to that observed at 0.4 g s mL^{-1} W/F ratio; however, the highest yield to acetonitrile is close to 74%.

Because of the results obtained, we decided to optimize the feed composition, in the aim of using a feed composition which is as much as possible close to the stoichiometric composition. Various feeds were used, and the results are compared in Figure 14; the W/F ratio was equal to 0.1 g s mL^{-1}. It is possible to make the following considerations:

a) The conversion of ethanol and oxygen are very close to each other, for each set of experiments; this is due to the fact that in all cases the two reactants were fed in almost stoichiometric amount (molar ratio either equal to 1 or close to 1), and the most important reaction, the formation of acetonitrile, consumes 1 mole of oxygen per each mole of ethanol converted. Other reactions consume less than 1 mole oxygen (e.g., the oxidehydrogenation into acetaldehyde), others consume more than 1 mole (the combustion) per mole of ethanol converted.

b) The ammonia conversion is always lower than 100%, even under conditions of stoichiometric ratio with ethanol. This is due to the fact that the only reaction consuming ammonia is the formation of acetonitrile (the yield to both HCN is very low, and that to N_2 almost negligible), and at best the yield to acetonitrile is 74%. However, it is evident from the figure that the ammonia conversion is probably underestimated; for example, in the case of the feed ratio 5/5/5, a higher ammonia conversion is expected. It is necessary to consider that the error here is not probably attributable to the measurement of ammonia conversion, but rather to the inlet flow rate of ammonia. It is likely that indeed an amount of ammonia at least 10-20% higher than the measured one was fed in some cases.

c) If ethanol conversion at 350°C is taken into consideration, the following rank is inferred (ethanol/ammonia/oxygen): 5/6/6 > 10/12/10 > 2/3/2 > 5/5/5 ≈ 5/13/6. This comparison implies that using a slight excess of oxygen increases the conversion of ethanol (5/6/6 > 5/5/5), but using a large excess of ammonia, even in the presence of a slight excess of oxygen) inhibits the conversion of ethanol

(5/6/6 > 5/13/6). In other words, it is possible that ethanol and ammonia compete for adsorption over the same sites.

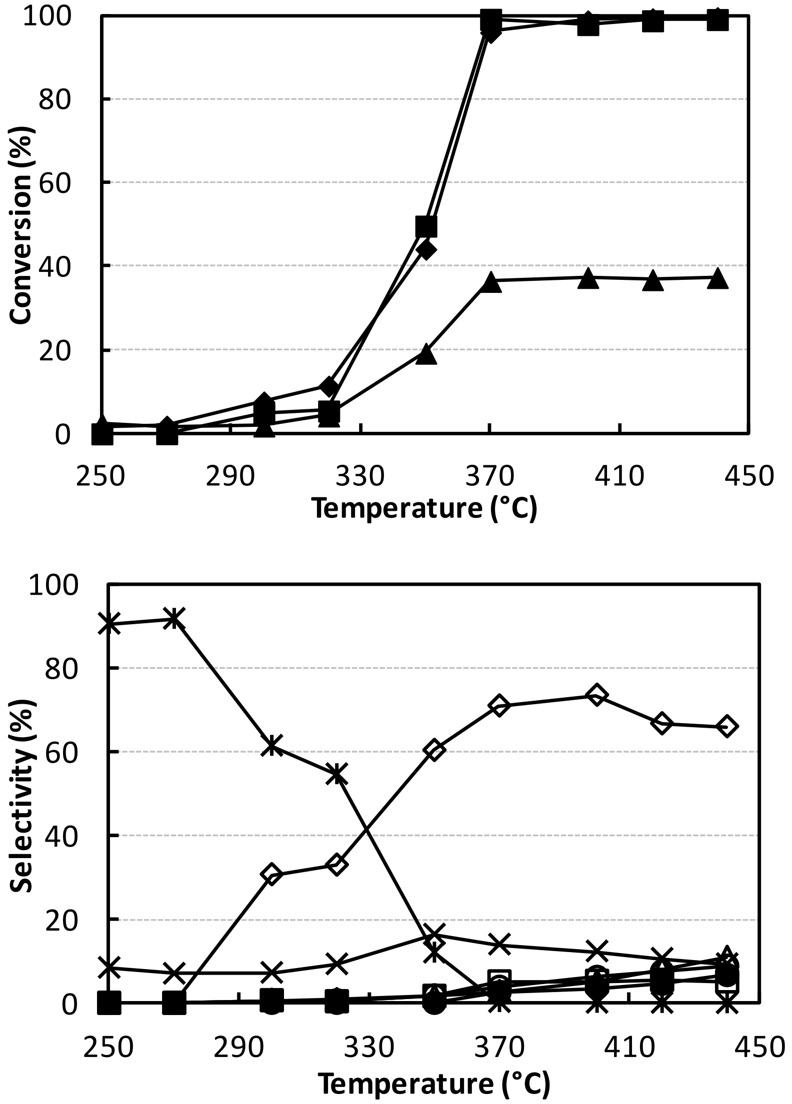


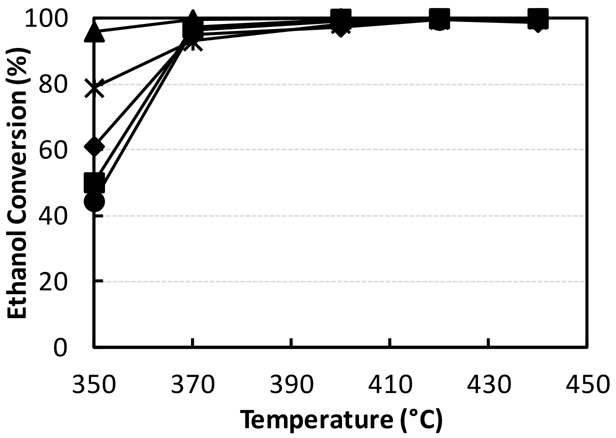
Figure 13. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/6. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO_2 (×), HCN (□), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V/Zr/O.

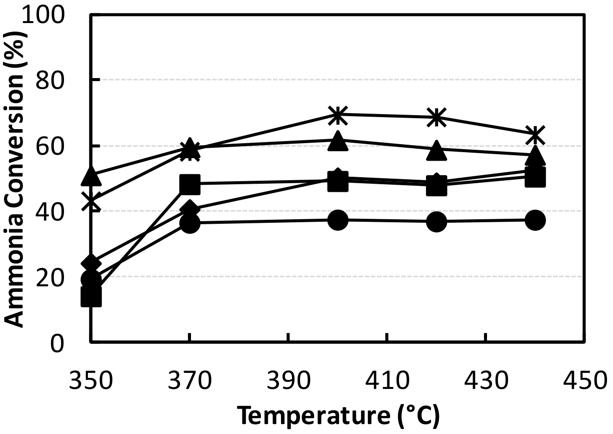
d) The relatively low conversion of ethanol obtained with 2/3/2 feed, which is an unexpected result because of the low ethanol concentration fed, is likely due to the presence of a “large” excess of ammonia (if compared to the ethanol fed), while the oxygen concentration is in stoichiometric amount. In the case of the 10/12/10 feed, the conversion is lower than that obtained with the 5/6/6 feed again because of the stoichiometric oxygen fed. Therefore, it can be concluded that regarding the conversion of reactants, the ammonia concentration should be fed in an amount as close as possible to the stoichiometric ratio (in order to both maximize its conversion and avoid inhibition effects on conversion), whereas the concentration of oxygen can be in slight excess or close to the stoichiometric amount. Moreover, apparently with this catalyst inlet concentrations of ethanol higher than 5% can be fed, without occurrence of any surface saturation effects; this is another important difference with respect to the VPP catalyst.

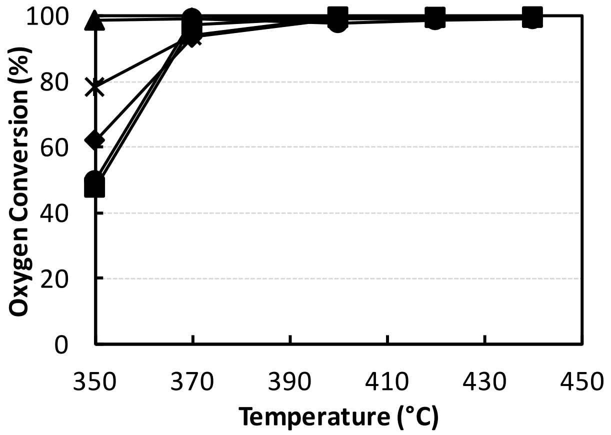
e) In regard to the maximum selectivity to acetonitrile, that for every set of experiments is obtained at 400°C, the rank is the following: 5/6/6 (selectivity 74%, yield 74%) ≈ 5/13/6 (selectivity 74%, yield 73%) > 10/12/10 (selectivity 71%, yield 70%) > 5/5/5 (selectivity 67%, yield 67%) >≈ 2/3/2 (selectivity 66%, yield 65%). Therefore, the best selectivity is obtained in the presence of excess ammonia (although very slight). An exception is the feed 2/3/2; in this case however, it is possible that because of the low concentration of the reducing reactants (ethanol and ammonia), the catalyst is overoxidized under reaction conditions, and hence more selective to combustion or oxidative degradation reactions. In fact, it is shown that the selectivity of CO was greater than it was with the other feeds.

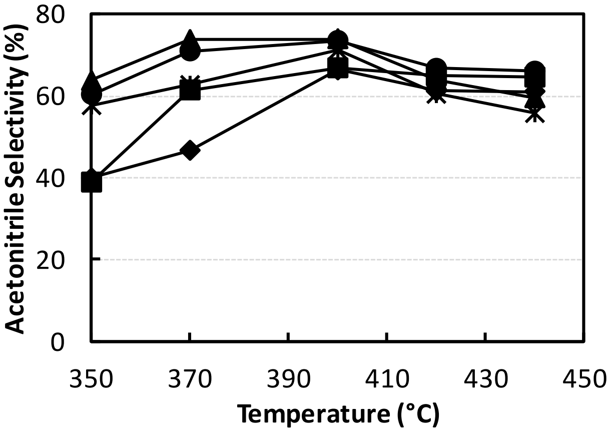
f) With the exception of the ethanol/ammonia/oxygen 2/3/2 feed, the lower selectivity to acetaldehyde at low temperature is shown in the case of the feed containing an excess of ammonia. This is not straightforward, however, because the selectivity to acetaldehyde is also a function of ethanol conversion, which is the lower for the 5/5/5, 5/13/6 and 2/3/2 feeds. The effect of feed composition on ethylene and CO_2 selectivity is low, although not negligible. Greater effects are seen in the case of selectivity to CO, the higher being shown by the 2/3/2 feed, the lower by the 5/13/6 feed.

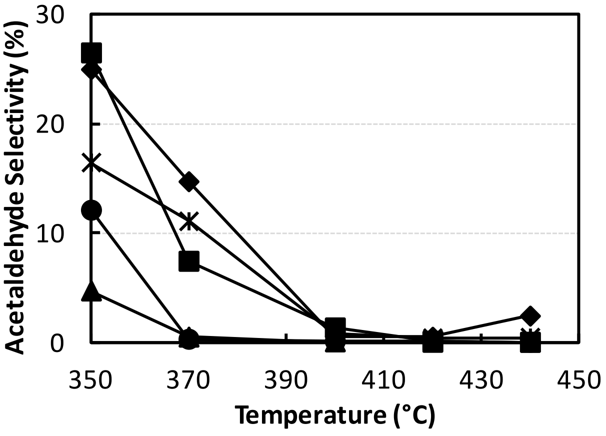
It can be concluded that the optimal feed composition in terms of yield to acetonitrile are ethanol/ammonia/oxygen (molar ratios) 5/6/6, 5/13/6 and 10/12/10, but in terms of reactants conversion the best feed compositions are 10/12/10 and 5/6/6; in terms of acetonitrile productivity the best feed is 10/12/10, since saturation effects were not observed even at such a high ethanol concentration.

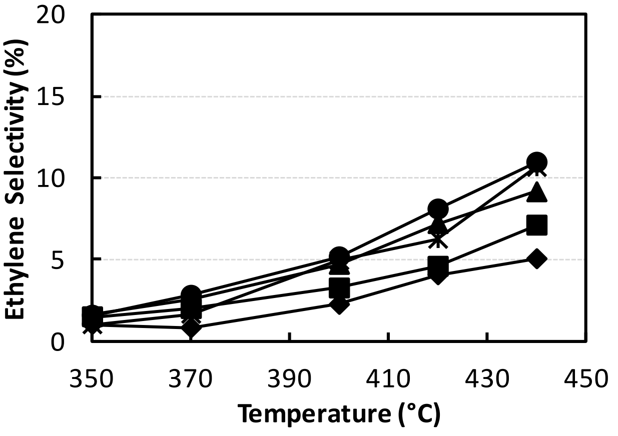

Ethanol Conversion (%)
0
20
40
60
80
100
350
370
390
410
430
450
Temperature (°C)


Ammonia Conversion (%)
0
20
40
60
80
100
350
370
390
410
430
450
Temperature (°C)


Oxygen Conversion (%)
0
20
40
60
80
100
350
370
390
410
430
450
Temperature (°C)


Acetonitrile Selectivity (%)
0
20
40
60
80
350
370
390
410
430
450
Temperature (°C)


Acetaldehyde Selectivity (%)
0
10
20
30
350
370
390
410
430
450
Temperature (°C)


Ethylene Selectivity (%)
0
5
10
15
20
350
370
390
410
430
450
Temperature (°C)

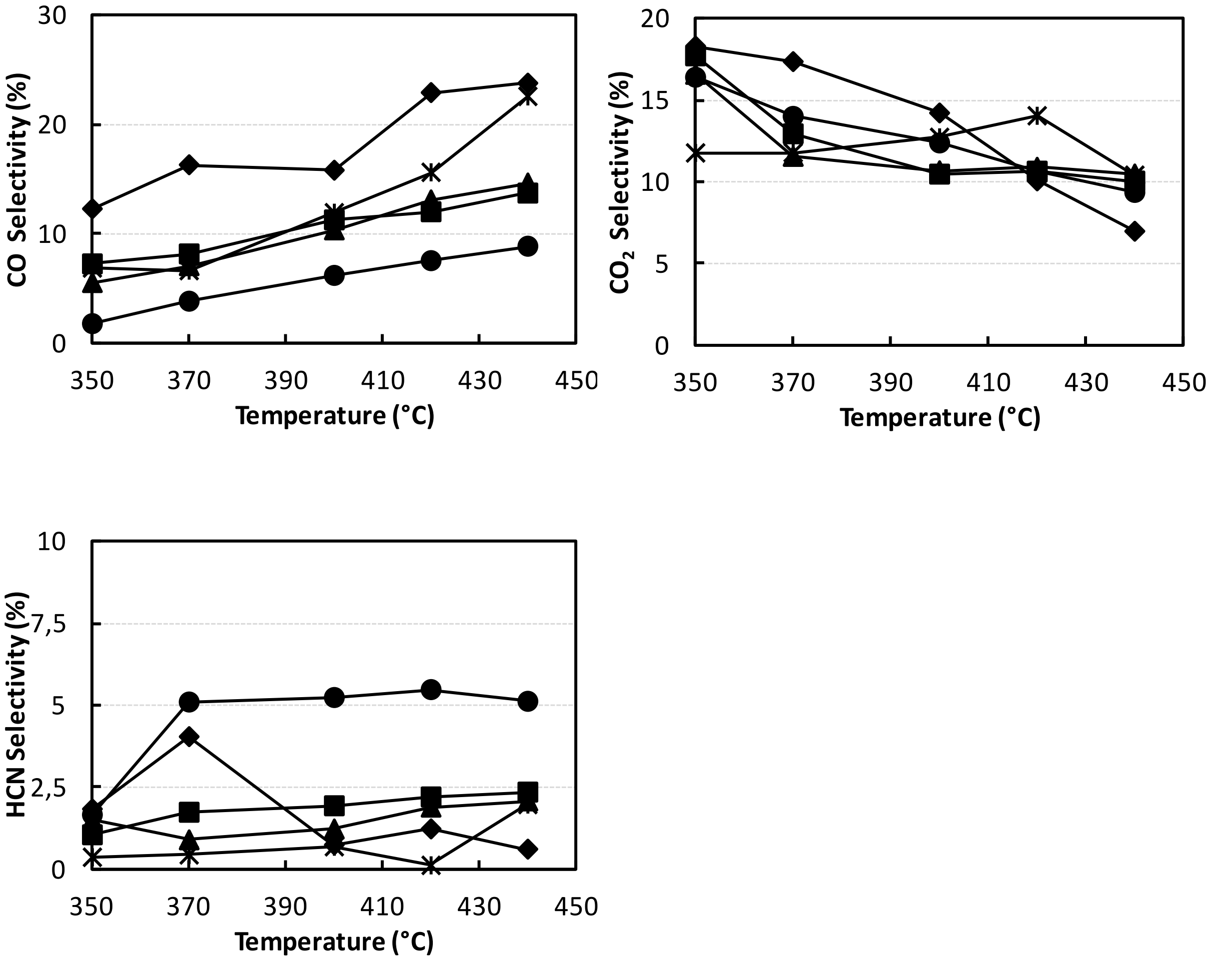


Figure 14. Effect of temperature on catalytic behavior for various feed compositions: Ethanol/ammonia/oxygen (molar ratios): 5/13/6 (●), 5/6/6 (▲), 5/5/5 (■), 2/3/2 (◆) and 10/12/10 (✱). W/F ratio 0.1 g s mL^{-1}; catalyst V/Zr/O.

Noticeably, at these conditions the carbon balance still is good, which confirms the absence of reactions leading to the formation of heavy compounds, typically observed under conditions of surface saturation with the VPP catalyst. Therefore, we decided to carry our experiments aimed at studying the short-term lifetime of the V/Zr/O catalyst, using the best conditions of 0.1 g s mL^{-1} W/F ratio, temperature 400°C, and feed composition ethanol/ammonia/oxygen 10/12/10. Results are reported in Figure 15. A slow deactivation effect is shown, whereas the selectivity to acetonitrile is stable, being approximately the 70%.

Finally, some experiments were carried out feeding paraldehyde (as an internal source of acetaldehyde); results of experiments are shown in Figure 16. Reaction conditions were: acetaldehyde/ammonia/oxygen (molar fractions %) 2/3/2. In the Figure, acetaldehyde is given as one of the products of transformation of paraldehyde. These data should be compared with those obtained by feeding ethanol/ammonia/oxygen with molar ratio 2/3/2 (Figure 14).

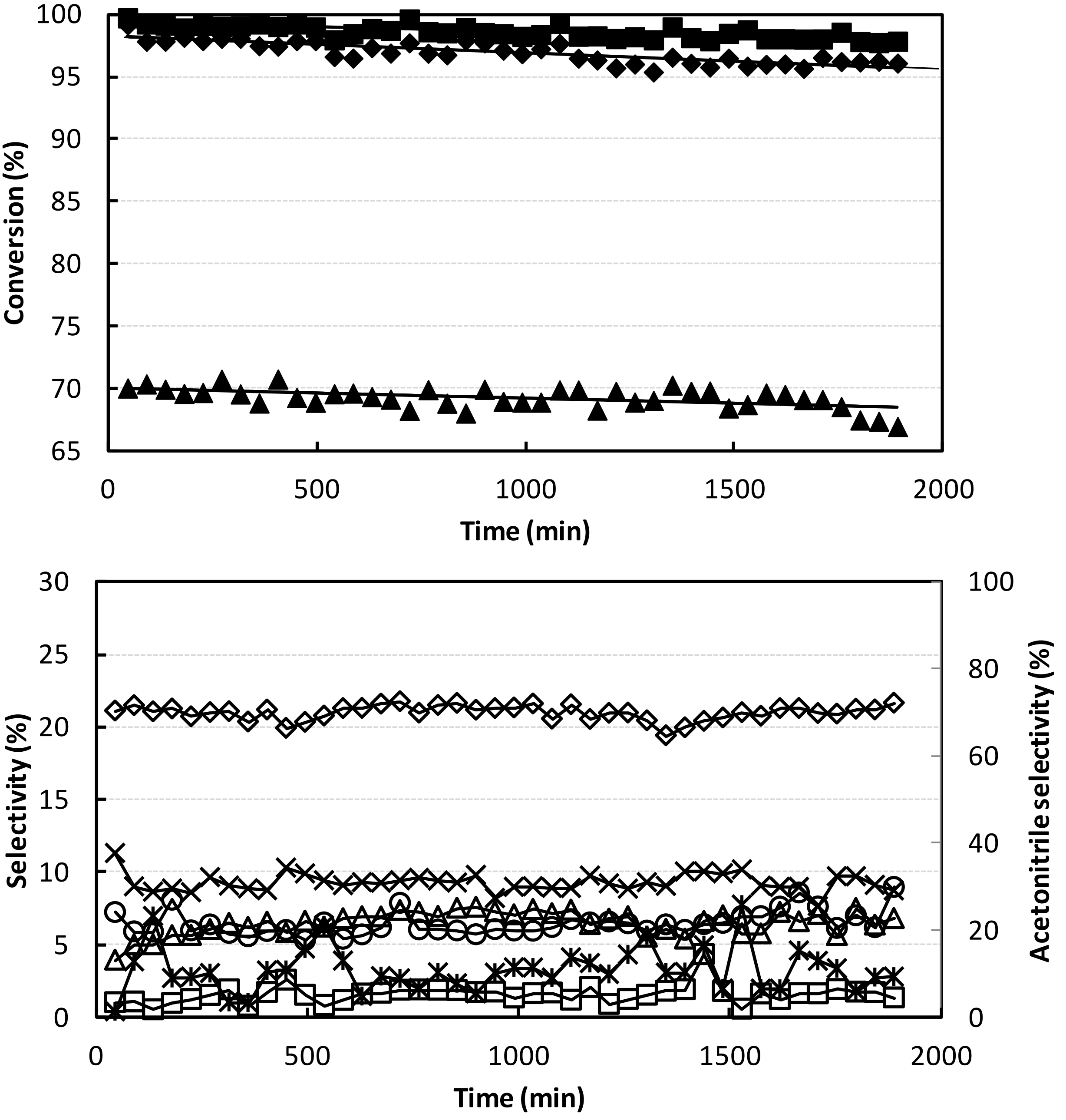
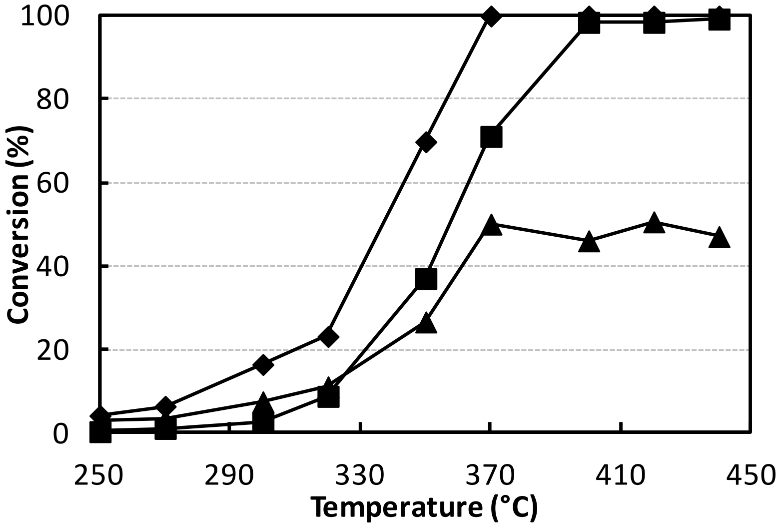


Figure 15. Effect of reaction time on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 10/12/10, temperature 400°C. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO_2 (×), and HCN (□). Catalyst V/Zr/O.



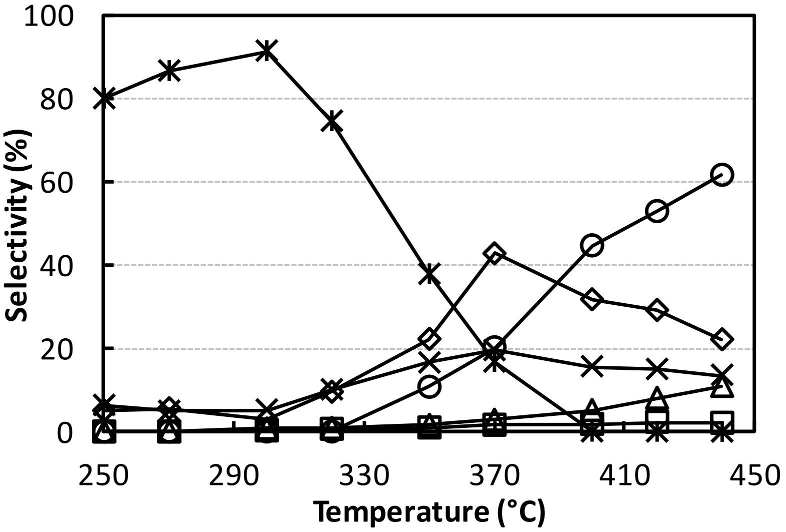


Figure 16. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): acetaldehyde (in the form of paraldehyde 0.66 mol%)/ammonia/oxygen 2/3/2. Symbols: paraldehyde conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO$_2$ (×), and HCN (□). Catalyst V/Zr/O.

Surprisingly, the yield to acetonitrile was lower than that obtained starting from ethanol under the same reaction conditions; conversely, the formation of CO was much higher. This effect might be interpreted assuming that with this catalyst the formation acetonitrile may occur by two different mechanisms, one *via* acetaldehyde and ethanimine formation, and another one *via* ethylamine formation.

Figures 17 and 18 compare the catalytic behavior of catalysts V/Ti/O and V/Zr/O, both containing the 7 wt% V_2O_5, at 0.1 g s mL^{-1} W/F ratio and feed composition ethanol/ammonia/oxygen (mol%) 5/6/6; the latter are amongst the best reaction conditions for the V/Zr/O catalyst.

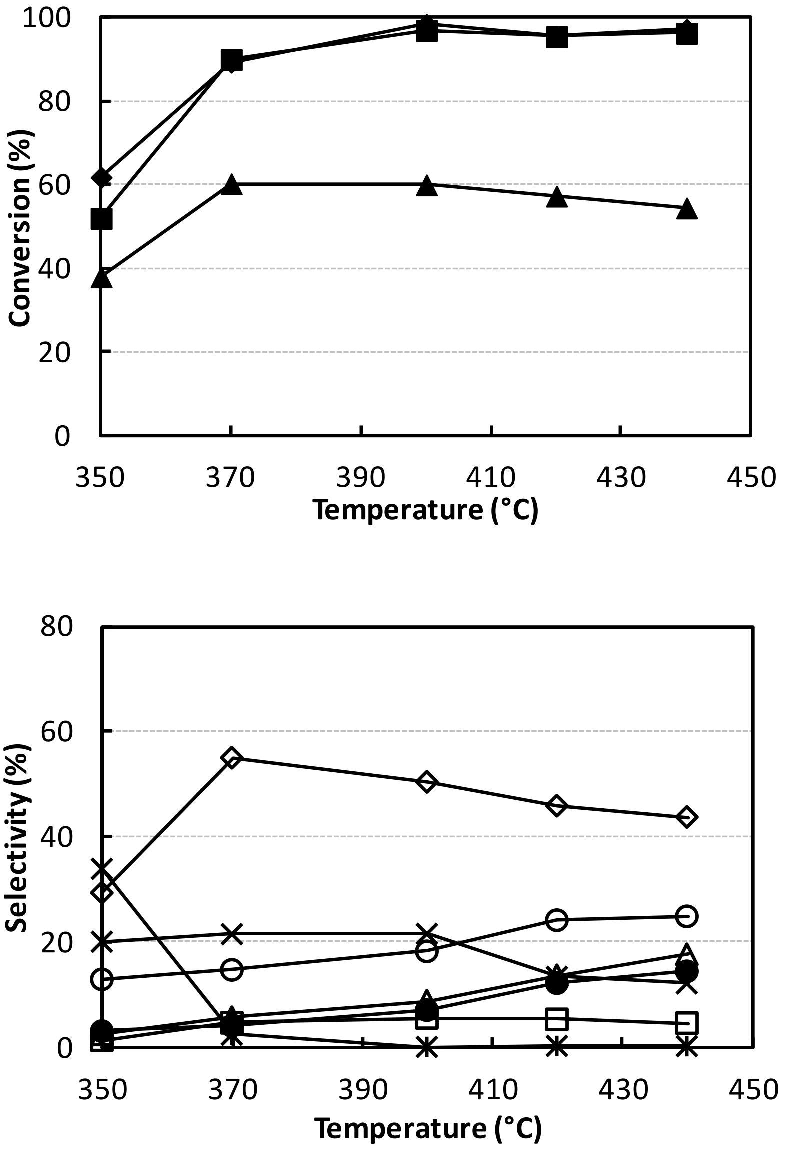


Figure 17. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/6/6. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO_2 (✕), HCN (□), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V7/Ti/O.

It is shown that the V/Zr/O catalyst shows a superior performance, because of the better yield and selectivity to acetonitrile, and of the higher ethanol conversion. The V7/Ti/O catalyst shows a greater selectivity to all by-products: CO, CO_2, HCN, ethylene and N_2 from ammonia combustion. This difference can be attributed to the different nature of the V species which develop at the surface of the support, and also to the nature of the support itself; in fact both titania (Figure 1 in Section A.2), and zirconia (Figure 8 in Section B.1) are active in ethanol ammoxidation.

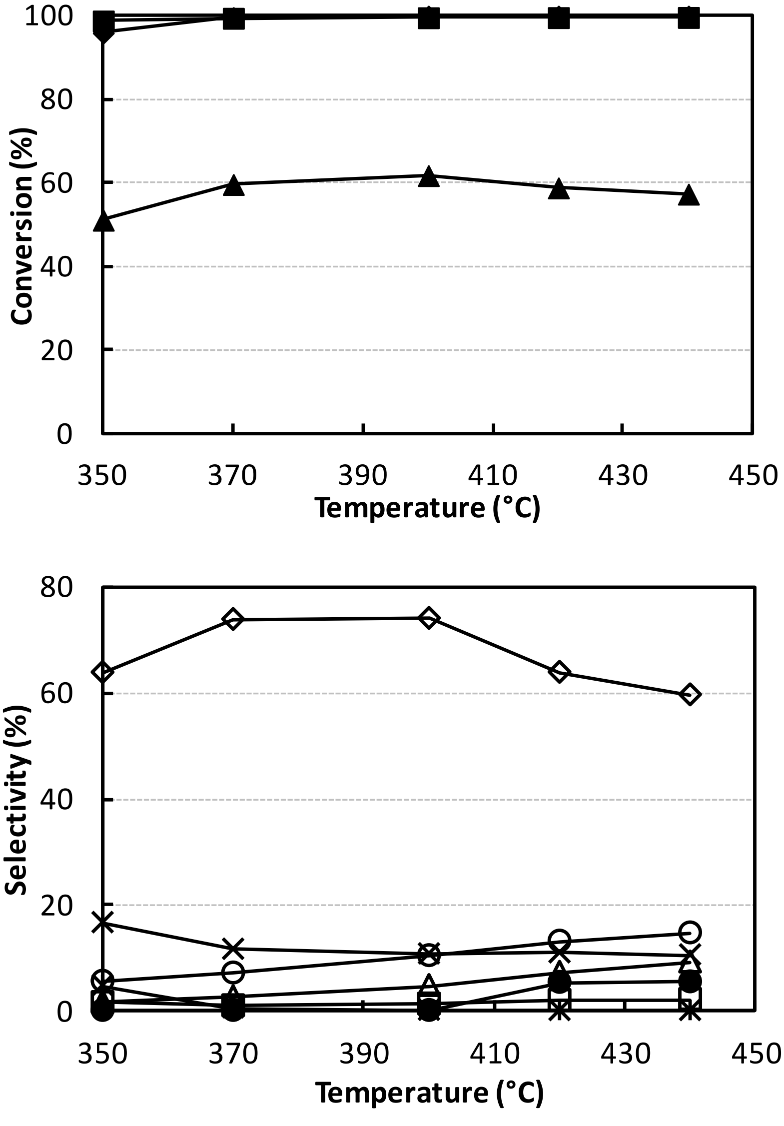


Figure 18. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/6/6. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO_2 (×), HCN (☐), and N_2 (calculated with respect to converted ammonia) (●). Catalyst V/Zr/O.

3. Ethanol ammoxidation with metal antimonates and metal molybdates catalysts

Other catalysts claimed to be active and selective in ammoxidation of hydrocarbons are based on either rutile-type mixed oxides (metal antimonates), or multimetal molybdates; the former give good performance in propane ammoxidation to acrylonitrile [15], the latter is used industrially for the ammoxidation of propylene [1].

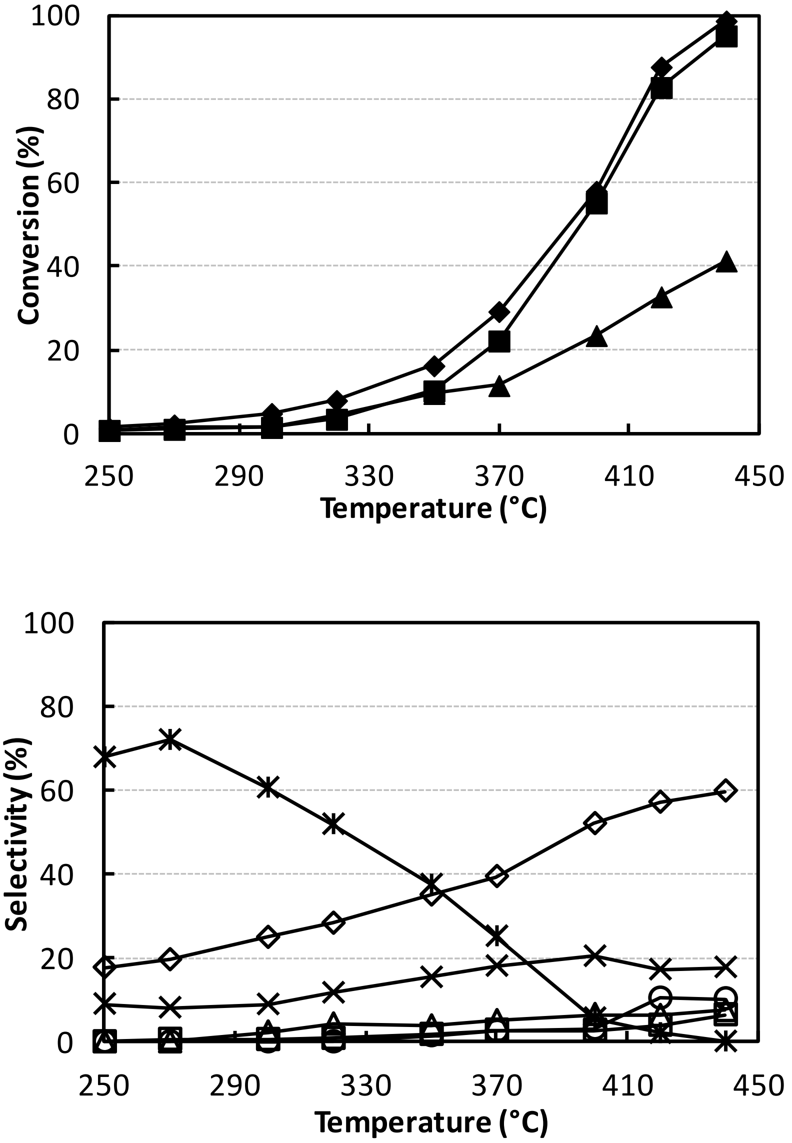


Figure 1. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/6. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO_2 (✕), and HCN (□). Catalyst Sn/V/Nb/Sb/O.

Figure 1 shows the catalytic behavior of a Sn/V/Nb/Sb/O catalyst (atomic ratio between elements 1/0.2/1/3), recently used for propane ammoxidation [15a]. Conditions used are: W/F ratio 0.1 g s mL^{-1}, feed composition ethanol/ammonia/oxygen (molar %) 5/13/6. The catalyst shows a behavior not much different from that observed with the supported vanadium oxide catalyst, but is clearly less active than the latter. One important peculiarity of this system is the very low degree of ammonia overoxidation to N_2, even at high temperature (because of this reason, the selectivity to N_2 is not reported in Figures). The maximum selectivity to acetonitrile is 60%, at 99% ethanol conversion.

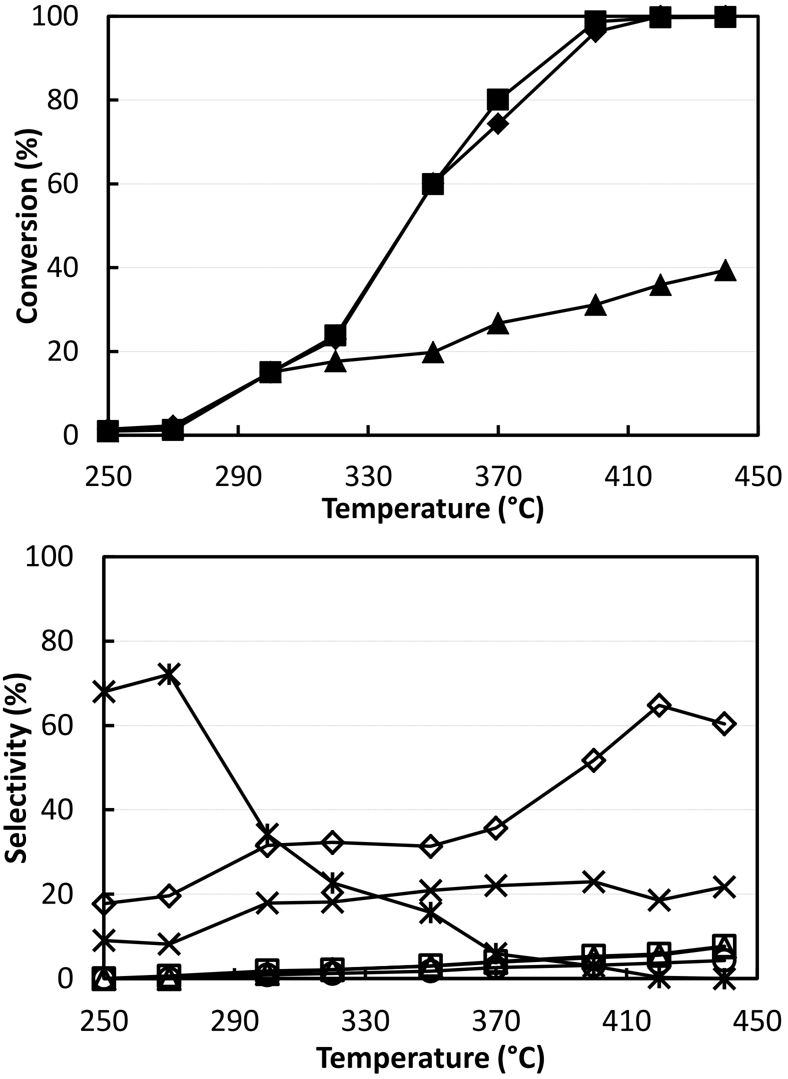


Figure 2. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.4 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope)/ammonia/oxygen 5/13/6. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CO_2 (×), and HCN (□). Catalyst Sn/V/Nb/Sb/O.

In the attempt of using lower reaction temperature while achieving acceptable conversion, we carried out experiments using W/F ratio 0.4 g s mL^{-1}; results are shown in Figure 2. Under these conditions, much higher reactants conversion were obtained; however, still the maximum selectivity was close to 60% (64%). Moreover, we noticed the formation of heavy compounds in the temperature interval 300-to-400°C; in fact, in this T range the decline of selectivity to acetaldehyde did not lead to a corresponding increase of selectivity to acetonitrile, but instead to that of heavy compounds. Only at high temperature we noticed the increase of selectivity to acetonitrile, and a decrease of that to heavy compounds.

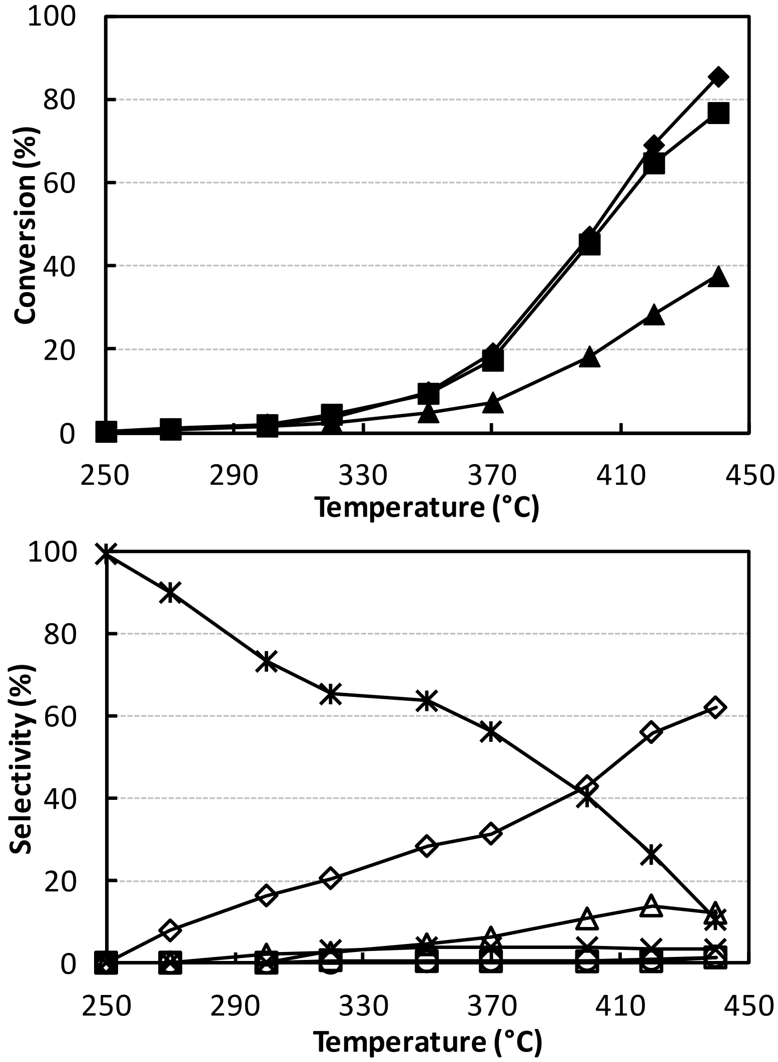


Figure 3. Effect of temperature on reactants conversion (top figure) and on selectivity to products (bottom figure). Reaction conditions: W/F ratio 0.1 g s mL^{-1}, feed composition (molar %): ethanol (azeotrope ethanol/water 95.6/4.4 wt%)/ammonia/oxygen 5/13/6. Symbols: ethanol conversion (◆), ammonia conversion (▲) and oxygen conversion (■). Selectivity to: acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (O), CO_2 (×), and HCN (□). Catalyst multimetal molybdate Bi/Fe/Co/Cr/Mo/O.

The reactivity of a multimetal molybdate catalyst (more specifically, of the C41 catalyst formerly used industrially for acrylonitrile synthesis) is illustrated in Figure 3; conditions used are W/F ratio 0.1 g s mL^{-1}, and feed composition (molar %): ethanol/ammonia/oxygen 5/13/6. It is worth reminding that in some patents [1] the co-feed of ethanol and propylene is claimed as a way to improve acetonitrile yield during acrylonitrile synthesis; in this latter process, the catalyst used is based on multimetal molybdate.

The catalytic behavior shown is similar to that observed with the rutile antimonate; also in this case, the most important peculiarity is the very low selectivity to N_2 (not reported, because negligible), and the very low selectivity to CO and CO_2; on the other hand, the catalyst looks poorly active, and the maximum selectivity to acetonitrile is 62%, at 85% ethanol conversion.

Conclusions

The reaction of ethanol ammoxidation to acetonitrile can be classified as a “facile” reaction, in the sense that it may be catalyzed by various catalytic systems, ranging from metal molybdtates, to supported vanadium oxide, to vanadyl pyrophosphate. However, the yield to acetonitrile obtained can range from medium values (30-40%) up to good and very good values (between 60 and 75%). In order to obtain an acetonitrile yield higher than 70%, it is necessary to carefully design both the catalyst and the reaction conditions to use. Specifically, the following results are worth of being mentioned:

a) The surface acidity must be very low, because acidity catalyzes several undesired reactions, such as the formation of ethylene, and of heavy compounds as well.

b) Supported vanadium oxide is the catalyst showing the best catalytic behavior, but the role of the support chosen is of crucial importance. The support not only affects the nature of the V active site, but also directly contributes to the reaction.

c) Metal molybdates and antimonates show interesting catalytic behaviors, but are poorly active, and probably require harder conditions than those used with the V oxide-based catalysts.

d) One key point in the reaction network is the rate of reaction between acetaldehyde (the first intermediate compound) and ammonia, compared to the parallel rates of acetaldehyde transformation into by-products (CO, CO_2, HCN). The catalysts showing the higher efficiency in this reaction are those based on supported Vanadium oxide.

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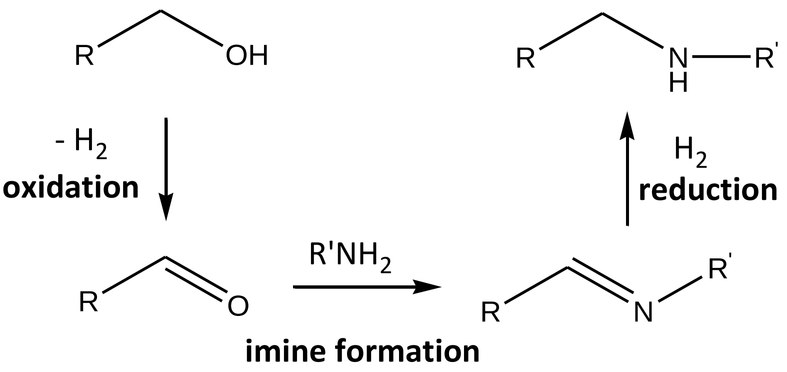
B. The amination of ethanol to acetonitrile

Introduction

The reaction between an alcohol and an amine leads to the alkylation of the amine (**N-alkylation**), with elimination of water. When the reaction is catalyzed by catalysts containing elements active in dehydrogenation reaction (eg, Ni, Co, Fe, Cu), it is also called **amination**; however, when the reaction is carried out in the presence of a large excess of hydrogen, it is referred to as **hydroamination**. N-alkylation (or amination with acid catalysts), amination and hydroamination are methods conventionally used for the synthesis of various substituted (alkylated) amines [1].

In **N-alkylation** over acid catalysts, the key-step of the process is NOT the dehydrogenation of the alcohol into acetaldehyde, but the exchange between –OH and –NH_2. This implies that starting from a primary amine, both di and tri-alkylated amines may form, in function of the ratio between the amine used and the alcohol. When ammonia is used, mono-, di- and tri-alkylated amines may form, and the control of the process selectivity may become a hard task, when a specific amine is the desired one. In fact, the selectivity to the secondary amine is generally low because the nucleophilicity of amines is increased by the *N*-alkylation.

Conversely, the mechanism of the **amination** occurs according to the reaction scheme made of the following consecutive steps: (a) the dehydrogenation of an alcohol into a carbonyl compound, (b) the imine formation by reaction between the carbonyl compound and the amine, and (c) the hydrogenation of the imine to an alkylated amine, using the hydrogen borrowed from step (a) (because of this reason, amination is also referred to as **reductive amination**) (Scheme 1). Usually, the reaction is carried out in the liquid-phase, in the presence of a base, and a catalyst (typically made of a transition metal ion) is necessary for the first and third step.



Scheme 1. General network for reductive amination.

Other methods for the synthesis of secondary and tertiary amines include (a) N-alkylation with alkyl halides [2], (b) reductive amination of carbonyl compounds [3], (c) amination of aryl halides [4], and (d) hydroamination of unsaturated hydrocarbons with amines [5]. However, these conventional procedures suffer significant disadvantages, such as the use of environmentally unfriendly halides, the use of expensive amines as starting materials, the production of large amounts of wasteful salts, and often low selectivities.

Homogeneous transition metal catalysts, especially copper-, ruthenium- and iridium-based, can be used for the synthesis of secondary amines, usually with great selectivity [6]. However, homogeneous catalysts have disadvantages of the recovery and reuse of expensive catalysts and/or the indispensable use of co-catalysts such as bases and stabilizing ligands. The synthesis of alkylated amines using heterogeneous catalysts such as solid acids or transition metal-based catalysts has also been widely described in the literature [7].

Other more recent references are [8]; catalysts used include Ru(II) or Ir(I) complexes, metallic Pd (supported over MgO), Cu/Ni colloidal systems, supported $Ru(OH)_3$. Recently, the alkylation of primary (aromatic) amines with alcohols to produce secondary amines was reported by Mizuno et al, using a $Ru(OH)_3/Al_2O_3$ catalyst [8a]. In another paper [8b], the same authors report about the use of the same catalyst for the synthesis of secondary and tertiary amines by reaction between an alcohol and urea.

An overview of the mechanisms and catalysts for alcohols **amination** to alkylated amines is reported in the review by Hamid et al [8f].

In regard to the synthesis of primary amines, many efficient catalytic procedures using copper, ruthenium, rhodium, and iridium complexes have been reported using ammonia or its related compounds as nitrogen sources [9]. As for the selective catalytic synthesis of tertiary and secondary amines using ammonia or its related compounds, there are only a few reports [10]: palladium-catalyzed N-arylation of ammonia with aryl halides and iridium-catalyzed N-alkylation of ammonium salts such as NH_4OAc and NH_4BF_4 with alcohols.

Finally, the gas-phase and photocatalytic N-alkylation reactions of ammonia with alcohols have also been reported [11]. In the gas-phase acid-catalyzed reaction between methanol and ammonia, products formed include methylamine, dimethylamine and trimethylamine, and a partial control of selectivity can be achieved by using a shape-selective effect due to the limited pore size of selected zeolite, such as H-mordenite [11f]. Thermodynamic data on the reaction between ethanol and ammonia are reported in ref [12].

When the final step of the process is not an hydrogenation, but a **dehydrogenation**, and ammonia is used as the reactant instead of an amine, a **nitrile** is the product of the process (even though the alkylated amines can be formed as by-products); we can refer to this reaction as **non-reductive amination.** Worth of note, in **hydroamination** (that is an amination carried out in the presence of hydrogen), the catalysts used are similar to those used for the non-reductive amination.

In the following sections we shall discuss more in detail the literature on the dehydrogenation of primary amines into nitriles (in the aim of studying a two-step process including first ethylamine synthesis by means of N-alkylation, and then ethylamine dehydrogenation into acetonitrile), on hydroamination, and on non-reductive amination.

The (oxi)dehydrogenation of primary amines into nitriles

In regard to the transformation of a primary amine into a nitrile, there are two different approaches for the transformation of alkylamines into the corresponding nitriles: (a) a dehydrogenation reaction, and (b) and oxidehydrogenation reaction.

The oxidative approach is usually carried out at mild temperatures, in the liquid phase. Although several oxidation procedures that use stoichiometric reagents for the synthesis of nitriles from amines have been reported [13], only a few catalytic procedures have been described [14]. Ruthenium complexes have been described for the oxidation of amines with O_2, but usually these systems show low turnover numbers, form significant amounts of by-products, and also may exhibit severe deactivation of the catalysts. Mizuno et al reported outstanding yield to nitrile in the oxidation of various benzylamines with oxygen, using Ru/Al_2O_3 [15a] or $Ru(OH)_3/Al_2O_3$ [15b] catalysts, which proved to be a fully heterogeneous system. When a Manganese oxide octahedral molecular sieves (OMS-2) was used, primary amines were transformed into primary amides, because the catalyst could act as an efficient, reusable heterogeneous bifunctional catalyst for the sequence of oxidative dehydrogenation to the nitrile and successive hydration of the latter to the amide [15c].

Catalysts investigated in the literature for the dehydrogenation of alkylamines to the corresponding nitriles include Al_2O_3, SiO_2 and ZrO_2. Reactions occurring include deamination to the olefin (dealkylation), disproportionation and dehydrogenation to the nitrile. In the case of alumina, catalytic sites for deamination are those having hydroxo groups, while those for dehydrogenation are defects produced by the removal of water from the surface; conversely, other authors underline the role of surface Lewis sites. Tanabe [16] reported that deamination (dealkylation) occurres over the strong acid sites of SiO_2-Al2O_3, while the dehydrogenation is promoted over strong basic sites (for example, over MgO). However, the amphoteric ZrO_2 showed the highest activity and selectivity for the formation of nitriles, especially in the decomposition of secondary and tertiary amines. In the latter case, in fact, the deamination of the tertiary amine leads first to the formation of the secondary amine (plus ethylene) and then of the primary amine, both reactions being catalyzed by the acid sites of ZrO_2. The latter is finally dehydrogenated to the nitrile over the basic sites, or further deaminated to ethylene and ammonia over the acid sites.

The hydroamination of ethanol

The hydroamination is usually aimed at the synthesis of alkylated amines, as it is also for reductive amination; however, instead of using the hydrogen “internally” produced during the first step, the hydrogen is co-fed to the reactor. This is also a process used industrially, since short-chain aliphatic amines, important intermediates for the chemical industry, are produced by reaction between an alcohol and a primary or secondary amine, in the presence of hydrogen [17].

> The reaction is carried out with Co, Ni or Cu catalysts supported over silica or alumina. In general, it is believed that the active sites are the elements in the **metallic form**, because the latter is the species which develops at the reaction conditions used [18]. In regard to the hydroamination of alcohols with ammonia, the reaction has been investigated using Co-based catalysts [19], and Ni-based catalysts [20].

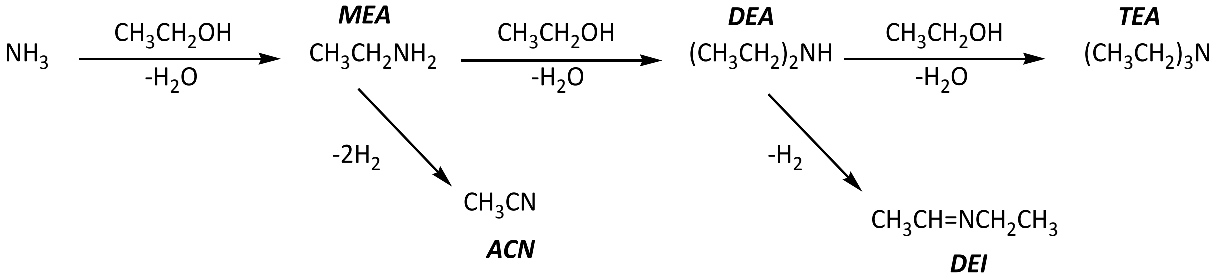
Still there are uncertainties in regard to the reaction mechanism; in fact, two different mechanisms have been proposed:

1. A first hypothesized mechanism involves the abstraction of the α-H atom from the alcohol R-CH_2OH, with generation of a fragment which is adsorbed on the Co surface [17]; an H abstraction also occurs from the amine R'R"NH, and this second fragment couples with the former one to generate an amino alcohol, R-CH(OH)-NR'R". Finally, the elimination of the OH species and the addition of H generates the amine.
2. The mechanism proposed by Jackson [21] also involves a first step of H abstraction from the alcohol (ethanol in this case), but after this step an adsorbed ethylidene species may form by the release of the OH group. This species reacts with ammonia to form ethylamine.

Several products are obtained during hydroamination: amines, imines, enamines, nitriles and hydrocarbons [17-22]. Hydrocarbons are particularly undesired, and are formed by hydrogenolysis of the amines. A drawback of the process is the formation of carbonaceous deposits, and of metal carbides and metal nitrides as well. Deactivation is retarded by the presence of hydrogen [23], but even in the presence of hydrogen there is some deactivation, which is again attributed to the accumulation of coke; another reason for deactivation, especially occurring in the absence of hydrogen, is the strong interaction of ammonia with the catalyst [20].

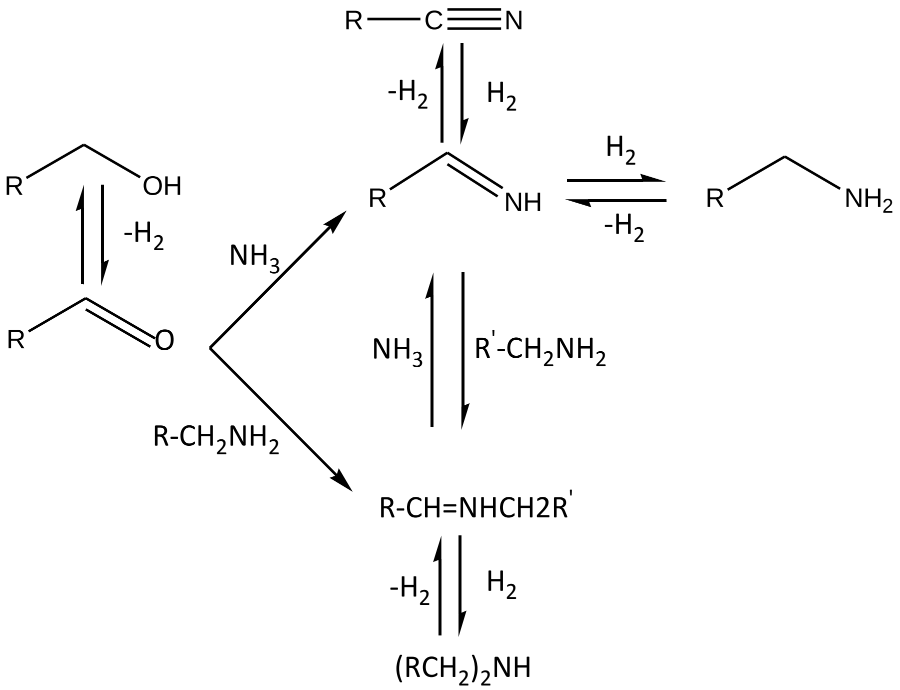
Rausch et al [20] also investigated the effect of main reaction parameters with Co-silica catalyst; the reaction was typically carried out at 210°C, with feed composition (molar ratios) ethanol/ammonia/inert/hydrogen equal to: 2/7/14/80; under these conditions, conversion of ethanol was between 70 and 90%, with selectivity to hydrocarbons between 10 and 20%. The latter was affected by the amount of Co loading, and by the degree of Co reduction. It is worth noting that under these conditions acetonitrile was only a minor product; major products were the amines and the hydrocarbons.

The general reaction scheme proposed by the authors is reported below (Scheme 2):



Scheme 2. Reaction network in ethanol hydroamination [20].

Card et al [24] also investigated Cu-alumina catalyst for octanol gas-phase hydroamination into octanenitrile, in the presence of hydrogen. The mechanism proposed by Card et al is shown in Scheme 3. It is evident that when the reaction is carried out with ammonia, one product can be the nitrile; in this case, the latter step is not the hydrogenation, which would lead to the primary amine, but a dehydrogenation. Since the reaction is carried out in the presence of hydrogen, it may be expected that the nitrile is only a minor product, because the dehydrogenation of the intermediately formed imine into nitrile should be less favoured than its hydrogenation into the alkylated amine. In fact, in many cases the nitrile is only a minor product. However, this is not the case according to what reported in some patents; specifically, the use of co-fed hydrogen is explicitly claimed as necessary to obtain high yield to butyronitrile from 1-butanol and ammonia, while limiting the extent of catalyst deactivation [25]; the catalyst is based on pre-reduced supported Cu.



Scheme 3. Reaction network proposed by Card et al [24].

The non-reductive amination of ethanol

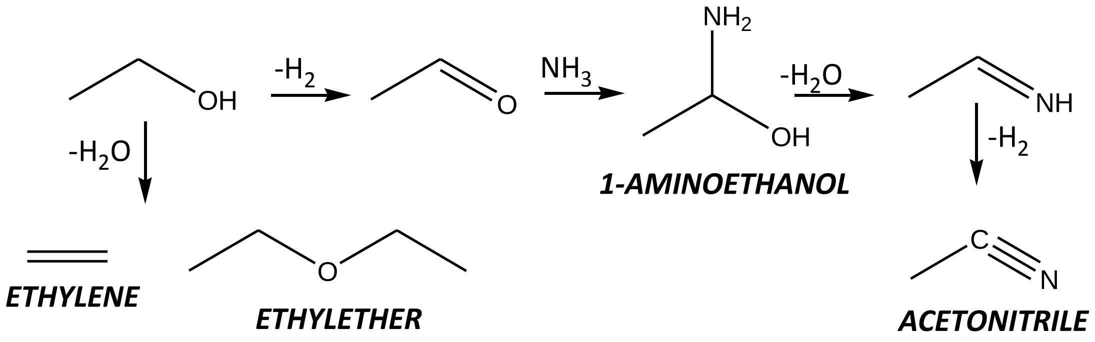
In contrast to the reductive amination, the **non-reductive amination** (also referred to as **amination-dehydrogenation**) is carried out in the absence of co-fed hydrogen; under these conditions, the formation of the nitrile may be more favoured than the alkylamine, in function of the reaction conditions used [26].

$C_2H_5OH + NH_3 \rightarrow CH_3CN + H_2O + 2\ H_2$

In regard to the catalysts used in amination of ethanol to acetonitrile, in 1960s Kryukov et al. [27] first reported the conversion of alcohols to acetonitriles by amination-dehydrogenation over a fused iron catalyst.

Various other systems have then been investigated:

a) CuOx-alumina [28]. The mechanism proposed is shown in Scheme 4; the main intermediate is acetaldehyde, which is then converted into the imine and finally dehydrogenated into the nitrile.

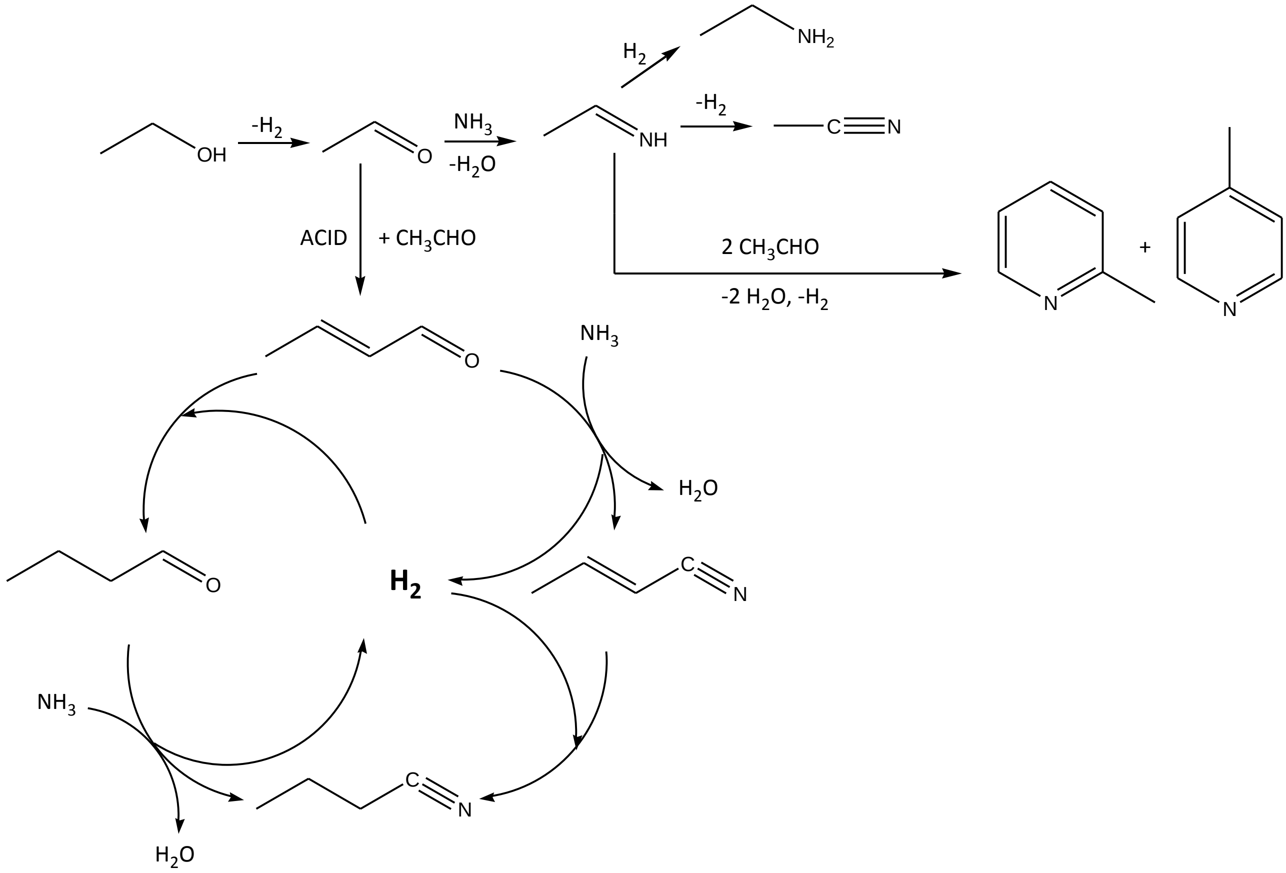


Scheme 4. Proposed reaction scheme for ethanol amination [28].

The authors obtained almost total conversion of ethanol at 290°C, with 92.6% selectivity to acetonitrile, using a feed ratio NH_3/ethanol equal to 7. It is important to note that the catalyst was pre-reduced with H_2/N_2 at 250°C; therefore, metallic Cu is considered as the active species. When CuO (unsupported) was used, the reaction led to the prevailing formation of an heavy compound, the 1-aminoethanol trimer. This was interpreted as being due to the fact that the acid contribution of the support alumina is fundamental in the aim of dehydrating the 1-aminoethanol into the imine, so limiting the accumulation of the intermediate and the formation of the trimer. On the other hand, the presence of acid sites favours the formation of ethylene and diethylene ether at high temperatures. Finally, the optimal temperature is claimed to be between 270 and 290°C.

Finally, a Cu/Ni/Ba-based colloidal catalyst has been used for the **reductive-amination** of dodecyl alcohol and of monomethylamine (MMA) by Kimura et al [8d]. Systems based on Cu are also used for the one-step amination of fatty alcohols and dimethylamine (DMA) to N,N-dimethyl-long-alkyl tertiary amines (DMTA), or of (MMA), to produce dialkylmethyl tertiary amines (DDMAs), intermediates for quarternary ammonium salts as softening agents; these processes are also used commercially. In the amination reaction, the active hydrogen, required for the hydrogenolysis of aldehyde-DMA adduct to DMTAs, was effectively supplied by dehydrogenation of a starting alcohol itself.

b) CoOx/NiO-alumina [29]. Scheme 5 shows the reaction network proposed by the authors. The authors checked the reactivity of various catalysts, based on Cu-, on Ni-, and Co-, all supported over alumina. The worst performance was shown by the CuO-alumina catalyst, which yielded methylpyridines and ethylamine as the prevailing by-products. The best performance was shown by the CoOx-alumina catalyst, especially that one also containing Ni as a promoter. With the latter system, the best performance of 92.5% yield to acetonitrile was obtained at 420°C (or 380°C), with the ethanol azeotrope in feed (95/5 ethanol/water), and a ammonia/ethanol molar ratio equal to 7 (or 5). The selectivity slightly declined during lifetime experiments, which was due to coke accumulation and formation of metal carbides. By-products were butyronitrile, ethylene, pyridine and other heavy compounds.



Scheme 5. Reaction network reported by Zhao et al. [29]

Results and Discussion

1. The synthesis of acetonitrile by a two-step process: (a) Ethanol amination to ethylamine, and (b) Ethylamine dehydrogenation to acetonitrile.

1.1 The first step: Ethanol amination to ethylamine over acid catalysts

Figure 1 shows the results obtained using a H-Mordenite catalyst with Si/Al ratio 20 (Sud-Chemie 1/16” extrudates, code 303 H/02). Reaction conditions were: W/F ratio 0.8 g s mL-1, feed composition 5% ethanol, 13% ammonia, remainder He. It is shown that ethanol was converted by the 90% at 350°C; the main products formed were ethylene, ethylamine (selectivity 42% at 90% ethanol conversion), and even acetonitrile. This indicates that the formed ethylamine undergoes easily dehydrogenation into the nitrile, which is quite a surprising effect. It is possible that the reaction indeed is catalyzed by the alumina binder used to prepare the H-Mordenite extrudates; in fact, experiments described below show that non-redox metal oxides, especially those showing amphoteric properties, may be efficient in the dehydrogenation of ethylamine.

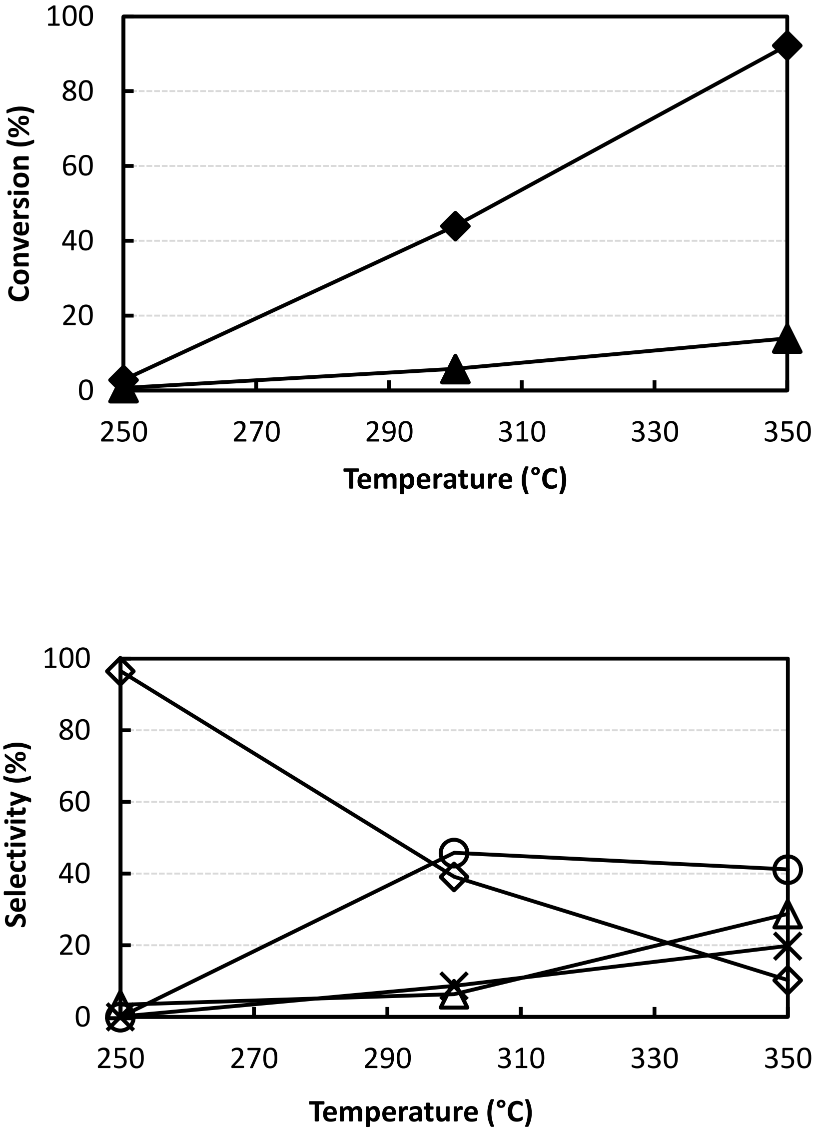


Figure 1. Effect of temperature on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol (azeotrope), 13% ammonia, W/F ratio 0.8 g s mL-1. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), to ethylene (△), to ethylamine (○) and to Others (diethylamine, triethylamine, diethylether) (✕). Catalyst H-Mordenite Si/Al 20.

Even more surprising is that fact that selectivity to acetonitrile decreases when the temperature is raised; in fact, dehydrogenation should be clearly more favored at high temperature. We cannot exclude the presence of an alternative mechanism for acetonitrile formation; in fact, if the catalyst is able to catalyze the dehydrogenation of ethylamine, it should also favor the dehydrogenation of ethanol into acetaldehyde, which might then react to yield ethanimine, precursor for acetonitrile formation. At the moment, we do not have a clear explanation for the formation of such a large amount of acetonitrile, in the low temperature range. Other by-products formed were diethylether, diethylamine and triethylamine (all have been lumped into the term Others). The same experiments were carried out using a H-Mordenite catalyst containing more Al (Si/Al ratio equal to 7.5; Toyo Soda HSZ-620 H0A), but in the powder form (therefore, it does not contain alumina binder). Figures 2 and 3 show the results obtained with 13% and 40% ammonia in feed, respectively.

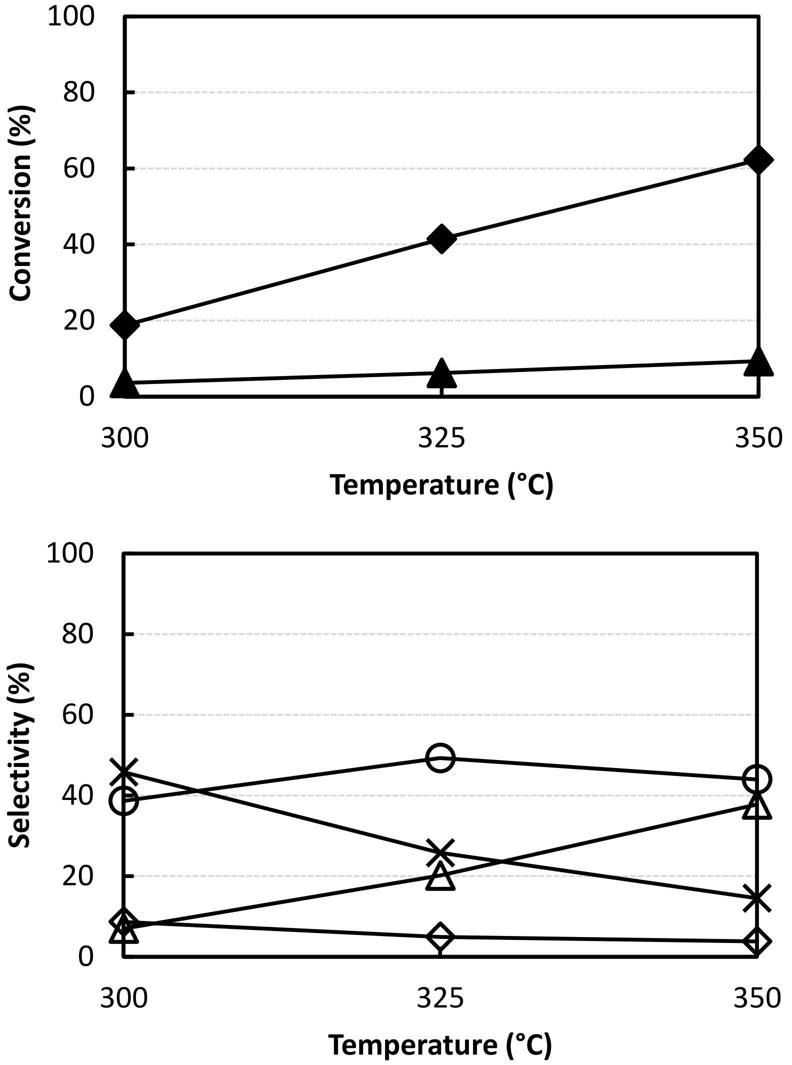


Figure 2. Effect of temperature on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 13% ammonia, W/F ratio 0.4 g s mL-1. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), to ethylene (△), to ethylamine (○) and to Others (diethylamine, triethylamine, diethylether) (✕). Catalyst H-Mordenite Si/Al 7.5.

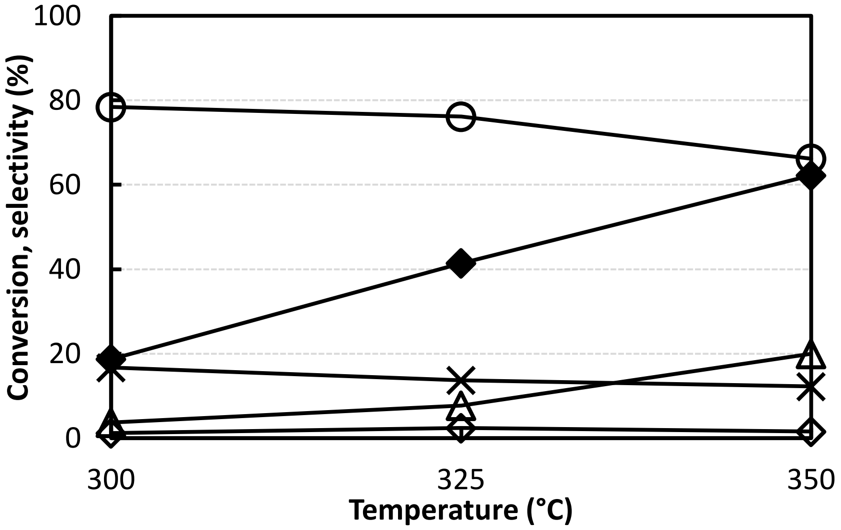


Figure 3. Effect of temperature on ethanol conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 40% ammonia, W/F ratio 0.4 g s mL-1. Symbols: ethanol conversion (◆),selectivity to acetonitrile (◇), to ethylene (△), to ethylamine (○) and to Others (diethylamine, triethylamine, diethylether) (✕). Catalyst H-Mordenite Si/Al 7.5.

In this case, the selectivity to acetonitrile is much lower than that obtained with the H-Mordenite containing less Al. Again, the selectivity to ethylamine is around 40%; at low temperature diethylether and polyalkylated amine are the prevailing by-products, but when the temperature is raised, ethylene becomes the dominant by-product.

The selectivity to ethylamine increases remarkably when the reaction is carried out using a large excess of ammonia (ethanol 5%, ammonia 40%). In fact, as shown in Figure 3, selectivity is about 66% at 62% ethanol conversion.

The effect of ammonia partial pressure is summarized in Figure 4. It is shown that an increase of ammonia partial pressure leads to a considerable increase of selectivity to ethylamine, and to a corresponding decrease of selectivity to polyalkylated amines. Surprisingly, the conversion of ethanol is not so much affected by ammonia partial pressure. This might indicate that the rate determining step of the process does not involve ammonia; a possibility is that indeed ethanol is dehydrogenated to acetaldehyde (the rate-determining step of the process), which then reacts with ammonia to yield ethanimine, and the latter finally is hydrogenated to ethylamine using the hydrogen borrowed from the first step. However, this hypothesis can be excluded, since a much higher yield to acetonitrile should be observed by means of ethylamine dehydrogenation, which instead is not the case.

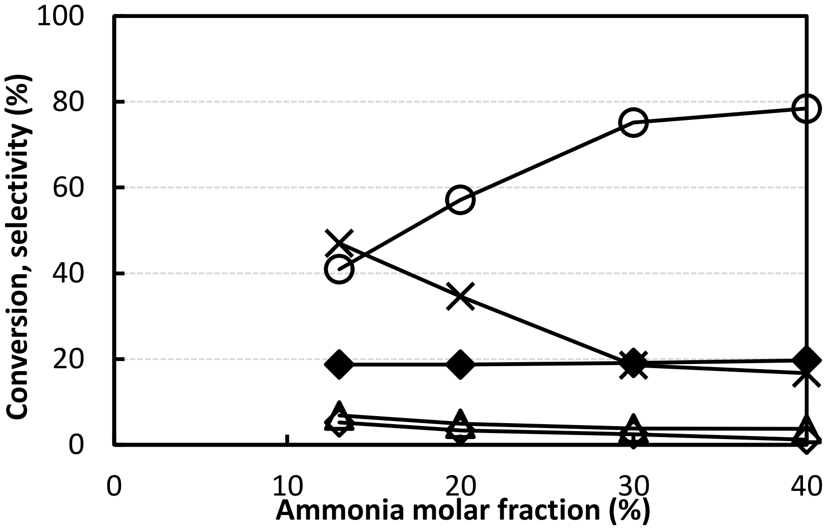


Figure 4. Effect of ammonia partial pressure on ethanol conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, W/F ratio 0.4 g s mL-1, temperature 300°C. Symbols: ethanol conversion (◆), selectivity to acetonitrile (◇), to ethylene (△), to ethylamine (○) and to Others (diethylamine, triethylamine, diethylether) (✕). Catalyst H-Mordenite Si/Al 7.5.

An alternative possibility is that the rate determining step is the activation of either ethanol or ammonia (or both) over the acid sites; in the presence of a surface saturation effect, an increase of ammonia partial pressure would not lead to an increase of ethanol conversion, because the concentration of adsorbed activated reactant would be a function of the acid sites concentration only.

These experiments demonstrate that it is possible to obtain about 50% yield to ethylamine under optimal conditions of a large excess of ammonia, and of temperature as high as 350°C.

1.2. The second step: ethylamine (oxi)dehydrogenation to acetonitrile

Table 1 summarizes the main features of the catalysts used; all samples were calcined at 450°C.

Table 1. Main features of catalysts used for ethylamine dehydrogenation.

Catalyst	Surface area, m^2/g	Atomic ratio
ZrO_2	30 (from Polynt)	-
MgO	80 (Synthesized)	-
Mg/Al/O	164 (Synthesized)	Mg/Al = 8
Mg/Si/O	50 (Synthesized)	Mg/Si = 3

Figure 5 compares the catalytic behavior of samples at 500°C, and Figure 6 reports the effect of temperature on the catalytic behavior of ZrO_2. Reaction conditions used for catalytic experiments were: W/F ratio 0.1 g s mL-1, feed composition 1% ethylamine, remainder inert (He). Under the conditions used, the only catalyst showing an acceptable activity is ZrO_2, which show ethylamine conversion as high as 50% at 450°C, and almost complete conversion at 500°C. All the other catalysts showed negligible conversion at both 400 and 450°C, and a conversion around 20-30% at 500°C; at the latter conditions, however, an important contribution of thermal homogeneous reactions cannot be excluded. The differences of reactivity observed between MgO and ZrO_2 agree with what already reported in the literature [16a, 16b].

In regard to the distribution of products, based on literature results we should expect the higher selectivity to ethylene (via deamination/dealkylation) over the acid systems, such as the mixed Mg/Al/O and Mg/Si/O and the amphoteric ZrO_2, whereas the higher selectivity to acetonitrile is expected with over the purely basic system, MgO. Indeed, the mixed Mg/Al/O and Mg/Si/O systems exhibit both basic and acid sites [30a, 30b], and hence should exhibit a catalytic behavior similar to that shown by ZrO_2.

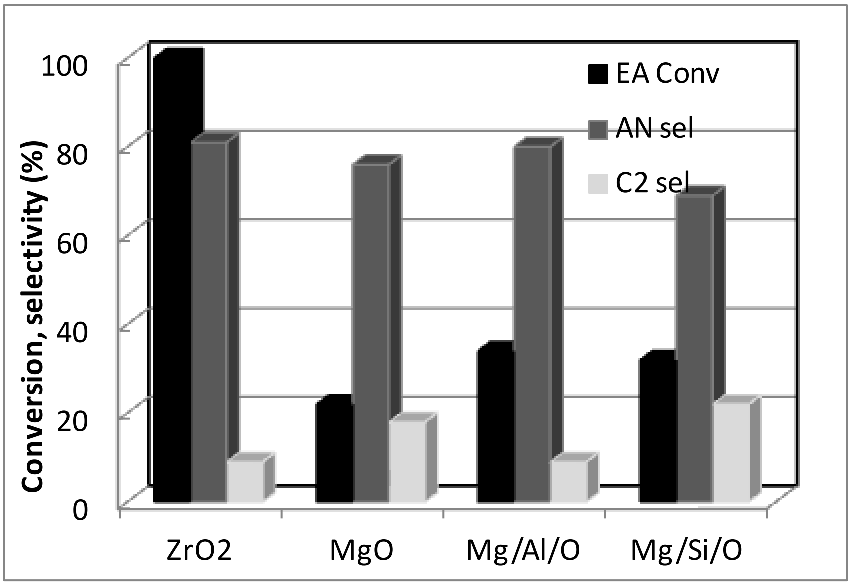


Figure 5. Conversion of ethylamine (EA), and selectivity to acetonitrile (AN) and ethylene (C2) over different catalysts, at 550°C reaction temperature. Other conditions: feed 1% ethylamine in He, W/F ratio 0.1 g s mL-1.

The only products formed were ethylene (via deamination) and acetonitrile (via dehydrogenation). The best selectivity to acetonitrile at 500°C is shown by ZrO_2, ca 80% (which also was the yield to acetonitrile, because ethylamine conversion is complete). With this catalyst, surprisingly the selectivity to acetonitrile and ethylene is not much affected by temperature (Figure 6).

We also carried out an experiment with ZrO_2 by adding O_2 in feed, in order to transform the dehydrogenation reaction into an oxidehydrogenation, and favor the direct transformation of ethylamine into acetonitrile while limiting the parallel deamination reaction. We also increased the W/F ratio (0.4 g s mL-1 instead of 0.1 g s mL-1), in order to lower the reaction temperature and limit the reactions of combustion. The results are summarized in Figure 7; ethylamine shows a moderate conversion already at 300°C. However, the predominant reaction products are carbon oxides, and selectivity to acetonitrile was not higher than 30%. We also detected the formation of diethylamine, which suggests the presence of a disproportionation reaction:

$2\ CH_3CH_2NH_2 \rightarrow (CH_3CH_2)_2NH + NH_3$

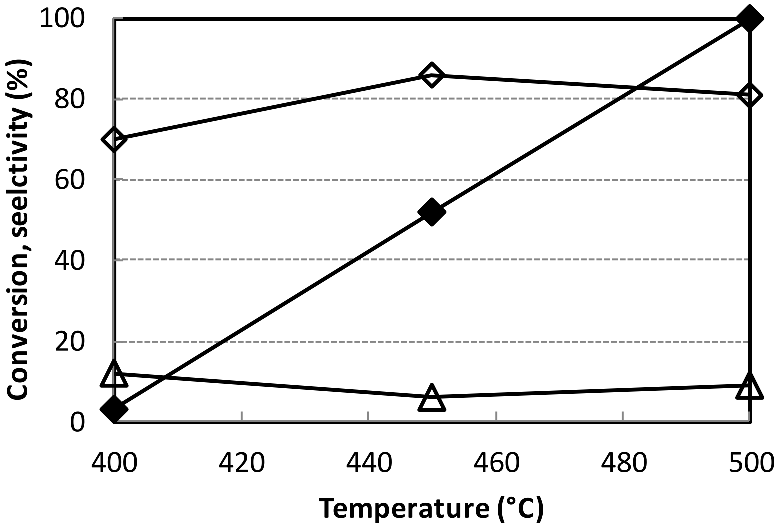


Figure 6. Effect of temperature on ethylamine conversion and selectivity to products. Reaction conditions: feed 1% ethylamine in He, W/F ratio 0.1 g s mL-1. Symbols: ethylamine conversion (◆), selectivity to acetonitrile (◇) and to ethylene (△). Catalyst ZrO_2.

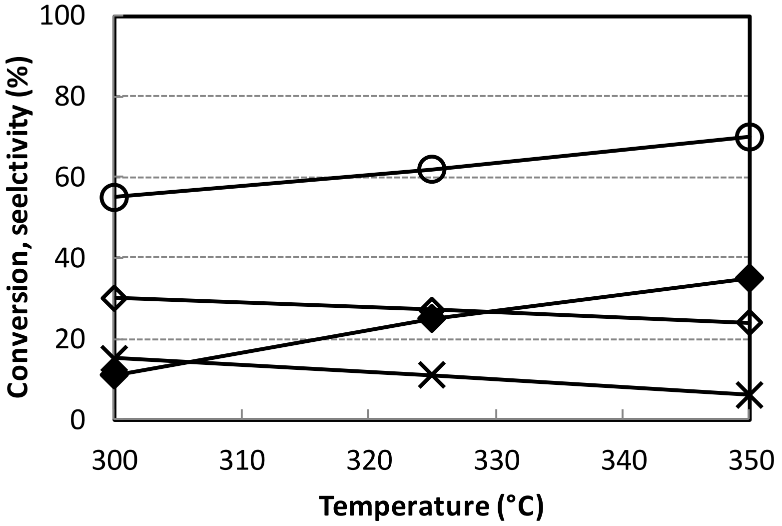


Figure 7. Effect of temperature on ethylamine conversion and selectivity to products. Reaction conditions: feed 1% ethylamine, 6% oxygen in He, W/F ratio 0.4 g s mL-1. Symbols: ethylamine conversion (◆), selectivity to acetonitrile (◇), to $CO+CO_2$ (○), and diethylamine (✕). Catalyst ZrO_2.

Concluding, the best result with the two-step approach was obtained with an H-Mordenite (Si/Al ratio 7.5) for the first step (selectivity 66% at ethanol conversion of 62%, at reaction conditions: feed composition ethanol 5%, NH_3 40%, W/F ratio 0.4 g s mL-1), and a ZrO_2 catalyst for the second step (81% selectivity at 100% ethylamine conversion, reaction conditions: feed 1% ethylamine, W/F ratio 0.1 g s mL-1, temperature 500°C). In overall, the best yield achieved in the two-step process, in which each step should be carried out at the optimal conditions inside a single reactor unit, would be around 33%.

1.3 Combining the two steps on either bifunctional or basic catalysts

The two steps examined, the amination of ethanol to ethylamine and the dehydrogenation of the latter into acetonitrile, require the presence of two different active sites, acidic and basic (dehydrogenating), respectively. Therefore, it is possible to use some of the catalysts already investigated, such as ZrO_2, Mg/Al/O and Mg/Si/O as bi-functional system for the one-pot transformation of ethanol into acetonitrile. In order to check for the feasibility of this option, we reacted ethanol and ammonia over the mentioned catalysts. This bi-functional approach should however be examined taking into account that the acid properties (necessary to carry out the first step) can be detrimental for the second step, because may favor the deamination of the intermediately formed ethylamine into ethylene and ammonia. On the other hand, the basic (dehydrogenative) properties, which are necessary for the second step, may also accelerate the direct dehydrogenation of ethanol to acetaldehyde; the latter might further react with ammonia to give ethanimine and then the nitrile. Therefore, this would provide an additional pathway for acetonitrile synthesis, likely more efficient than that one including ethanol amination + ethylamine dehydrogenation. It is also worth noting that the reaction pathway including ethanol dehydrogenation + acetaldehyde reaction with ammonia to ethanimine + final dehydrogenation of the imine to acetonitrile needs only basic sites. Therefore, if this latter mechanism prevails over the former, we should see a similar behavior for both basic (MgO) and bifunctional systems.

Figure 8 compares the catalytic behavior of the four catalysts shown in Table 1. Reaction conditions used were: feed composition 5% ethanol, 13% ammonia, W/F ratio 0.1 g s mL-1.

The results obtained lead to the following considerations:

a) The more active catalyst is again ZrO_2, as it was in the case of experiments carried out by feeding ethylamine. However, the difference of reactivity between ZrO_2 and the other samples is not so large as it was in the case of ethylamine dehydrogenation.
b) All the MgO-based catalysts show a similar behavior, with formation of acetaldehyde as the prevailing compound at low temperature; the raise of temperature leads to a decrease of selectivity to acetaldehyde, with a corresponding increase of selectivity to ethylene and acetonitrile. However, the product showing the greater increase is ethylene, and the selectivity to acetonitrile finally is no higher than 30%. With these

systems, the mechanism of reaction includes the dehydrogenation of ethanol to acetaldehyde (and not the amination of ethanol to ethylamine) as the first step.

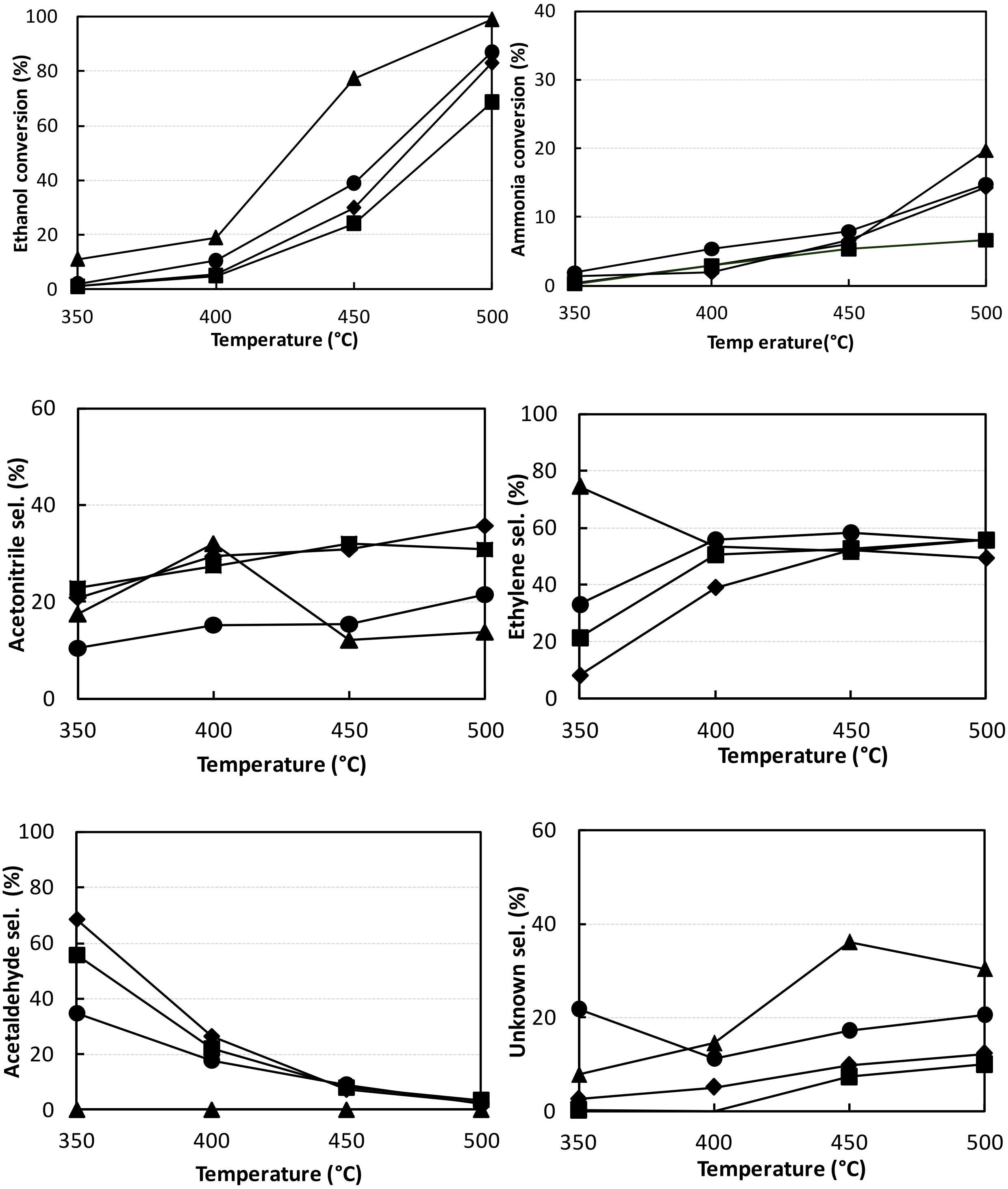


Figure 8. Effect of temperature on reactants conversion and on selectivity to products. Reaction conditions: feed composition 5% ethanol azeotrope, 13% ammonia, W/F ratio 0.1 g s mL-1. Symbols: MgO (■), Mg/Al/O (●), Mg/Si/O (◆), ZrO_2 (▲).

c) The peculiarity of ZrO_2 catalyst is that it does not show the formation of acetaldehyde at all. Moreover, the selectivity to ethylene is high even at low temperature; this means that the catalyst is much more efficient in ethanol dehydration than in its dehydrogenation. This agrees with the fact that acidity of ZrO_2 is stronger than that of the MgO-based catalysts, and supports the hypothesis that with this catalysts the acid-catalysed reaction of ethanol amination is the first step of the reaction pathway leading to acetonitrile.

d) Another peculiarity of the ZrO_2 is that the selectivity to acetonitrile declines at temperatures higher than 400°C, with a concomitant raise of the selectivity to a single by-product, which still has not been definitely identified (an hypothetical attribution is toluene). This by-product also forms with the other catalyst, but in lower amount than with the ZrO_2 catalyst.

We also carried out some experiments with the ZrO_2 catalyst by using the same feed composition, but at 0.8 g s mL-1 W/F ratio, in order to decrease the reaction temperature; however, still the best selectivity to acetonitrile is 32%, with 19% ethanol conversion at 300°C.

Concluding, the results clearly indicate that the one-pot approach is not possible, either because the mechanism does not occur *via* ammonia exchange + dehydrogenation, but instead takes place *via* dehydrogenation + condensation with ammonia + dehydrogenation (this pathway is usually referred to as "non-reductive amination, as described in Section 2), and the catalysts here investigated are not the best one for this reaction type, or because even though the mechanism is the expected one, the selectivity to acetonitrile is very low due to the presence of parallel reactions occurring over ethanol.

1.4 Ethanol "ammoxidation" on acid catalysts

One further reaction we investigated with acid catalysts is the reaction of ethanol and ammonia in the presence of oxygen. We have not discussed this reaction in the Section dealing with ammoxidation, because in this case we do NOT expect a redox mechanism, but a mechanism in which the ethylamine formed by ammonia exchange on acid sites, is afterwards transformed into acetonitrile. During this latter step, oxygen might eventually favor the dehydrogenation of the amine, even though this type of reaction (oxidehydrogenation) is not expected to occur neither on acid nor on basic sites. Another reason why we decided to investigate this reaction on acid catalyst is that in literature one paper reports about a very efficient ammoxidation of ethanol to acetonitrile over SAPO catalysts, systems which hold acid sites and do not possess redox properties [31]. We investigated this reaction with the H-mordenite catalyst (Si/Al ratio 7.5), and with a SAPO catalyst synthesized by us.

The catalytic behavior of the H-Mordenite catalyst is shown in Figure 9. Reaction conditions used were: 5% ethanol, 40% ammonia, 6% oxygen, W/F ratio 0.4 g s mL-1; such a large ammonia content was used because the reaction between ethanol and ammonia to yield ethylamine was greatly favored at high ammonia concentration (see Figure 4). It is shown that the catalytic behavior is not much different from that obtained in the absence of oxygen (Figure 3); however, the selectivity to ethylamine is lower than in the latter case, especially at low temperature. No formation of CO_x is detected.

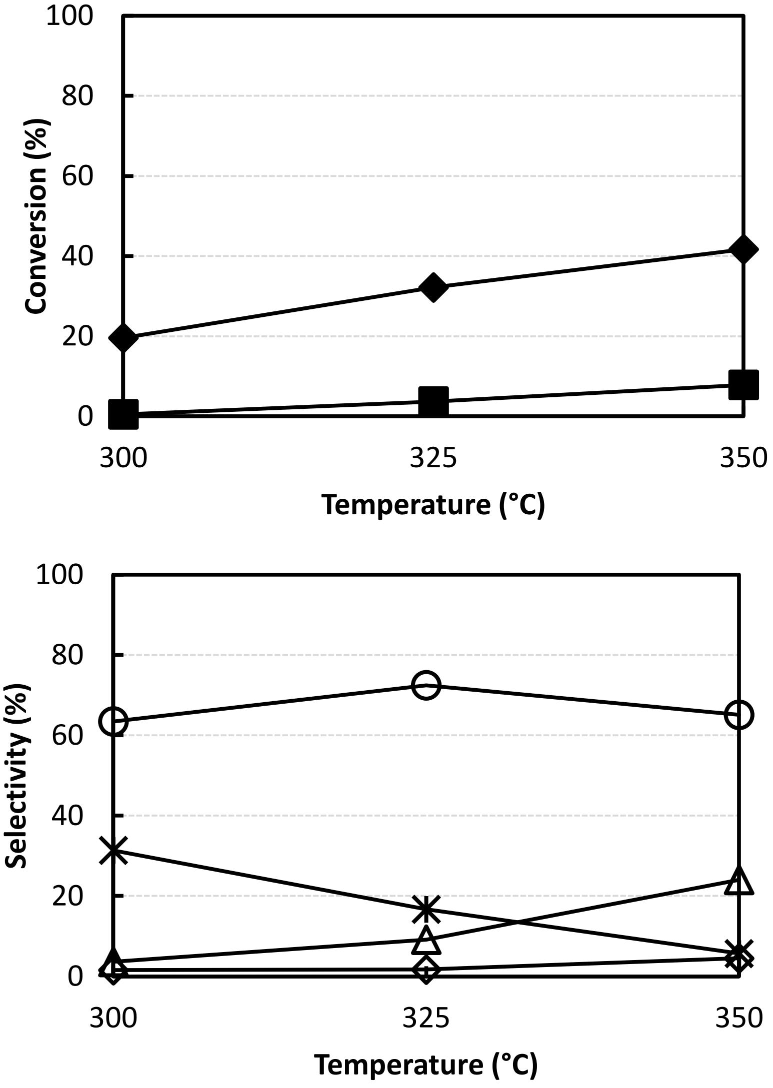


Figure 9. Effect of temperature on reactants conversion and in selectivity to products. Reaction conditions: feed 5% ethanol azeotrope, 40% ammonia, 6% oxygen, W/F ratio 0.4 g s mL-1. Symbols: ethanol conversion (◆), oxygen conversion (■), selectivity to acetonitrile (◇), to ethylene (△), to ethylamine (○) and to Others (diethylamine, triethylamine, diethylether) (✕). Catalyst H-Mordenite Si/Al 7.5.

The SAPO catalyst was synthesized according to the procedure reported in ref [32]. The XRD pattern of the sample is shown in Figure 10; the pattern corresponds to that of the SAPO-40 structure.

Catalytic experiments with the SAPO catalyst were carried out at the following conditions: ethanol/ammonia/oxygen (molar fractions %) 5/13/6, W/F ratio 0.1 g s mL-1 (Figure 11) or 0.4 s (Figure 12). Under both conditions used, the conversion of ethanol reaches a maximum value at ca 400°C; further raise of temperature does not lead to greater ethanol conversion. Another important result is that oxygen conversion is negligible up to 350°C; prevailing by-products in the low temperature range (250-350°C) are diethylether, diethylamine and even the extremely toxic methylisocyanate CH_3-N=C=O; both diethylether and diethylamine form by acid-catalyzed reactions, which explains the fact that no oxygen is converted. Moreover, neither acetaldehyde nor COx form in this temperature range, which allows us to exclude that either dehydrogenative or oxidative reactions take place at these conditions. There is however a non-negligible formation of acetonitrile, the selectivity of which increases when the temperature is raised, with a concomitant decrease of diethylamine. This means that acetonitrile forms by dehydrogenation of ethylamine (the latter being formed by direct amination of ethanol), and that the amine either dehydrogenates to acetonitrile, or reacts further with ethanol to form diethylamine. The increase of temperature leads to a greater contribution of the former reaction, at the expense of the latter one. On the other hand, the raise of temperature leads also to an increase of selectivity to ethylene, which becomes the predominant product at above 380°C. At high temperature and 0.4 g s mL-1 W/F ratio, small amounts of CO+CO_2 are also formed. Under both conditions, the ammonia conversion shows a maximum value at about 350°C, which also corresponds to the temperature at which the decline of acetonitrile selectivity is observed.

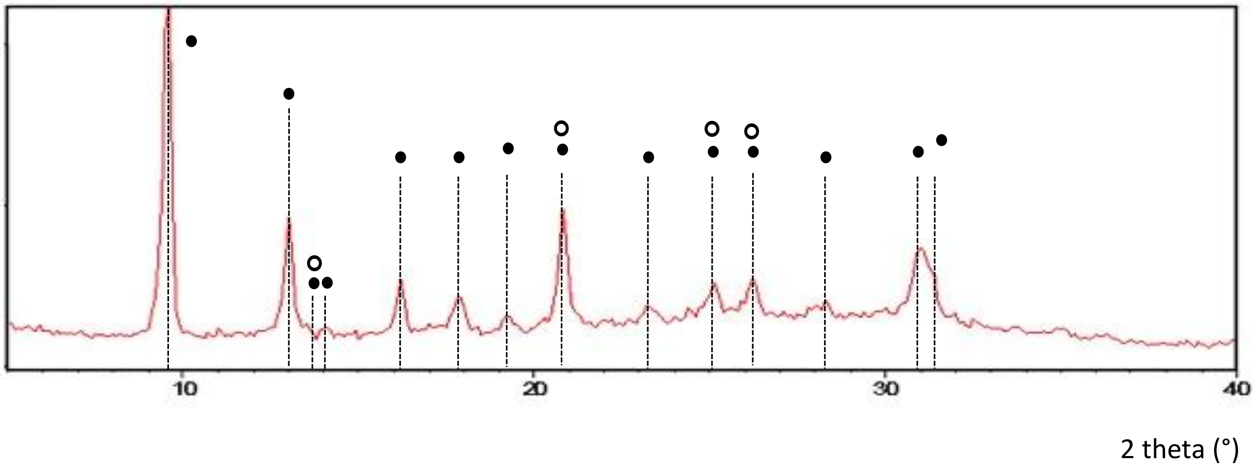


Figure 10. XRD pattern of the SAPO sample synthesized. Symbols: SAPO-5 (○), SAPO-40 (●).

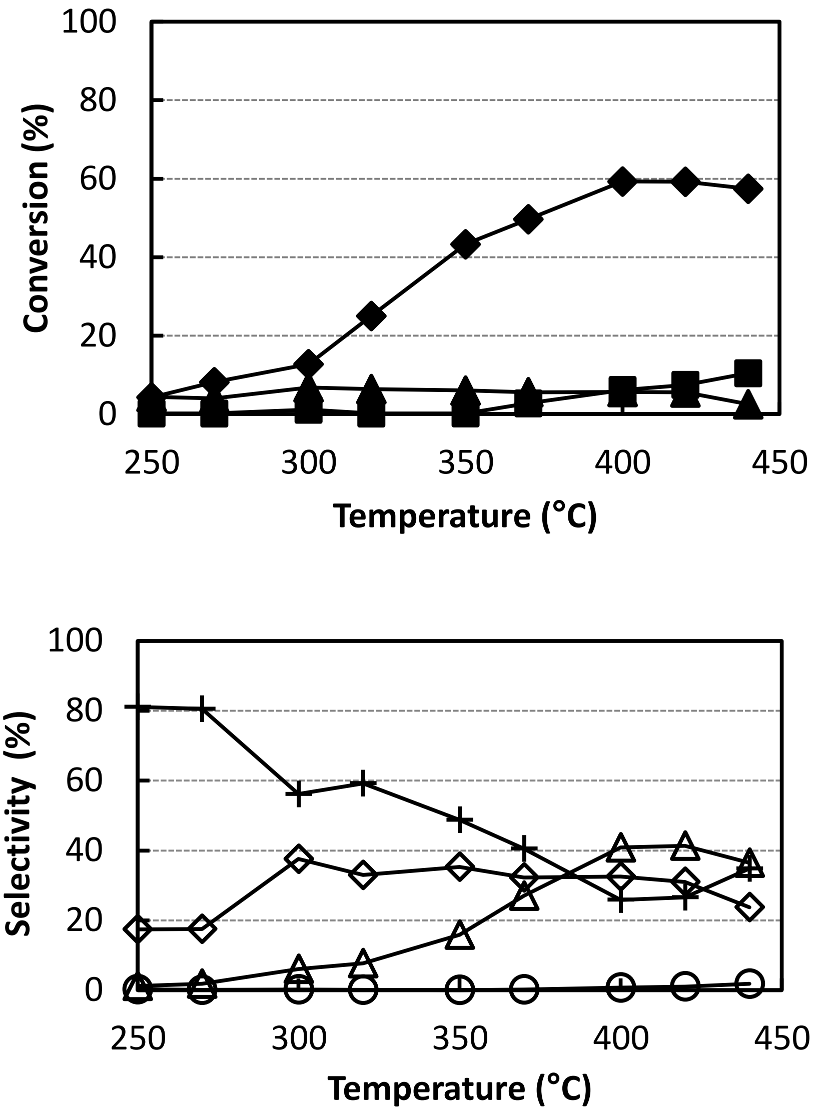


Figure 11. Effect of temperature on reactants conversion and in selectivity to products. Reaction conditions: feed 5% ethanol azeotrope, 13 % ammonia, 6% oxygen, W/F ratio 0.1 g s mL-1. Symbols: ethanol conversion (◆), oxygen conversion (■), ammonia conversion (▲), selectivity to acetonitrile (◇), ethylene (△), CO + CO_2 (O), and others (+). Catalyst SAPO.

Concluding, the SAPO catalyst is very efficient in the formation of ethylamine and in dehydrogenation of the latter into acetonitrile, but side reactions such as the formation of diethylamine and ethylene limit the selectivity to ethylamine and finally to acetonitrile. The catalyst also shows good dehydrogenating properties, which are quite surprising (the selectivity to acetonitrile shown by the H-Mordenite catalyst is by far lower than that obtained with the SAPO). At the moment, we do not know whether oxygen may play a role on this dehydrogenating property, although the very low oxygen conversion allows us to disregard this hypothesis, at least in the low temperature range.

Scheme 1 summarizes the reaction occurring in the acid-catalyzed amination of ethanol, and in the basic-catalyzed dehydrogenation of ethylamine into acetonitrile.

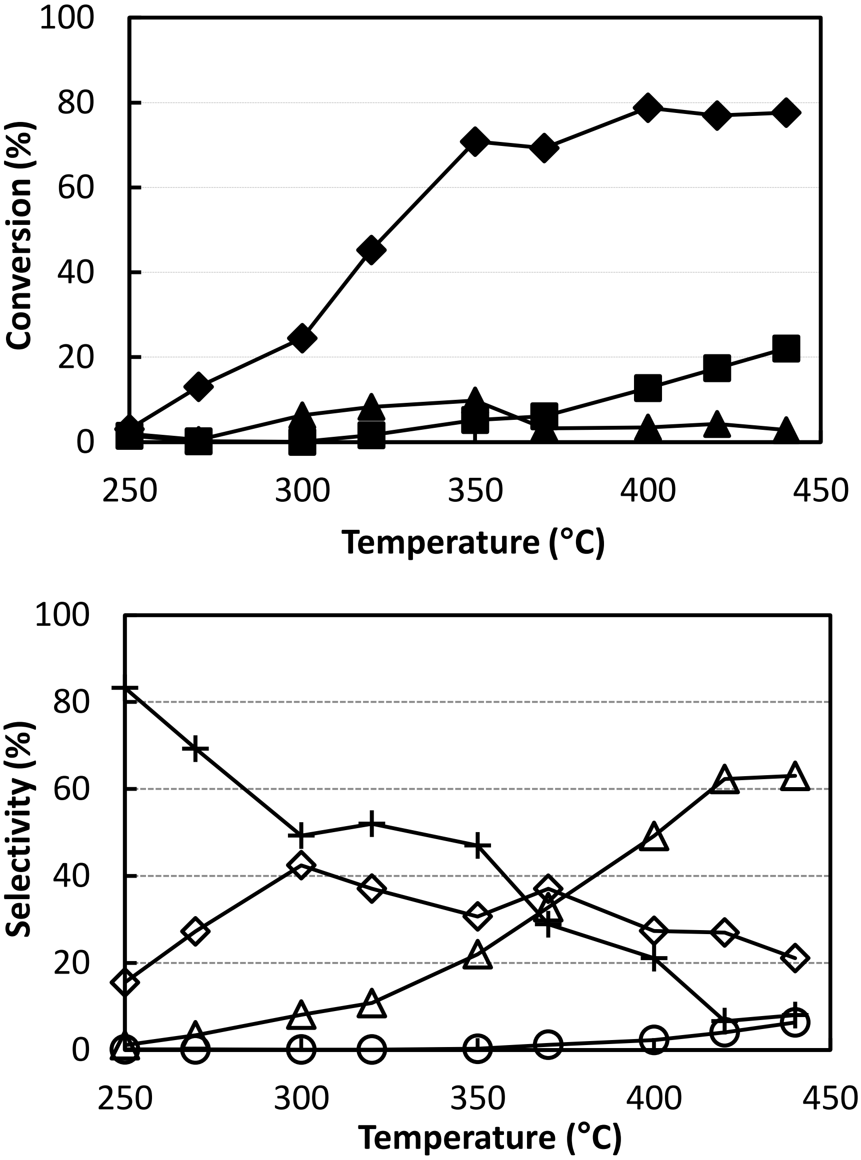
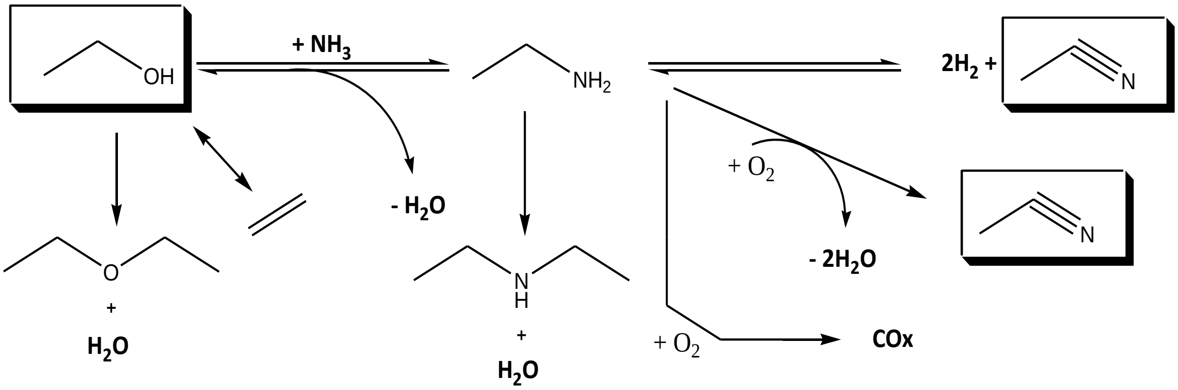


Figure 12. Effect of temperature on reactants conversion and in selectivity to products. Reaction conditions: feed 5% ethanol azeotrope, 13 % ammonia, 6% oxygen, W/F ratio 0.4 g s mL-1. Symbols: ethanol conversion (◆), oxygen conversion (■), ammonia conversion (▲), selectivity to acetonitrile (◇), ethylene (△), CO + CO_2 (○), and others (+). Catalyst SAPO.

Concluding, in this chapter we have discussed the results on the synthesis of acetonitrile from ethanol by means of a two-step process: (a) the amination of ethanol to ethylamine, and (b) the dehydrogenation of ethylamine to acetonitrile. The acid-catalyzed transformation of ethanol into ethylamine requires a large excess of ammonia, in order to observe good yield to ethylamine; this is likely due to thermodynamic limitations on the exchange reaction between water and ammonia. The step of ethylamine dehydrogenation to acetonitrile takes place with 80% yield on ZrO_2 catalyst. Combining the two steps over a single bifunctional catalyst, in the absence of oxygen (again with ZrO_2, showing both acid and basic properties), or with oxygen (with the SAPO catalyst, which is very efficient in the acid catalyzed amination, but also is active in ethylamine dehydrogenation) does not lead to satisfactory results, because of the several side reactions taking place.



Scheme 1. A summary of reactions occurring in the two-step transformation of ethanol into acetonitrile.

2. The non-reductive amination of ethanol over dehydrogenating catalysts

As described in the Introduction, one approach reported in the literature for the synthesis of acetonitrile is the non-reductive amination of ethanol. We have carried out reactivity experiments using catalysts based on Co and Cu oxides, dispersed over supports.

2.1 Preparation of catalysts

For samples supported on SiO_2, we used commercial silica produced by Grace Catalyst Carriers, with the following specifications: - Grade: 432, S.A. (m^2/g): 320, Pore Volume (mL / g): 1.2, pH (5% suspension): 6.5, Particle size: 30-100 μm, Particle shape: granular, Production code: QS02. For the sample supported on γ-Al_2O_3, we used an alumina produced by BASF, with the following specifications: S.A. (m^2/g) 190, Product code AL 3992, Article 5565952. The source of cobalt for Co20/SiO2, Co20/Al2O3 and Co10/SiO2 samples was cobalt (II) nitrate hexahydrate provided by Sigma (pur.> 98%); the source of copper for samples Cu10/SiO2 and Cu20/SiO2 was copper (II) nitrate trihydrate (pur.> 99 %); the source of nickel for the samples Co20Ni3/SiO2 and Co20Ni3/Al2O3 was nickel (II) nitrate hexahydrate (pur.> 98%).

Sample Co20/SiO2 was prepared as follows: 9.8107 g of cobalt nitrate hexahydrate are dissolved in 25 mL of distilled H_2O in a flask under stirring at room temperature; after the complete dissolution of the salt, 10.0350 g of SiO_2 are added slowly. The slurry obtained is left under stirring for 1 hour. The water is subsequently removed from the flask by means of a rotary evaporator at the relative pressure of 90 kPa and at a temperature of 70°C. The solid obtained is dried in an oven at 120°C overnight. The catalyst is then calcined using the thermal treatment in static air in a muffle, with the following temperature program: - Isotherm at 120°C for 2 hours; - heating with a rate of 10°C / min, until 550°C; - Isotherm at 550°C for 5 hours; - Cooling down to ambient temperature. The same procedure was used for all samples. The Co10/SiO2 catalyst was prepared using the same procedure as reported above, but using 4.9035 g of cobalt nitrate hexahydrate. The final amount of Co deposited was measured by means of ICPEOS, after digestion of the sample in microwave; for sample Co20/SiO2, the exact amount of Co (wt%) turned out to be 19.9%, for Co10/SiO2 sample 8%.

The Co20/Al2O3 was prepared as follows: in a beaker 9.8107 g of cobalt nitrate hexahydrate are dissolved in 25 mL of distilled H_2O, are then 10.0350 g of Al_2O_3 are added slowly. The slurry obtained is left under stirring for 1 hour. The water is subsequently removed from the flask by means of a rotary vapory evaporator at the relative pressure of 90 kPa and at a temperature of 70°C. The solid obtained is dried in an oven at 120°C for one night, and finally calcined as reported above. The Co20Ni3/Al2O3 catalyst was prepared in the same way, by dissolving 1.4914 g of nickel nitrate hexahydrate in 5 mL of distilled H_2O in a separate beaker under stirring at room temperature; then the two solutions, containing the Co and the Ni salts, respectively, were mixed under stirring.

The Cu20/SiO2 catalyst (19.5 wt% Cu by means of ICP analysis) was prepared using 7.9106 g of copper nitrate trihydrate. The Cu10/SiO2 catalyst (13.2 wt% Cu) was prepared using 3.9553 g of copper nitrate trihydrate.

2.2 Catalytic experiments

We first tested the reactivity of the Co20/Al2O3 catalyst, using the reaction conditions: ethanol 5 mol%, ammonia 25 mol%, W/F ratio 1 g s mL^{-1}. The results are shown in Figure 1. The conversion of ethanol is almost complete at 400°C; at low temperature, we noticed the formation of acetaldehyde and ethylamine; this indicates that both mechanisms, take place ie, (a) N-ethylation + dehydrogenation and (b) dehydrogenation + amination.

Other important by-products at low temperature are diethylether (the prevailing product at 350-370°C; however, the selectivity then decreases and becomes nil at 400°C), crotonaldehyde (shown in traces at 370°C), butadiene and butyronitrile; these two latter compounds are present over the entire T range, and in the T range 400-to-440°C they are the only by-products detected. In the figure, all the by-products have been grouped into the term "Others". These results indicate that due to the basic properties of the catalyst (maybe because of alumina, an amphoteric oxide), the acetaldehyde formed undergoes condensation reactions to yield C_4 compounds. However, the major by-product is ethylene; the selectivity to acetonitrile shows the maximum value of 60% at 400-420°C.

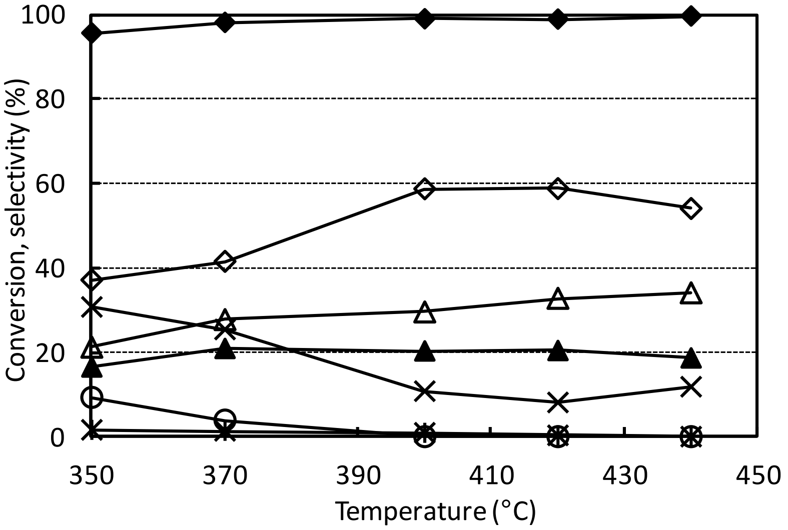


Figure 1. Effect of temperature on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, W/F ratio 1 g s mL^{-1}. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), to ethylene (△), to ethylamine (○), to acetaldehyde (✱), and to Others (✕). Catalyst Co20/Al2O3.

Figure 2 shows the catalytic behavior of the Co20/SiO2 catalyst; in this case we decided to investigate also temperatures lower than 350°C. Besides acetaldehyde several by-products form at 250-320°C, such as: 2-methylpyridine, diethylamine, 2-butenenitrile, isobutyronitrile, and butanedinitrile; selectivity to acetonitrile is no higher than 20-30%. However, at above 300°C, the selectivity to by-products declines rapidly, and correspondingly that to acetonitrile raises, until the high value of ≥ 96% (by-products being CO and traces of CO_2), obtained at almost total ethanol conversion. Such a high selectivity is due to the very low selectivity to formation, which forms in negligible amount even at high temperature. The best result is obtained at 370°C.

Figures 3 and 4 show the results obtained with the Co20Ni3/Al2O3 and Co20Ni3/SiO2 catalysts; we both systems, we investigated reaction temperatures higher than 350°C (W/F ratio 1 g s mL^{-1}). The behavior shown by the two catalysts is quite different; in the former case, several by-products form (as it is in the case of the catalyst without Ni), but the selectivity to acetonitrile is not much affected by temperature. Conversely, with the latter catalyst high acetonitrile selectivity (≥ 96%) is shown at 350°C, with total ethanol conversion (as in the case of the corresponding sample without Ni); the only by-products are CO, 1% CO_2 and ethylene, with no CH_4 produced. The selectivity to acetonitrile decreases when the temperature is raised, with a corresponding raise of both ethylene and products of acetaldehyde decomposition, CH_4+CO, which formed in an almost equimolar amount, with no formation of CO_2.

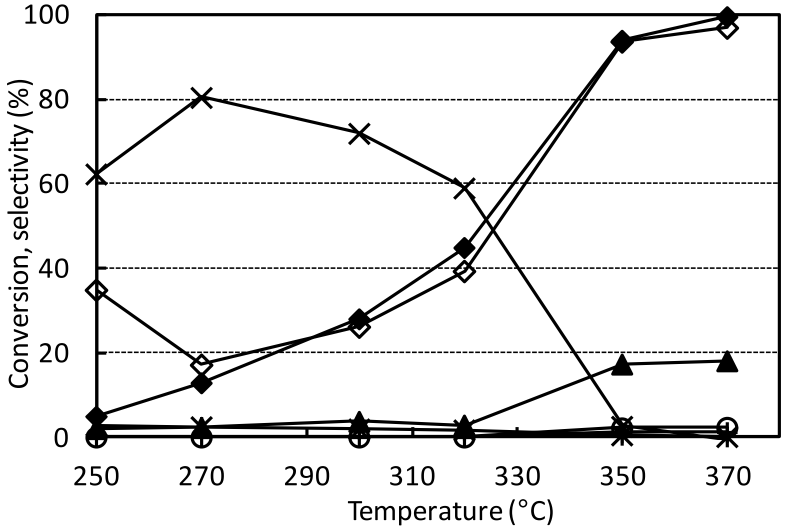


Figure 2. Effect of temperature on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, W/F ratio 1 g s mL^{-1}. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), CO (○), CO_2 (+), acetaldehyde (✱), and to Others (×, including methane, formed at T ≥ 350°C). Catalyst Co20/SiO2.

Therefore, the active Co/Ni phase deposited on silica is very selective at 350°C, but then it catalyzes the decomposition of ethanol or acetaldehyde, either because of a direct contribution of silica, or because of the specific nature of the Co active site that forms by the interaction with the silica support. The catalytic performance shown at 350°C remained stable for 4 hours, during an experiment aimed at the identification of short-term deactivation phenomena.

Concluding, we can say that alumina is not a good support, because of the several by-products produced under conditions at which ethanol conversion is higher than 90%. Conversely, the use of silica as the support leads to a very active and selective catalyst (selectivity close to 96-97% at almost total ethanol conversion), at 350°C. Lower temperatures lead to both lower conversion and selectivity, and higher temperatures lead to a decline of selectivity.

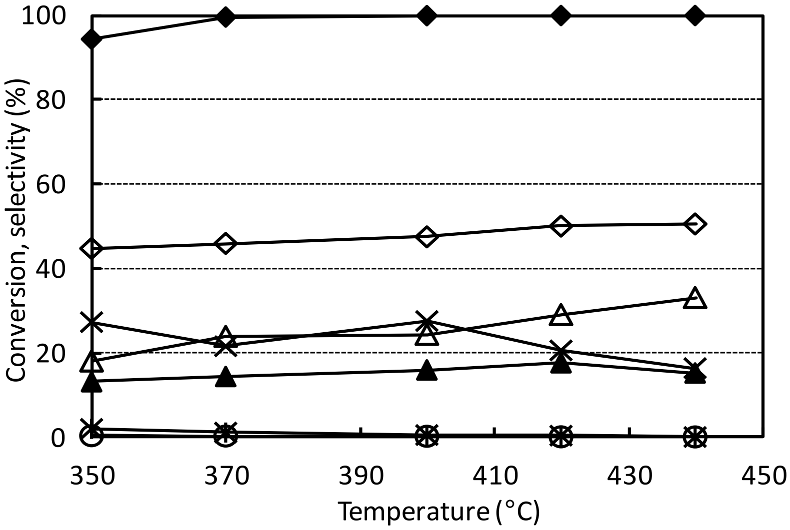


Figure 3. Effect of temperature on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, W/F ratio 1 g s mL^{-1}. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), to ethylene (△), to HCN (○), to acetaldehyde (✱), and to Others (✕). Catalyst Co20Ni3/Al2O3.

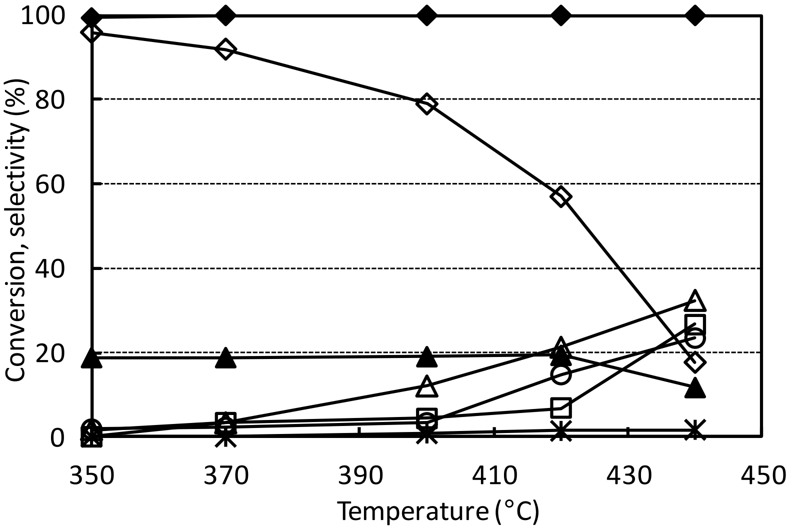


Figure 4. Effect of temperature on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, W/F ratio 1 g s mL^{-1}. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), acetaldehyde (✱), ethylene (△), CO (○), CH_4 (☐), and Others (✕). Catalyst Co20Ni3/SiO2.

We also carried out some experiments with the Co10/SiO2 catalyst; at 350°C, this catalyst gives 90% conversion only, with 89% selectivity to acetonitrile. By-products are CO, with smaller amounts of CO_2, HCN and ethylene. At 370°C, the conversion obtained is 98.6%, and the selectivity to acetonitrile is 92.8%, the remaining being CO + CH_4 and minor amounts of ethylene. Therefore, it seems fundamental to have a high coverage of the silica support, in order to develop an active and selective catalyst.

We then carried out experiments by decreasing the ammonia content in feed (in fact, under the conditions shown in Figures 1-4 ethanol is the limiting reactant), with the Co20Ni3/SiO2 catalyst, at 350°C and 1 g s mL^{-1} W/F ratio, feeding 5% ethanol and variable concentrations of ammonia; results are shown in Figure 5. It is shown that a decrease of ammonia partial pressure leads to a decline of ethanol conversion, and to the raise of selectivity to acetaldehyde; moreover, we also noticed the formation of CH_4 (included in Others) and CO (the products of acetaldehyde decomposition), and of small amounts of ethylene too. Therefore, an excess of ammonia is fundamental not only in the aim of pushing the conversion of ethanol and of the intermediately formed acetaldehyde, but also to selectively poison the sites that are responsible for the decomposition to CO and CH_4. This is a point that is worth of being investigated further; it may be hypotized that silica is responsible for the decomposition of ethanol or acetaldehyde, which explains why lower Co oxide content finally leads to a worse catalytic behavior.

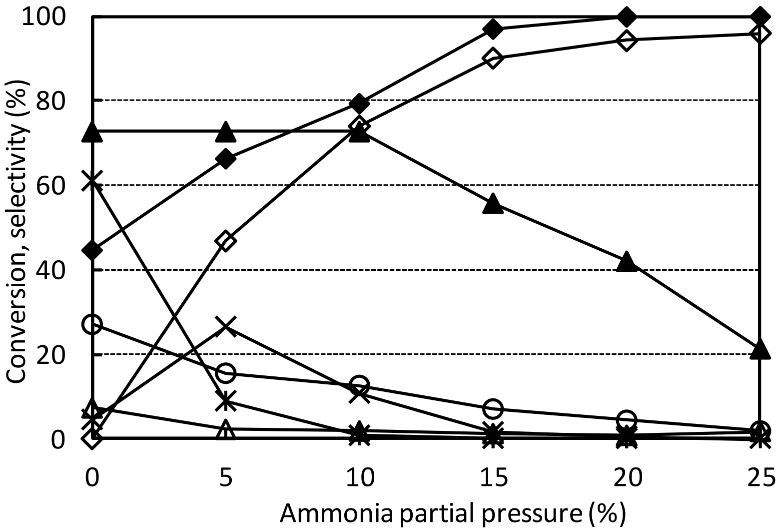


Figure 5. Effect of ammonia partial pressure on reactant conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, W/F ratio 1 g s mL^{-1}, temperature 350°C. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), CO (○), acetaldehyde (✱), ethylene (△), and to Others (✕, including CH_4). Catalyst Co20Ni3/SiO2.

We carried out lifetime experiments using the Co20/SiO2 catalyst, under the best conditions found: ethanol 5%, ammonia 25%, temperature 370°C, W/F ratio 1 g s mL^{-1}. Results are plotted in Figure 6. A deactivation phenomenon is shown: during the very first period of time-on-stream, the conversion falls from > 98% to ca 93%, and then it declines more slowly; this occurs with a concomitant decline of selectivity to acetonitrile, and a corresponding increase of selectivity to CO and acetaldehyde, whereas that to CO_2 becomes negligible. Methane forms with selectivity always lower than 0.5%; a worsening of the C balance also occurs. It can be assumed that the fresh oxidized catalyst (see the section dealing with the characterization of fresh and used catalysts) is extremely selective to acetonitrile, but the reduction of the Co oxide leads to a less active and less selective system. The decrease of activity is likely to be attributed to the accumulation of coke (as it will be shown later).

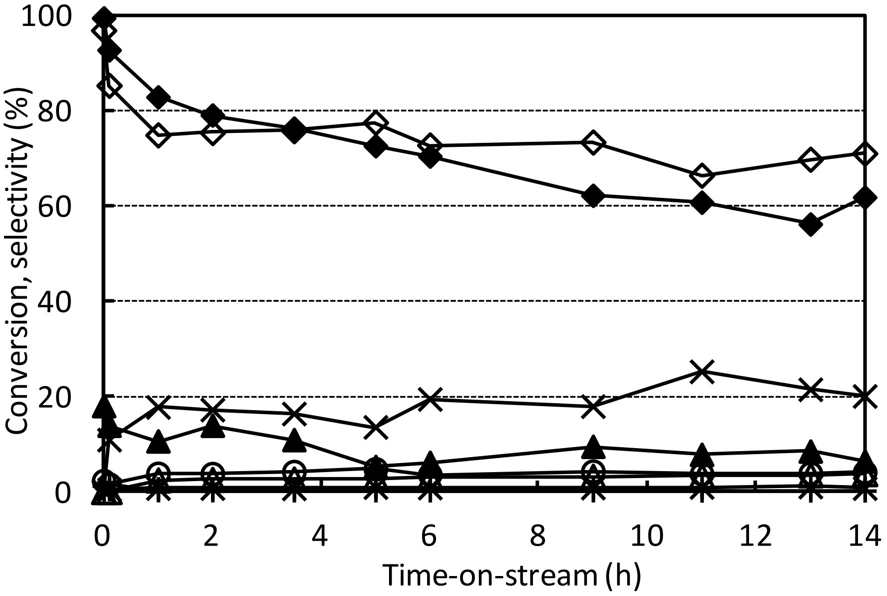


Figure 6. Effect of temperature on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, W/F ratio 1 g s mL^{-1}, temperature 370°C. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), CO (○), CO_2 (+), acetaldehyde (✱), ethylene (△), and to "loss in C balance" (×). Catalyst Co20SiO2.

The lifetime test was also carried out at 350°C (Figure 7). In this case, the decline of ethanol conversion is much slower than at 370°C, but still a decrease of selectivity to acetonitrile is observed. It is interesting to note that the decline of selectivity first occurs with a concomitant increase of selectivity to CO and CH_4; however, after a few hours the formation of these two latter compounds also decreases, and a rapid raise of the loss in C balance is shown. This confirms that the fully oxidized catalyst is very selective to acetonitrile (however, at 350°C conversion of ethanol is not complete; however also a 1.5% selectivity to CO_2 is observed with the fresh catalyst), but the incipient reduction of Co enhances the decomposition reactions leading to the formation of methane and CO. Thereafter, the catalyst starts to accumulate "coke" on the surface, with an increase of the "loss in C balance" and a concomitant progressive decline of selectivity to acetonitrile. Acetaldehyde is also formed (not shown in the Figure); its selectivity increases along with catalyst deactivation, but is always less than 1.5%. After 31 h time-on-stream, we also carried out a regeneration of the catalyst in air; in order to limit the local hot spots due to coke combustion, we raised slowly the temperature while feeding air from 300 to 450°C, with intermediate isothermal steps. Then we started the reaction again; indeed, an increase of conversion is observed after the regeneration treatment, however with a lower selectivity to acetonitrile, to CO and CH_4, and an higher formation of coke.

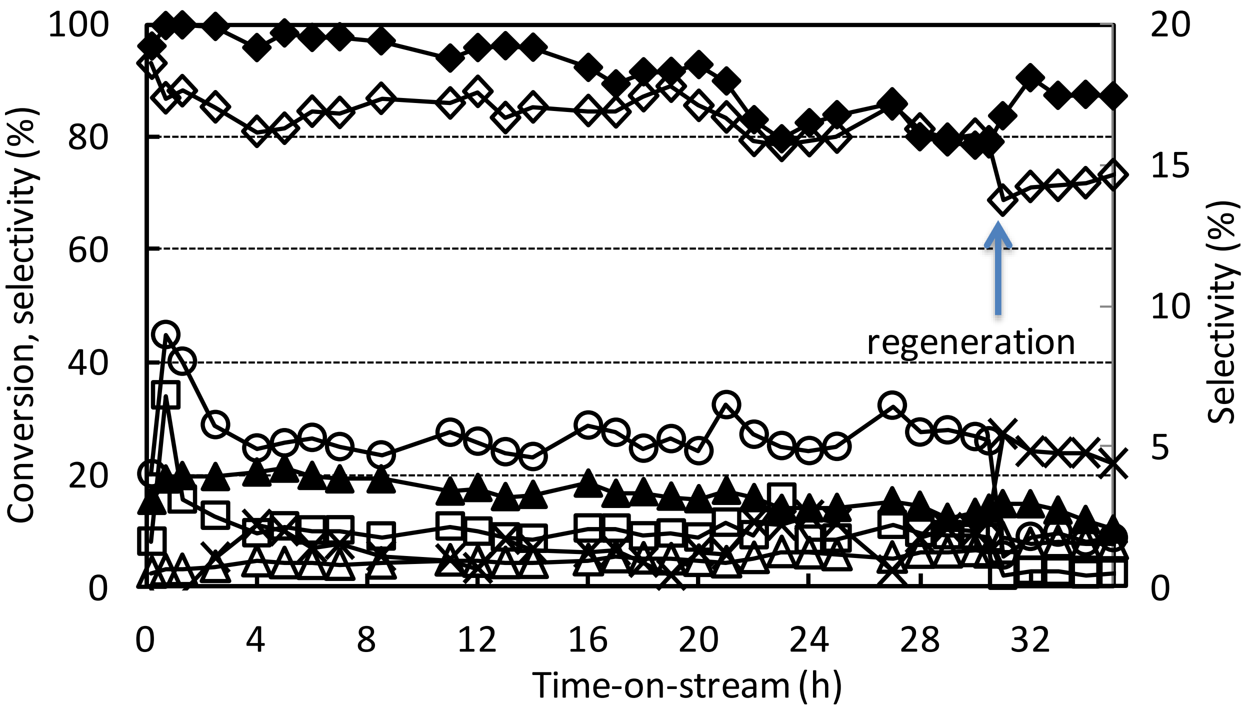


Figure 7. Effect of time-on-stream on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, W/F ratio 1 g s mL^{-1}, temperature 350°C. Symbols: ethanol conversion (◆, on left scale), ammonia conversion (▲, on left scale), selectivity to acetonitrile (◇, on left scale), CO (○, on right scale), ethylene (△, on right scale), methane (□, on right scale) and to loss in C balance (✕, on left scale). Note: CO_2 and acetaldehyde are also present (selectivity less than 1.5% each), but have been omitted. Catalyst Co20/SiO2.

The short-term lifetime experiments clearly highlight that the catalyst undergoes deactivation phenomena, likely because of the accumulation of carbonaceous residues on its surface, precursors for coke formation. The latter event is also attributable to the reduction of the Co ion by ethanol, which during the first hours reaction time is oxidized to acetaldehyde and CO_2, with coproduction of water (NH_3 probably is not oxidized, since we did not detect the formation of N_2). Therefore, we carried out some experiments with co-feeding of components which might limit the accumulation of coke and/or the reduction of Co, with the Co20/SiO2 catalyst. Specifically, we co-fed:

a) Steam, in the aim of carrying out the reforming of coke to CO/H_2 while the former is generated on the surface; moreover, it is known that metallic Co can be reoxidized by steam (water being reduced to H_2) under mild temperature conditions [33]. In fact, the oxidation of Co by steam is thermodinamically more favoured at low temperature, whereas the opposite reaction, the reduction of Co ion to metallic Co by H_2 is more favored at high temperature.

b) Hydrogen, in the aim of carrying out the reduction of coke to methane while it is generated on the catalyst surface. Some patents claim this operation in order to avoid the deactivation of Co-based catalysts [34]. One possible drawback might be the transformation of a non-reductive amination reaction into an amination-hydrogenation, with the hydrogenation of the intermediately formed ethanimine to ethylamine being preferred over its dehydrogenation into acetonitrile.

c) Oxygen, in the aim of burning the coke while being formed. In this case, one possible drawback would be the formation of CO_2 + H_2O by direct combustion of either ethanol or some intermediate or even acetonitrile itself.

Figure 8 shows the results of the experiments carried out with the co-feeding of steam; reaction conditions were: temperature 370°C, ethanol 5%, water 13%, W/F ratio 1 g s mL^{-1}. The presence of water has a strong negative effect on catalytic behavior. Ethanol conversion is much lower than that obtained without co-fed steam; moreover, the selectivity to acetonitrile is no higher than 40-45%, and declines after ca 10 hours time-on-stream. At the same time, an increase of selectivity to carbonaceous residues and to other heavy compounds is registered. Minor by-products are acetaldehyde and ethylene.

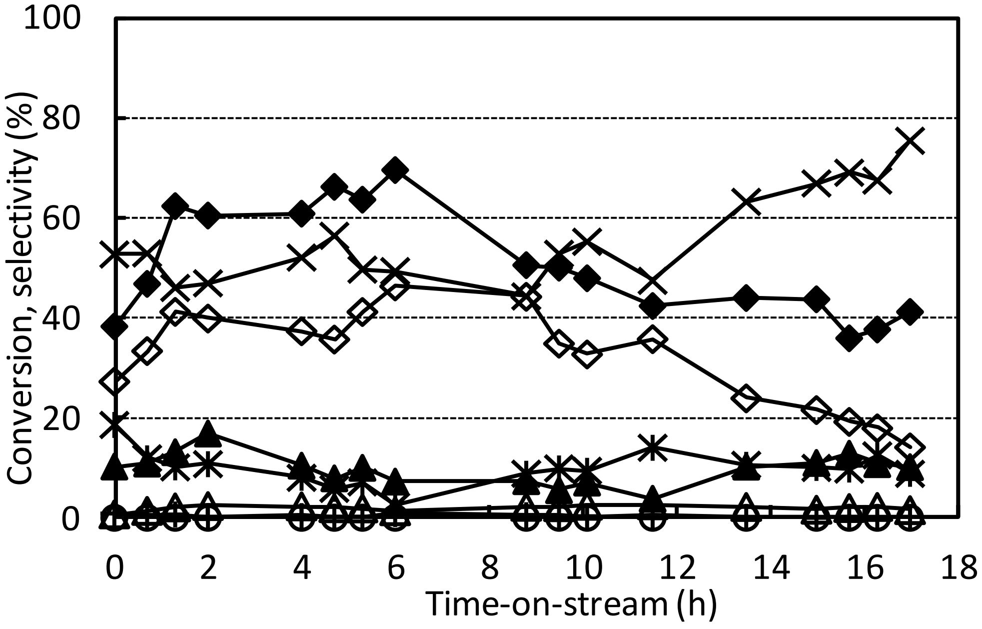


Fig conditions: 5% ethanol azeotrope, 25% ammonia, steam 13%, W/F ratio 1 g s mL^{-1}, temperature 370°C. Symbols: ethanol conversion (◆), ammonia conversion (▲), selectivity to acetonitrile (◇), CO (○), CO_2 (+), acetaldehyde (✱), ethylene (△), and to “loss in C balance” (✕). Catalyst Co20/SiO2.

The effect of oxygen co-feeding is shown in Figures 9, 10 and 11, for two different oxygen concentration in feed and different temperatures as well. The following effects are shown:

a) At 350°C, with 2% oxygen co-fed (Figure 9), during the first 10 h time-on-stream we observe a decline of ethanol conversion with a concomitant increase of selectivity to acetonitrile, and a decrease of selectivity to other "heavier" by-products, amongst which we identified acetamide and ethylacetate; indeed, after ca 10 h the selectivity to acetonitrile is above 90%, and that to other heavier by-products is close to zero. There are also minor amounts of CO (0.4% selectivity), CO_2 (4-5%), CH_4, (0.3%), ethylene (selectivity increasing from 0.5% to 1%) and acetaldehyde (3-4%). During the same period, oxygen conversion is almost total, but after ca 8 h it starts to decline.

b) After 10 h reaction time, however, the trends change: oxygen conversion becomes 100%, ethanol conversion is around 65%, but the selectivity to acetonitrile decreases rapidly down to 60%, with a parallel increase of selectivity to heavy compounds/carbonaceous residues and to CO_2.

Similar experiments were carried out at 370°C, using two different oxygen concentrations in feed (2%, Figure 10, and 4%, Figure 11). In the former case, the behavior shown is that of a continuous decrease of both ethanol conversion and selectivity to acetonitrile (also the ammonia conversion decreases), with a raise of selectivity to carbonaceous materials (from 0% to 25% after 20 h time-on-stream); worth of note, the C balance is very good during the first 3-4 h reaction time, a clear indication of the absence of C residues accumulating on the catalyst. The oxygen conversion remains very high and constant during the experiment time. Minor by-products are CO (selectivity increasing from 0.5 to 0.9%), CO_2 (increasing from 4 to 8%), acetaldehyde (decreasing from 3 to 2%) and ethylene (about 1.5-1.7% during the reaction time).

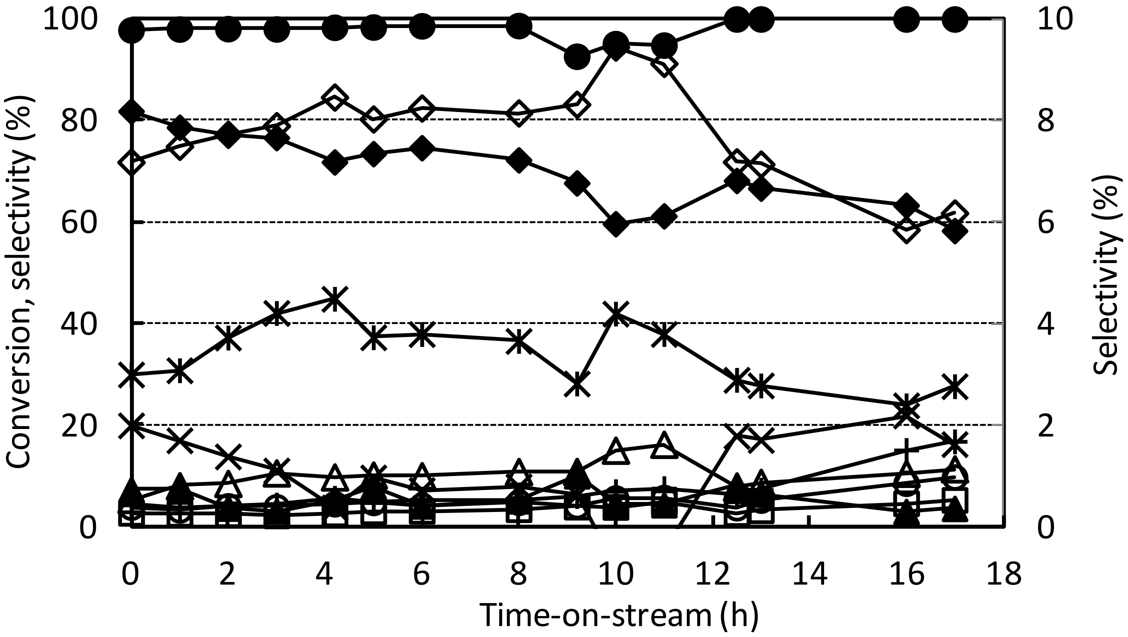


Figure 9. Effect of time-on-stream on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, oxygen 2%, W/F ratio 1 g s mL^{-1}, temperature 350°C. Symbols: ethanol conversion (◆, on left scale), ammonia conversion (▲, on left scale), oxygen conversion (●, on left scale), selectivity to acetonitrile (◇, on left scale), CO (○, on right scale), ethylene (△, on right scale), methane (□, on right scale), acetaldehyde (✱, on right scale), CO_2 (+, on left scale), and to loss in C balance (×, on left scale). Catalyst Co20/SiO2.

These results suggest that even though the oxygen co-fed may play an important role, however 2% concentration in feed is probably too low; in consequence of this, the final fraction of the catalytic bed is not contacted with oxygen, because the latter has been already completed converted in the top (upstream) section of the bed. Therefore, we carried out the experiment shown in Figure 11, with 4% oxygen in feed. We observe the following: (i) the ethanol conversion shows a slow decline (from 98% down to 91% after 21 h time-on-stream; (ii) the selectivity to acetonitrile first increases from 88 to 93% and then declines from the latter value down to 80%; these changes occur with a concomitant and complementary change of CO_2 selectivity, which first decreases down from 12 to 6% and then increases again up to 12%; (iii) other by-products are: acetaldehyde (selectivity increasing from 0.6 to 1.7% and then decreasing down to 1%), CO (selectivity around 1%), CH_4 (0.3%), ethylene (increasing from 0.6 to 1.3%); (iv) ammonia conversion is stable, and oxygen conversion first decreases from 100 down to 93%, and then raises up to 98%; (v) the C balance is very good during the first 15-16 h reaction time (with an amount of C residues which is close to 0%), and finally is systematically around 95-97% (3-5% of heavy compounds or carbonaceous residue).

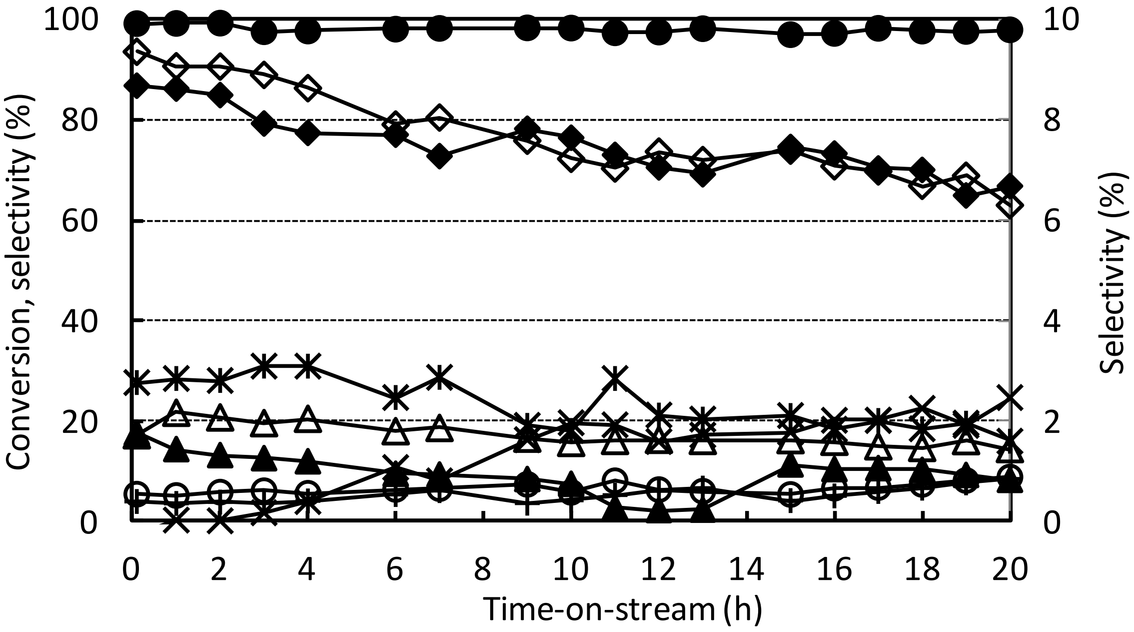


Figure 10. Effect of time-on-stream on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, 2% oxygen, W/F ratio 1 g s mL^{-1}, temperature 370°C. Symbols: ethanol conversion (◆, on left scale), ammonia conversion (▲, on left scale), oxygen conversion (●, on left scale), selectivity to acetonitrile (◇, on left scale), CO (○, on right scale), ethylene (△, on right scale), acetaldehyde (✱, on right scale), CO_2 (+, on left scale), and to loss in C balance (×, on left scale). Catalyst Co20/SiO2.

The results obtained can be interpreted as follows:

a) At 350°C, with ethanol and ammonia only (Figure 7), the fresh catalyst (containing the spinel Co_3O_4 as the main component of the active phase, see the characterization section) is in part reduced during the very first reaction time (from 0 to ca 2 h), by reduction of the Co^{3+} species to Co^{2+}; this leads to an initial increase of conversion but to a decline of selectivity to acetonitrile, because of the higher formation of CO and methane; during this period, however, there is no accumulation of C residues.

b) After ca 2h, the partially reduced catalyst starts to accumulate C residues, precursors for coke formation, and the activity starts to decline; first, this leads to a decline of selectivity to acetonitrile, CO and CH_4; however, after ca 4 h reaction time, the distribution of products remains substantially unchanged until 20 h time-on-stream, while the conversion keeps on decreasing. These results indicate that the spinel phase is the most selective catalyst for acetonitrile formation, but that the unavoidable reduction of Co^{3+} is the event which leads to the formation of coke.

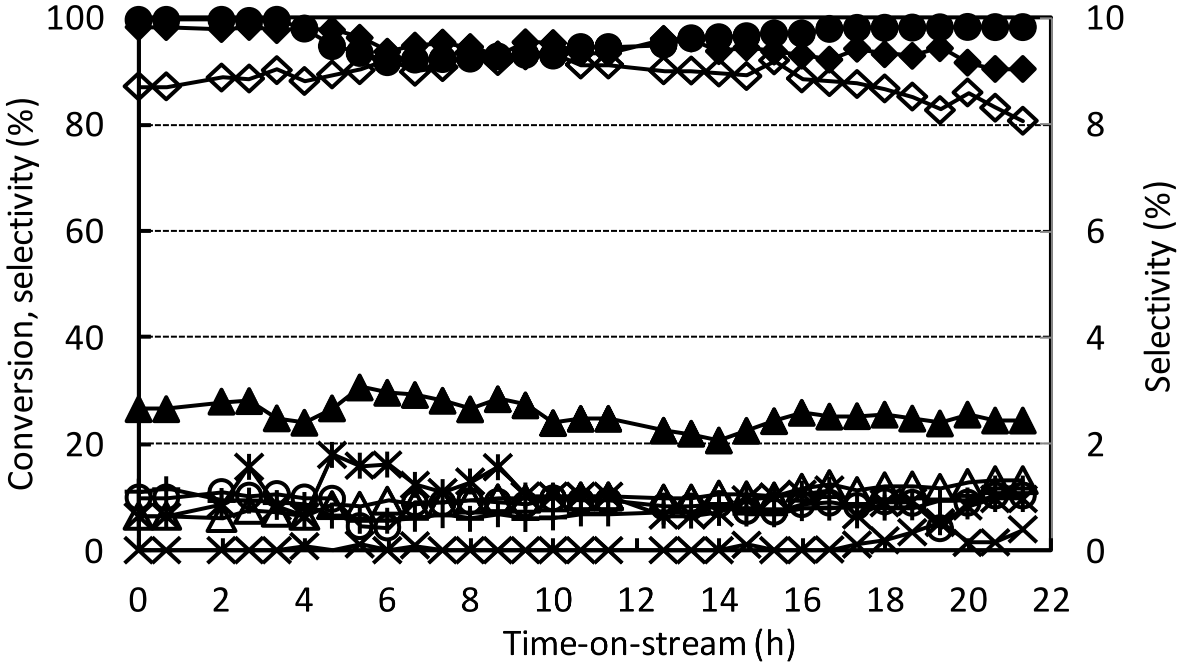


Figure 11. Effect of time-on-stream on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, 4% oxygen, W/F ratio 1 g s mL^{-1}, temperature 370°C. Symbols: ethanol conversion (◆, on left scale), ammonia conversion (▲, on left scale), oxygen conversion (●, on left scale), selectivity to acetonitrile (◇, on left scale), CO (○, on right scale), ethylene (△, on right scale), acetaldehyde (✱, on right scale), CO2 (+, on left scale), and to loss in C balance (×, on left scale). Catalyst Co20/SiO2.

c) The presence of oxygen should help in keeping the catalyst oxidized, with high activity and selectivity to acetonitrile. However, results obtained (Figure 9) provide contrasting information. In fact, the catalyst shows an initial low selectivity to acetonitrile, with 20% selectivity to other oxydized by-products (acetamide and ethylacetate). On the other hand, during the first 10 h reaction time the selectivity increases, with a concomitant progressive decline of selectivity to the cited by-products; meanwhile, the selectivity to CO_2 remains low. Since the oxidation of the spinel to Co_2O_3 is unlikely, we can formulate the hypothesis that three different phenomena overlap: (i) the formation of C residua, probably due to the fact that the oxygen co-fed is too low to keep the entire catalytic bed "clean"; this event causes the continuous decrease of both ethanol conversion and selectivity to acetonitrile; (ii) the action of oxygen that keeps the spinel oxidized, contrasting the reducing effect of ethanol; this effect has not much role on activity, but is important for selectivity since it tends to contrast and even reverse the negative effect of coke accumulation on selectivity; and (iii) the formation of oxidized by-products which also lower the selectivity to acetonitrile. On the fresh spinel, the third effect is the prevailing one, which explains the low selectivity to acetonitrile during the 0-4 h reaction time, and the formation of acetamide and ethylacetate, both compounds being possibly formed from acetic acid. However, this effect soon vanishes, probably because the reactivity of the spinel starts to be affected by both a reduction of the surface and the formation of some coke. The second effect is the prevailing one during the intermediate reaction time, from 4 to 10 h, at which the selectivity to acetonitrile is relatively high. During this period, still the amount of coke is not relevant, and the catalyst is not strongly reduced yet. Finally, the first effect is the prevailing one after 10 h reaction time; this is likely unavoidable, because even though the coke accumulation (and the Co^{3+} reduction as well) are probably slowed down due to the presence of oxygen, however they are not completely avoided.

d) At 370°C, with only ethanol and ammonia fed (Figure 6), the only evident phenomena is the progressive decline of both activity and selectivity, and the concomitant increase of the amount of carbonaceous residues, precursors for coke formation; the latter is very rapid at the beginning of the reaction time, and then, although still present, becomes slower.

e) In the presence of water (Figure 8), the picture changes completely; the conversion decreases dramatically, an event which may be due to a competition between ethanol and water for adsorption over the same sites, but the most negative effect is on the distribution of products. Different hypothesis can be put forward, such as (i) an increased catalyst acidity, because of the in-situ generation of hydroxylated species; or (ii) the hydration of acetonitrile, with formation of compounds finally converted into heavy compounds.

f) With 2% oxygen co-fed only (Figure 10), the picture is not much different from that shown without oxygen. However, it is worth noting that on the fresh catalyst, and during the initial period (0-3 h reaction time), there is no formation of C residues. In practice, the presence of oxygen slows down both the deactivation and the loss of selectivity, which however still are both present.

g) Co-feeding 4% oxygen considerably changes the picture (Figure 11). The behavior is now very similar to that shown in Figure 9 (T 350°C, 2% oxygen co-fed); therefore, the results here can be interpreted in a similar way. It is important to note that the amount of oxygen that gives rise to the above mentioned events (i.e., the overlapping of different phenomena), is a function of the reaction temperature used.

We finally carried out experiments by co-feeding hydrogen, at 370°C; results are shown in Figures 12 and 13. With 4% hydrogen co-fed, a slight decline of conversion is shown during the first 10 h, which however becomes quicker afterwards; at the same time, the selectivity to acetonitrile first increases during the first 2 h reaction time, then remains approximately constant, and finally declines rapidly. The initial increase of selectivity to acetonitrile corresponds to a similar decline of selectivity to methane, whereas the acetonitrile decrease is accompanied by a concomitant increase of the selectivity to carbonaceous residues (coke). This indicates that the presence of hydrogen facilitates the methanation of coke precursors, a process which is very efficient at the beginning of reaction time; afterwards, however, the methanation becomes less efficient, and coke starts to accumulate on catalyst surface. Therefore, the amount of hydrogen co-fed finally is not enough to contrast the accumulation of coke. We also carried out a regeneration treatment of the catalyst, and then started up the reaction again. As shown in Figure 12, this treatments leads to a recovery of both ethanol conversion and yield to acetonitrile (which however is 82% only) and to methane.

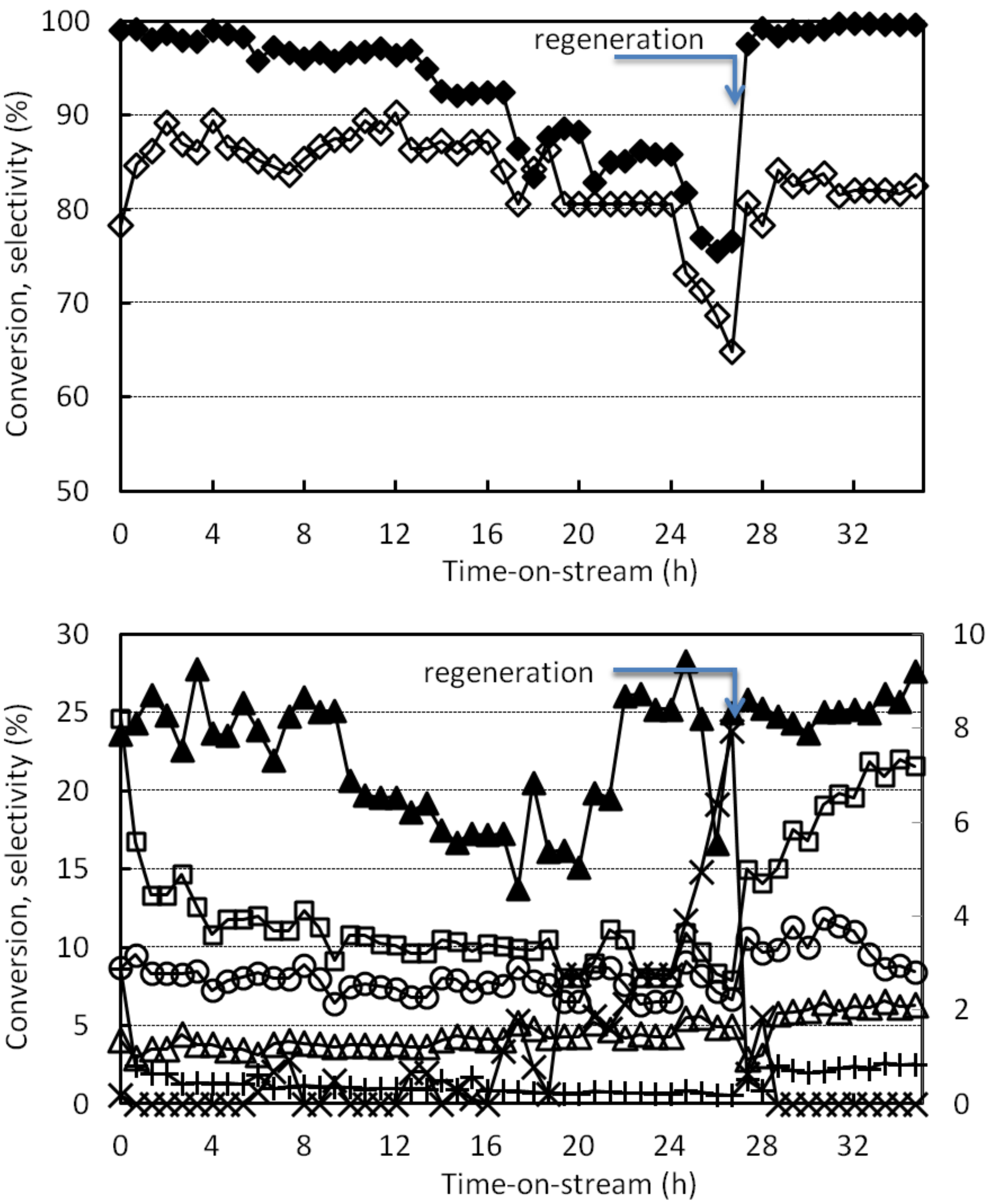


Figure 12. Effect of time-on-stream on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, hydrogen 4%, W/F ratio 1 g s mL^{-1}, temperature 370°C. Symbols: ethanol conversion (◆, on left scale), ammonia conversion (▲, on left scale), oxygen conversion (●, on left scale), selectivity to acetonitrile (◇, on left scale), CO (○, on left scale), CH_4 (□, on right scale), ethylene (△, on right scale), CO_2 (+, on right scale), and to loss in C balance (×, on left scale). Catalyst Co20/SiO2.

Figure 13 shows the results obtained with 10% hydrogen co-fed. In this case, the ethanol conversion remains stable, in the range 95 to 99%, over the entire reaction time examined, but still the selectivity to acetonitrile declines, and also with the fresh catalyst is no higher than 75%; an increase of selectivity to C residues is shown. It is also important to notice that during experiments with co-fed hydrogen we never registered the formation of ethylamine.

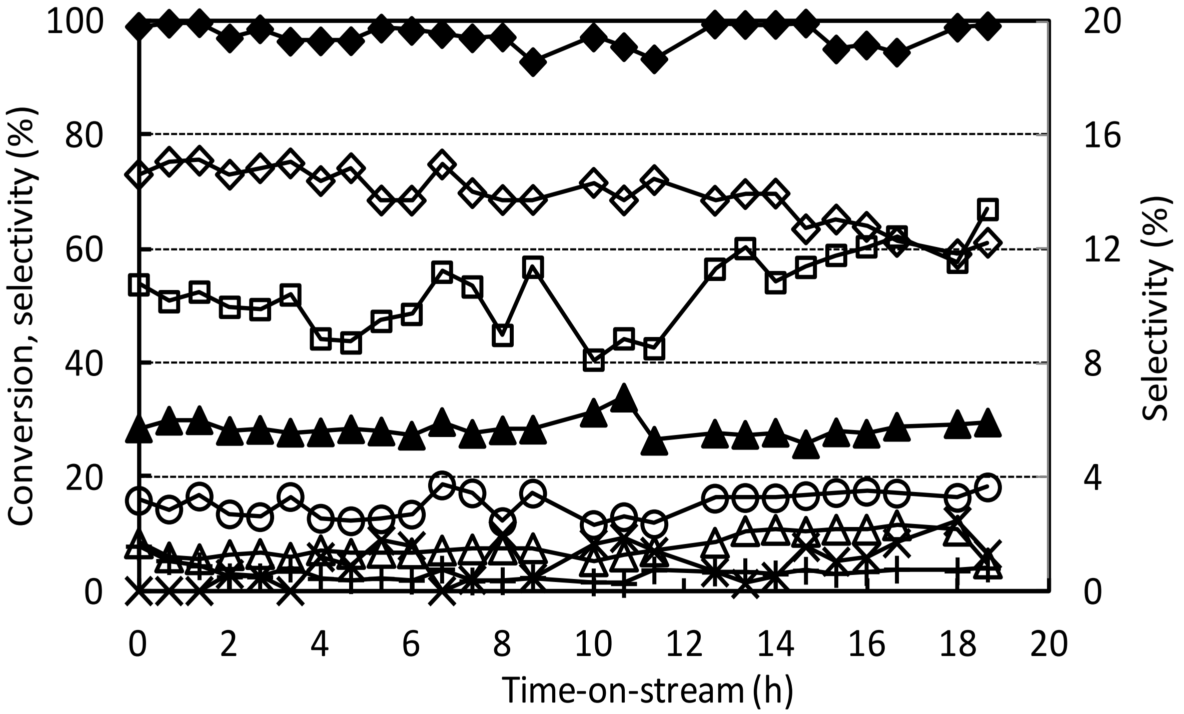


Figure 13. Effect of time-on-stream on reactants conversion and selectivity to products. Reaction conditions: 5% ethanol azeotrope, 25% ammonia, hydrogen 10%, W/F ratio 1 g s mL^{-1}, temperature 370°C. Symbols: ethanol conversion (◆, on left scale), ammonia conversion (▲, on left scale), oxygen conversion (●, on left scale), selectivity to acetonitrile (◇, on left scale), CO (○, on left scale), CH_4 (□, on right scale), ethylene (△, on right scale), CO_2 (+, on right scale), and to loss in C balance (×, on left scale). Catalyst Co20/SiO2.

Figures 14 and 15 compare the conversion of ethanol and the selectivity to acetonitrile at 370°C, in function of time-on-stream, for the Co20/SiO2 catalyst, using the different co-fed gas-phase promoters. It is shown that co-feeding either 10% hydrogen or 4% oxygen allows maintaining a relatively high ethanol conversion, whereas co-feeding 4% hydrogen only has a less relevant, although non-negligible, effect. Adding 2% oxygen only has a marginal effect, whereas co-feeding steam clearly has a negative effect.

On the other hand, co-feeding 10% hydrogen has no improvement effect on acetonitrile selectivity, compared to the test without gas-phase promoter, whereas co-feeding either 4% hydrogen or 4% oxygen allows maintain the selectivity to acetonitrile above 80% for 20 h time-on-stream. No effect on selectivity to acetonitrile is observed in the presence of 2% oxygen, and the presence of steam again leads to a worse selectivity.

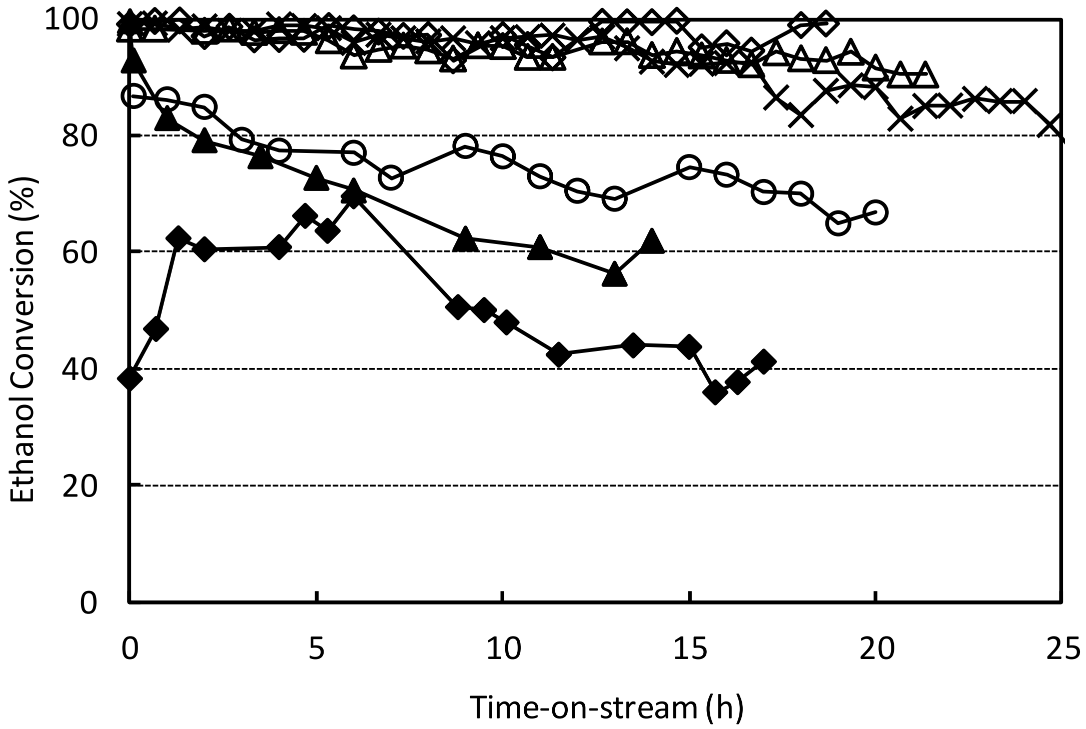


Figure 14. Effect of time-on-stream on ethanol conversion with the Co20/SiO2 catalyst, at 370°C, and various co-fed components. Feed: 5% ethanol, 25% ammonia. Symbols: none (▲), 13% H2O (◆), 4% H2 (✕), 10% H2 (◇), 2% O2 (○), 4% O2 (△). Catalyst Co20/SiO2.

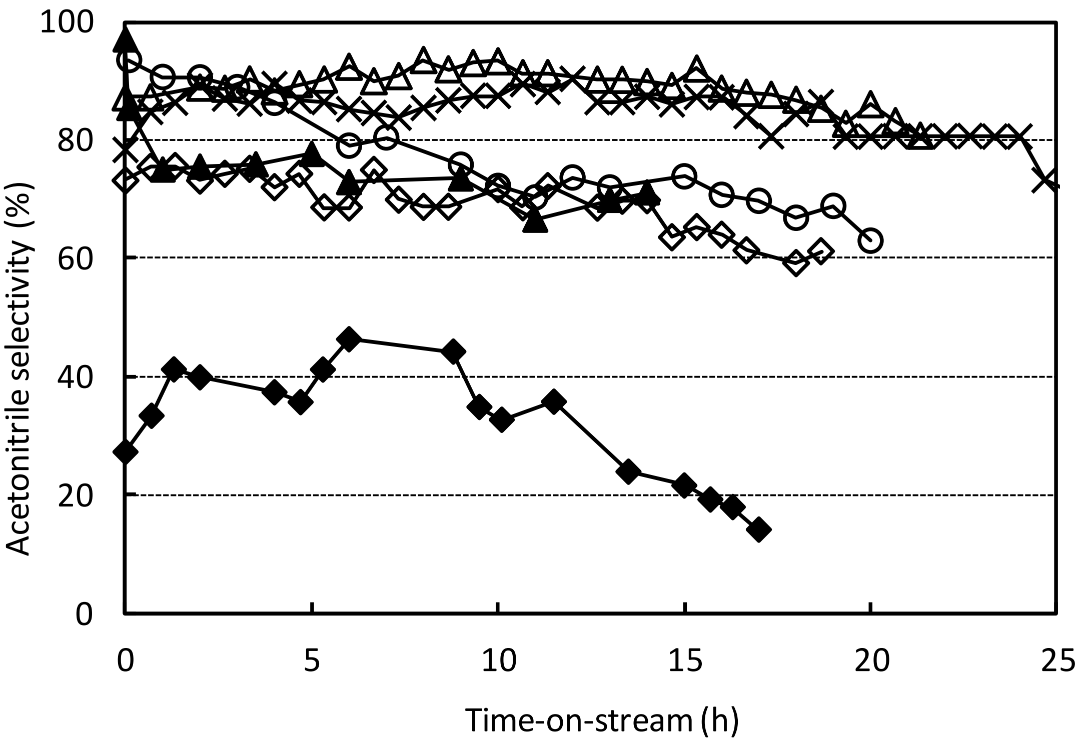


Figure 15. Effect of time-on-stream on acetonitrile selectivity with the Co20/SiO2 catalyst, at 370°C, and various co-fed components. Feed: 5% ethanol, 25% ammonia. Symbols: none (▲), 13% H2O (◆), 4% H2 (✕), 10% H2 (◇), 2% O2 (○), 4% O2 (△). Catalyst Co20/SiO2.

Some experiments were carried out using the Cu10/SiO2 and Cu20/SiO2 catalysts. With both samples, both ethanol conversion and selectivity to acetonitrile were very low. For example, with the former catalyst ethanol conversion is 60% at 430°C (W/F ratio 1 g s mL-1, feed 5% ethanol, 25% ammonia), with 5% selectivity to acetonitrile; best selectivity is 28%, at 320°C (ethanol conversion 26%). We registered the formation of several by-products, amongst which the most important are: butyronitrile, 4-butenenitrile, 2-butenenitrile, 3-methylpyridine, diethylamine, acetamide, 1,2-dimethylaziridine, lactonitrile, besides ethylene and diethylether; acetaldehyde is not formed. Results were not better with the Cu20ISiO2 catalyst; in this case, we carried out experiments in function of time-on-stream; at 270°C, the initial ethanol conversion was 54%, but it rapidly declined, and was 10% only after 1.5 h reaction time. The initial selectivity to acetonitrile was remarkable (73%), but then decreased down to less than 20% in a very short time. At these conditions, the same N-containing compounds already identified with the Cu10/SiO2 catalyst were also found, and also 3-4% selectivity to acetaldehyde was registered.

2.3 The characterization of catalysts

In Figure 16a and 16b are shown the XRD patterns of Co20Ni3 supported on γ-alumina and silica, respectively. In both samples we can see the reflects at 18.9, 31.2, 36.8, 38.5, 44.8, 55.6, 59.3, 65.2, 78.3 °2θ, attributable to the Co_3O_4 spinel [34], while reflects at 45.8, 67.0 °2θ are characteristic of γ-alumina [35] (Figure 16a), and signal at 21.9 °2θ is characteristic of silicon oxide [36] (figure 16b). Regarding the nickel, in this case it was not possible to identify clearly the presence of specific crystalline phases. In literature [19a] it is reported that the presence of small amounts of nickel favor the dispersion of cobalt on the surface of the catalyst.

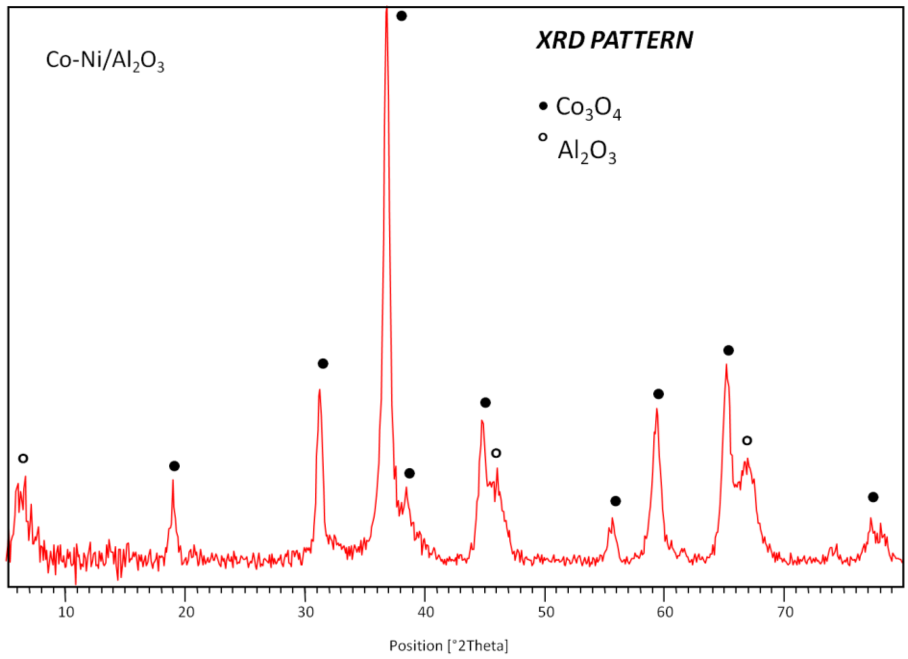


Figure 16a. XRD patterns of Co20Ni3 supported on γ-alumina.

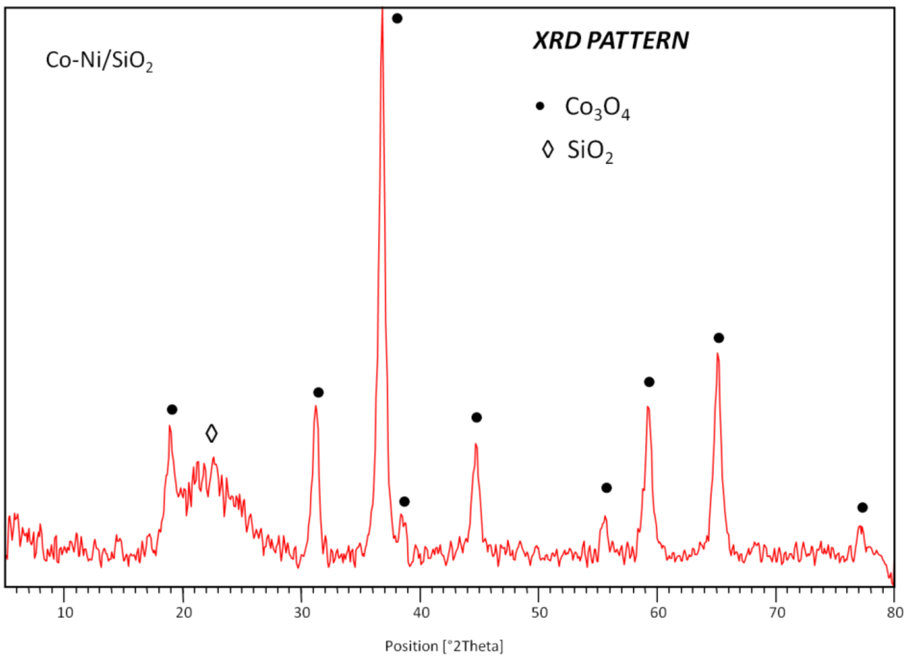


Figure 16b. XRD patterns of Co20Ni3 supported on silica.

Figure 17 shows the Raman spectra of the Co20/SiO_2 sample before reaction and after reaction. Relating to the catalyst before reaction (blue line) the following bands were found: 689, 618, 519, 480, 192 cm^{-1} Raman shift. According to the literature [37] it can be concluded that Raman shift found, except that at 192 cm^{-1} correspond to those typical of the spinel Co_3O_4. Probably the signal at 192 cm^{-1} is attributable to the silica support. The red spectra shows the surface catalyst after 14 hours of reaction at 370 °C; we can see clearly two bands at 1593 and 1319 cm^{-1} typical of the ordered coke (crystalline). Because of the high drift line, it is impossible to attribute the bands in the spectrum of fresh catalyst (blue line). However, it is important to note that any information concerning cobalt on the surface of the catalyst after reaction is lost due to the presence of crystalline coke that generates the intense drift signal.

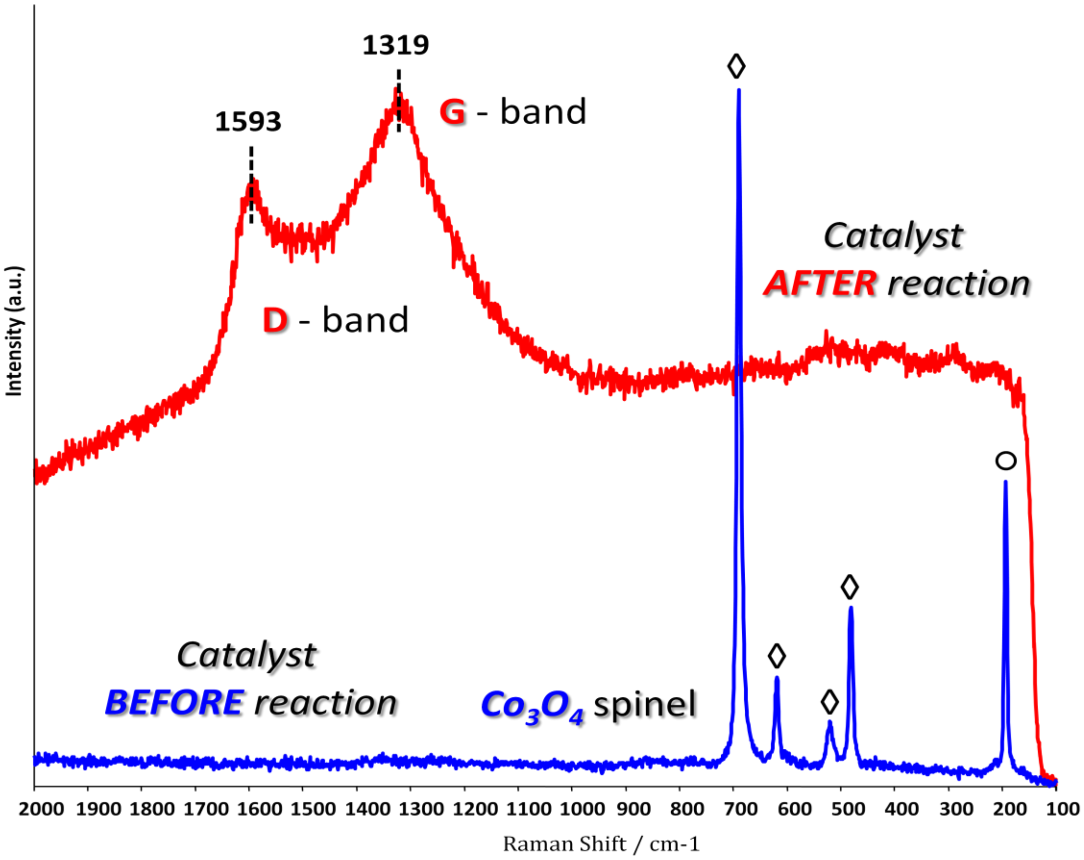


Figure 17. Raman spectra of the Co20/SiO_2 ◊ = Co_3O_4 spinel. ○ = Silica. Before reaction blue line, after reaction red line.

Figure 18 shows the temperature programmed oxidation profile of the Co20/SiO_2 sample after reaction. It is observed a consumption of oxygen at about 300 °C (peak with shoulder) and about 480 °C, at 920 °C; a negative peak is observed, probably due to the development of CO or CO_2, which, therefore, may be associated the combustion of coke formed on the surface of the catalyst. In literature [39] the first two peaks are attributed to the oxidation of adsorbed heavy compounds, coke precursors and amorphous coke; however if this were the case, should be negative due to the formation of CO and CO_2, hence is more likely attributable to the oxidation of Cobalt.

Figure 17 shows the XPS spectra of the Co20/SiO_2 sample before reaction (fresh calcined catalyst) and after prolonged reaction in ethanol amination-dehydrogenation. According to the literature [40], the shifting between spin-orbital components Co $2p_{3/2}$ and Co $2p_{1/2}$ (ΔBE) demonstrates that in the used catalyst there is an excess of Co^{2+} on the surface and the intense peak P2 as well as its satellite P6 indicates the CoO form. However, no metallic Co is present. Therefore, the used catalyst contains both CoO and the spinel Co_3O_4. The latter compound is instead the only one present in the fresh calcined sample. This indicates that the catalyst during reaction undergoes only a minor change of the oxidation state of Co, but there is no deep reduction down to metallic Co. In other words, metallic Co cannot be active species in ethanol amination-dehydrogenation.

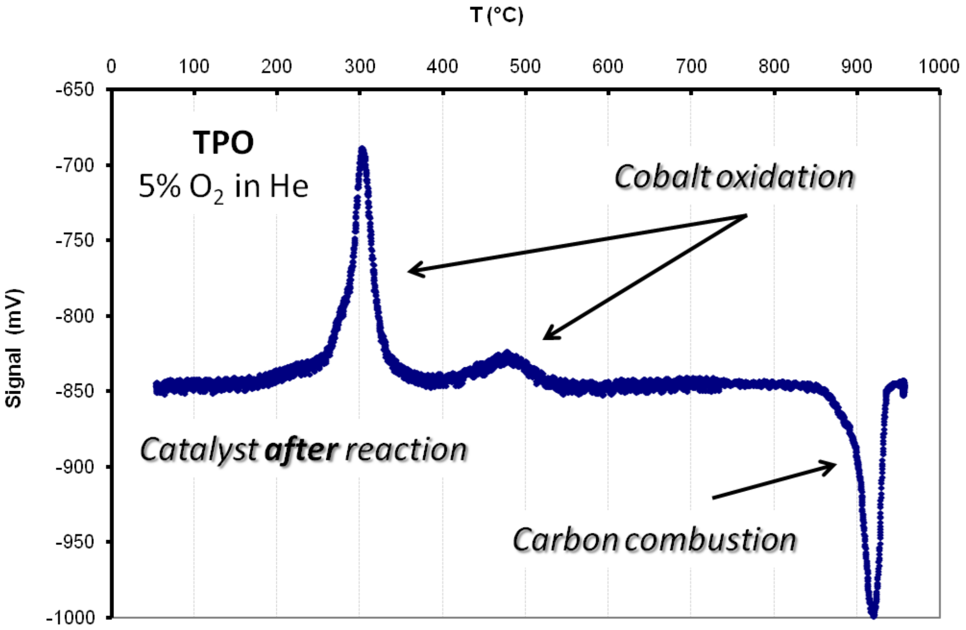


Figure 17. TPO analysis of Co20/SiO_2 sample after reaction. Used gas 5% of O_2 in He.

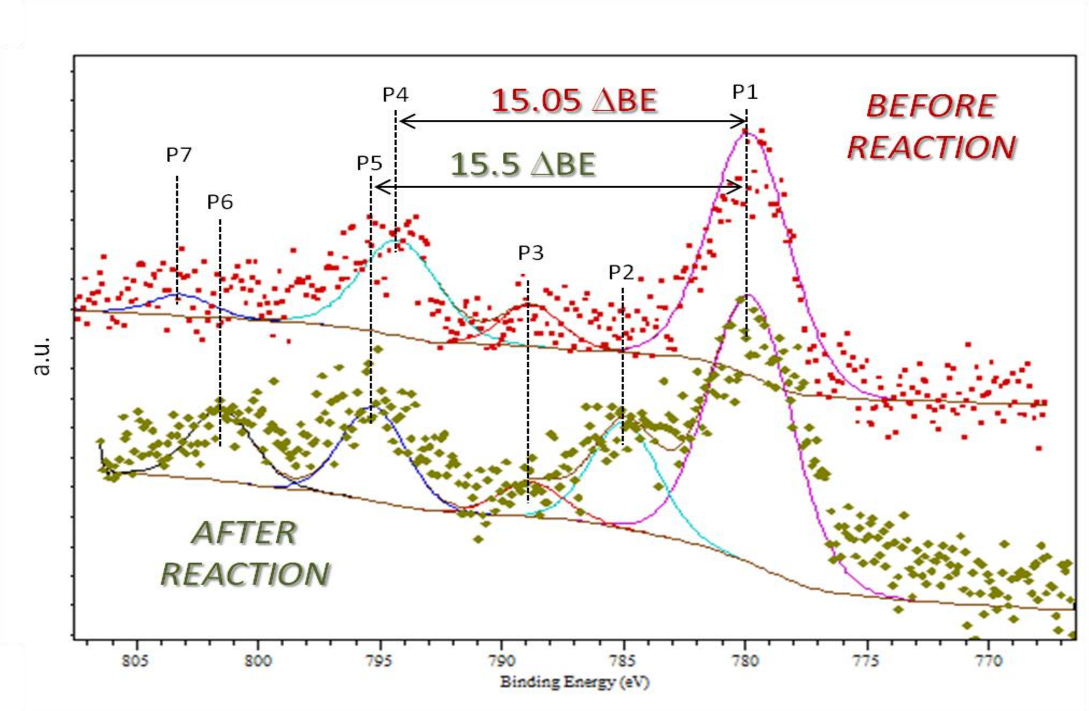


Figure 17. XPS spectra of the Co20/SiO$_2$ sample before and after reaction. **P1** = Main spin-orbital component Co 2p3/2 **P2** = Shake-up Co^{II} **P3** = Satellite peak Co^{III} **P4 /P5** = Main spin-orbital component Co 2p1/2 **P6** = Satellite peak Co^{II} **P7**= Satellite peak Co^{III}

Conclusions

We have investigated the reactivity of catalysts based on Co oxide as the main active component for the direct non-reductive amination of ethanol to acetonitrile. The optimal catalyst is made of Co oxide supported over silica, whereas supporting over alumina leads to poor catalytic performance, in contrast with what reported in the literature. The deactivation of the catalyst, mainly due to the accumulation of C residues, precursors for coke formation, can be slowed down by the co-feeding of either hydrogen, or oxygen; in the latter case, the decrease of the deactivation rate is less relevant than with hydrogen, but the selectivity to acetonitrile is higher. The characterization of catalysts evidenced that the spinel Co$_3$O$_4$ (the main component of the fresh calcined catalyst) is only in part reduced during reaction, and there is no formation of metallic Co.

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