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Catalysts study of adipic acid synthesis from 1,6-hexanediol

Tesi di laurea sperimentale

Candidato

NOEMI CAPECE

RELATORE

PROF. FABRIZIO CAVANI

CORRELATORE

DR ROBERT WOJCIESZAK

PROF. SÉBASTIEN PAUL

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Abstract

Sustainable chemicals currently have a very limited market share due to current low production but biomass is expected to become one of the major renewable energy and fine chemicals sources in the coming years. Bearing in mind the compromise of all nations to climatic change remediation, the industries will need to use efficient catalysts and green processes to meet the requirements of emissions and efficiency. This project is expected to develop new catalysts to convert 1,6-hexanediol to adipic acid through a green approach based on the "nano-catalysis" and "green chemistry" concepts. Supported Au and Pd nanoparticles were used to study one-pot reaction of HDO oxidation to AA using O_2 as a final oxidant and H_2O as a solvent. Catalytic results showed that under low pressure O_2 atmosphere and low temperature ($< 120°C$) AuNPs supported on basic-supports are more active then acid and amphoteric oxides. The effect of basic oxide (MgO) addition to MgF_2 was studied. The study showed that doping of MgF_2 with MgO increased significantly the activity of the catalyst. The best results were obtained with the $Au/0.4MgF_2$-$0.6MgO$ sample, which gave the selectivity to AA of 33% at HDO conversion of 62%.

Summmury

Abbreviations and acronyms

HDO: 1,6-hexanediol

HA: 6-hydroxyhexanoic acid

AA: adipic acid

GA: glutaric acid

SA: succinic acid

HP: hydrogen peroxide

X: conversion

Y: yield

S selectivity

CB: carbon balance

M: metal

NPs: nanoparticles

VO: vapor phase oxidation

LO: liquid phase oxidation

HPLC: high performance liquid chromatography

TEM: Transmission Electronic Microscopy

TPD: temperature programmed desorption

XRF: X-ray fluorescence

XRD: X-ray diffraction

1. Introduction

Adipic acid is one of the most important aliphatic dicarboxylic acid with the highest world production and it is primarily used as a starting reagent in the preparation of nylon-6,6 polyamide, fibers, plasticizers, food additives and many other applications[1]. Global production in 2014 reached 2839 ktons and demand for adipic acid continues to grow with about 2% increase each year. It is due also to the non-nylon applications, which are growing faster than the nylon sector[2,3].

Adipic acid is generally synthesized using HNO_3 in a two-step process involving oxidation of cyclohexanone and cyclohexanol (KA oils) and which is seriously harmful to the environment leading huge mark on global warming. Indeed, the nitrous oxide (N_2O) produced in this process is an unavoidable stoichiometric waste that is commonly designed as a major factor of the global warming and ozone depletion. Moreover, it is also responsible for acid rains and smog. Every years more than 400,000 metric tons are emitted into the atmosphere, which corresponds to about 5–8% of the worldwide N_2O production[4].

Actually, one of the most difficult challenges of the industrial chemistry is the development of new sustainable and "green" processes, due to increasing environmental problems, which affect our planet. One of the main objectives in the reduction of the environmental impact of this process is the use of greener oxidizing agents and renewable starting materials. With the purpose to move on this direction, the main aim of this project was the design of an heterogeneous catalyst to carry out the synthesis of adipic acid starting from 1,6-hexanediol, as a possible alternative to the traditional process of the oxidation of cyclohexane obtained from hydrogenation of benzene. 1,6-hexanediol could be easily obtained from cellulose derived from lignocellulosic biomass wastes[5], making it a promising feedstock for the production of biobased chemicals and energy[6,7,8,9,10].

2. Adipic Acid

2.1 Physical and chemical properties of adipic acid

At room temperature and atmospheric pressure, adipic acid is a colourless, odourless crystal having an acidic taste. It is highly soluble in methanol and ethanol, soluble in water and acetone, and only slightly soluble in cyclohexane and benzene. It is normally crystallized from aqueous solutions as flat, slightly elongated, hexagonal, monoclinic plates. Adipic acid (IUPAC name hexanedioic acid) has a molecular weight of 146,14g/mol, pKa values of 4,43 and 5,41 and chemical formula $HOOC(CH_2)_4COOH$ $(C_6H_{10}O_4)$[11]. Its melting point is 152°C and boiling point is 338°C. It is stable in air in mild conditions, however if heated over 200°C it decomposes and volatile acidic vapours of valeric acid and other substances can be produced[12]. The tendency of adipic acid to form a cyclic anhydride by loss of water is much less pronounced compared to glutaric or succinic acids. Its carboxylic acid groups easily react to form salts, esters, amides, nitriles, etc. It is quite stable to most oxidizing agents, as demonstrated by its production in nitric acid. However, nitric acid can attack adipic acid auto-catalytically above 180°C, producing carbon dioxide, water, and nitrogen oxides. Its fundamental chemical and physical properties are listed in Table 1[11].

Table 1: Chemical and physical properties of Adipic acid [11]

Property	Value
molecular formula	$C_6H_{10}O_4$
molecular weight	146.14
melting point, °C	152.1 ± 0.3
specific gravity	1.344 at 18°C (sol)
	1.07 at 170°C (liq)
coefficient of cubical expansion, K^{-1}	4.0×10^{-4} at 35–150°C (sol)
	10.3×10^{-4} at 155–168°C (liq)
vapor density, air $= 1$	5.04
vapor pressure, Pa^a	
solid at °C	
18.5	9.7
32.7	19.3
47.0	38.0
liquid at °C	
205.5	1,300
216.5	2,000
244.5	6,700
265.0	13,300
specific heat, kJ/kg K^b	1.590 (solid state)
	2.253 (liquid state)
	1.680 (vapor, 300°C)
heat of fusion, kJ/kg^b	115
entropy of fusion, J/mol K^b	79.8
heat of vaporization, kJ/kg^b	549
melt viscosity, mPa s($=$cP)	4.54 at 160°C
	2.64 at 193°C
heat of combustion, kJ/mol^b	2,800

2.2 Adipic acid uses and production

Adipic acid is a high-volume bulk petrochemical commodity (1650€/t). It is the most important aliphatic dicarboxylic acid in the chemical industry and ranks as one of the top 50 chemicals in the United States[11]. Adipic acid is used in polyamide-6,6 fibers and some resins accounts for ∼75% of the total output, it is also used for polyurethane production, as a reactant to form polyester polyols, plasticizers, lubricant components, and food acidulant (E 355). Almost 90% of the domestic U.S. adipic acid is used to produce nylon-6,6. Indeed its production trends are closely correlated with consumption trends of this polymer. The current adipic acid market volume is ∼2,6 Mt/yr, with an average annual demand growth rate forecast of 3%−3,5%. The global capacity distribution is as follows: East Asia, 1035 kt; European Union (EU), 935 kt; USA, 910 kt; rest of the world (ROW), <100 kt. Major global adipic acid producers (2011) include Invista (formerly Du Pont Textiles and Interiors), Rhodia, Ascend (formerly Solutia, Inc.) and BASF Figure 1[11].
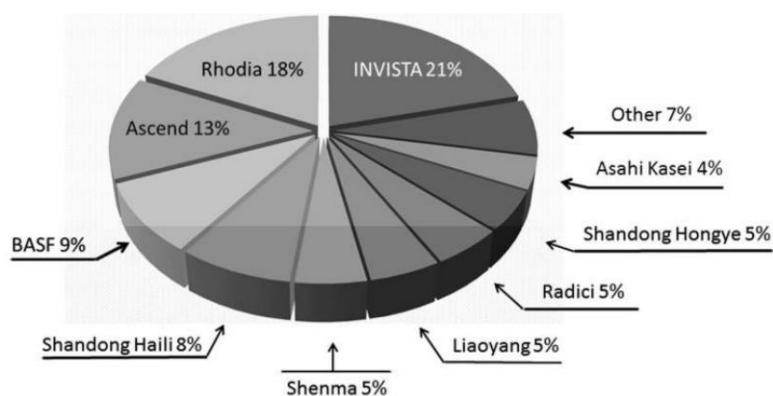
Figure 1: Adipic acid manufactures.

(Copyright 2011, Dr. Gary Diamond.)

2.3 Current synthesis of AA: Oxidation of cyclohexane to adipic acid by two-steps

Currently, adipic acid is obtained by two-step oxidation process. In the first step the oxidation of cyclohexane to a mixture of cyclohexanone/cyclohexanol (One/Ol, KA Oil) is performed by air and in the second step the oxidation of KA Oil to adipic acid with HNO_3.
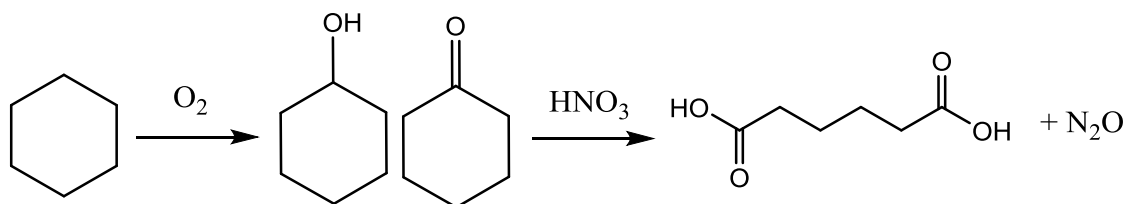
Scheme 1: Conventional process for the manufacture of adipic acid from KA Oil. [13]

2.3.1 First step: oxidation of cyclohexane to KA Oil with air

Cyclohexane derives from either by the hydrogenation of benzene, or from naphta fraction but only in a small amount. The oxidation of cyclohexane to KA Oil has been already industrialized by DuPont in the early 1940s. The reaction conditions are temperature between 150°C and 180°C and air pressure in the 10-20atm range, catalyzed by Co or Mn organic salts in liquid phase. Products of this oxidation are KA Oil (selectivity 75-80 %) as the main one and carboxylic acids (mainly succinic and glutaric acid) as by-products.
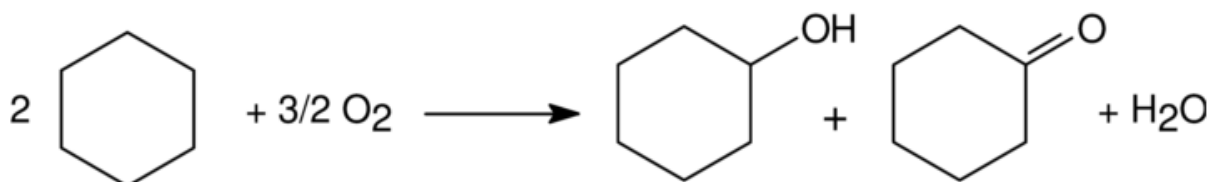
Scheme 2: Oxidation of cyclohexane to KA Oil.

The reaction is carried out in three in-series reactors (Figure 2). Cyclohexane is fed in the first reactor and air is distributed to the three reactors, allowing a better control of the reaction and improvements of safety. In the first reactor, cyclohexane is oxidized to cyclohexylhydroperoxide and this is the rate-limiting step of the process. For this reason the decomposition of hydroperoxide is carried out in the second reactor, where catalyst amount and reaction conditions are optimized, allowing the Ol/One ratio to be controlled. During the process the products are washed with water and subsequently with caustic solution, in order to reduce acid impurities.
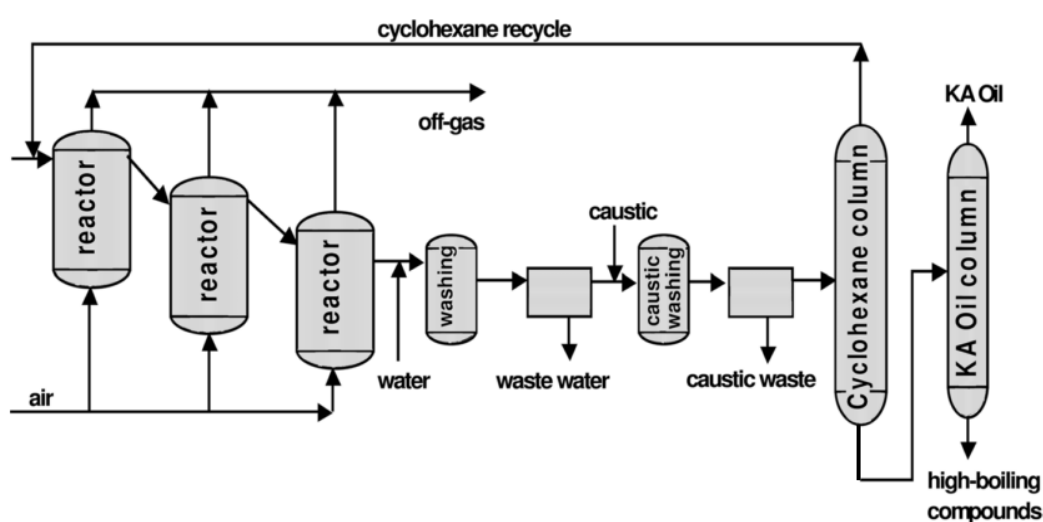
Figure 2: Semplified flow-sheet of the process for the oxidation of cyclohexane with air

a – reactor of oxidation by air, b – washing, c – decantation of water, d – reactor of decomposition of decantation, e – caustic dentation, f – column of recuperation of cyclohexane, g – column of recuperation of KA oil

The current step adopted a variation characterized by the use of substantial quantities of anhydrous meta-boric acid (Bashkirov Oxidation). No other catalyst is necessary in this process. Boric acid reacts with cyclohexanol to give a borate ester that stabilizes the product and reduces its tendency to be oxidized further to form either cyclohexanone or degradation products. Results show a conversion of 10% (or even 15%) and selectivity of 90%, with a molar ratio Ol/One of around 10. The borate ester formed is easily hydrolyzed by hot water to boric acid and cyclohexanol. After distillation, a 99,5% Ol/One mixture is obtained.[14]

7

Alternately in this process there are other two variations currently employed: i) hydrogenation of phenol to KA Oil and ii) hydration of cyclohexene to cyclohexanol (Scheme 3).

Concerning the hydrogenation of phenol, this process is safer than that based on cyclohexane oxidation, leading to reduced investment costs. Moreover, by increasing the amount of ketone it is possible to use less nitric acid in the next oxidation step.

In regards to the other oxidation option, cyclohexane is obtained from benzene by partial hydrogenation. Due to the difficult to stop the hydrogenation of benzene to cyclohexene it is necessary to work with catalyst consisting of Pt or Ru powder, coated with a layer of an aqueous solution of zinc sulfate. The reaction is carried out in a bi-phasic system composed of benzene and water solution. Since cyclohexene is less soluble in the aqueous phase it migrates preferentially to the organic phase, avoiding further hydrogenation. Cyclohexane is obtained with 80% of selectivity and further hydrated on ZMS-5 catalyst to produce cyclohexanol. Less hydrogen is consumed in this process and fewer by-products are formed if compared to above-mentioned methods, but more nitric acid must be used in the subsequent oxidation step.
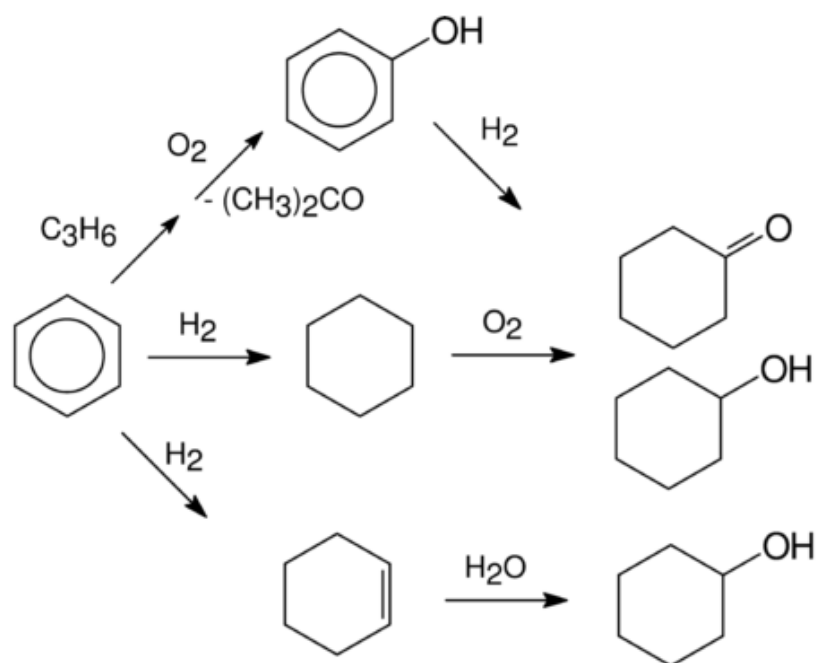
Scheme 3: Alternative synthesis of KA Oil from benzene compared to cyclohexane (in the middle);
i) hydrogenation of phenol to KA Oil (top);
ii) hydration of cyclohexane to cyclohexanol (bottom).

2.3.2 Second step: oxidation of KA oil to AA with nitric acid

The second step in the synthesis of adipic acid from cyclohexane is the further oxidation of KA Oil with 65% nitric acid in molar ratio HNO_3/Ka Oil at least 7/1 () and in presence of Cu (II) and ammonium metavanadato catalyst.
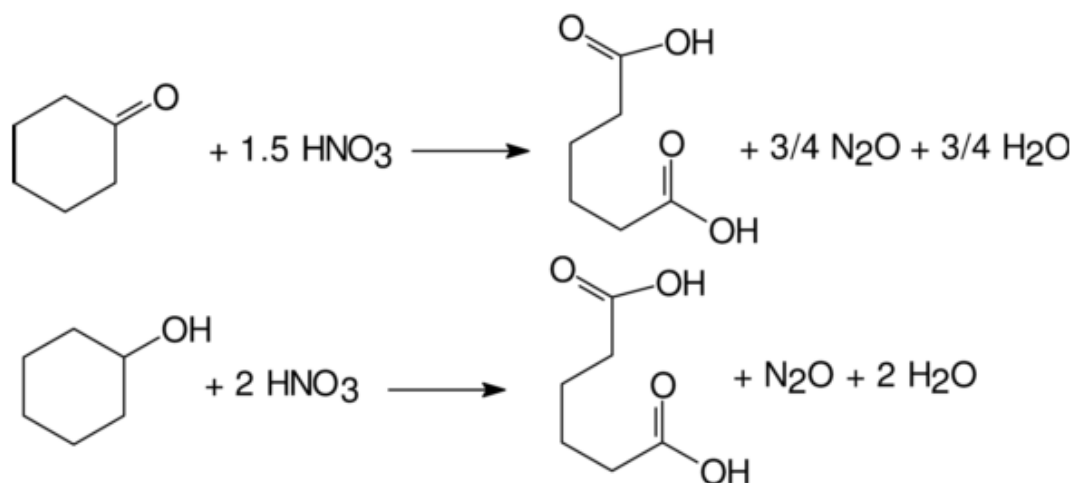
Scheme 4: Oxidation of cyclohexanol and cylohexanone to adipic acid with nitric acid.

The reaction mechanism is known since 1963 and discussed in detail by van Asselt and van Krevelen (Scheme 5). In the first step nitric acid oxides cyclohexanol to cyclohexanone and the latter is further nitrosated to 2-nitrosocyclohexanone by nitrous acid. Many reactions occur during this step, however the main pathway is the formation of 2-nitro-2-nitrosocyclohexanone, which is hydrolyzed to 6-nitro-6-hydroximinohexanoic acid. The final step is the oxidative hydrolysis of the latter product to adipic acid [14].
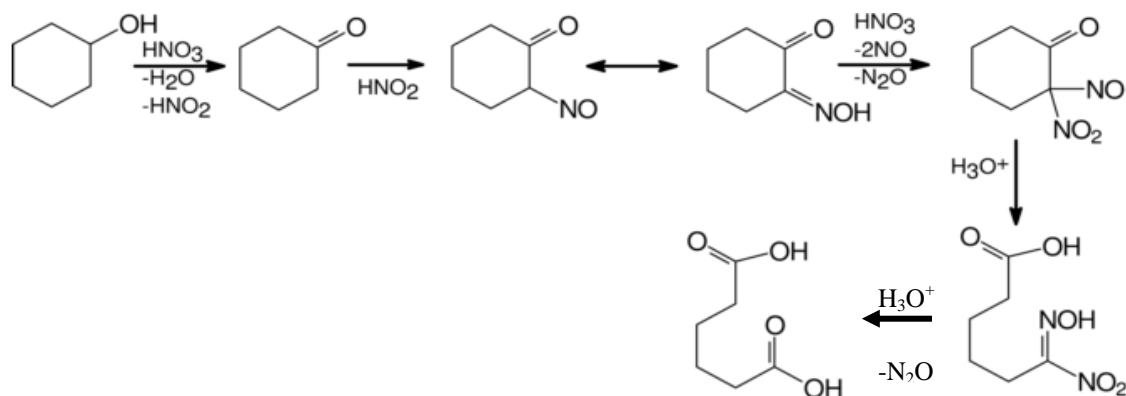
Scheme 5: The main reactions involved in the oxidation of KA Oil.

The reaction is carried out in two in-series reactors: the first one operates at 60-80 °C, the second one at 90-100°C under a pressure of 1-4 atm (Figure 3). KA Oil conversion is 95% and by-products are glutaric acid (selectivity 3%) and succinic acid (selectivity 2%).

Due to the exothermicity of the reaction, in order to avoid run-away, the KA Oil mixture is added in small amounts to the solution of the nitric acid and the catalyst in the first reactor. In the second reactor the products are stripped by air to separate nitrogen oxides (NOx) and nitrous oxide (N_2O). Nitrogen compounds and others gas streams deriving from the first two reactors are adsorbed in water. Last step allows converting nitrogen oxides in nitric acid to recycle the reagent for the oxidation of KA Oil, nitrous oxide is treated to reduce the dangerous emission. The aqueous phase, carrying the main products, is passed through the crystallizer. The first crystallization permits to separate the adipic acid form the solution, and then the recrystallization is done again to purify the product. After the separation of adipic acid the solution is concentrated to obtain nitric acid with the concentration about 60%. One part of this liquid is recycled while the other is purged and the catalyst is recovered.[15]
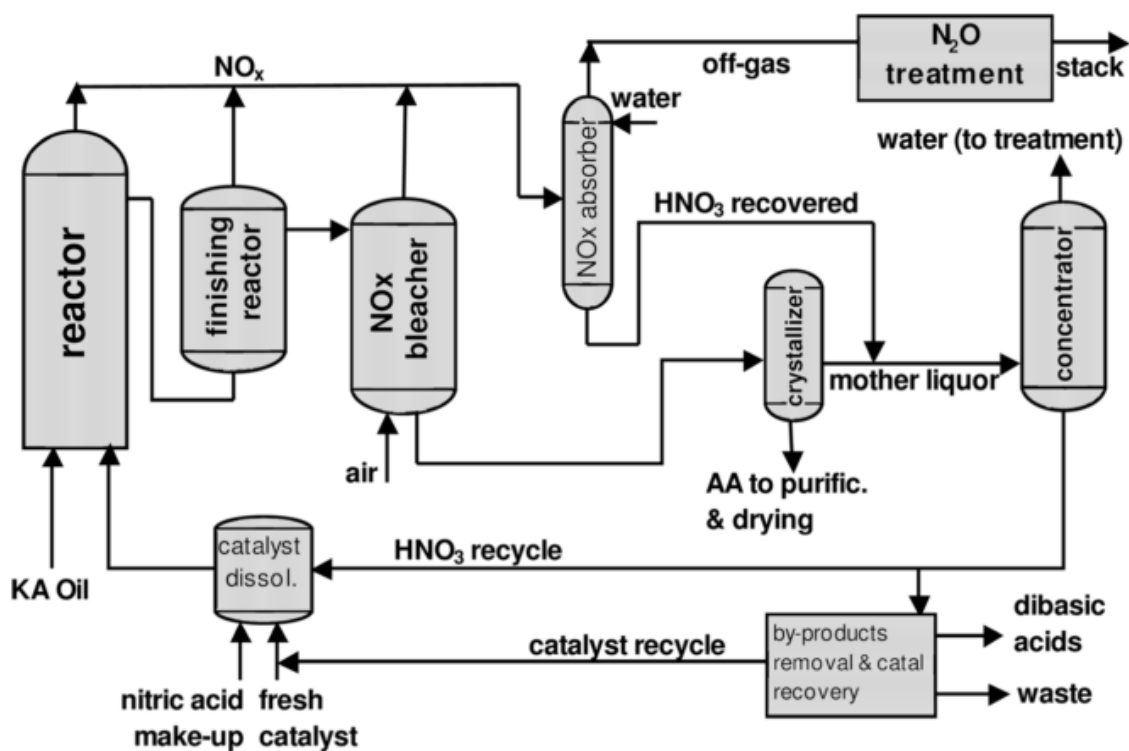
Figure 3: Simplified flow sheet of oxidation of KA Oil to adipic acid.

Last step of oxidation process could be also carried out under air atmosphere using Cu-Mn acetate. In this case the reaction mixtures rich in cyclohexanone are used. Oxidation is conducted in acetic acid solution at about 80-85 °C and 6 bar of air pressure over Cu and Mn acetate catalysts. This process has the advantage that no HNO_3 is used avoiding corrosive and environmental problems. Rohm & Hass in the USA produced for several years thousands tons of adipic acid by this way, but the project was abandoned due to poor product quality.

This industrial process has many disadvantages that includes:

- Low overall product yield (4-11%).
- Corrosion of reactors and pipes due to nitric acid.
- High-energy consumption.
- Emission of greenhouse gas N_2O (0,3 $kgN_2O/kg_{adipic\ acid}$)

2.3.3 Environmental impact of AA production and N_2O abatement

The KA Oil oxidation by nitric acid produces NOx and N_2O as the main by-product gas. The first ones are easily recovered as nitric acid by compression in the presence of excess oxygen and further adsorption, according to the following reactions:

$$2NO + O_2 \rightarrow 2NO_2 \tag{1}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \tag{2}$$

Differently the N_2O is harder to reduce because of its low solubility in aqueous solution. Moreover, N_2O is classified as longed lived greenhouse gases LLGHGS (others are CH_4, CO_2 and radioactively active constituents such as ozone and different types of aerosols), which contributes to the climatic changes. The estimated atmospheric lifetime of N_2O is 150 years and the impact of N_2O on the ozone depletion layer increase is estimated to be about 6%.

$$N_2O + O(1D) \rightarrow NO + NO \ (61{,}7\%) \tag{3}$$

$$N_2O + O(1D) \rightarrow N_2 + O_2 \ (38{,}3\%) \tag{4}$$

The equation (3) shows that the major part of N_2O is converted to NO, which is implicated in catalytic ozone destruction[16].

The two industrial processes contributing most to N_2O emissions are the production of nitric acid and that of adipic acid. N_2O emissions from adipic and nitric acid production contribute to about 0,2% of global emissions (roughly 100 $MtCO_2$/eq), which is equivalent to 24% of non-CO_2 greenhouse gas (GHG) emissions from key industrial processes. *(4)*

By 1999 all major adipic acid producers have implemented N_2O abatement technologies and, as a result, this source has been decreased substantially. At the moment there are three different methods to restrict the pollutant emission of N_2O[17]:

- Catalytic dissociation of N_2O to N_2 and O_2
- N_2O decomposition in boilers – thermal destruction
- Conversion of N_2O into recoverable NO

Catalytic abatement is considered the simplest removal method for N_2O. Catalyst such as noble metals (Pt, Au), pure or mixed oxides (spinel, perovskite – types, hydrotalcites),

supported systems (metal or metal oxides on alumina, silica, zirconia) and zeolites are considered suitable for the catalytic dissociation reaction. Unfortunately there are some problems linked to the strong exothermicity of the reaction such as:

- Sintering of the catalyst or their supports.

- High investment costs for the careful selection of special heat resistant materials for reactors bodies.

- Difficulty in respecting the environmental regulation: with increasing temperature of the catalytic bed the risk of NOx formation increases (NOx concentration is limited by the law).

Thermal abatement occurs in two ways, depending on the conditions: oxidizing or reducing. In the first case, N_2O is oxidized into NO and NO_2 and these ones are absorbed in water to recover a modest amount of nitric acid, which can be recycled in the process upstream. In the second case, a reducing atmosphere is generated by adding an excess of methane to the gas mixture fed. Excess of methane produces an unburnt share (CO and H_2), which is a driving force for the reduction of nitrogen oxides to nitrogen. Equations (5-9) show the thermal abatement of N_2O in reducing method[14].

$$4\ N_2O + CH_4 \rightarrow CO_2 + 2\ H_2O + 4N_2 \tag{5}$$

$$4\ NO + CH_4 \rightarrow CO_2 + 2H_2 + 2\ N_2 \tag{6}$$

$$2\ O_2 + CH_4 \rightarrow CO_2 + H2O \tag{7}$$

$$H_2O + CO_2 + 2\ CH_4 \rightarrow 3CO + 5\ H_2 \tag{8}$$

$$N_2O \rightarrow \frac{1}{2}\ O_2 + N_2 \tag{9}$$

An alternative and innovative method to recover N_2O has been proposed by Solutia and Boreskov Institute of catalysis[18]. It consists in using nitrous oxide as a reactant for hydroxylation of benzene to phenol in the presence of a ZSM-5 catalyst exchanged with Fe (III). Phenol can be further hydrogenated to cyclohexanol, which is used for the synthesis of adipic acid (Scheme 6).
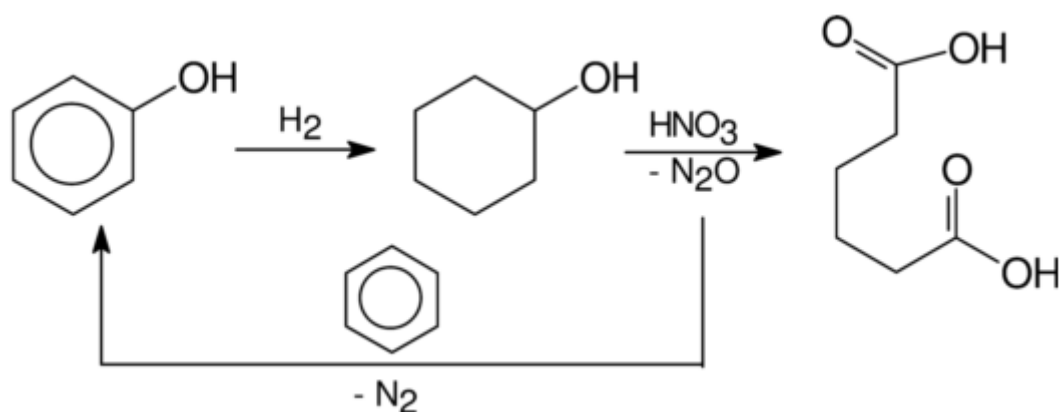
Scheme 6: N₂O cycle for the synthesis of phenol

Although high selectivity in phenol is achieved (95%), this process has not been put into commercial operation due to the rapid catalyst deactivation caused by tar deposition.

Another interesting application of N_2O is its use in the synthesis of cyclododecanone, a raw material for Nylon. BASF proposed to use N_2O as oxidizing agent for oxidation of cyclododecatriene to produce cyclododecanone (Scheme 7) and this process is more eco-friendly compared to the classical methods of synthesis of cyclododecanone[19].
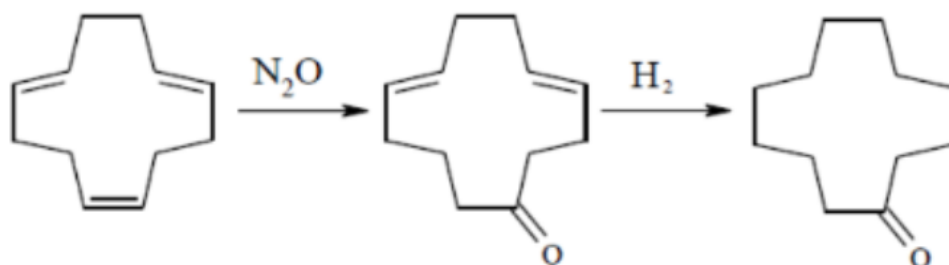
Scheme 7: Oxidation of cyclododecatriene to cyclododecanone using N₂O.

14

3. Alternative starting reagents

Vigorous efforts lavished in the research of alternative starting reagents are the attempt to get a pathway as close as possible to the principles of Green Chemistry.

3.1 Green Chemistry

Green Chemistry is the tendency to realize free-pollution processes or processes that produce only few amounts of pollutant agents, using safe and renewable products for the environment and people and low energy demand. Here below are reported the twelve principles of Green Chemistry [20]:

1. *Prevention*

   It is better to prevent waste than to treat or clean up waste after it has been created.

2. *Atom Economy*

   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. *Less Hazardous Chemical*

   Synthesis wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. *Designing Safer Chemicals*

   Chemical products should be designed to affect their desired function while minimizing their toxicity.

5. *Safer Solvents and Auxiliaries*

   The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. *Design for Energy Efficiency*

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. *Use of Renewable Feedstocks*

   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. *Reduce Derivatives*

   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. *Catalysis*

   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. *Design for Degradation*

    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. *Real-time analysis for Pollution Prevention*

    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. *Inherently Safer Chemistry for Accident Prevention*

    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

3.2 Cyclohexane

Cyclohexane is the main reagent used in the current industrial synthesis of adipic acid and for this reason it is important to develop new methods to improve the efficiency and the

sustainability of the process starting from this reagent. In the next chapters are reported some studies for the development of new catalytic systems for the synthesis of adipic acid.

3.2.1 Ce/AlPO-5 catalyst for solvent-free liquid phase oxidation of cyclohexane by oxygen

CeO2 and CeO2-based materials have attracted much attention in catalysis because of their unique catalytic activities associated with environmental concerns. The facile redox cycle of Ce4+/Ce3+ leads often to higher oxygen storage capacity (OSC) with reversible addition and removal of oxygen in the fluorite structure of ceria [21]. In 1982, Wilson and co-workers developed a new class of zeolite-like molecular sieve of AlPO-n (n denotes a structure type) type [22]. Their structures are typically built up from strict alternation of AlO4 and PO4 tetrahedral through corner sharing to form a neutral open-framework. Some of the Al sites can be replaced by catalytically active transition metal ions. One of the important promising applications of AlPO-n is the linear and cyclic hydrocarbons oxidation in air. They are also present in the growing field of solvent-free industrial reactions in the important area of clean technology. The authors reported the first example of a cerium doped AlPO-5 microporous molecular sieve and its catalytic performance in the oxidation of cyclohexane in a solvent-free system, with O2 as an oxidant [21].

The catalytic oxidation was carried out in a 25 ml stainless steel reactor equipped with a magnetic stirrer. In a typical reaction, cyclohexane (2 mL) was mixed with Ce/AlPO-5 catalysts (10 mg) and heated to 140 °C under a 0,5 MPa O2 atmosphere. After reaction, the reactants and products were directly analyzed by GC or GC-MS. This reaction was also tested using bare AlPO-5 as a catalyst and only trace amount of oxidative products were detected. Thus, it is clear that Ce plays an important role in the reaction and probably Ce ions are the active sites of Ce/AlPO-5 material. In this case the major products were cyclohexanol and cyclohexanone (KA Oil). The total conversion of cyclohexane was 13,5% with selectivity to KA Oil of 91%. The selectivity to adipic acid was only 8,2%. Higher selectivity in adipic acid were obtained in the presence of acetic acid used as solvent (≈100%) but only 6% of cyclohexane conversion was achieved with the drawback due to the solvent use. Other tests indicated that the leaching of cerium from the catalysts was very low and recycling experiment confirmed that no changes in conversion and selectivity were observed. In

conclusion these heterogeneous catalysts are found to be very stable and suitable for the first step of cyclohexane oxidation to KA oil but not enough active to its final oxidation to adipic acid in solvent-free conditions [21].

3.2.2 Direct synthesis of adipic acid by air oxidation of cyclohexane

Rodia patent proposed a lipophilic catalyst that can be easily separated from the reaction mixture and recycled together with the unconverted cyclohexane. At the end of the reaction, water is added to the solution to solubilize the AA. The reactant, the catalyst and the intermediate products cyclohexanol and cyclohexanone form an immiscible phase and are recovered and recycled (Figure 4). AA is crystallized from the aqueous solution by cooling, and finally filtered and dried.
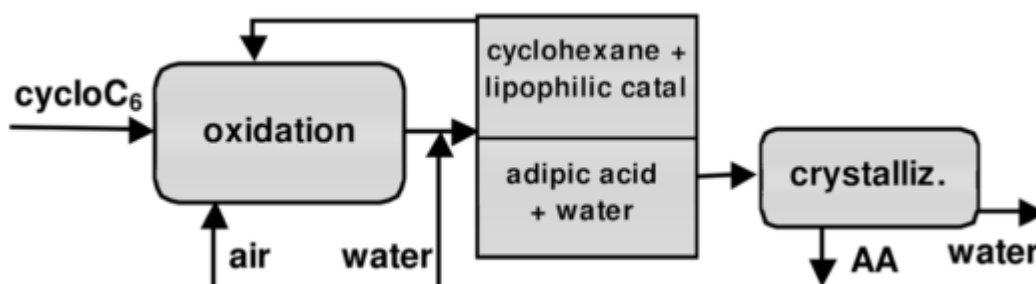
Figure 4: Schematic flow chart for a one-step adipic acid synthesis from cyclohexane.

In front of the presence of the extraction step, the catalyst must be very hydrophobic to avoid loss, as well as thermally stable, cheap, available at industrial scale. Authors studied a combination of manganese and cobalt salts with different carboxylic acids as homogeneous catalyst, which have revealed to be active at very low concentrations.

In terms of productivity and selectivity the best results were achieved with 10-12 wt% of 4-tert-butylbenzoic acid at 130 °C and 20 bar of air. Under these continuous conditions a 56% selectivity into adipic acid and 10,4% of conversion were obtained. After organic phase recycling, selectivity increased to 70,6% and the measured productivity of adipic acid exceeded 96 g L^{-1} h^{-1}.

18

This study has demonstrated the potential of the free-solvent system in the oxidation of cyclohexane to adipic acid using suitable oxidizing agent such as air and avoiding the final nitric oxidation step which generates a strong greenhouse gas [23].

3.2.3 Oxidation of cyclohexane to adipic acid catalyzed by Mn-doped titanosilicate with hollow structure

Titanosilicalite catalysts are well known to be very active in the oxidation of cyclohexane to KA oils with H_2O_2. The titanosilicate-catalyzed oxidation process is believed to be a "green" route to substitute old processes still in use. One-pot process for the direct oxidation of cyclohexane to adipic acid with O_2 in free-solvent condition is reported by Shi et al. They have developed an efficient titanosilicate catalyst with hollow structure (HTS) for use in the oxidation of cyclohexane, which showed higher active than TS-1 using H_2O_2 as oxidant [24].

The hollow structure with bigger intra-particle pores dimensions can intensify the transport of reactants and products in and out of the crystal channels [25]. This catalyst permits to obtain better selectivity to adipic acid (molecule diameter of 1.00 nm) due to the bigger diameter with respect to cyclohexanone (0,51 nm) and cyclohexanol (0,58 nm).
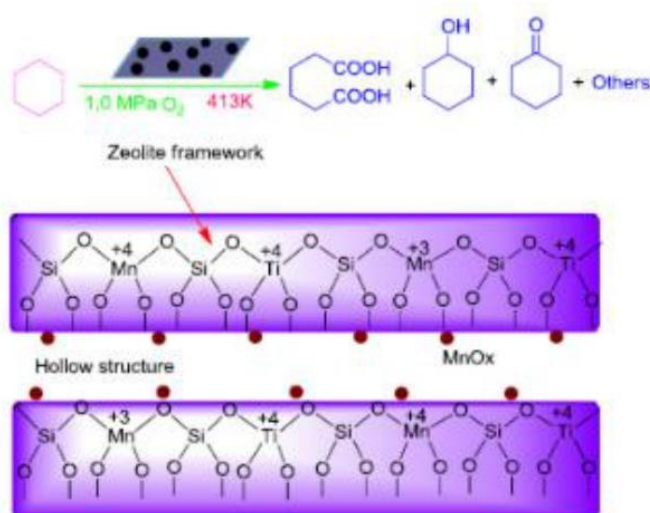

Figure 5: Illustration for the cyclohexane oxidation over the synthesized catalyst.

The reaction has been conducted under a constant oxygen pressure, without solvent in a 100 mL stainless steel reactor equipped with a Teflon beaker and magnetic stirrer. The Mn-HTS catalyst gave the highest selectivity of AA, 57,7%, with a relatively high cyclohexane conversion, 8,6%, which was attributed to the nature of the metal used. There was also tested the recyclability of the catalyst and the results showed that the selectivity of AA on regenerated catalyst was almost equal with that over fresh catalyst, disclosing the stability of the catalyst and its possibility to be reused.

The mechanism proposed for the oxidation of the cyclohexane to adipic acid consists in a series of radical oxidations as shown in Scheme 8.
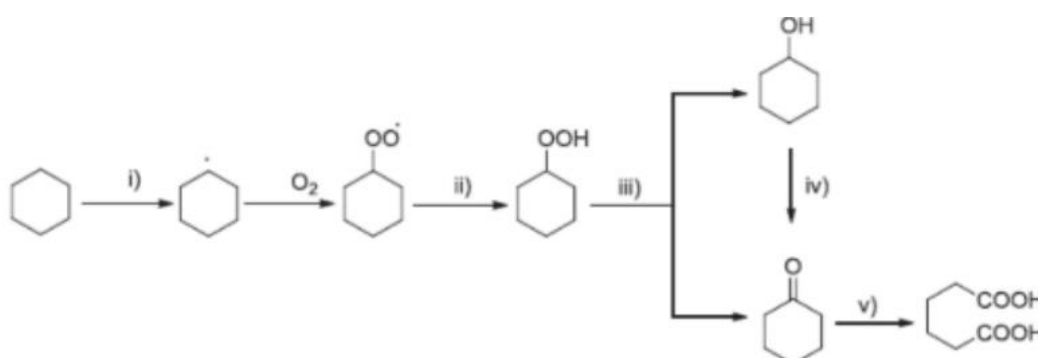
Scheme 8: A plausible reaction path for oxidation of cyclohexane to AA over Mn-HTS.

i) O_2 or Ti-oxygen complex; ii) R-H; iii) Ti or Mn active site; iv) Ti-O_2 or Mn-O_2; v) Ti/Mn-O_2

3.2 Cyclohexene

Cyclohexene is already used as a precursor in the two-step synthesis of the adipic acid [26], therefore a one-step synthesis with less environmental impact oxidants could be a better alternative respect the current process. Cyclohexene can be obtained by partial hydrogenation of benzene, dehydrohalogenation of cyclohexyl halides or partial cyclohexane dehydrogenation. Asahi studied benzene hydrogenation to cyclohexene [27]. However, even if good cyclohexene selectivity was obtained, the problems with catalyst deactivation occurred. The method of dehydrohalogenation of cyclohexyl halides would have a potential advantage of recycling hazardous halogenate compounds. Hydrogen treatment of cyclohexyl chloride using silica supported nickel catalyst gave 97% cyclohexene selectivity at temperatures between 200 and 300°C[28].

3.2.1 Direct oxidation of cyclohexene with hydrogen peroxide

Actually the best one-step synthesis of adipic acid is direct oxidation of cyclohexene using hydrogen peroxide as oxidant. However, from the industrial point of view the high cost of this reagent and low availability of cyclohexene make difficult to develop it at an industrial scale.
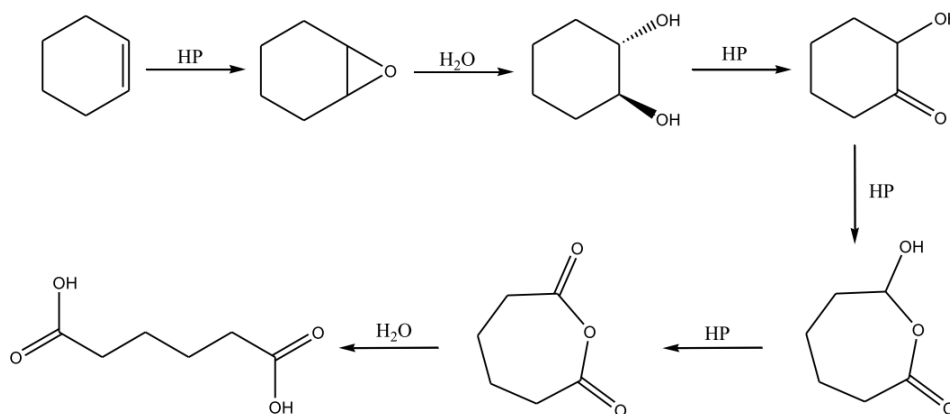
Scheme 9: Direct oxidation of cyclohexene to AA with HP

It is worth to note that the most of the reactions described in the literature occur in a biphasic system composed by cyclohexene and a solution of HP (30% v/v). Usually the reactions are carried out in the presence of homogenous catalysts based on W, Pd, Os, Mn and a Phase Transfer Catalyst (PTC) [29].

Sato *et al.*[26] described an efficient oxidation reaction of cyclohexene in free-solvent condition at low temperature 75-90 °C using HP as oxidant. In these conditions a quantitative yield has been obtained using only a little surplus of HP with respect to the theoretical amount. In this work a W based catalyst reacts with the oxidizing reagent (HP). The anionic peroxo species formed are then extracted by the quaternary ammonium cation of PTC from the organic solution to the aqueous one. The problem of this process is the oxidative degradation of the ligands in the presence of ammonium salts and the instability of catalysts.

Further studies proposed an alternative to the PTC based quaternary ammonium salts. These compounds are toxic and expensive. In particular the ligands based on organic acids able to transfer the anionic peroxo species from the organic to the aqueous solution were used. Thanks to these new improvements, the process permitted to obtain high purity adipic acid

21

(99%) with the yield of about 80-88%. Nevertheless all these processes do not permit to reproduce them in a large industrial scale due to the high cost of HP.

3.2.2 Direct oxidation of cyclohexene with oxygen or air

When oxygen is used in the oxidation of cyclohexene the main product formed is 2-cyclohexen-1-one [30,31], which may be further hydrogenated to cyclohexanone. The reaction follows the autoxidation-type mechanism forming first cyclohexene hydroperoxide. If the reaction is carried out in the presence of a co-reducing agent (for example, isobutyraldehyde), high selectivity to the epoxide is obtained (88-94% with complete conversion of substrate) [32]. Asahi has proposed the oxidation of cyclohexene with O_2 using isopolyoxomolybdates [27]. The primary products were cyclohexene oxide, cyclohexandiol and 2-cyclohexene-1-ol (Scheme 10). The two former compounds are intermediates in the AA synthesis. After 24 hours at 50°C and 1 atm of oxygen, 37% of cyclohexene was converted was obtained with 90% selectivity to the three primary products.
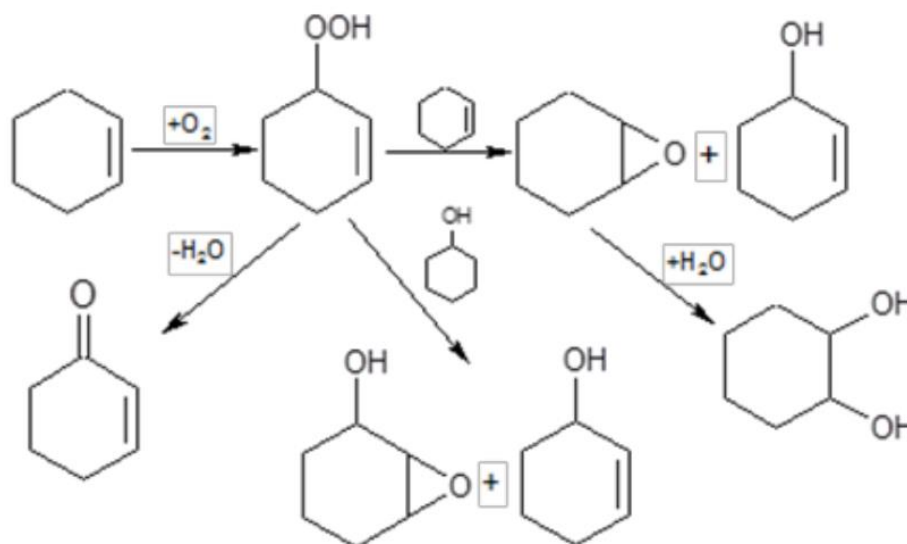
Scheme 10: Oxidation of cyclohexene with O_2.

When the system based on Pd (II) and P/Mo/V heteropoly-compounds is used, the reaction follows a Wacker-type mechanism that is different from the radical-type autoxidation. The primary product in this case is cyclohexanone, which can be further oxidized with oxygen to

AA. Many systems belonging to this class of catalysts were investigated. The best results were achieved with $Pd(NO_3)_2/CuSO_4/H_3PMo_{12}O_{40}$ catalyst in aqueous solution of acetonitrile at 80°C and 10 atm of oxygen: cyclohexene conversion was 49% with 97% selectivity to cyclohexanone [33]. More recently, at 80°C and 50 atm of air, using the same catalyst, >>99% selectivity to cyclohexanone with 80% cyclohexene conversion were reported [34].

3.3 Butadiene

Adipic acid synthesis can be carried out through methoxycarbonylation of butadiene. This process, developed by BASF, is composed by three steps: addition of CO, addition of methanol and subsequent hydrolysis of the esters to obtain AA[35]. Homogeneous catalyst based on Co and pyridine are essential to avoid oligomerization reactions and the process permits to achieve a total yield of AA of about 72% referred to butadiene, with product purity of 99,9%. The major by-products obtained are esters such as methyl valerate and dimethyl esters of dicarboxylic acids with four carbon atoms, which could however, find uses in other applications. The development of this process has not reached yet the industrial scale due to economic and technical issues, such as the high cost to work due to the high pressures (150-300 atm) [36].
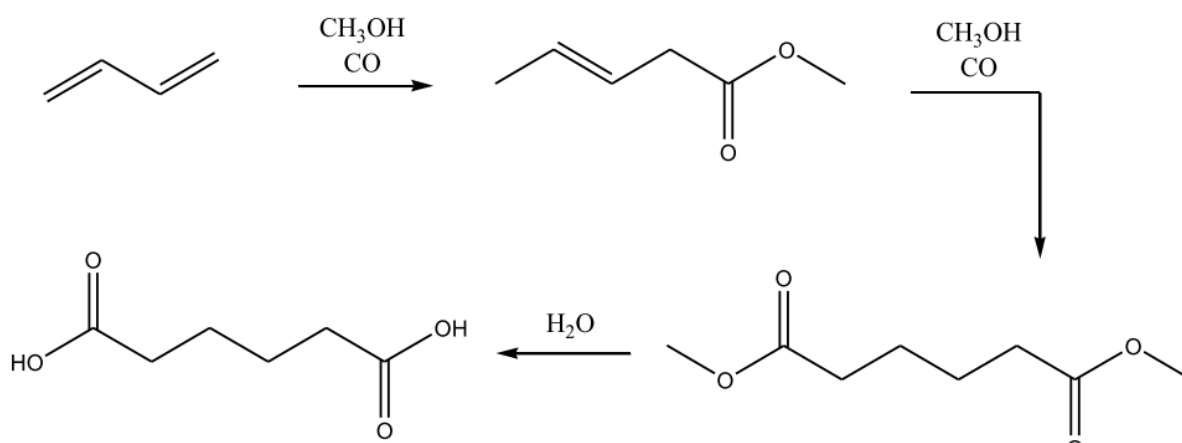
Scheme 11: Methoxycarbonylation of butadiene to AA.

DuPont and DSM studied a new approach consisting in the hydroxycarbonyalation of butadiene by CO and H2O at 100 °C and 80 atm. This method is cheaper from the raw materials point of view, but higher cost in the BASF process derives from catalyst and difficulties in catalyst recovery (Scheme 12) [37].
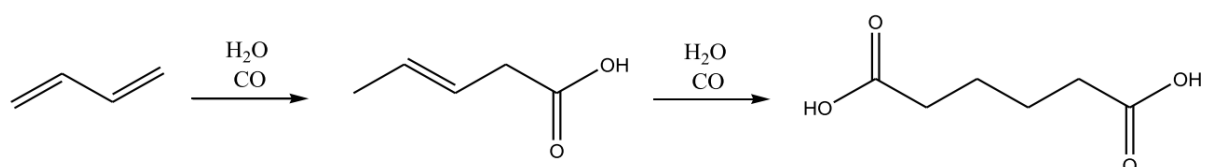
Scheme 12: Hydroxycarbonylation of butadiene to AA.

Other variations of methoxycarbonylation have been studied by Rhone Poulenc [38] and Shell Chemicals [39,40], which developed a new catalyst able to convert butadiene into AA with CO and water. Because with this catalyst the mono-olefins are not carboxylated, the use of crude C4 fractions as starting material is allowed. This new process, however, was stopped at the level of bench-scale: the main limit for the industrialization is the use of a complex as homogeneous catalyst, composed of precious metals and phosphine ligands, which are very expensive.

3.4 n-Hexane

One of the main difficulties of the actual catalysis is the oxidation of the linear alkanes terminal carbons; in particular, the direct oxidation of n-hexane on C1 and C6 would lead directly to AA (Scheme 13). About this process, one problem is the limited availability of the reagent, which is mainly derived from cracking plants, where it is easily converted to benzene.
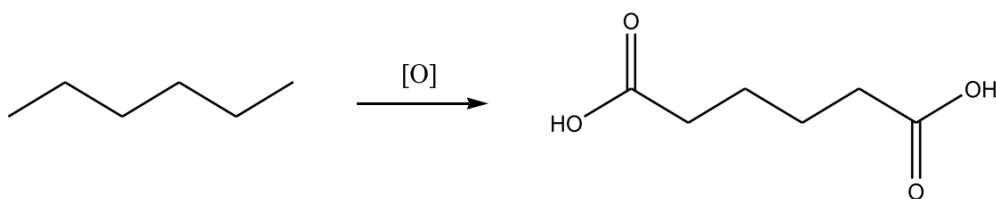
Scheme 13: Direct oxidation of n-hexane to AA.

This reaction can be carried out in the presence of enzymes provided with active centers based on Fe that react with air to produce AA starting from n-hexane. High selectivity (near 100%) can be achieved in this reaction, but the attempt to replicate these properties in non-biological systems for use in industrial plants gave poor results. Chemical systems were tried, such as Mn-porphyrins, Co and Mn alluminophosphates or supported on zeolites, but AA yields higher than 35% have been never reached. The major by-products obtained were hexanol, hexanal and methyl-butyl ketone [41].

3.5 Glucose

Deaths and Frost proposed an AA two-steps synthesis starting from D-glucose. The process consists in a conversion of the sugar in to cis,cis-muconic acid by genetically modified Escherichia coli followed by hydrogenation on a Pt active carbon supported catalysts or using Pt-Ru nanoparticles supported on silica. The first process works at room temperature and 35 bar of H_2 while the latter is carried at 80 °C and 30 bar [42].
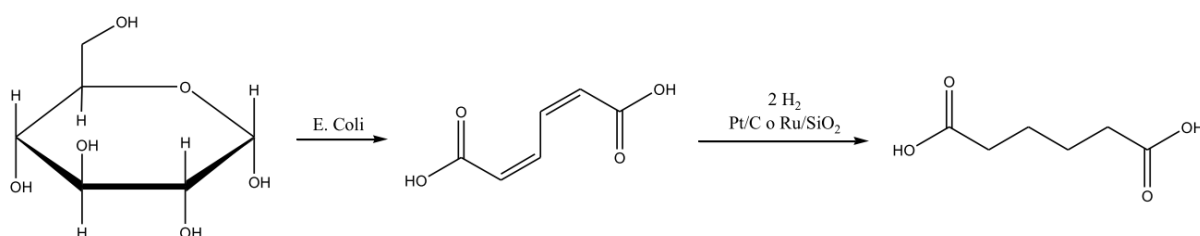
Scheme 14: Synthesis of AA starting from D-glucose.

The yield of the first step is about 25% while the second step gives a yield of 95% for both catalysts. This route from glucose presents environmental and economic advantages, since it uses a renewable source that can be obtained even from lignocellulosic biomass, starting from a low-cost raw material and at the same time providing added value to a waste compound. The main problem of this method is represented by the final product cost that is not competitive with that obtained by the traditional process. Furthermore, the scale-up of the biotechnological process needs to be improved to produce AA in large scale [42,43].

3.6 Conclusion concerning alternative starting reagent

In literature several methods for AA synthesis are reported. From the more conventional to more alternatives, all these processes try to develop a more sustainable chemistry. As reported in the previous chapters, many reagents can be used as starting material for AA synthesis. In particular cyclohexane, cyclohexene, butadiene, n-hexane and D-glucose were discussed. Scheme 15 summarizes some possible synthetic routes to AA. From an industrial point of view, the main limiting factors are linked to the economic issues. In the synthesis of AA or other products, several green approaches are presented, but very often only a few examples are really sustainable in terms of both environmental and economic points of view.
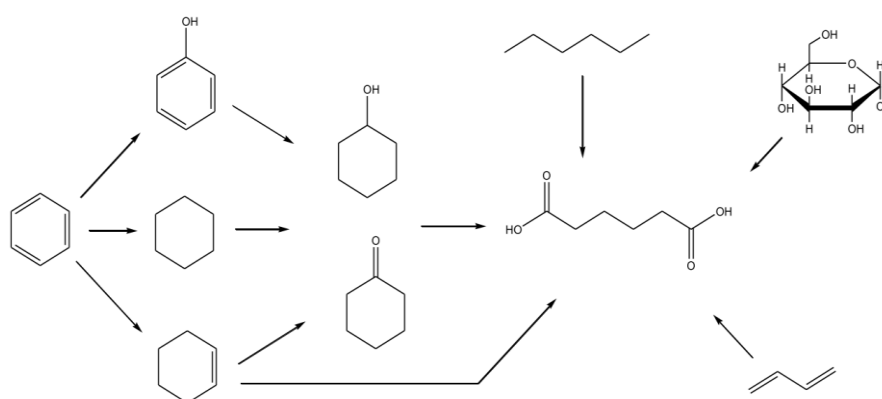
Scheme 15: Summary of the various pathways for AA synthesis.:

In the case of glucose using as a starting material the synthesis of AA can be consider green, but the high cost of the final product is not competitive with that obtained by the traditional

process. Even if the direct synthesis of AA from cyclohexene perfectly adheres to the Green Chemistry principles, the use of large amounts of HP makes these processes economically uncompetitive. One of the main problems concerning other processes is the use of acetic acid as the solvent that requires additional costs for handling and special materials.

3.7 Sustainable Chemistry

The main problem of Green Chemistry is that often, the respect and the implementation of all the principles, is not convenient for an economic point of view or is difficult or completely not applicable from technical aspects. For these reasons, in the last years it has been understood that a Green process is not enough, it should be mostly Sustainable. Sustainable Chemistry is a more general concept, which includes economic, social and environmental aspects. A chemical process must produce a profit and optimize the resources use, taking in to account the necessity of the company and reducing the impact on people and on environment. One of the main aspects where the industry is focused is safety; this aspect can be improved following some key words that help to increase the economic and environment sustainability of a process [44]:

- **Intensification (also called Minimization)**: reducing the presence or amounts of a hazardous material or produce them in situ, trying to maintain the same process productivity.

- **Substitution**: replacing a hazardous material with a non-hazardous or less-hazardous material. The classic example of substitution is the use of water as a coolant instead of combustible and highly corrosive thermal oil. Using non- combustible materials instead of low flash point hydrocarbons is another example such as the substitution of supercritical carbon dioxide instead of hexane solvent in the extraction of caffeine from coffee beans. The hazards of fire and explosion from the solvent are eliminated.

- **Attenuation**: using less hazardous process conditions or a less hazardous form of material. Attenuation is commonly achieved by using lower temperatures and pressures. It may be achieved through process chemistry (i.e., a new process with less

potentially energetic effects). It might also be achieved by using less flammable or corrosive materials.

- **Limitation of Effects**: designing a facility to minimize the impact of a release of material or energy. The most common example of Limitation of Effects is proper siting and location of facilities. Space separation can reduce the impact of an energetic release at one location from impacting another by minimizing radiant heat and explosion-generated pressure effects and projectiles.

- **Simplification and Error Tolerance**: designing a facility so that operating errors are less likely or the process is more forgiving if errors are made. An example is ergonomic design of control systems and control panels. The easier it is for an operator to respond and find the correct shutoff button (for example) the better chance of an orderly safe shutdown.

From a sustainable point of view, the oxidation catalysis shows large improvement opportunities, especially if the following guidelines for research are followed:

a) study of new processes for the intermediate and monomer synthesis from alkanes instead alkenes and aromatics (the traditional building blocks);

b) new heterogeneous catalytic systems for liquid phase oxidation that permit better oxidants from environmental point of view;

c) better working conditions which permit to minimize the production of wastes improving the selectivity and productivity.

3.8 Aspects of the catalytic oxidation in liquid phase

Catalytic aspect is important because catalyst used permit to avoid stoichiometric reactions (reducing the amount of solvent and waste produced), intensification of the processes (working with smaller reactor and in continuous instead discontinuous), operate in mild conditions (less temperature and pressure), reduce the consumption of energy and obtain better selectivity.

Homogeneous catalysis presents large advantages in terms of selectivity and possibility to change the features of the catalyst, but in industrial scale is less used than heterogeneous catalysis due to high costs of catalyst recovery costs (separation and re-use) and the low productivity per reactor unit volume. Furthermore, the use of organometallic complexes puts strong restrictions to the operating conditions due to their stability, so it could be better work in diluted solution (having less productivity) and the ligand cost can be very high. For all these reasons processes using heterogeneous catalysts are preferred.

An alternative that respects the principles of the sustainable chemistry is represented by biocatalysis: usually reactions are conducted in aqueous solutions with low pressures and temperatures, the catalyst has high activity, the chemical selectivity, regiochemistry and stereochemistry are specific even with substrates that show multifunctionality, without the use of protector or activator groups.

These properties permit to obtain more suitable processes from the environmental and economic point of view, thanks to their greater simplicity. However, biocatalysis, using mainly enzymes and other biological systems, has big problems about the processes scale-up because of the fragility of the catalysts. Even the oxidant has an important role on the sustainability of a process. Stoichiometric oxidants as nitric acid, chlorine, permanganate or dichromate can be very efficient but has some drawbacks as large coproducts production that must be separated and treated appropriately.

An alternative-oxidizing reagent can be hydrogen peroxide, it has a large amount of active oxygen and its co-product is water. The HP use does or may lead several disadvantages:

- the presence of water as co-product can carry on some problems in the reaction mixture;
- it needs a catalyst to be activated because HP is a weak oxidant;
- from HP decomposition high level of oxygen can be generated increasing the pressure inside the reactor and causing flash problems if organic compounds are present;
- if excess of HP is used the final cost of products increases.

Organic hydroperoxides have similar problems, such as the formation in the reaction solution of the corresponding carboxylic acid or its salt that needs to be eliminated from the final product; furthermore these compounds are expensive and dangerous due to their instability.

Another suitable opportunity is the use of air or pure oxygen as oxidant. This permits to avoid the formation of co-products derived from oxidation that can cause problems in the reaction

mixture. In particular oxygen, instead of air, permits to reduce the volume of gas flows that has to be treated after reaction, operating pressure in some cases permits to increase the selectivity and the productivity of the process, improving the reagents contact and the transfer mass in the case of several phases. But the choice of pure oxygen has some drawbacks: oxygen is more expensive than air and decreases the security of the process because of the high possibility to form explosive mixtures. Nevertheless, oxygen and air remain the best oxidants from an environmental perspective.

Another important aspect to take into account in the study of oxidation processes is the choice of the phase: gaseous (VO) or liquid (LO). Generally VO requires high temperatures (300-500 °C), higher than temperatures used in LO (80-200 °C), also the different density plays an important role, indeed liquid phase reactions achieve better productivity. The high temperature used in VO causes the cleavage of C-C bond with the possibility of the formation of light and combustion products such as CO and CO_2, reducing the reaction selectivity.

From an engineering point of view, liquid phase oxidations are easier: generally they are carried out in the CSTR (Continuous-flow Stirred-Tank Reactor) or bubble columns, with the advantage of a better heat exchange. In the case of VO, reactors are tubular or multitubolar fixed beds, more complicated and difficult to build.

Concerning the control of the reaction, the LOs are easier to handle, with less possibility of run-away and a greater number of hydrocarbons suitable for reactions instead of VO. Generally, working in gaseous phase is cheaper than liquid, but very often the low selectivity of VO reaction reduces drastically this advantage. [43,45,46].

3.9 New system for the synthesis of adipic acid

3.9.1 1,6-hexanediol

For the reasons discussed above, chemical industry has a high interest in developing new ways for more sustainable processes in the synthesis of adipic acid. Reason why in recent years scientific attention has been oriented toward another reagent, which is 1,6-hexanediol.

Although 1,6-hexanediol may be normally obtained by crude oil, the interest for this reagent lies in the possibility of obtaining it from processing renewable resources such as corn grain

(maize), sugar cane, sugar beet, wheat, potato, cassava and rice as well as alternative sources such as energy crops, plant biomass, agricultural wastes, forestry residues, sugar processing residues and plant-derived house-hold wastes. If processes for the production of 1,6-hexanediol from renewable feedstock at a cost less than the current cost for producing the same from oil-derived adipic acid could be commercialized, 1,6-hexanediol could become a vital building block chemical uses for and production volume of which would expand exponentially. In light of the changing environment toward utilization of cheaper, renewable feedstocks, the discovery of new, industrially scalable methods for the selective and economical production of adipic acid from 1,6-hexanediol could have extraordinary value in near future.

3.9.2 Transformation of 1,6-hexanediol to adipic acid

As appeared from the literature the noble metals such as Au, Pd and Pt catalyze the oxidation of alcohol groups to carboxylic groups [47]. Concerning fifth point of the list of principles of Green Chemistry, as previously explained in Chapter 3.1, auxiliary substances, like the solvent, should be less innocuous as possible and water reveals to be the best solvent. Considering these conditions the best results up to now come recently from Rennovia Inc. This company brought to the market an environmentally friendly manner that consists of using water as solvent, dioxygen as the oxidant in the presence of supported Pt and Au NPs. Many systems belonging to this class of catalysts were investigated. The best results were achieved with Pt/zirconia catalyst in aqueous solution of HDO, 140°C and 6 bar of oxygen and 34 bar of nitrogen. In these conditions 1,6-hexanediol conversion was 100% with >99% yield to adipic acid [48].

Despite the excellent results, this process could be further improved under temperature and pressure point of view. In fact more recently there was an attempt to work at 70°C and 40 bar of air. They have been tested the alloying of Pd or Pt with Au [49] since it has been shown in recent years that alloying permits to enhance significant activity and stability [50,51,52,53,54,55] of the catalysts. The Au-Pt catalysts have been shown to show higher catalytic activity than Au-Pd. The highest yield of the desired dicarboxylic acid (96%) was reached for the catalysts having a Au/Pd or Au/Pt atomic ratio of 1. Furthermore, the Au-Pt catalyst on zirconia showed good stability and maintained a high performance over 6 runs.

Modibo Mounguengui-Diallo *et al*. [49] hypothesized the reaction pathway of the 1,6-hexanediol oxidation to adipic acid (Scheme 16). 1,6-hexanediol is firstly oxidized to the intermediate 6-hydroxyhexanal which has a structural isomer with ε-caprolactol, the intermediate is subsequently oxidized to 6-hexanoic acid which has a structural isomer with ε-caprolactone. The final steps are the oxidation to 6-oxohexanoic acid and the oxidation to adipic acid.
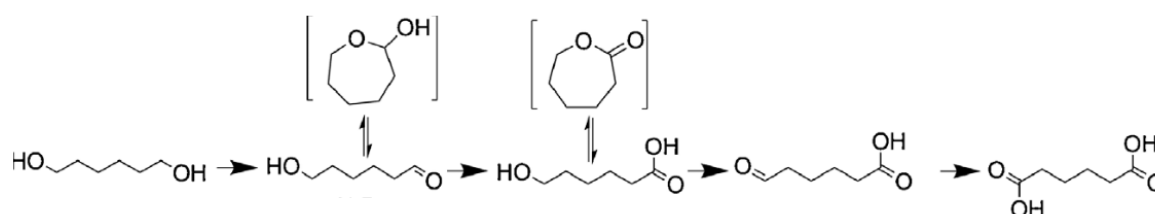
Scheme 16: Scheme of reaction of HDO oxidation to AA

Oxidation of the second alcohol group in HA is less rapid than the oxidation of the first alcohol group in HDO. This general reaction pathway was also observed during oxidation of HDO acetic acid acqueous solution over Pt/C [56].

3.9.3 Nanoparticles system

The International Organisation for Standardisation (ISO) defines the term "nanomaterial" as "material with any external dimensions in the nanoscale or having internal structure or surface structure in the nanoscale". The term "nanoscale" is defined as size range from approximately 1nm to 100 nm. Everything has a surface (or interface) and both physical and chemical properties depend on the nature and breadth of the surface regardless of whether it is a bulk material of a nanoscale material. At constant volume, if the surface increases the physical-chemical phenomena due to interactions with the external environment become much more relevant. Besides the surface atoms possess more energy than bulk atoms, consequently surface atoms is more chemically reactive, which means that nanoparticles possess enhanced chemical reactivity. The study of noble metals-based catalysts has grown significantly in

recent years in front of the their surprisingly activity in the form of nanoscale particles. Due to the high selectivity of noble metals catalysts, expensive purification processes are not necessary. Gold and Palladium are not active metals from a catalytic point of view if they are used as bulk material, because of its low tendency to chemisorption due to its electronic configuration respectively [Xe] $4f^{14}5d^{10}6s^1$ and [Kr] $4d^{10}$. In fact the chemical adsorption on a transition metal is made possible by the interaction of the HOMO and LUMO orbitals. From the catalytic point of view, the force of the chemical adsorption must be sufficiently strong to allow an effective interaction, but not too much, otherwise, an excessive retention of the molecule to the metal surface, would reduce the activity. Because of their electronic configuration, when a molecule adsorbs on metallic bulk surface, a strong effect of back bonding to the antibonding orbital is observed. A very weak interaction with the adsorbate does not allow a correct activation.

Besides the metal–support interaction was declared to be essential for the formation of a stable catalyst system [57,58]. Some authors reported different catalytic activity using different type of carbon supports with the same metal particle size indicating a specific metal–support interaction. Ishida *et al.* observed that gold particle size influences the catalytic effect more significantly than the nature of the support comparing carbon and different metal oxide supports such as Al_2O_3, ZrO_2, TiO_2, CeO_2 [59,60].

3.9.4 Supports for gold nanoparticles

The support plays a crucial role of dispersing the active phase, of stabilizing it in the desired state, in order to preserve properties of active phase during the chemical reaction and the treatments to which the catalyst will be subjected. The main features are: high thermal stability, high surface area and good mechanical properties.

Non-supported gold nanoparticles have a very high surface energy, so they are easy to agglomerate. Therefore, they should be dispersed on a suitable support to maintain their stability and catalytic activity. Gold and palladium nanoparticles should have good wetting capability and should interact with the high surface area support. Au and Pd NPs can be supported on metal oxides, activated carbon, zeolite and other supports by different methods of preparation including impregnation, precipitation, sol-immobilization or microemulsion.

33

Oxide supports are divided into basic supports, such as MgO, NiO, BaO, acid supports like Al_2O_3 and zeolites, and amphoteric supports like TiO_2,. For Au or Pd catalysts supported on active materials (which participate in the reaction mechanism), the dominant reaction pathway involves adsorption of a mobile molecular oxygen species on the support, dissociation at the interface that supply with reactive oxygen. While for inert supports, where the oxygen supply most likely proceeds via direct dissociative adsorption on the Au particles, the size of the latter plays a decisive role. Therefore, the use of supported gold and palladium catalyst to catalyze 1,6-hexanediol oxidation reaction, after choosing suitable support, requires that more attention be paid to the influence of preparation method on metal NPs size.

In industrial projects is preferred to support the active phase on metal oxides. Thus, the choice of the right support and adequate percentage of metals presumes a very delicate and complex process.

4. Objective of thesis

The main objective of this thesis concerns the synthesis of adipic acid from 1,6-hexanediol. In particular the aim of the work is to develop new process compatible as much as possible with the principles of Green and Sustainable Chemistry. To meet these requirements, the study was focused on the development of new heterogeneous catalysts able to oxidize the starting reagent in aqueous phase, using an economic and clean oxidizing agent. As described in the previous chapters, it was decided to work with the two best oxidants from environmental and economic perspectives, which are oxygen and air.

With the aim to develop a new process which could be able to exploit interest in renewable feedstock in accordance with Green Chemistry it was decided to work with a matter which is obtained by cellulose-derived [61]. At the same time this reagent responds to the Sustainable Chemistry on the Substitution point of view, namely it has the intent to replace a toxic reagent such as benzene. For these reasons 1,6-hexanediol was used as a starting reagent.

The first part of the thesis was dedicated to the synthesis and testing of different kind of catalysts; in line with the Sustainable Chemistry principles only heterogeneous catalysts were studied. These catalytic systems allow easily separating the catalyst from the final reaction mixture making the process less complicated and saving a lot of energy and money from the industrial point of view. Once the best catalytic systems have been chosen, the second part of the thesis was dedicated to the study of reaction conditions, in particular: using air replacing oxygen, changing molar ratio substrate/M, in order to bring the conditions closer to those that could be the most suitable from a large scale industrial point of view.

5. Experimental Part

5.1 Catalysts

The research objective of this thesis was to develop an alternative process, with a less environmental impact, for the synthesis of adipic acid. For this reason is necessary to develop a catalyst that is easy to prepare, active and selective, easy to separate and recovery from the final mixture and with a low tendency to deactivation.

For this study supported gold, palladium nanoparticle catalysts were used. Different supports among acid, amphoteric and basic ones were screened. All the catalysts were synthesized and characterized in collaboration with Adam Mickiewicz University in Poznań, Poland (MgO, MgF_2-based catalysts) and Departamento de Química Fundamental, of the São Paulo University in Brazil (MnO_2, BaO based catalysts).

5.1.1 Supports

- **NiO, TiO$_2$, MgO, CaO oxides,** and **Activated Carbon** (AC) were purchased from Sigma Aldrich® and used them as received.

TiO$_2$ and Activated Carbon show both kind of sites, acid and basic as reported in TPD characterization [62,63,64].

Basic proprieties of NiO, MgO, CaO contains are well known [65,66,67] .

- **VPP** were purchased from DuPont® and used them as received.

Acid sites are well known and divided in acid sites of Lewis, for the presence of V^{4+}, and acid sites of Brφnsted, for the presence of hydroxyl groups linked to Phosphorus [68].

- **Supports used for NC2 and NC1**catalysts preparation were purchased from Saint-Gobain NorPro's Denstone® and used as received. NC 1 support: SZ 39140 (wt %) = ZrO$_2$ 58%, TiO$_2$

41%, HfO_2 1,1%, SiO_2 0,46%; NC 2 support: SZ 61143 (wt %) = ZrO_2 83,2%, WO_3 15,3%, HfO_2 1,5%.

The corresponding supports have been characterized with NH_3-TPD and CO_2-TPD [69] and they show acidic proprieties.

- **MgF_2** and **MgF_2-MgO** supports with different MgF_2/MgO ratios were obtained by reacting a basic magnesium carbonate [$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$] powder with controlled amounts of a 40 wt.% aqueous solution of hydrofluoric acid, as described in [70,71]. The amount of HF was chosen to ensure 40, 60 and 100 mol.% of MgF_2 in the support. The resulting dense gels of MgF_2-unreacted magnesium carbonate were subjected to ageing for 40 h at room temperature then dried at 80 ^{o}C for 24 h before being calcined under air flow (50 mLmin^{-1}) at 500 ^{o}C for 4 h. The MgF_2-MgO samples were labelled as $0.4MgF_2$-0.6MgO and $0.6MgF_2$-0.4MgO.

Characterization of MgF_2 has been led using TPD, analysis showed both kind of sites, basic and acid [72].

- **MnO_2** nanoflowers were obtained by a hydrothermal approach [73,74,75]. In a typical procedure for the synthesis of nanoflowers, 0,4 g of $MnSO_4 \cdot H_2O$ and 1,0 g of $KMnO_4$ were dissolved in 30 mL of deionized water. This solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated and stirred at 140 °C for 1 h and then allowed to cool down to room temperature. The products were collected by centrifugation and washed three times with ethanol (15 mL) and three times with water (15 mL) by successive rounds of centrifugation and removal of the supernatant. As prepared materials were then dried at 80 °C for 6 h in air.

- **BaO** was obtained calcining 1g of $BaNO_3$ (Sigma-Aldrich) at 600°C for 6h (20 °C/min).

5.1.2 Catalyst preparation

Supported nanoparticles were prepared following a method based on the available literature [76,77] using the sol-immobilization method with PVA as stabilizer. First, a 2% (w/w) solution of PVA in distilled water was prepared considering the ratio PVA/Au (w/w) = 1.2 and when the PVA was completely dissolved the solution was added to an aqueous solution of $HAuCl_4$ (0.5 mM) under vigorous stirring (400 rpm). A freshly prepared $NaBH_4$ solution (0.1 M) was prepared considering the molar ratio $NaBH_4$/Au = 5 and then added drop by drop to form the metallic sol. The colour of the sol was deep purple. After 30 minutes of sol generation, the Au nanoparticles were immobilized by adding different supports under vigorous stirring. The amount of support was calculated to give a final metal loading of 2 wt.%. After 2 hours the slurry was filtered, the solid washed with 100 mL of hot water (T=50-60 °C) and 50 mL of ethanol and after was dried in the oven at 100 °C for 1 hour. The solid was finally grinded. Using this preparation method, it is expected to prepare gold nanoparticles with a diameter around 2-4 nm.

Au/0.6MgF$_2$-0.4MgO

Au / MgF_2-MgO (6040) wt% support chemical composition is MgF_2 60%, MgO 40%

2 wt% of Au

$m_{support}$ = 100 mg

m_{Au} = $m_{support}$ · 2/100 = 100 mg · 2/100 = 2 mg

n_{Au} = n_{HAuCl4} = m_{Au} / MW_{Au} = 2 mg / 196,97 g/mol = 0,0102 mmol

V_{HAuCl4} = n_{HAuCl4} / C_{HAuCl4} · 10^3 = 0,0102 mmol / 0,19 mol/L · 10^3 = 53 μL

PVA/Au 1,2% w/w

m_{PVA} = m_{Au} · 1,2 = 2 mg · 1,2 = 2,4 mg

V_{PVA} = m_{PVA} · 100/2 = 2,4 mg · 100/2 = 120 μL

$NaBH_4$ (0,1 M $NaBH_4$ / Au = 5 n/n)

$n_{NaBH4} = n_{Au} \cdot 5 = 0{,}0102 \text{ mmol} \cdot 5 = 5{,}1 \cdot 10^{-2} \text{ mmol}$

$m_{NaBH4} = n_{NaBH4} / MW_{NaBH4} = 5{,}1 \cdot 10^{-2} \text{ mmol} \cdot 37{,}83 \text{ g/mol} = 1{,}9 \text{ mg}$

$V_{H2O} = n_{NaBH4} / C_{NaBH4} = 5{,}1 \cdot 10^{-2} \text{ mmol} / 0{,}1 \text{mol/L} \cdot 10^{3} = 508 \text{ }\mu L$

Water (HAuCl$_4$ 0,5 mM)

$V_{H2O} = n_{Au} / C_{HAuCl4} = 0{,}0102 \text{ mmol} / 5 \cdot 10^{-4} \text{ mol/L} = 20 \text{ mL}$

Au/NC1

NC1 has Saint-Gobain support whose chemical wt% composition is: ZrO_2 58%, TiO_2 41%, HfO_2 1,1%, SiO_2 0,46%, (SZ 39140).

2 wt% of Au

$m_{support} = 1000 \text{ mg}$

$m_{Au} = m_{support} \cdot 2/100 = 1000 \text{ mg} \cdot 2/100 = 20 \text{ mg}$

$n_{Au} = n_{HAuCl4} = m_{Au} / MW_{Au} = 20 \text{ mg} / 196{,}97 \text{ g/mol} = 0{,}101 \text{ mmol}$

$V_{HAuCl4} = n_{HAuCl4} / C_{HAuCl4} \cdot 10^{3} = 0{,}101 \text{ mmol} / 0{,}19 \text{ mol/L} \cdot 10^{3} = 532 \text{ }\mu L$

PVA/Au 1,2% w/w

$m_{PVA} = m_{Au} \cdot 1{,}2 = 20 \text{ mg} \cdot 1{,}2 = 24 \text{ mg}$

$V_{PVA} = m_{PVA} \cdot 100/2 = 24 \text{ mg} \cdot 100/2 = 1200 \text{ }\mu L$

NaBH$_4$ (0,1 M NaBH$_4$ / Au = 5 n/n)

$n_{NaBH4} = n_{Au} \cdot 5 = 0{,}101 \text{ mmol} \cdot 5 = 0{,}505 \text{ mmol}$

$m_{NaBH4} = n_{NaBH4} / MW_{NaBH4} = 0{,}505 \text{ mmol} \cdot 37{,}83 \text{ g/mol} = 19 \text{ mg}$

$V_{H2O} = n_{NaBH4} / C_{NaBH4} = 0{,}505 \text{ mmol} / 0{,}1 \text{mol/L} = 5 \text{ mL}$

Water (HAuCl$_4$ 0,5 mM)

$V_{H2O} = n_{Au} / C_{HAuCl4} = 0{,}102 \text{ mmol} / 5 \cdot 10^{-4} \text{ mol/L} = 204 \text{ mL}$

Figure 5: *Typical purple colour of Au-PVA solution after NaBH$_4$ adding(left)*
NC1 2% w/w: Au$_{NP-PVA}$ / ZrO$_2$-TiO$_2$ (right)

5.1.3 Catalyst characterization

X-ray Diffraction

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern. The dominant effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of those X-rays from atoms within the target material. In materials with regular structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is described by Bragg's Law, $n\lambda = 2d \sin\theta$. The directions of possible diffractions depend on the size and shape of the unit cell of the material. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure. However, most materials are not single crystals, but are composed of many tiny crystallites in all possible orientations called a polycrystalline aggregate or powder. When a powder with randomly

oriented crystallites is placed in an X-ray beam, the beam will see all possible interatomic planes. If the experimental angle is systematically changed, all possible diffraction peaks from the powder will be detected. X-ray diffraction has been applied to many different types of applications including thin film analysis, sample texture evaluation, monitoring of crystalline phase and structure, and investigation of sample stress and strain[78]. The X-ray analyses have been carried out by using Bruker-D8 Advance XRD. Powder Xray diffraction (XRD) patterns were recorded on a Bruker D8-Advance X-ray powder diffractometer operated at an accelerating voltage of 40 kV and an emission current of 40 mA with Cu Kα radiation. Samples were scanned over the range of 10° - 70°, step size of 0,014° and a time of 19,2 s par step. The setting of 10 mm divergence, fent primaire Soller 2,5° were used.
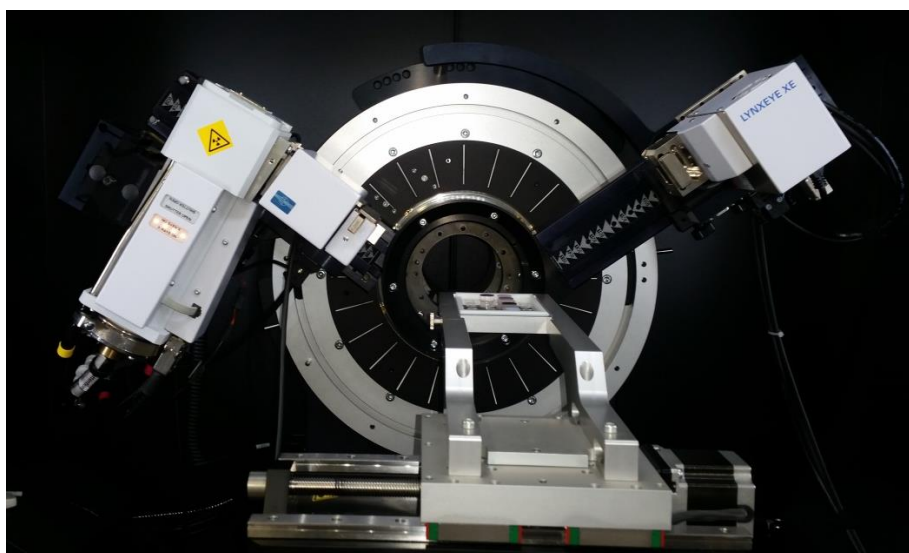
Figure 6:XRD apparatus

X-ray Fluorescence

X-ray fluorescence (XRF) is a powerful quantitative and qualitative analytical tool for elemental analysis of materials. It is ideally suited to the measurement of film thickness and composition, determination of elemental concentration by weight of solids and solutions, and identification of specific and trace elements in complex sample matrices. XRF analysis is used extensively in many industries including semiconductors, telecommunications, microelectronics, metal finishing and refining, food, pharmaceuticals, cosmetics, agriculture,

plastics, rubbers, textiles, fuels, chemicals, and environmental analysis. The method is fast, accurate, non-destructive, and usually requires only minimal sample preparation. When elements in a sample are exposed to a source of high intensity X-rays, fluorescent X-rays will be emitted from the sample at energy levels unique to those elements. The basic concept for all XRF spectrometers is a source, a sample, and a detection system. The source irradiates the sample and a detector measures the fluorescence radiation emitted from the sample. In most cases for XRF, the source is an X-ray tube. Alternatives are a radioactive source or a synchrotron. There are two main types of XRF instruments: Energy Dispersive X-ray fluorescence (EDXRF) and Wavelength Dispersive X-ray Fluorescence (WDXRF). X-ray optics can be used to enhance both types of XRF instrumentation. For conventional XRF instrumentation, typical focal spot sizes at the sample surface range in diameter from several hundred micrometers up to several millimeters. Polycapillary focusing optics collect X-rays from the divergent X-ray source and direct them to a small focused beam at the sample surface with diameters as small as tens of micrometers. The resulting increased intensity, delivered to the sample in a small focal spot, allows for enhanced spatial resolution for small feature analysis and enhanced performance for measurement of trace elements for Micro X-ray Fluorescence applications. Doubly curved crystal optics direct an intense micron-sized monochromatic X-ray beam to the sample surface for enhanced elemental analysis [56]. Elemental concentration of analyses in the catalysts was determined with the use of an energy dispersive micro-X Ray Fluorescence spectrometer M4 TORNADO (Bruker). This instrument is equipped with 2 anodes a Rhodium X-ray tube 50 kV/600 µA (30 W) and a Tungsten X-Ray tube 50 kV/700 µA (35 W). For sample characterization, the X-rays Rhodium with a polycapillary lens enabling excitation of an area of 200 µm was used. The detector used was a Silicon-Drift-Detector Si(Li) with <145 eV resolution at 100000 cps (Mn Kα) and cooled with a Peltier cooling (253°K). The elements, that can be measured by this instrument unit range from sodium (Na) to uranium (U). Quantitative analysis was done using fundamental parameter (FP) (standardless). The measurement was done under vacuum (20 mbar). A small drop of reaction solution sample is deposited on the layer and, once it is fully evaporated, several points were measured for each sample in order to cover the sample surface with a spot size of 200 µm for each point.

Transmission Electronic Microscopy

The transmission electronic microscope (TEM) analysis with EDS probe (Figure 7) is based on the electron-matter interaction and it is useful to know about composition, phases presented, crystallinity degree and particles size with a resolution of 0,2 nm, for the high-resolution instruments.
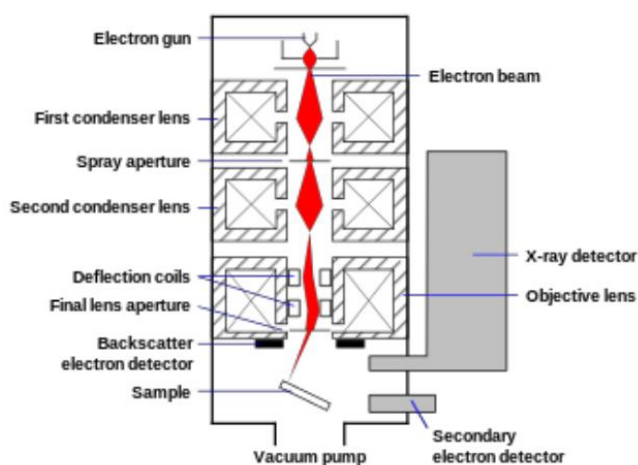
Figure 7: TEM simplified scheme.

During the analysis, a beam of electrons is accelerated with an electric potential in high vacuum and focused on the sample using magnetic lenses. The beam can traverse through a very thin sample layer and it is partially diffracted and partially it does not undergo any deviation. Subsequently, both of electron beams come to a fluorescent screen that allows to see the greatly enlarged bi-dimensional projection. The TEM analyses were performed to know the metal nanoparticles distribution and them size. The most active catalysts were characterized in the morphology and in the metal dispersion on the surface. Before the analysis, the catalysts were dispersed in EtOH and left for 10 minutes in the ultrasonic bath. To perform the analyses, the suspensions were deposited on the copper grill\grate and the instrument used was the microscopy TEM/STEM FEI TECNAI F20 combined with an Energy Dispersive X-ray Spectrometry (EDS) a 200 keV.

5.2 Laboratory set up

The catalytic tests were performed in a multiphase semi-batch reactor equipped with mechanical stirrer and external heating system and on a SPR High Pressure reactor on the REALCAT platform. All equipment used is described below.

5.2.1 Bench scale reactor

The TOPIndustry Autoclave is a steel reactor used to perform the catalytic tests. The autoclave used is built so as to control and take action on different parameters, such as: rotation, amount of catalyst charged, reagents concentration and temperature of reaction. In fact the reactor is equipped with a high precision heating system and a mechanical stirrer. It is possible to perform tests up to 250 °C (using refrigeration system on the top of the reactor) and 100 bar of pressure. Temperature and stirring rate are controlled with and external electronic device. Liquid reagents are insert in the vessel of the autoclave, which has a total volume of 30 mL. The flow system is fitted with two valves, one linked with a pure O_2 tank (total CnHm < 500 PPB, H_2O < 3 PPB), which permits to charge oxygen in the reactor, and another one, opposite placed to purge. Technical scheme of the reactor is given in the following Figure 8.
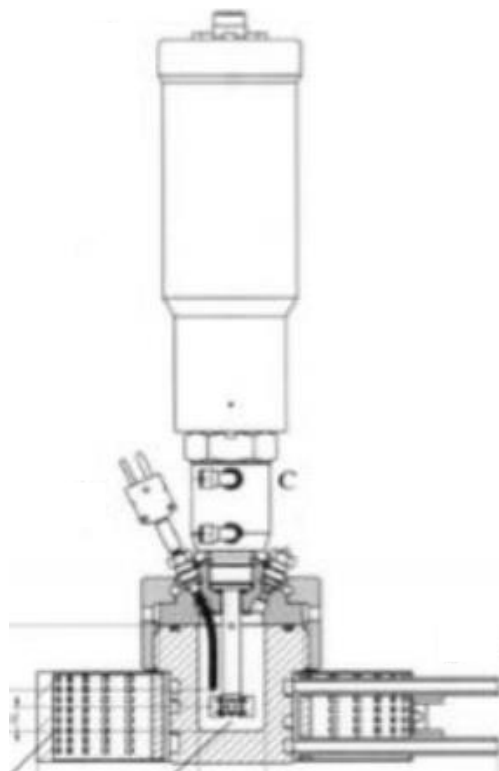
Figure 8: TOPIndustry autoclave reactor scheme.

5.2.2 Reactor settings and conditions

The reactor was used in batch conditions, therefore firstly it was charged with the reagent solution and catalyst, finally with O_2 at whose tank it was linked. The reaction solution was prepared adding a certain amount of 1,6-hexanediol in 21 mL of total volume of H_2O stirring the solution with an ultrasonic bath to dissolve 1,6-hexanediol before adding it in the vessel. While 1 mL of that solution was taken off for HPLC analysis of the t_0. Then a very precise amount of catalyst was weighted considering the desired molar ratio between the M and the substrate and then added to the autoclave.

After this, the reactor was closed and purged with a flow of oxygen. The pression used (6 bar) was reached and after that the heating system turned on. The time necessary to reach the desired temperature was not considered in the reaction time, indeed the 2 hours of reaction started just when the system reached the right temperature. At the end of the reaction the air cooler system decreased the temperature till room temperature at which the final solution was discharged. The reaction mixture was taken away and filtered with a nylon membrane filter

0,2μm for syringe. 1 mL of the final solution was diluted with water for HPLC analysis of the t_f and the rest of the solution was stored in the fridge for further analyses. The relative TOPIndustry Autoclave results are shown in the Results and Discussion chapter of this thesis.

5.2.2 Screening Pressure Reactor (SPR)

The Screening Pressure Reactor (SPR) is an automated high pressure, high temperature reactor that accelerates catalyst discovery and reactions optimization located in REALCAT platform. This high throughput system can screen hundreds of reaction conditions, explore new synthetic routes, optimize reaction yield and identify alternate reaction conditions to reduce costs or identify a suitable solvent. The SPR has very wide applications like: hydrogenation/dehydrogenation, oxidation, acid/base reactions, biomass processing, petrochemicals, fine chemicals. For this project, it was useful to test and screen several catalysts in shorter time. The relative SPR results are shown in the Results and Discussion II chapter of this thesis.

As explained above SPR possesses many characteristics, the main ones of which are following listed:

- High throughput runs: catalysts testing in parallel (24 samples) and examine multiple variables simultaneously for rapid and high information content screening.
- Flexible reaction scales: 2 mL x 48 glass vials or 6 mL x 24 stainless steel vials.
- Wide process window: temperatures up to 400 °C and pressures up to 200 bar.
- Automated operation: temperature, pressure, and flow profiles controlled automatically based on a user defined recipe.
- Powerful mixing: High intensity vortexing (up to 800 rpm) provides for good solid/gas/liquid contacting during reaction and limits mass transfer issues.

Figure 9: Screening Pressure Reactor (SPR)

5.3 Analysis of the products

The quantitative analysis of the components of the reaction mixture was carried out by means HPLC.

5.3.1 Qualitative and quantitative analysis by HPLC

High Performance Liquid Chromatography (HPLC) was developed in the late 1960s and early 1970s. Today it is widely applied for separations and purifications in a variety of areas including pharmaceuticals, biotechnology, environmental, polymer and food industries. HPLC has over the past decade become the method of choice for the analysis of a wide variety of compounds. Its main advantage over GC is that the analytes do not have to be volatile, so macromolecules are suitable for HPLC analysis. HPLC is accomplished by injection of a small amount of liquid sample into a moving stream of liquid (called the mobile phase) that passes through a column packed with particles of stationary phase. Separation of a mixture into its components depends on the different degrees of retention of each component in the column. The extent to which a component is retained in the column is determined by its partitioning between the liquid mobile phase and the stationary phase. In HPLC this partitioning is affected by the relative solute/stationary phase and solute/mobile phase interactions. Thus, unlike GC, changes in mobile phase composition can have an enormous impact on the separation. Since the compounds have different mobilities, they exit the column at different time. The retention time is the time between injection and detection. There are numerous detectors, which can be used, in liquid chromatography such as UV, RI and MS. Detector is a device that senses the presence of the different components from the liquid mobile phase and converts that information to an electrical signal. It is important to remember that any changes in operating conditions will affect the retention time, which will affect the accuracy of identification. Quantitative analysis is often accomplished with HPLC. An automatic injector providing reproducible injection volumes is extremely beneficial, and it is standard on modern commercial systems. The HPLC apparatus consists of a mobile phase reservoir, which is just a clean solvent jug, a solvent delivery system consisting of a pump for delivering precise, reproducible and constant amount of mobile phase, a sample inlet, the column, a detector with associated electronics, and some kind of interface to the outside world

such as a computer. The pump, which is used to deliver the mobile phase solvent at a uniform rate often, operates at pressures ranging from 500 - 5000 psi. These high pressures are needed because the stationary phase column packing consists of very small, tightly packed particles. High pressure should be applied to push the mobile phase through this stationary phase at a reasonable flow rate. HPLC is just one type of liquid chromatography, meaning the mobile phase is a liquid. Reversed phase HPLC is the most common type of HPLC. What reversed phase means is that the mobile phase is relatively polar, and the stationary phase is relatively non-polar. Thus non-polar compounds will be more retained (i.e. have longer retention times) than a polar compound. In normal phase HPLC, the mobile phase is relatively non-polar and the stationary phase is relatively polar. Other more general types of HPLC include partition, adsorption, ion-exchange, size-exclusion, and thin-layer chromatography [79]. The instrument used in the UCCS laboratory is a Shimadzu for Ultra Fast Liquid Chromatography composed by: 20ACHT UFLC version Auto-Sampler, LC-20AD Solvent Delivery Unit, DGU-20A3 Online Degasser, CTO-20A Column Oven and SPD-20A UFLC version UV-VIS Detector.

HPLC method:

- Column: Rezex ROA – organic Acid H+ (8%).

- Length: 30m.

- Inner diameter: 7,80 mm.

- Eluent: sulfuric acid 5 mM.

- Flow: 0,5 mL/min.

- Volume injected: 20 uL.

- Run time: 60 min.

- Column pressure: 40 bar.

- Detector: UV, λ= 210 nm; IR.

5.3.1.1 HPLC calibration

1,6-hexanediol

Mother solution of 1,6-hexanediol (11,5 mg) in water (5 mL) was prepared. Other solutions have been gotten at different concentration by dilution of mother solution. RI detector was used to detect.

Table 2: 1,6-hexanediol HPLC calibration output

C_{HDO} (mM)	$Area_{HDO}$
0,0	0,0
4,9	3,0
9,7	6,4
14,6	9,1
19,5	12,2

Retention time of HDO: 53,5 min
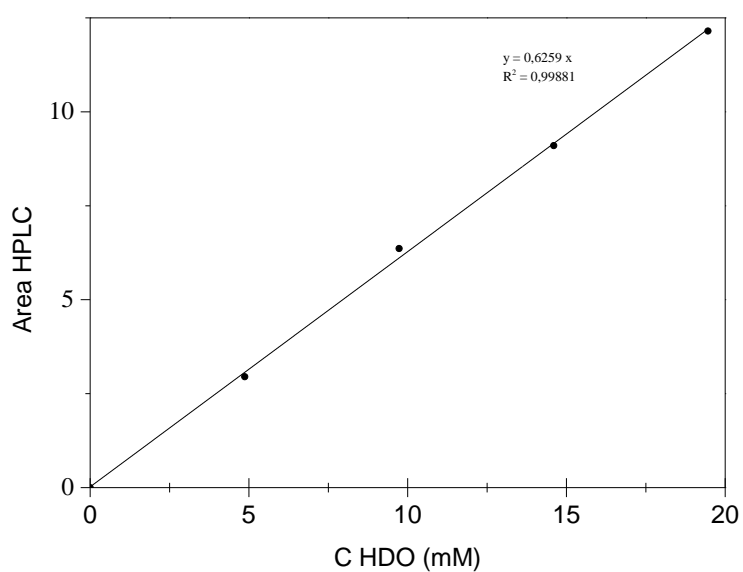
Figure 10: 1,6-hexanediol calibration curve

6-hydroxyhexanoic acid

Mother solution of 6-hydroxyhexanoic acid (15,4 mg) in water (9 mL water and 1,1 mL NaOH 10^{-2} M). Other solutions have been gotten at different concentration by dilution of mother solution. HA has been detected by UV detector at 210nm of wavelength.

Table 3: 6-hydroxyhexanoic acid HPLC calibration output

C_{HA} (mM)	$Area_{HA}$
0,0	0,0
1,2	2,2
2,9	5,9
5,8	11,3
8,7	17,1
11,5	22,3

Retention time of HA: 34,8 min
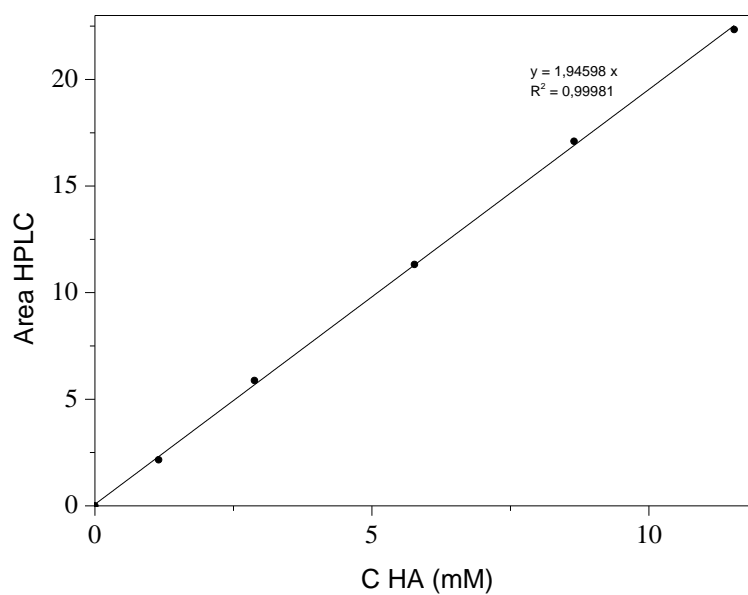
Figure 11:*6-hydroxyhexanoic acid calibration curve*

Adipic acid calibration

Mother solution of adipic acid (44,7 mg) in water (5 mL) was prepared. Other solutions have been gotten at different concentration by dilution of mother solution. AA has been detected using UV detector at 210nm of wavelength.

Table 4: Adipic acid HPLC calibration output

C_{AA} (mM)	$Area_{AA}$
0,0	0,0
1,0	4,1
5,1	19,5
10,2	39,3
15,3	58,9
30,4	77,8

Retention time of AA: 25,0 min
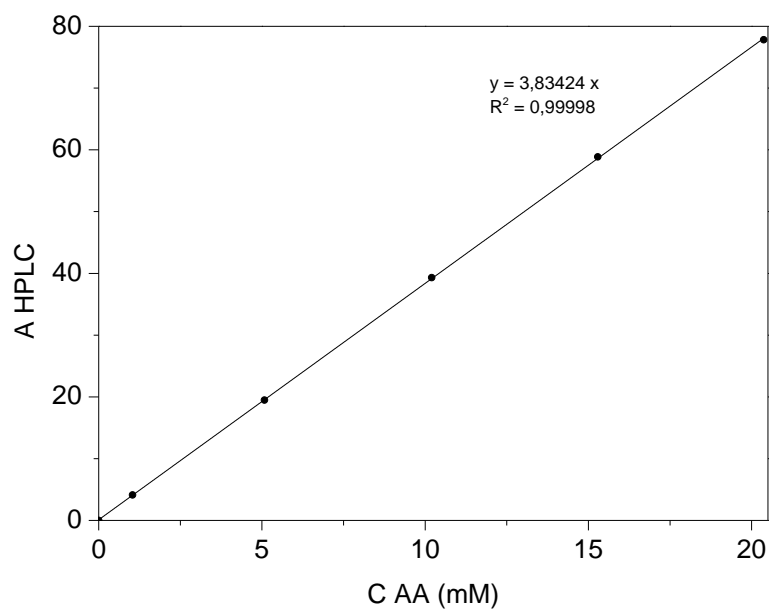
Figure 12:Adipic acid calibration curve

5.3.2 Catalytic data analysis

The aim of this thesis was to verify and improved the catalytic activity of the catalysts screened in oxidation of 1,6-hexanediol to adipic acid in water. Quantitatively, the work has been possible thanks to the integration peaks obtained by HPLC-analysis and calibration curves of each single compound. It was therefore possible to calculate conversion, yield, selectivity and carbon balance, according to the following formulas.

$$CB = \frac{n\ HDO\ f + n\ AA + n\ HA}{n\ HDO\ i} \cdot 100\%$$

$$X\ HDO = \frac{n\ HDO\ i - n\ HDO\ f}{n\ HDO\ i} \cdot 100\%$$

$$Y\ product = \frac{n\ product}{n\ HDO\ i} \cdot 100\%$$

$$S\ product = \frac{n\ product}{n\ HDO\ i - n\ HDO\ f} \cdot 100\%$$

n HDO i = initial moles of HDO

n HDO f = final moles of HDO

n product = final moles of product

6. RESULTS AND DISCUSSION I

The aim of this part of the thesis is to screen the best catalytic system for the base-free oxidation of 1,6-hexanediol to adipic acid in aqueous phase.

All results reported here concern reactions carried out in the TOPIndustry Autoclave reactor, described in the Experimental Part (Chapter 5.2.1) and in the conditions listed below:

- Temperature of reaction: 100°C
- Time of reaction: 3 hours
- Pressure O_2: 6 bar
- Starting reactant solution: 20 mL
- Molar ratio HDO/M: 100
- Stirring: 600 rpm

All catalytic tests and final solutions treatments were performed using the methodology described in the Chapter 5.3. The catalyst and the aqueous solution of 1,6-hexanediol were manually introduced into the reactor. The catalyst was weighed with an analytical balance while the starting reagent solution was prepared mixing HDO, weighed with an analytical balance, and water withdrawn with a calibrated pipette. The temperature of the reflux condenser was set up at 10 °C. Once this temperature was reached the pressure was set to the desired value. Then the stirring system and the temperature were also set up to the desired values. At the end of the reaction, the temperature of the reactor was cooled down to room temperature, the stirring was stopped and the pressure released. The solution has been then filtered to remove the catalyst and 200 μL of that solution was withdrawn with a micropipette prior to the HPLC analysis. The final volume of the reactant mixture was measured using a graduated pipette to calculate the conversion, yield and selectivity.

6.1 Metal effect

One of the most important factors that influence the catalytic activity is the nature of the metal used as the active phase. In our study we have compared Au and Pd based catalysts. The study has been led using MgO as the support and the conditions mentioned above. Since the

metal concentration on the support was different between gold (2%) and palladium (1%), formula showed in Chapter 5.3.2 has been adapted considering the number of moles of metal used. In this way the conversion is expressed as the percentage of the rate of number of moles of reagent converted on moles of metal used and the yield as the percentage of the rate of number of moles of product produced on moles of metal used. Results are reported in Table 5.

Table 5: Metal effect on MgO support at 100 °C, 6 bar O_2, 600 rpm, 3h, HDO/M = 100

Metal	X_{HDO} (%)	Y_{HA} (%)	Y_{AA} (%)	CB (%)
Au	58	37	15	94
Pd	27	16	4	93

The results presented in Table 5 shows that carbon balance was always higher than 90%. It was calculated considering that the main compounds obtained were: non-reacted 1,6-hexanediol, 6-hydroxyhexanoic acid, the intermediate, and adipic acid, the expected product.
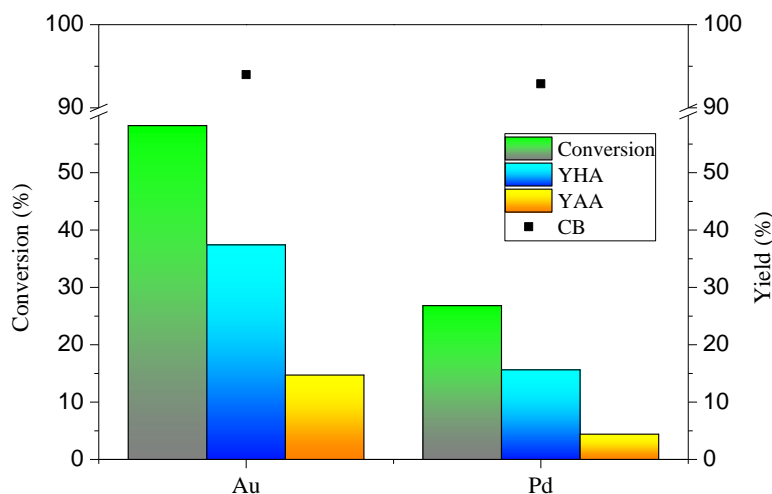

Figure 13: Metal effect on HDO conversion at 100 °C, 6 bar O_2, 600 rpm, 3h, HDO/M = 100

Results shown in Table 5 and Figure 1 show that the nature of the metal plays a fundamental role in HDO oxidation. In fact, maintaining the same conditions and support, gold NPs are more active than Pd NPs. Au NPs activity is almost double of that showed by Pd NPs (58% versus 27).

In both cases the main product of the reaction was 6-hydroxyhexanoic acid, the intermediate. This result suggests that both catalysts oxidize preferentially HDO and the HA desorption is the determining step of the reaction.

6.2 Support Effect

It was previously demonstrated that the nature of the metal plays a crucial role in 1,6-hexanediol oxidation. As gold resulted in more active materials; therefore it has been decided to study in deep the role of the support on the catalyst activity using gold catalysts. In particular, the attention is focused on the acid/basic sites of the supports. For this purpose several supports have been selected among acidic, amphoteric and basic ones. Results are reported in Table 6.

The following supports were considered:

- NC2: ZrO_2 83,2%, WO_3 15,3%, HfO_2 1,5%
- VPP
- NC1: ZrO_2 58%, TiO_2 41%, HfO_2 1,1%, SiO_2 0,46%
- AC
- MgF_2
- TiO_2
- NiO
- MnO_2
- MgO
- CaO
- BaO

All catalysts screened had total gold loading of 2%, therefore it was possible to use formula presented in Chapter 5.3.2.

Table 6: Support effect in HDO oxidation on supported Au_{NP}. 3h at 100°C, 6bar O_2, 600rpm

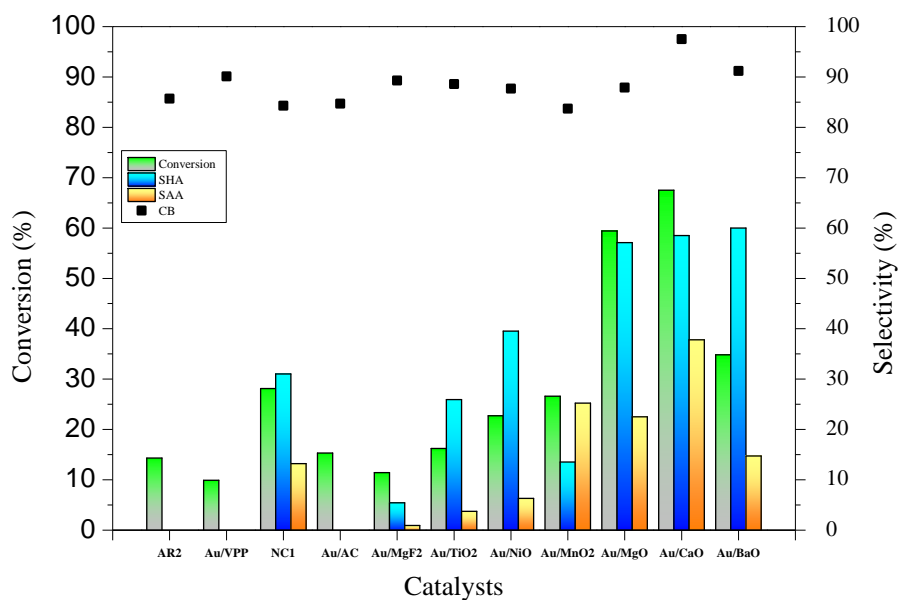| Catalyst	X_{HDO} (%)	HA		AA		CB (%)
		Y (%)	S (%)	Y (%)	S (%)	
Au/NC 2	14	0	0	0	0	86
Au/VPP	10	0	0	0	0	90
Au/NC 1	28	9	31	4	13	84
Au/AC	15	0	0	0	0	85
Au/MgF$_2$	11	1	5	0	1	89
Au/TiO$_2$	16	4	26	1	4	89
Au/NiO	23	9	40	1,4	6	88
Au/MnO$_2$	27	4	14	6,7	25	84
Au/MgO	59	34	57	13	23	88
Au/CaO	68	40	59	26	38	97
Au/BaO	35	21	60	5	15	91

Figure 14:Support effect for Au_{NP}. after 3h, 100°C, 6 bar O2, 600rpm, HDO/M = 100

First observation from these results is that the support plays a crucial role in the 1,6-hexanediol oxidation using Au NPs. In all cases the carbon balance was always higher than 84

%. The most important observation is that the kind of acid/basic properties of the support used influences the catalyst activity. In fact, there is a clear distinction among results obtained with acid, amphoteric and basic supports.

Acid supports have negative effect on HDO oxidation on Au nanoparticles (Figure 2). In case of VPP and NC 2 the conversion is low and no AA was observed in the final products. The only exception for acid supports is NC1, which has the chemical composition of ZrO_2 58%, TiO_2 41%, HfO_2 1,1%, SiO_2 0,46%. This catalyst showed good results with the HDO conversion of 28% and selectivity to AA of 13%.

Amphoteric supports showed also low activity in HDO oxidation, among which Au/TiO_2 reached the highest values. HDO conversion reached 16% and selectivity of 4% to AA was obtained.

Last supports screened, reported in Table 2, are those with basic properties (NiO, CaO, MgO). All of them showed high activity in HDO oxidation. Considering basic Lewis definition for "an electron pair donor" basicity increases with growing of atom size, because it is easier to push away the external electrons from the nucleus. Rearranging metal basic-supports in order of increasing size (Ni > Mn > Mg > Ca > Ba) there is an increasing of conversion of HDO from Ni to Ca and an unexpected decrease of activity for Ba. The most active catalyst was Au/CaO ($X_{HDO} = 67\%$), followed by Au/MgO ($X_{HDO} = 59\%$) in conditions tested. Indeed, as already observed by Davis et al. [80] the use of basic support would increase the population of hydroxyl species on the surface of the catalyst and thus promote the oxidation of HDO. In our case, the supports we used confirmed this observation. MgO and CaO are typical basic oxide and will react with water forming $Mg(OH)_2$ or $Ca(OH)_2$ acting as a weak base [81] and increasing the pH of the reactant solution. In contrary, much less basic TiO_2 and acidic AC [82] will not change the acid pH of the reactant mixture. As expected, the Au-based catalysts supported on neutral or acidic supports (MgF_2, VPP) showed low or no yield of AA besides presenting some conversion. The catalytic activity observed here followed a similar trend to that reported by Ebitani et al., which reported that catalysts using basic supports displayed higher activity than those using neutral or acidic supports [hydrotalcite (HT) > MgO > Al_2O_3 > activated carbon (AC) > SiO_2] [83]. While the activity might be related to the basic sites on the metal oxide surface, the basic oxides used as supports (CaO, MgO, NiO) form HO^- ions when in aqueous solutions, and then part of the support is dissolved. Previous studies from Zope et al. with Au/TiO_2 and hydrotalcite (HT) as

a solid base for HMF oxidation showed that leaching of Mg^{2+} from HT actually occurred[84]. XRF measurements and determination of pH values obtained after catalytic tests (results discussed below) confirmed the dissolution of the supports that, according to literature [81], resulted from an acid-base reaction, once the formed acid lowered the pH of the reaction medium and consumed the basic solid support. Then, the support dissolution is intensified by the formation of acids as reaction products (AA and HA), which lowers the reaction pH. It means that the catalysts with basic supports are very active, but might not resist to recycling tests, owing to the leaching of the support. Moreover, in such a case, a neutralization reaction will be required to isolate the acid, which means an additional step to the process.

Subsequently pH measures were taken for the most interesting family of catalysts previously screened and they are listed below.

- Au/NC 1
- Au/MnO_2
- Au/MgO
- Au/CaO

pH measures were made using pH-meter FE20 FiveEasy. pH measures were carried out before and after reaction in the conditions listed above and after the results reported in Table 7. For reagent solution, pH was measured only for one HDO solution (m_{HDO} = 32,3 mg, V_{H2O} = 20 mL) to have an order of magnitude of initial pH of reagent solution, pH measured is 7,64. Product solution pH expected is acid because product awaited was adipic acid (pKa_1 4,41 and pKa_1 5,41[85]).

Table 7: pH of reaction solution after 3h at 100°C, 6bar O_2, 600rpm

Solution after filtration of catalysts	pH
Au/NC 1	4,18
Au/MnO_2	5,47
Au/MgO	9,35
Au/CaO	7,03

Only solutions corresponding to the catalysts NC1 and MnO_2 catalyst showed an acid pH, but other parameters could influence these values. For this reason XRF analysis was performed on the same solutions used for pH measures to provide qualitative information about the presence of metals (Table 8). Samples for analysis were got after evaporation of a few solution drops on a polymer substrate as showed in Figure 15.

Figure 15: Sample preparation for XRF analysis

Table 8: XRF analysis

CT	Metals				
	Ca	**Mg**	**Mn**	**Zr**	**Ti**
Au/MgO	-	X	-	-	-
Au/CaO	X	-	-	-	-
Au/MnO$_2$	-	-	X	-	-
NC 1	-	-	-	-	-

XRF results showed that almost all samples examined presented some leaching: the presence of Mg was detected in the corresponding solution of Au/MgO, Ca in Au/CaO and Mn in Au/MnO$_2$. Different behaviour for only NC1 which didn't show leaching because Zr and Ti were not detected. In contrary, as expected any leaching was observed for NC1 sample.

6.3 Basicity Effect

Unfortunately, during the catalytic tests leaching issues at the end of the reaction have been noted. Nevertheless, apparently the basic properties of the supports contribute significantly to the catalytic activity of the final materials. Their catalytic performances strongly depend on the basicity of the support.

For this reason, the basicity effect was studied changing the amount of MgO and MgF_2 in MgO-MgF_2 mixed phases. Basic sites added to MgF_2 would improve the catalyst activity in HDO oxidation to AA and, at the same time, the presence of MgF_2 could decrease the MgO leaching. The preparation of mixed phases allowed the control of the content of basic sites in the support by diluting them under the form of a mixture of MgF_2 and MgO phases [86,87,88]. The catalytic tests carried out with the MgF_2-MgO based catalysts are presented in Table 9 and Figure 16.

Table 9: MgO addition effect on Au/MgF$_2$ catalysts in HDP oxidation after 3h at 100°C, 6bar O$_2$, 600rpm

wt. % MgO	X_{HDO} (%)	HA		AA		CB (%)
		Y (%)	S (%)	Y (%)	S (%)	
0	11	1	5	0	1	89
40	42	17	41	14	33	89
60	62	34	54	20	33	92
100	59	34	57	13	23	88

Carbon balance was always close to 90%, which suggests that adipic acid, unreactive 1,6-hexanediol and 6-hydroxyhexanoic acid (the intermediate) were major products of the reaction.

Au/MgF$_2$ displayed a rather low catalytic activity, similar to those of titania- and AC-based catalysts (11 % of HDO conversion) although it was less prone to the formation of AA. The presence of the catalyst did not yield any change in the reaction pH, then there was no evidence of leaching. Therefore, degradation and/or side reactions and lower catalytic performance can be attributed to the acidic reaction medium, which does not favor the Au-based solid catalytic functions. Increasing the content of MgO in the mixed phase support (MgO-MgF$_2$) resulted in higher conversions, AA yields and carbon mass balances, as

highlighted in Figure 16. The addition of basic sites to MgF_2 effectively improved the catalyst activity. In fact the HDO conversion passed from 11% for MgF_2 to 42% for 40% of MgO and 60% of MgF_2. Surprisingly, Au/0.4MgF$_2$.0.6MgO showed a slight better activity compared to Au/MgO (62% and 59% respectively), however, the main effect was on AA selectivity, 33% and 23%, respectively. Results obtained showed that Au/MgF$_2$MgO 4060 is more selective to AA than Au/MgO and the reaction pathway favoured HDO oxidation to HA. Therefore it has been hypothesized a synergic effect between MgF_2 and MgO, whose presence is essential to have high yield of AA.

At the end, XRF analysis was also performed to verify the presence of leaching with the new catalysts. Few drops of solutions after reaction and filtration were dried to prior to analysis. Traces of Mg have been detected in both catalysts but an ICP analysis showed much lower Mg leaching (82 ppm) in case of mixed phases than in the case of MgO (110 ppm) [89].
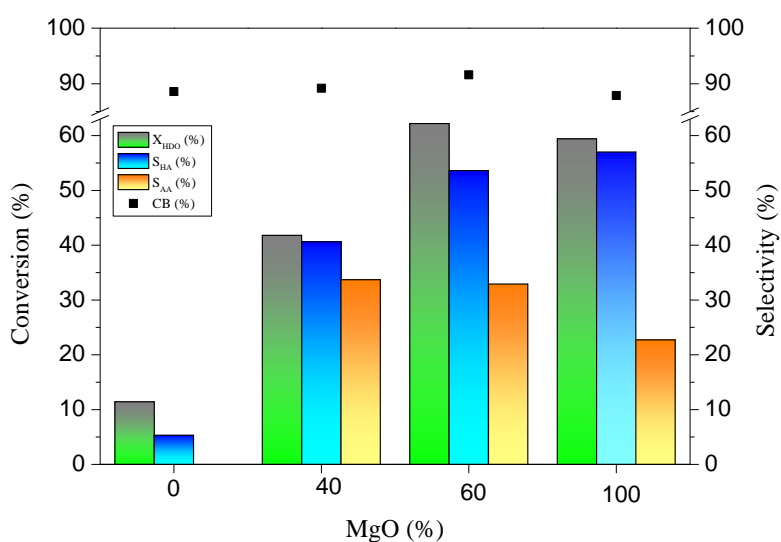

Figure 16: Supports effect for Au nanoparticles in HDO conversion and AA selectivity

6.4 Catalysts characterization

X-ray diffraction

XRD analysis enables determining the crystalline structure of materials and also estimating the chemical composition of the prepared catalysts under certain conditions.
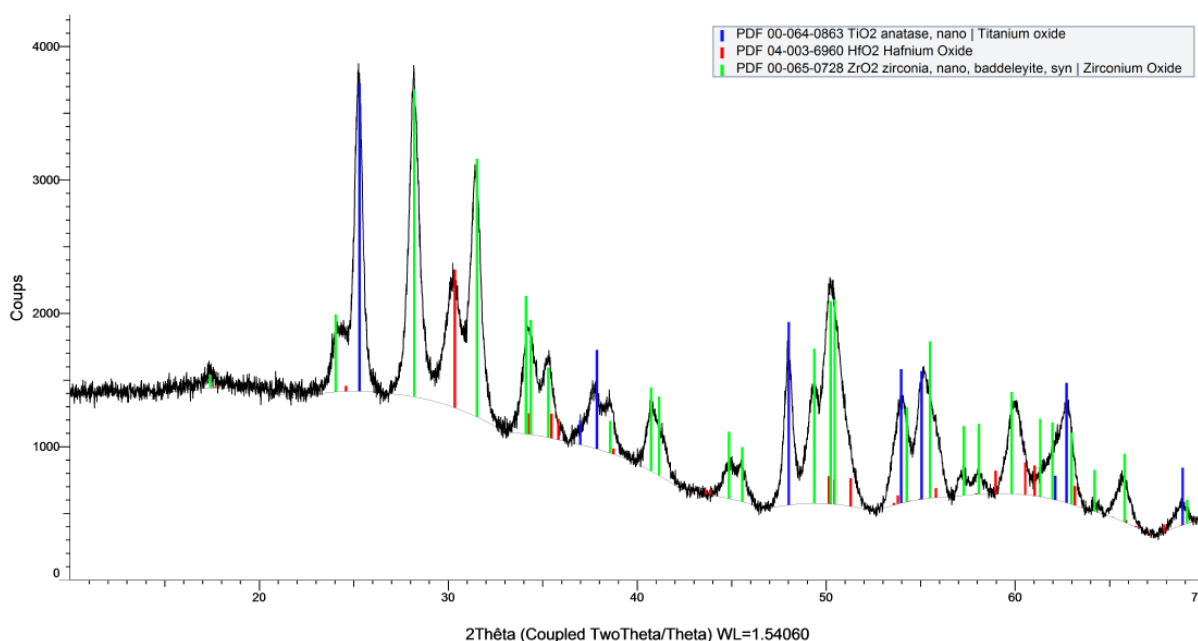
XRD Au/NC 1

Figure 17: X ray diffraction spectra of Au/NC 1

NC 1 composition is ZrO_2 58%, TiO_2 41%, HfO_2 1,1%, SiO_2 0,46%. The diffraction patterns presented in Figure 17 show all characteristic peaks originated from NC 1 compounds: titanium oxide in the mineral form of anatase, zirconium oxide in the mineral form of baddeleyite and hafnium oxide. Silica oxide peaks are not visible because it is amorphous.

In addition, no peaks originated from gold were present. This could be explained by very small size of the gold particles (smaller than 3 nm) or by the low Au content and the good dispersion of the NPs.
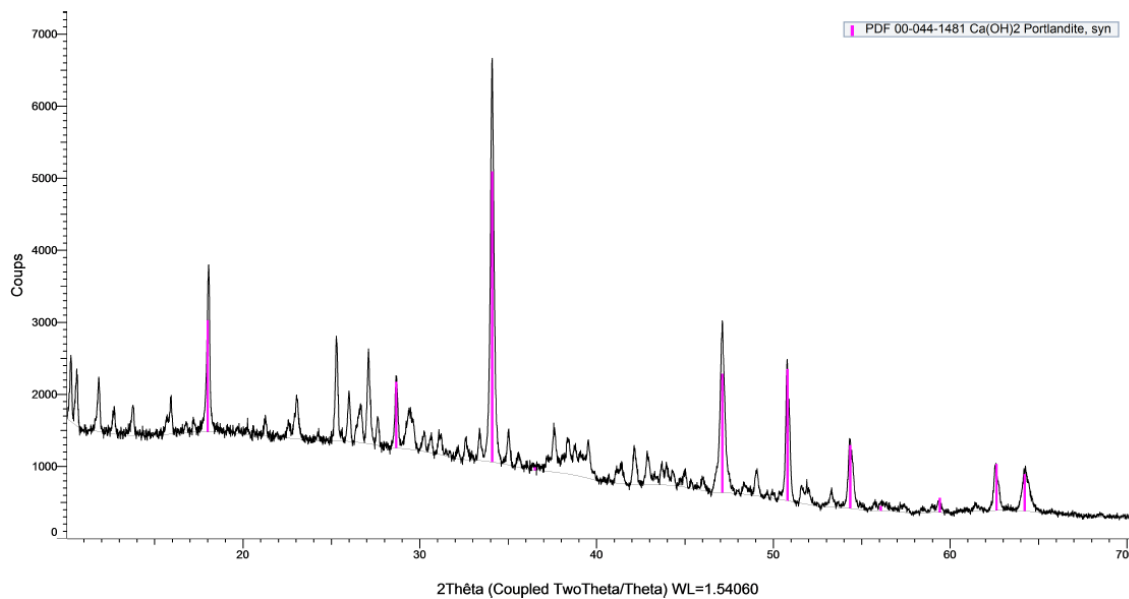
Figure 18: X ray diffraction spectra of Au/CaO

The diffraction patterns presented in Figure 18 show characteristic peaks originated from portlandite, the mineral form of $Ca(OH)_2$. Calcium hydroxide could have been formed by reaction between Calcium oxide and water, as reported in the following formula

$CaO + H_2O \rightarrow Ca(OH)_2$.

In addition, no peaks originated from gold were present. This could also confirmed very small size of the gold particles (smaller than 3 nm).

XRD Au/MnO$_2$

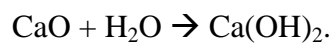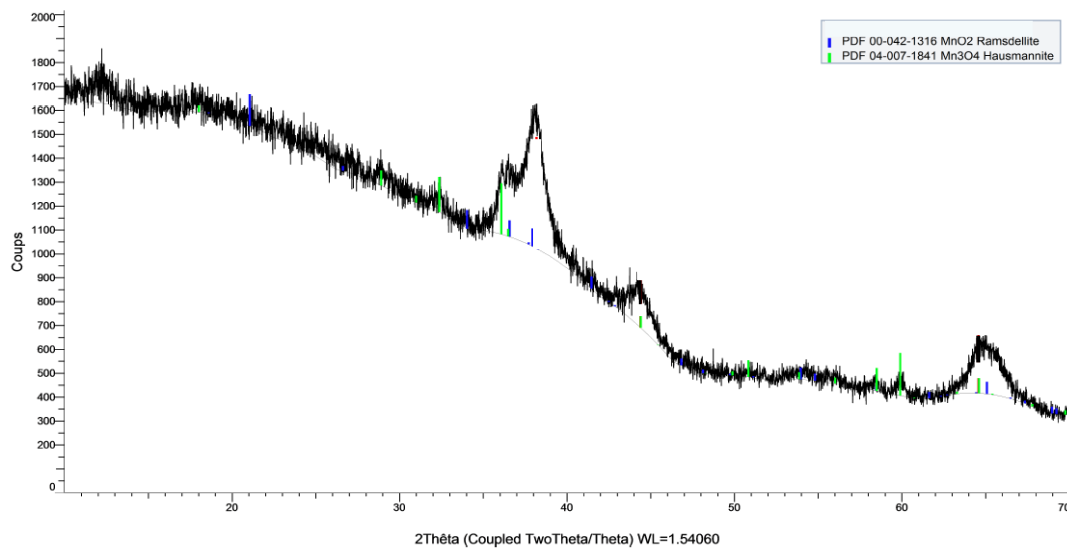*Figure 19: X ray diffraction spectra of Au/MnO$_2$*

The diffraction patterns presented in Figure 19 show characteristic peaks originated from Au and MnO$_2$, ramsdellite form. There are also present characteristic peaks originated from hausmannite Mn^{2+}Mn$^{3+}_2$O$_4$. The spectra aspect corresponds to an amorphous compound. In addition, no peaks originated from gold were present.

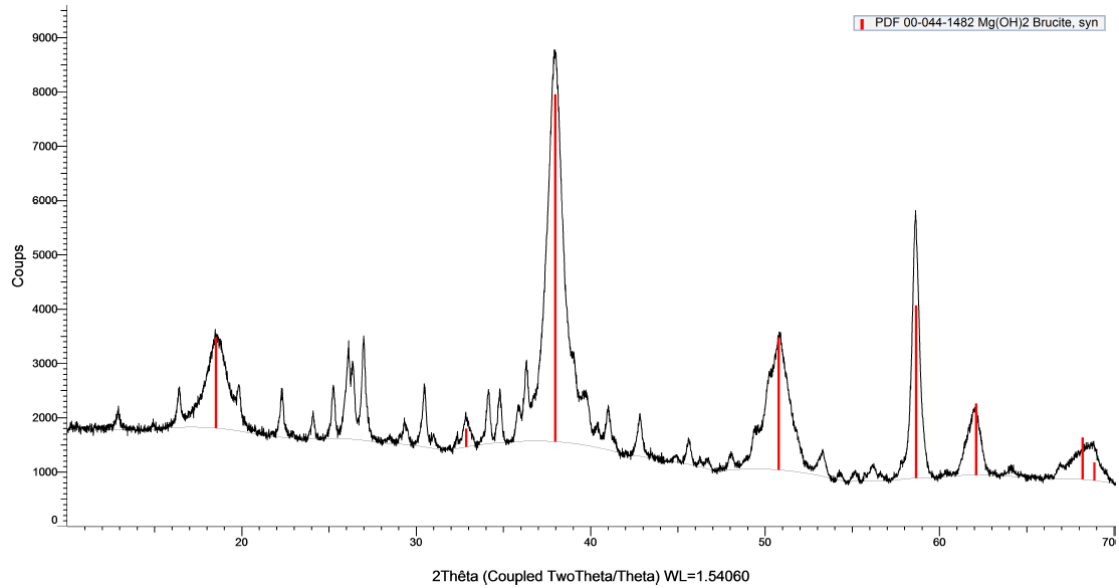***Figure 20:*** *X ray diffraction spectra of Au/MgO*

The diffraction patterns presented in Figure 20 show characteristic peaks originated from brucite, the mineral form of $Mg(OH)_2$. Magnesium hydroxide could been formed by reaction between magnesium oxide and water, as reported in the following formula

$MgO + H_2O \rightarrow Mg(OH)_2$.
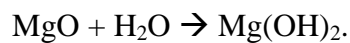
In addition, no peaks originated from gold were present.

XRD Au/0.4MgF$_2$-0.6MgO
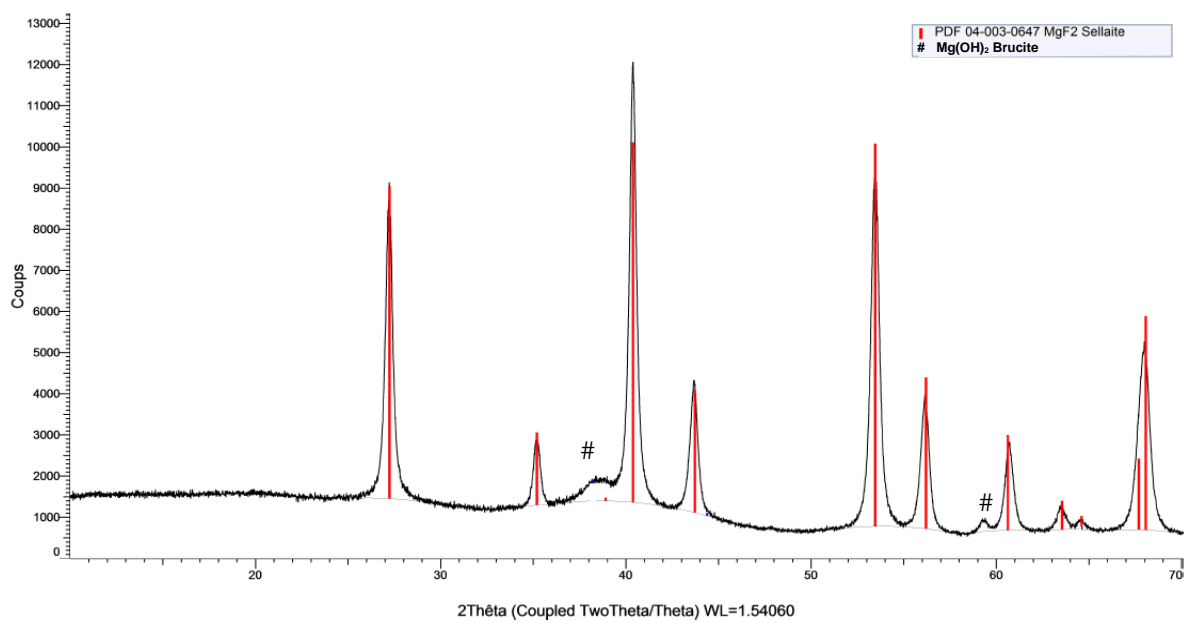
Figure 21: X ray diffraction spectra of Au/0.4MgF$_2$-0.6MgO

The diffraction patterns presented in Figure 21 show characteristic peaks originated from Sellaite, MgF$_2$. In addition, no peaks originated from gold were present. The sample presented the most intense peaks originated from brucite, the mineral form of Mg(OH)$_2$, indicated with "#", by reference MgO PDF 00-044-1482, whose formation has been explained for Figure 20.

TEM analysis

The Au-based catalysts were prepared using the two-step sol immobilization method, in which gold nanoparticles of homogeneous sizes are first prepared and then immobilized over all the different supports through a reproducible method. PVA-stabilized Au NPs with an average size of 3 nm, as determined by TEM (Figure 22a), had their size preserved after immobilization on different supports (Figure 22b-d) (basic supports and MgF_2-MgO materials). Indeed, the Au NPs deposited on the supports were monodispersed with an average size of 3.6 nm ± 0.8 nm and no significant agglomeration of gold nanoparticles was detected. The aforementioned big differences in specific surface areas between the MgO and MgF_2 samples did not impact the average particle size of the deposited gold nanoparticles. Apparently, the modification of the MgO materials with gold nanoparticles did not change the structural and morphological properties of the support. Considering the same average Au particle size and metal loading, it can be expected that the catalytic performances would mostly be governed by the structure and the physico-chemical properties of the support.
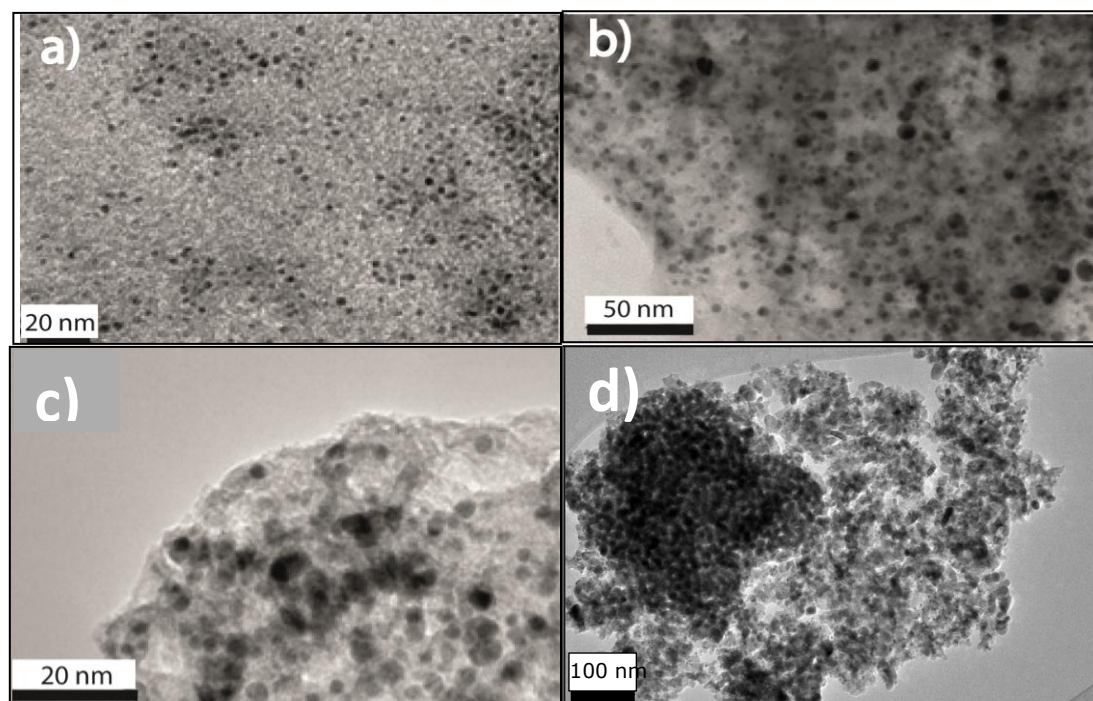

Figure 22: TEM images of the (a) unsupported gold nanoparticles, (b) supported Au/MgO, (c) supported Au/0.4MgF₂-0.6MgO, d) supported Au/NC1

7. RESULTS AND DISCUSSION II

The objectives of this part of the thesis were to study new catalytic systems, and the optimization of the reaction conditions, in particular use of air instead of oxygen, changing molar ratio substrate/M, in order to work in the conditions more suitable for a large scale industrial application.

All the following reactions discussed below were carried out in the Screening Pressure Reactor (SPR), described in the Experimental Part (Chapter 5.2.2) and in the conditions listed below:

- Temperature of reaction: 110°C
- Time of reaction: 4 hours
- Pressure air: 15 bar
- Total reagent solution: 2 mL
- Water as solvent
- Stirring: 600 rpm

The catalyst and the aqueous solution of 1,6-hexanediol were manually introduced into the reactor. The catalyst was weighed with an analytical balance while the starting reagent solution was prepared mixing HDO and water and withdrawn with a calibrated pipette. All reactors were filled at the same time and then connected to the workstation. Once the reaction program has been set on the PC connected to the workstation, temperature and pressure increased to the desired values. At this point the stirring started. At the end of the reaction the temperature was cooled down to room temperature by a flux of N_2, the stirring was stopped and the pressure decreased. Hence the solution has been filtered to remove the catalyst and 200 μL of that have been withdrawn with a micropipette prior to the HPLC analysis. The eventual loss of weight during reaction has been checked by weighting before and after all reactors with catalyst and reaction solution. Since the weight remained fix, it has been assumed that the volume did not change.

7.1 Molar ratio effect

In order to optimize the reaction conditions to be more suitable for a large-scale industrial application, the oxygen was firstly replaced with air, which is cheaper and more safe to handle. Secondly, the effect of molar ratio HDO and the metal was studied in in order to increase the concentration of the substrate. Increasing molar ratio between the substrate and the catalyst a decrease in conversion is expected because less active sites are available for the reaction.

All reactors were filled with the same amount of catalyst (10 mg) and HDO solution (2mL) considering the different molar ratio HDO/M. The following catalysts were screened:

- Au/NC1
- Au/MgO
- Au/0.6MgF$_2$-0.4MgO
- Au/CaO

7.1.1 HDO/Au = 100 and 150

Table 10: HDO/Au = 100, 110°C, 4 h, 15 bar of air, 600rpm

Catalysts	X$_{HDO}$ (%)	HA		AA		CB (%)
		Y (%)	S (%)	Y (%)	S (%)	
NC1	51	22	43	10	20	81
Au/0.6MgF$_2$ 0.4MgO	44	19	43	19	43	94
Au/MgO	77	41	53	35	46	99
Au/CaO	46	21	46	14	30	89

Table 11: HDO/Au = 150, 110°C, 4 h, 15 bar of air, 600rpm

Catalysts	X_{HDO} (%)	HA		AA		CB (%)
		Y (%)	S (%)	Y (%)	S (%)	
NC1	39	20	52	7	18	88
Au/0.6MgF$_2$ 0.4MgO	37	18	48	13	34	93
Au/MgO	71	41	59	27	38	98
Au/CaO	60	30	50	25	42	95

Carbon balance was always close to 90%, which suggests that main compounds obtained were adipic acid, unreacted 1,6-hexanediol and 6-hydroxyhexanoic acid.

Increasing the molar ratio between HDO and Au affected significantly the catalytic activity. In fact in the case of Au/NC1, Au/MgO and Au/MgF$_2$-MgO samples the conversion of HDO decreased as the HDO/M ratio increased. Interestingly, in case of Au/CaO sample the conversion had opposite trend. It passed from 46 % at 100 to 60 % at 150 molar ratio.

In both molar ratio tested the most active catalyst was Au/MgO. At HDO/Au = 100 it gave a HDO conversion of 77 % and selectivity to AA of 46 %, while at HDO/Au = 150 it gave a HDO conversion of 71% and selectivity in AA of 38%.

In the conditions tested and in both molar ratio tested Au/0.6MgF$_2$-0.4MgO showed a lower activity to HDO oxidation than Au/MgO and at HDO/Au = 100 showed not preferential pathway for oxidation. In fact selectivity to 6-hydroxyhexanoic and AA was almost the same of (S_{HA} = 43 %, S_{AA} = 43 %).
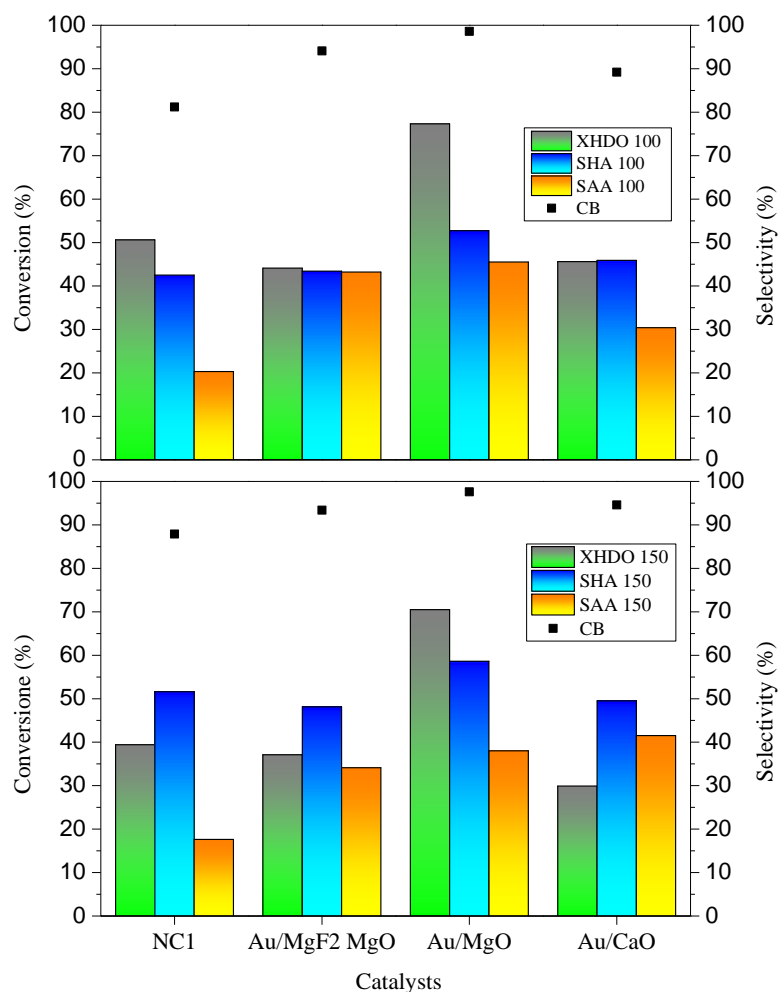
Figure 23:Molar ratio effect for supported Au NPs after 110°C, 4 h, 15 bar of air, 600rpm, HDO/Au = 100 (up) and 150 (down)

7.1.2 HDO/Au = 180 and 200

The increase of HDO/Au molar ratio effectively showed generally a negative effect on catalyst activity. However Au/CaO catalyst disclosed an opposite behaviour. For this reason molar ratio was further increased to 180 and 200, screening the catalysts previously mentioned.

The procedure of preparation of reactors and software of SPR for reaction follows what it has been explained in the previous chapter 7.1.1 and all the tests and treatments of the final solution were performed as described in the Chapter 5.3. All results are presented in Table 12 - Table 14 and Figure 24.

Table 12: Molar ratio effect for supported Au NPs after 110°C, 4 h, 15 bar of air, 600rpm

Catalysts	X_{HDO} (%) 100	X_{HDO} (%) 150	X_{HDO}(%) 180	X_{HDO}(%) 200
NC1	51	39	32	35
Au/0.6MgF$_2$-0.4MgO	44	37	49	46
Au/MgO	77	71	61	58
Au/CaO	46	60	53	50

In Table 12 reports HDO conversion at different molar ratio for the catalysts tested. Au/MgO shows the expected behaviour. The HDO conversion decreased with the increase of HDO/M ratio. It passed from 77% at 100 to 58% at 200.

The other catalysts tested showed a not predictable behaviour, such as NC1 showed a little increase in activity at 200 as compared to 180 (35% and 32% respectively). Similarly Au/CaO presented an increase in activity at 150 ($X_{HDO} = 60\%$) and a subsequent decrease at 180 and 200.

The Au/0.6MgF$_2$-0.4MgO sample showed almost no changes in activity in the HDO/M ratio range.

Detailed data obtained for the HDO oxidation ate HDO/M ratios of 180 and 200 are presented in Table 13 and Table 14.

Table 13: HDO/Au = 180, 110°C, 4 h, 15 bar of air, 600rpm

Catalysts	X_{HDO} (%)	HA		AA		CB (%)
		Y (%)	S (%)	Y (%)	S (%)	
NC1	32	17	53	4	13	89
Au/0.6MgF$_2$ 0.4MgO	49	22	44	17	34	89
Au/MgO	61	42	68	19	31	99
Au/CaO	53	30	57	20	38	97

Table 14: HDO/Au = 200, 110°C, 4 h, 15 bar of air, 600rpm

Catalysts	X_{HDO} (%)	HA		AA		CB (%)
		Y (%)	S (%)	Y (%)	S (%)	
NC1	35	16	47	4	13	86
Au/0.6MgF$_2$ 0.4MgO	46	22	49	12	26	88
Au/MgO	58	40	69	16	28	99
Au/CaO	50	18	37	16	31	84

Carbon balance was always close to 90%, which suggests that the increase of the HDO/Me ratio did not affected the carbon balance.

In both molar ratio tested the most active catalyst was Au/MgO. At HDO/Au = 180 it reached a HDO conversion of 61% and selectivity to AA of 31%, while at HDO/Au = 200 it reached a HDO conversion of 58% and selectivity to AA of 28%.
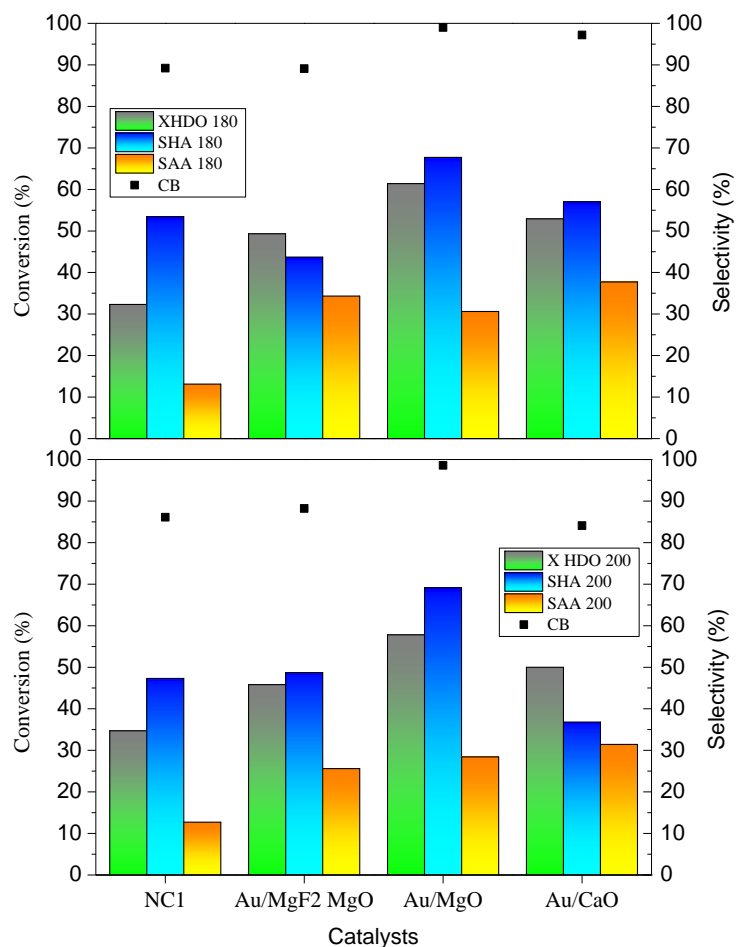

Figure 24: Molar ratio effect for supported Au NPs after 110°C, 4 h, 15 bar of air, 600rpm, HDO/Au = 180 (up) and 200 (donw)

74

8. Conclusions

The aim of this master thesis was to study a new catalytic process for the production of adipic acid under "green conditions" under base-free conditions using heterogeneous catalysts, which would be more sustainable if compared to the traditional homogeneous ones.

For this reason Green and Sustainable Chemistry principles have been taken into account in order to design the new route for adipic acid production. To meet these requirements this project was conducted using only H_2O as solvent, pure oxygen or air and Gold nanoparticles immobilized on supports. At the same time the starting reagent, 1,6-hexanediol, can be obtained from cellulose-derived (tetrahydrofuran-2,5-diyl)dimethanol, hence deriving from biomass and replacing the current toxic reagent, benzene.

In the first part of thesis a first catalytic screening permitted to identify AuNPs as being more active than Pd NPs. From this study it was possible to screen different supported AuNPs and find the most active catalysts. In the conditions tested (100 °C, 6 bar O_2, time of reaction 3 h, 600rpm, HDO/metal = 100) the main products obtained were 6-hydroxyhexanoic acid and adipic acid, with a higher selectivity to 6-hydroxyhexanoic acid. Among all catalysts tested in the conditions reported above, the most active one was Au/CaO with a X_{HDO} = 68% and S_{AA} = 38%.

This work highlights the advantages of Au-basic oxides catalysts for the selective oxidation of HDO. Their catalytic performances showed that conversions and AA selectivity strongly depend on the basicity of the support. For this reason basicity effect was studied by changing the amount of MgO and MgF_2 in mixed support. Basic sites added on MgF_2 make the catalyst actives in HDO oxidation to AA. Au/$0.4MgF_2 0.6MgO$ showed a slight better activity in the HDO oxidation respect to Au/MgO, respectively 33% and 23%. Results obtained showed that Au/$0.4MgF_2 0.6MgO$ was more selective in adipic acid production compared to Au/MgO, respectively S_{AA} = 33% vs S_{AA} = 23%. In both cases the pathway favoured was HDO oxidation to the intermediate.

Although the catalysts with basic supports are very active, they might not resist to recycling, owing to the leaching of the support. NC1catalyst (Au/ZrO_2 58%, TiO_2 41%, HfO_2 1,1%, SiO_2 0,46%), even being an acid support, resulted active in HDO oxidation (X_{HDO} = 28%, S_{AA} = 13 %) and in addition it did not show any leaching issues.

The second part of the thesis was focused on the optimization of the reaction conditions. In particular it was studied the effect of using air in place of oxygen, of changing the molar ratio substrate/metal, in order to bring the conditions closer to those that could be the most suitable from an industrial point of view.

In the conditions tested (110 °C, 15 bar air, time of reaction 4 h, 600rpm), the main products obtained were the same as those found in the first part of the thesis, namely 6-hydroxyhexanoic acid and adipic acid, with a higher selectivity to 6-hydroxyhexanoic acid. This result permits to extend the research using air, which is cheaper and safer to handle than pure oxygen. The trend in product obtained was different for $Au/0.6MgF_2$-$0.4MgO$ sample at HDO/M=100 which showed the same selectivity to AA and HA ($X_{HDO} = 44\%$, $S_{HA} = 43\%$, $S_{AA} = 43\%$).

Increasing HDO/Au molar ratio (150, 180, 200) a decrease of catalyst activity was observed due to the decrease of the number of active sites available for reagent molecules. This behaviour was confirmed for Au/MgO. Instead Au/CaO showed an activity peak at HDO/M ratio of 150 ($X_{HDO} = 60\%$, $S_{HA} = 60\%$, $S_{AA} = 42\%$), while for the others catalysts (Au/NC1 and $Au/0.6MgF_2$-$0.4MgO$) conversion assumes almost a constant value, respectively around an average amount of 35% and 45%. For what concerns AA selectivity, NC1 maintained a constant value of 13% after 180 molar ratio, while $Au/0.6MgF_2$-$0.4MgO$ and Au/MgO showed a slight decrease, but values always respectively higher than 26% and 28%.

Further studies will be carried out in order to improve the catalytic system based on mixed oxide supports $ZrO_2/TiO_2/HfO_2/SiO_2$ support and MgF_2/MgO in order to understand the path of reaction and the reaction mechanism.

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