

# 1. INTRODUCTION

Catalysis is an important field in the chemistry which almost 90% of chemical processes involving catalysts in at least one of their steps. In the table 1.1 is illustrated a historical background of some catalytic processes.

**Table 1. 1. Historical background of catalytic processes<sup>1</sup>**

Catalytic process	Catalyst	Main author	Year
<i>Sulfuric acid</i>	Lead chamber	Roebuck	1746
<i>Dehydration of alcohols</i>	Acid	Priestley	1778
<i>Esterification of organic acids</i>	Acid	Scheele	1782
<i>Dehydrogenation of alcohols (ethanol)</i>	Metal	Van Marum	1796
<i>Oxidation of alcohol</i>	Pt black	Priestley & Döbereiner	1810
<i>Decomposition of H<sub>2</sub> O<sub>2</sub> and NH<sub>3</sub></i>	Metals	Thénard	1813
<i>Hydrolysis of starch to glucose</i>	Acid	Kirchoff	1814
<i>Combustion</i>	Pt	Davy	1817
<i>Decomposition NH<sub>3</sub></i>	Fe > Cu > Ag > Au > Pt	Dulong	1823
<i>Oxidation</i>	Pt	Fusinieri	1824
<i>Oxidation SO<sub>2</sub> to SO<sub>3</sub> (contact process)</i>	Pt	Phillips	1831
<i>Definition of catalysis</i>		Berzelius	1836
<i>Oxidation of NH<sub>3</sub> to nitric acid</i>	Pt	Kuhlmann	1838
<i>HCl + O<sub>2</sub> → Cl<sub>2</sub></i>	Cu	Deacon	1875
<i>Esterification of acid</i>	Acid	Bertholet	1879
<i>Sulfuric acid</i>	V <sub>2</sub> O <sub>5</sub>		1875
<i>Friedel-Crafts reactions</i>	Lewis acids (AlCl <sub>3</sub> )	Friedel & Crafts	1877
<i>Nitric acid synthesis</i>	Pt gauzes		1904
<i>NH<sub>3</sub> synthesis from N<sub>2</sub> and H<sub>2</sub> under high pressure</i>	Fe	Haber	1909
<i>Hydrogenation</i>	Ni	Sabatier	1912
<i>Active site concept</i>		Michaelis	1913
<i>Theory of adsorption</i>		Langmuir	1915
<i>Industrial process of NH<sub>3</sub> synthesis under pressure</i>	Fe	Haber	1918
<i>CO + H<sub>2</sub> → CH<sub>3</sub> OH</i>	ZnO-chromia	BASF	1923
<i>CO + H<sub>2</sub> → hydrocarbons</i>	Fe, Co	Fischer & Tropsch	1923
<i>Contact catalysis theory</i>		Taylor	1925
<i>Hydrogenation vegetable oils</i>	Ni	Raney	1926
<i>Catalytic cracking of petroleum</i>	Acid	Houdry	1930
<i>Synthesis gas</i>		Bergius & Bosch	1931
<i>Alkylation reaction for gasoline fuel</i>	Acid	Ipatieff & Pines	1940
<i>Synthetic zeolites</i>		Barrer & Breck	1946
<i>Exhaust gas treatment</i>		General Motors & Ford	1976

The focus of the catalysis is the transformation of organic or inorganic substances in other more important or relevant, although, at present, due to environmental issues and our dependence on fossil fuels such as coal, petroleum, and natural gas, the fuel production is the industry as major demand of novel catalytic materials. However, world reserves are diminishing inexorably and this situation cannot last for long time so are urgently needed promoting materials of new energies, for example those that are capable of producing electricity, breaking H<sub>2</sub>O bonds with the separation of H<sub>2</sub> and O<sub>2</sub>, and storing the energy either in batteries or as molecular hydrogen.

Catalytic processes more efficient, require improvements in the catalytic activity and selectivity whereby it becomes important to tailor the design of catalytic materials with the desired structures and the desired dispersion of active sites, which can be found in materials such as zeolites<sup>1</sup>, LDHs<sup>2</sup> (*Layered double hydroxides*), CNTs<sup>3</sup> (*Carbon nanotubes*), PILC<sup>4</sup> (*Pillared interlayer clays*), MOFs<sup>5</sup> (*Metal organic frameworks*), offer a variety of these possibilities, with controlled large and accessible surface areas of the catalysts.

These materials may possess specific chemical properties, such as acid-base, redox, dehydrogenating, hydrogenating, oxidizing and physical properties like porosity, high surface area, thermal and electrical conductivity.

On the other hand, scientist also search that the catalysts being inexpensive and easily obtained to multigram scale.

Recently, hexacyanometallates, which are a serial of materials with molecular formula M<sup>II</sup>[M<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub>·nH<sub>2</sub>O, have been used as heterogeneous catalysts for the industrial ring epoxide aperture with alcohols leading to polyetherols.<sup>6</sup> However, these material offer many other possibilities as polycarbonates and poly-oles synthesis<sup>7-9</sup> and for hydroamination of alkenes and alkynes.<sup>10, 11</sup> All of these reactions with high catalytic activity.

Once exposed above, has been suggested as thesis subject, the evaluation of catalytic activity in oxidation reactions, of a serie of hexacyanocobaltates which contain mixture of divalent metals such as Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup>.

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These materials were made in order to have present in the solid hexacyanocobaltates, ions that can provide the structural integrity and also they can interact with oxygen and introduce Lewis acidity to bind some organic molecules that contain Lewis bases sites.

For which arise the next general objective:

✿ ***Synthesis, characterization and evaluation by gases chromatography of catalytic activity of hexacyanocobaltates in oxidation process.***

And as specific objectives:

✿ Synthesis of hexacyanocobaltates of formula  $M^A_x M^B_{3-x} [Co(CN)_6]_2 \cdot nH_2O$  with metal divalent mixture of  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  by precipitation technique.

✿ Characterization of hexacyanocobaltates by means of:

- Infrared spectroscopy
- X-ray diffraction
- Thermogravimetric analysis
- X-ray Fluorescence

✿ Evaluation of catalytic activity of hexacyanocobaltates as heterogeneous catalyst and monitoring the process of reactions by Gases Chromatography in:

- Oxidation reaction of Oximes to ketones
- Oxidative coupling of naphthalenethiol and naphthalene

Characterization of products by separation with Gases Chromatography and their identification by Mass Spectrometry.