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**Dehydrocyclization of n-Hexane to
Cyclohydrocarbons over
Heteropolyoxometalates Catalysts**

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Dedication

**to my beloved Family:
my parents, my brothers, my sister, my wife, my son and my daughters**

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Table of Contents

Dedication.....	2
Acknowledgements	3
Table of Contents	4
General Introduction	7
Abreviation	11
CH I Polyoxometals, Literature Study	12
I.1 Introduction	13
I.1.1 Nomenclature	13
I.1.2 Historical Perspective	14
I.2 Definition and Structure of Heteropolyanion	15
I.2.1 Definition of Heteropolyanion	15
I.2.2 Structure of the Heteropolyanion	15
I.2.2.1 The Structural Properties of Polyoxometallates	15
I.2.2.2 Basic Structural Units	16
I.2.2.3 The Clathrate-Like Structure	17
I.2.2.4 Chemical Elements Taking Part in POMs	18
I.2.2.5 Features of POMs	20
I.3 Geometric Structures of Representative Types of Polyanions	20
I.3.1 The Keggin Structure	21
I.3.1.1 Primary Structure	22
I.3.1.2 Secondary Structure	23
I.3.1.3 Tertiary Structure	23
I.3.2 The Wells-Dawson Anions Structre	23
I.3.3 The Anderson Structre	24
I.3.4 The Lindqvist Type Structre	25
I.3.5 Lacunary Species	26
I.4 Properties of Heteropolyanions	29
I.4.1 Acidity of heteropoly compound	29
I.4.1.1 Bronsted Acidity of Solution	29
I.4.2.1 Bronsted Acidity of Solid State	30
I.4.1.3 Lewis Acidity	31
I.4.2 Heteropolycompounds Oxidation-Reduction Properties	32
I.4.2.1 In Solution	32
I.4.2.2 In Solid State	32
I.4.3 Stability of Heteropolyanions	34
I.4.3.1 Thermodynamic Stability of Heteropolyanions in Solution	34
I.4.3.2 Thermal Stability of Heteropolyanions	34
I.4.3.3 Structural Stability of Heteropolyanions	38
I.4.3.4 Improvement of Structural Stability by Acting on the Process	38
I.4.3.5 Improvement of Structural Stability by Acting on the Catalyst	39
I.4.4 Charastics of HPA Surface	39
I.4.4.1 Surface Acidity	39
I.4.4.2 Availability of Surface Mobile Oxygen Species	40
I.4.5 Solubility	40
I.5 Calalysis in the Heteropolyanions	41
I.5.1 What is the Catalyst	41
I.5.2 Homogeneous Catalysis	41
I.5.2.1 Acidic Catalyzed Reactions	41
I.5.2.2 Redox Catalyzed Reactions	42
I.5.3 Heterogeneous Catalysis	43
I.5.3.1 Acidic Catalyzed Reactions	43

I.5.3.2 Redox Catalyzed Reactions	44
I.5.4 Classification of Catalytic Reactions	45
I.5.4.1 Surface Reaction (Surface-Type)	45
I.5.4.2 Heart Reaction Type I (Bulk Type I)	45
I.5.4.3 Heart Reaction Type II (Bulk Type II)	46
I.6 Transformation of Alkanes by Heteropolycompounds	46
I.6.1 Transformation of Ethane by Heteropolycompounds	47
I.6.2 Transformation of Propane by Heteropolycompounds	47
I.6.3 Transformation of n-C4 on Heteropolycompounds	48
I.6.4 Transformation of Isobutane on Heteropolycompounds	48
I.7 Hydroisomerization of n-Paraffins	49
I.7.1 The Purpose of the Hydroisomerization of n-Paraffins	49
I.7.2 Industrial Processes for the Isomerization of n-Paraffins	50
I.7.3 Generations of n-Paraffins Isomerization Catalysts	51
I.8 Reactions Mechanism	52
I.8.1 Monofunctional mechanism on Bronsted acid sites	53
I.8.2 Monofunctional mechanism on Lewis acid sites	53
I.8.3 Bifunctional Mechanism	53
I.9 Transformation of n-Hexane	53
References	55
 CH II Synthesis and Characterization of the Catalysts	 60
II.1 Introduction	61
II.2 Synthesis of Heteropolyacids	62
II.2.1 Synthesis of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, 13 H_2O	62
II.2.2 Synthesis of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, x H_2O	63
II.2.3 Synthesis of Heteropoly salts	65
II.2.3.1 Synthesis of $(\text{NH}_4)_4\text{HPMo}_{11}\text{MO}_{39}$, x H_2O salts with $\text{M} = \text{Ni}^{2+}$, Cu^{+2} and Co^{2+}	65
II.2.3.2 Synthesis of $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$, x H_2O Salt	66
II.2.3.3 Synthesis of $(\text{NH}_4)_4\text{HSiMo}_{11}\text{FeO}_{39}$, x H_2O Salt	66
II.2.3.4 Synthesis of $(\text{NH}_4)_{2.5}\text{Fe}_{0.1}\text{H}_{0.4}\text{PMo}_{12}\text{O}_{40}$, x H_2O Salts	67
II.2.3.5 Synthesis of $(\text{NH}_4)_{3-x}\text{Ni}_x\text{PMo}_{12}\text{O}_{40}$, x H_2O Salts	67
II.2.3.6 Synthesis of $(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{40}$ Salt	67
II.2.3.7 Synthesis of mixed salts: $\text{KFe PMo}_{12}\text{O}_{40}$	67
II.2.3.8 Synthesis of $\text{KFe PW}_{12}\text{O}_{40}$ Salts	68
II.2.3.9 Synthesis of $(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$ Salts	68
II.3 Technical Analysis	68
II.3.1 Introduction	68
II.3.2 Solid State Characterization	69
II.3.2.1 Analysis by infrared spectroscopy (FTIR)	69
II.3.2.2 Analysis by X-ray Diffraction (XRD)	74
II.3.2.3 Analysis by ^{31}P NMR Spectroscopy	80
II.3.2.4 Thermogravimetric Analysis	80
II.3.2.5 Characterization of residues by IFTR after thermogravimetric Analysis	83
II.3.2.6 Characterization by scanning electron microscopy	85
II.3.3 Solution Characterization	97
II.3.3.1 Analysis by ultraviolet-visible spectroscopy	97
II.3.3.2 Electrochemical Analysis	101
References	107

CH III Reactivity of Heteropolycompounds	109
III.1 Introduction	110
III.2 n-Hexane Reaction using H ₂ as Carrier Gas	111
III.2.1 Effect of time on the Catalytic Activity of Heteropolycompounds	111
III.2.2 Effect of chemical composition of heteropolycompounds on catalytic activity	115
III.2.3 Effect of Temperature	117
III.3 n-Hexane Reaction using N ₂ as Carrier Gas	120
III.4 Activation Energy	123
III.5 Mechanisms of transformation of n-hexane on heteropolyoxometallates	127
References	129
General Conclusion	130
Appendix	132
Abstract	140

General Introduction

Isomerization of light n-alkanes (n-pentane and n-hexane) is important for the production of clean and high-octane number fuels. The major commercial catalysts for light n-alkanes isomerization are Pt on chlorinated alumina or Pt/H-mordenite [1,2]. Pt on chlorinated alumina has high catalytic activity at low temperature (115–150 °C) where the production of branched isomers is favored in the equilibrium of production distribution [3]. However, this catalyst suffers from chlorine loss during the isomerization process and requires constant addition of chlorine-containing compounds. This chlorine-containing catalyst is also subjected to stringent environmental control. While Pt/H-mordenite does not have these disadvantages, it requires higher reaction temperature (260 °C) which is thermodynamically unfavorable for the formation of branched isomers.

Extensive researches have been devoted to the search for an environmentally friendly catalyst that can operate at low temperature. It has been known that modified zirconia catalysts offer a replacement for halogen-containing catalysts since they exhibit good potential for n-alkanes isomerization. Sulfated zirconias (SZ) have been found to be a strong solid acid for C₄/C₅/C₆ isomerization at low temperature, [4–7] SZ system, however, has the disadvantages of deactivation and sulfur loss during reaction and regeneration [8].

Due to their strong acidity and its amenability to “molecular tuning” (through their salts), the heteropolyanions (HPA), which are highly organized systems, are very good candidates for the catalyzation of alkane isomerization.

Keggin type heteropolyacids (HPAs) have been widely used in acid-catalysed reactions as well as oxidation reactions both in the heterogeneous and homogeneous systems [9–15]. Heteropolyacids have been lately pointed out as versatile green catalysts for a variety of reactions like: alkylation and acylation of aromatics, esterification, and liquid bi-phase processes [16,17]. There is an interest to substitute liquid catalysts (e.g. H₂SO₄, HF, p-toluenesulphonic acid) – which are corrosive, toxic and difficult to separate from reaction solution- by more environmentally friendly solid acids. Among many possible forms of heteropolyacids used as catalysts, there are their salts [18,26].

Catalysis by heteropoly acids (HPAs) and related polyoxometalate compounds is a field of increasing importance, where HPAs have several advantages as catalysts which make them economically and environmentally attractive. On the one hand, HPAs have a very strong Bronsted acidity approaching the superacid region. On the other hand, they are efficient

oxidants, exhibiting fast reversible multielectron redox transformations under rather mild conditions.

Their acid-base and redox properties can be varied over a wide range by changing the chemical composition. Solid HPAs possess a discrete ionic structure, comprising fairly mobile basic structural units heteropolyanions and counter-cations (H^+ , $H_2O_5^+$, etc.) unlike the network structure of, e.g., zeolites and metal oxides. This unique structure manifests itself to exhibit an extremely high proton mobility and a “pseudoliquid phase”^[16], while heteropolyanions can stabilize cationic organic intermediates.^[19] On top of that, HPAs have a very high solubility in polar solvents and fairly high thermal stability in the solid state. These properties render HPAs potentially promising acid, redox, and bifunctional catalysts in homogeneous as well as in heterogeneous systems. HPAs are widely used as model systems for fundamental research, providing unique opportunities for mechanistic studies on the molecular level. At the same time, they become increasingly important for applied catalysis. Most of the pioneering work has been done since the 1970s^[9-11].

In the last two decades, the broad utility of HPA acid and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selective transformations of organic substances. Several new industrial processes based on HPA catalysis, such as oxidation of methacrolein, hydration of olefins (propene and butenes), polymerization of tetrahydrofuran, etc., have been developed and commercialized.^[18]

HPAs are complex proton acids that incorporate polyoxometalate anions (heteropolyanions) having metal-oxygen octahedra as the basic structural units.^[24-31] The first characterized and the best known of these is the Keggin heteropolyanion typically represented by the formula $XM_{12}O_{40}^{x-8}$ where X is the central atom (e.g., Si^{4+} , P^{5+} , etc.), x is its oxidation state, and M is the metal ion (Mo^{6+} or W^{6+}). The M^{6+} ions can be substituted by many other metal ions, (e.g., V^{5+} , Co^{2+} , Zn^{2+} , etc). The Keggin anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner- sharing metal-oxygen octahedra MO_6 (Figure 1)^[31].

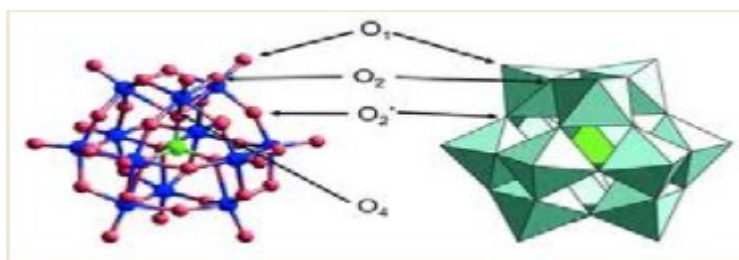


Figure 1. The Kegin structure of the $XM_{12}O_{40}^{x-8}$ anion (α -isomer): terminal (O^1), edge-bridging (O^2), and corner- bridging (O^3), P-O (O^4) oxygen atoms .

The octahedra are arranged in four M_3O_{13} groups. Each group is formed by three edges sharing octahedra and having a common oxygen atom which is also shared with the central tetrahedron XO_4 . Among a wide variety of HPAs, the Keggin's are the most stable and more easily available; these are the most important for catalysis. In this thesis HPAs are understood as the Keggin acids, unless otherwise stated.

The crystal structure of HPAs depends on the amount of hydration water. This water can be easily removed on heating, whereby the acid strength is increased due to the dehydration of protons. This is a reversible process accompanied by changing the volume of crystal cell. Unlike the rigid network structure of zeolites, in HPA crystal the Keggin anions are quite mobile. Not only water but also a variety of polar organic molecules can enter and leave HPA crystal. Such structural flexibility is important when using HPA as a heterogeneous catalyst.

In this work, the heteropolycompounds have been used in hexane dehydrocyclization reaction for the first time. The reaction may involve many products such as benzene, cyclohexane, cyclohexene, and cyclohexadiene, in addition to the unwanted methane product. The main goal is to maximize benzene production and minimize methane in the product mixture by investigating different catalysts, varying temperature, and carrier gas and retention time.

The study is structured as follows:

The first chapter summarizes the data of literature on the preparation methods, properties and on the structure of heteropolyanions (HPA) Keggin type as well as the activation of alkanes, in particular n-hexane

The second chapter deals with the preparation and characterization of synthesized solids by different methods (FTIR, XRD, UV-Visible, ^{31}P NMR, SEM, Electrochemical and thermal analysis)

The results of the study of the reactivity of polyoxometalates in the dehydrocyclization reaction of n-hexane are presented in Chapter III.

Finally, a conclusion summarizes the main results of this work.

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Abbreviations

HPA : Heteropolyanions

POM : Polyoxometalates

SZ : Sulfated Zirconias

Oh : Octahedral

TGA : Thermogravimetric Analysis

DTA : Differential Thermal Analysis

PMo_{12} : $\text{H}_3\text{PMo}_{12}\text{O}_{40}$

PMo_{11}V : $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$

PMo_{11}Fe : $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{40}$

PMo_{11}Co : $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{40}$

PMo_{11}Ni : $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{40}$

PMo_{11}Mn : $(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{40}$

PMo_{11}Cu : $(\text{NH}_4)_4\text{HPMo}_{11}\text{CuO}_{40}$

NiPMo_{12} : $\text{H}(\text{NH}_4)_4\text{NiPMo}_{12}\text{O}_{40}$

FePMo_{12} : $\text{H}(\text{NH}_4)_4\text{FePMo}_{12}\text{O}_{40}$

KFePMo_{12} : $\text{KFePMo}_{12}\text{O}_{40}$

PW_{11} : $(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$

CHAPTER I
Literature Study
Polyoxometals, n-Hexane Isomerization

I.1- Introduction:

The great majority of inorganic compounds are constructed of metallic atoms as principal entities. Inorganic molecules have great potential because the number of elements in purely inorganic molecules, combined with structural diversity, make them more powerful, particularly as far as their application is concerned. In fact, the search for new properties puts more importance on the elements in a framework than on the structure itself. Polyoxometalates (POMs) are polynuclear metal oxygen clusters usually formed of Mo, W or V that form a unique class of inorganic compounds because it is unmatched in terms of structural versatility and properties ^[1-6]. It is a family of ionic substances, non-toxic and non-odorous. They are composed of heteropolyanions (HPA) and counter-ions (protons, alkali, earth alkaline, transition metals, organic cations) and water molecules of hydration. The structure of HPA is called primary structure and the polyoxometallate is rated secondary structure. The latter depends on the nature of counter -ion and the degree of hydration . ^[7]

I.1.1- Nomenclature :

A systematic nomenclature of polyoxometalates has been developed.^[8,9] It uses a labeling system for the metal atoms and in some cases for oxygen atoms to avoid ambiguity. The resulting names however are too long, complicated, and never used for routine purposes .

In catalytic applications, only a relatively small number of well-known types of polyoxometalates have been involved so far, mostly limited to the Keggin compounds and their derivatives. Simplified conventional nomenclature, and sometime even trivial names are usually sufficient for reporting and retrieving information in the field. Here we adopt the current nomenclature that treats polyoxometalates (also referred to as heteropoly anions, polyoxoanions, or polyanions) as quasi coordination complexes. ^[8] The heteroatom, if present, is considered as the central atom of a complex, and the addenda as the ligands. In the formulas of heteropoly anions, the heteroatoms are placed before the addenda, and the counter-cations before the heteroatoms: the heteropoly anions are placed in square brackets and thus separated from the counter-cations, as illustrated by the following examples :

$[\text{SiW}_{12}\text{O}_{40}]^{4-}$	12-tungstosilicate or dodecatungstosilicate
$\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$	12-molybdophosphoric acid
$\text{Na}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	sodium decamolybdovanadophosphate

For simplicity, the counter-cations and the charge of polyanion and even the oxygen atoms may be omitted : for example, $\text{Na}_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}]$ may be abbreviated to $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]$ or P_2Mo_{18} .

I.1.2- Historical Perspective :

The first POM - the phosphomolybdate of formula $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ - was reported by Berzelius[10] in 1826. Marignac^[11] observed two isomeric forms of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$. In the early 1930s, Keggin solved the structure of the related anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ^[12]. Since then, countless structures have been synthesized and characterised. The turning point came when spectroscopic techniques were used for characterization. The end of the 19th century and the early decades of the 20th century were fruitful in theories that explained coordination chemistry^[13] and, particularly, the chemistry of POMs.^[14] In the last 40 years, a lot of experimental information has been collected. Today, POMs constitute an immense class of polynuclear metal-oxygen clusters^[15-17] usually formed by Mo, W or V and mixtures of these elements.

The vast field of heteropolyanion chemistry has been concentrated mostly around the preparation, characterization and application in analysis and catalysis chemistry. Although the number of heteropoly compounds is enormous, new classes of structure in them with often unexpected properties or reactivity and applications are still being prepared and characterized. However, These compounds have remarkable structures and features that allow them to be the subject of many studies. Day and Kempler^[18], Chen and Zubietta^[19], and Isobe and Pope^[20] have focused their work on the study of their structural properties. Their chemical nomenclature has been the subject of a study by Jeannin^[21] while Papaconstantinou^[22], Yamasa^[23] and Hill and Mc Carta^[24] have examined their photochemical and photocatalytic applications. Pope and Muller have obtained spectacular structures, creating a new field of investigation : the supramolecular chemistry of polyoxometallates^[25], they are used to assay uric acid of cholesterol, Biochemistry, their salts are used in medicine in the treatment of AIDS patients. In recent decades, the POM is used both in homogeneous and heterogeneous catalysis^[7, 26]. Most applications are related to their special ability to accept one or several electrons with minimal structural changes. Dozens of elements have been reported as taking part in POM compounds.^[6] In addition, beyond this chemical flexibility, they have an 'organic-like' structural diversity and the number of frameworks synthesized increases daily.

I. 2 - Definition and Structure of Heteropolyanion :

I.2.1 - Definition of Heteropolyanion :

The polyoxometallates are oxygen clusters with at least two different metals. The heteropolyanion general formula is : $(X_xM_mO_y)^{n-}$ ($x \leq m$).

Where: X: central atom or heteroatom. M: addenda atom or element.

Two cases arise depending on the nature of M:

* $X = Si^{IV}, Ge^{IV}, P^V$ and As^V where $M = Mo^{VI}$.

* $X = Si^{IV}, Ge^{IV}, P^V, As^V, B^{III}$ or element of the first series of transition in the case where $M = W^{VI}$.

I. 2. 2 - Structure of the Heteropolyanion

I.2.2.1 - The Structural Properties of Polyoxometallates

The polyoxometallates are synthesized and isolated from aqueous and non-aqueous solutions. The oxoanions transition metals such as $[MO_4]^{2-}$ (M: Mo, W) tend to polycondensation under acidic conditions to form clusters of anionic metal-oxygen commonly called polyoxometallates ^[27]. Polyoxometallates are one set of inorganic molecules in the vast field of coordination chemistry compounds. They are characterized by a central metal, M, which is surrounded by some atoms or groups of atoms. In POMs, ligands are normally oxygen atoms, although some derivatives with S, ^[28-32] F, ^[33] Br ^[34] and other p-block elements are known. So, in general, we have MO_n units, where n indicates the coordination number of M. Usually, $n = 6$, although it can be 4, 5 or 7, as well. Apart from M and O, other elements, which are usually labelled as X, can be part of the POM framework. As a general rule, they are 4-fold- or 6-fold- coordinated and lie in the center of the M_xO_y shell. Depending on whether X is present or not, we can distinguish two types of POM species. This classification is based on a purely structural criterion :

1- isopolyanions (IPAs) (Lindqvist structure) $[M_mO_y]^{p-}$, consisting of a single type of metal $[Mo_7O_{24}]^{6-}$ or $[V_{10}O_{28}]^{6-}$.

2- heteropolyanions (HPAs) $[X_xM_mO_y]^{q-}$ with ($x \leq m$), $[As_3Mo_5O_{15}]^{3-}$ containing in their structure one or more heteroatoms X.

In the case of heteropolyoxoanions, the heteroatoms are inside the cavity formed by octahedrons MO_6 . There are no chemical limitations for X and M by definition. The X elements are the so-called primary central or heteroatoms. In general, any element can

participate as X in a POM cluster since there are no strict physical requirements for this position. On the other hand, M are the so called secondary, peripheral or addenda atoms and only some M elements are typically found in such compounds. In a few cases, this distinction may be confusing or uncertain, but in the clusters dealt with here the distinction is clear. Despite the simplicity of formulas (1) and (2) above, the composition of a cluster can be highly complex, with various M elements taking part in the structure. In anions in which more than one M addenda-type is present in the framework, the molecule is known as a mixed-addenda cluster.

I.2.2.2 - Basic Structural Units

POMs are a family of medium-to-large-sized molecular (discrete) metaloxides. Metal-oxide aggregates with fewer than 3–4 metal centers are traditionally not POMs. Nevertheless, due to the increasing diversity of structures classified as such in the literature, the unequivocal definition of this group of compounds becomes gradually more and more diffuse. Countless reports,^[35] books^[36] and reviews^[37-38] have been published on this topic, showing an enormous molecular diversity amongst the inorganic family of molecules. This diversity is somehow a consequence of the rich, unprecedented and unusual properties associated with POMs. Many authors claim that they can be regarded as packed arrays of pyramidal MO_5 and octahedral MO_6 units (see **Figure 1.1**). These entities are, then, the fundamental structural units and are somewhat similar to the $-\text{CH}_2-$ unit in organic chemistry.



Figure 1.1 Ball-and-stick and polyhedral representations of the fundamental unit MO_6 .^[36]

Note that the M atom is displaced from the geometrical center of the A octahedron towards one of the oxygens, thus giving rise to a distorted C_{4v} unit.

The very important MO_6 units (and the MO_5 partner as well but to a lesser extent) are, then, packed to form countless shapes. They join to one another, apparently, in accordance with a few simple rules (as $-\text{CH}_2-$ does in organic molecules). Observing a representative set of POM clusters, and identifying the MO_6 blocks, we notice that the molecule as a whole is built by edge- and/or corner-sharing MO_6 octahedra. **Figure 1.2** shows these simple unions.

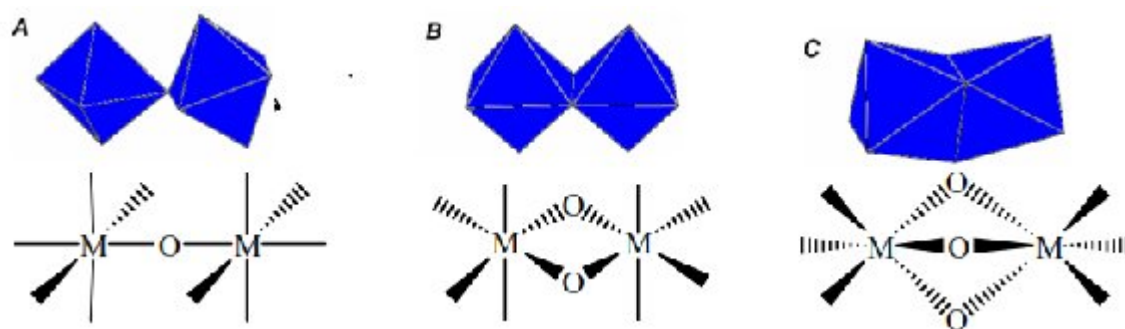


Fig. 1.2: Polyhedral models of the three possible unions between two MO_6 octahedral units. A) corner-sharing, B) edge-sharing and C) face-sharing

The most stable unions between two octahedra are the corner- and edge-sharing models,^[39] in which the M^{n+} ions are far enough from each other, and their mutual repulsion is modest (Table 1.1).

Table 1.1. Selected M–M distances (in angstrom units) of corner- and edgesharing octahedra in POMs.

Metal	corner-sharing	edge-sharing
W(VI)	3.7	3.4
Mo(VI)	3.7	3.5
V(V)	3.5	3.2

In **Figure 1.2 C**, the MO_6 octahedra are face-sharing, in such a way that the metallic centres are closer than in the other two cases (**A**, **B**) and, at such distances, the repulsion is not balanced by the stabilisation due to the chemical bonding in the 2-block unit. The latter form of union is uncommon.

1.2.2.3 - The Clathrate-Like Structure

Clathrate-like systems are molecular or supramolecular arrangements in which an internal unit is encapsulated by an external core. In metal-oxide polynuclear clusters it is a common phenomenon that has been discussed by experimentalists^[40-43] and computational chemists.^[44-46] A formulation for molecules that accomplish the requirements of a clathrate-like system was introduced by the way of I-E in which I and E are the internal and the external fragments (see **Figure 1.3**)

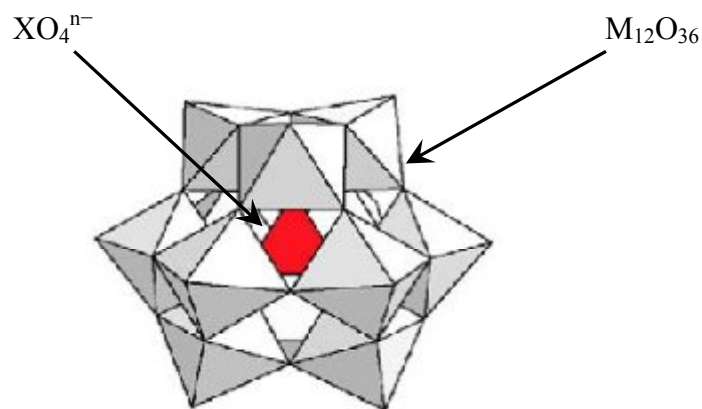


Figure 1.3. Polyhedral view of the clathrate-like structure of the Keggin anion. The external $M_{12}O_{36}$ core encapsulates the internal unit (represented as a red tetrahedron).

Keggin, Wells–Dawson anderson and Lindqvist anions were also formulated as :

$[XO_4]^{n-} - M_{12}O_{36}$ - Keggin,

$[XO_4]^{ni} - M_{18}O_{54}$ - Wells-Dawson

$[XM_6O_{24}]^{q-}$, anderson

$O^{2i} - M_6O_{18}$ - Lindqvist

where the external M_xO_y core is free of metallic electrons if the cluster is fully oxidized. This assumption can be very advantageous in the study of complex phenomena like the isomerism .

1.2.2.4 - Chemical Elements Taking Part in POMs

The addenda atoms 'M' have been identified as the most important entities in POMs. All the clusters included in this classification contain MO_n units, so the characteristics of M deserve further discussion. The fundamental structural block from which POM frameworks are built is the MO_6 unit,^[47] where M is a transition-metal element. Many M elements are known to form six-fold octahedral coordination compounds with oxygen, but not so many can take part in MO_6 units in a packed polynuclear metal-oxide aggregate. The structures of polyanions appear to be governed by the electrostatic and ionic radius principles of metal centers. That is, the only selected values of the charge/radius ratio are observed in M^{n+} in combination with O^{2-} ligands thus forming POMs. A few M's are commonly found or routinely included in a structure since these physical limitations control the stability of the metal oxide framework (see the values listed in **Table 1.2**).

Table 1.2. List of common metal cations, M^{n+} , taking part in POM frameworks. We especially highlight W and Mo for being the most typical as addenda atoms.

Metal ion	Octahedral radius (Å)	Observed coordination numbers in POMs
W^{6+}	0.74	6
Mo^{6+}	0.73	4, 6, 7
V^{5+}	0.68	4, 5, 6, 7
Ta^{5+}	0.78	6
Nb^{5+}	0.78	6
Tc^{7+}	0.70 a	
Ti^{4+}	0.74 a	
Sb^{5+}	0.74 a	

Table 1.2 contains early transition metal elements, from the left of the periodic table. In fact, there are other ions that have values of q and r with limits similar to those shown in **Table 1.2**. So, apart from other transition metals, some p-block elements could be, at least in principle, good candidates for being included in MO_6 units as addenda. However, charge and radius are not the only considerations to rule these assemblages of central metal units. Actually, an additional parameter related to M to be considered, is the ability to form metal-oxygen π -bonds. This affects the stability of these clusters, as well. It was observed long ago that, in octahedral MO_6 blocks, the central metal is not in the very middle of the polyhedron, but somewhat displaced from the geometrical centre towards one of the corners (see **Figure 1.4**).

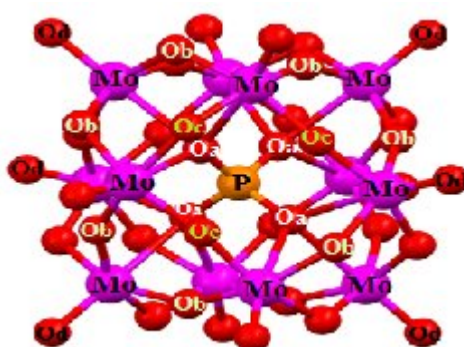


Fig. 1.4: Ball and stick representation of the Keggin type cluster;

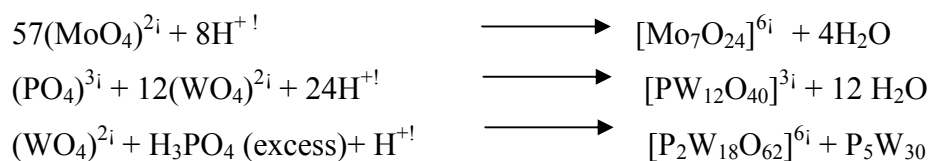
More precisely, it is displaced towards the corner that does not share another octahedron, and the oxygen at this position usually forms a double bond with the metal (see the

cluster in **Figures 1.4 and 1.5**). This is another of the requirements that the M center should comply with. These $p\pi-d\pi$ interactions are of the greatest importance in the stability of metal-oxide clusters, ^[48] and only the elements listed in **Table 1.2** are suitable for this purpose. The terminal (unshared) oxygens are, in general, essentially nonbasic since there is a strong inward polarisation of the oxygen's electron density. This accounts for the molecular (discrete) metal-oxide arrays of MO_6 units, instead of extended, insoluble infinite layers or solids.

It is precisely the ability to form $M=O$ double bonds that makes small POMs possible. After nearly two centuries of POM chemistry, almost all the elements of the periodic table have somehow been incorporated into a polyoxometalate framework.^[49] This accounts for the chemical variability of this field.

1.2.2.5 - Features of POMs

Heteropolyanions and isopolyanions are routinely prepared and isolated from both aqueous and non-aqueous solutions. The most common method of synthesis involves solving $[MO_n]^{mi}$ oxoanions which after acidification assemble to yield a packed molecular array of MO_6 units. For example,



Care must be taken with pH conditions so that the reaction can be controlled. The sequence in which the reagents are added to the reaction media is also important. One of the most important steps in synthetic procedures of POMs are the isolation of crystals so that their features can be studied in greater depth. Clusters are precipitated or crystallized by adding counter-cations (alkali metals, organic cations like TBA, etc.) and subsequent separation. Usually, the solid state structure of polyoxometalates is preserved in solution and an appropriate choice of the counterion allows the redissolution of a polyoxoanion in aqueous, organic or mixed aqueous/organic solvents. The structure of polyoxoanions is determined by single-crystal X-ray diffraction and the diamagnetic nature enables the use of multinuclear NMR, which is the most powerful technique for studying the structure in solutions. As far as preparation and storage conditions are concerned, it is worth noting that POMs are hydrolytically and thermally stable.

I.3 - Geometric Structures of Representative Types of Polyanions:

(Keggin, Lindqvist, Anderson-Evans and Wells-Dawson)

Dozens of structural types and stiochiometries of polyoxometalates are known to date. The minimum degree of condensation of addenda atoms is arbitrarily set to be in the range of 2 to 6. The maximum can go to as high as a few hundred. For example, the gaint heteropoly tungstate $[\text{La}_{16}\text{As}_{12}\text{W}_{148}\text{O}_{524}]^{76-}$ (relative molecular mass 40000, diameter 4 nm) includes 28 heteroatoms (La,As) and 148 addenda atoms (W) .

Two general principles apply to polyoxometalate structures ^[50,51] :

- 1- Addenda atoms occupy a metal-oxygen polyhedron MO_x that is most commonly an octahedron. In this polyhedron, the metal atom is displaced from the inversion center towards the peripheral vertice because of metal-oxygen π bonding
- 2- Structure with MO_6 octahedra that contain more than two free vertices are generally not found among the typical polyoxometalates. This is known as the Lipscomb restriction,[52] which may be explained as a result of the strong trans influence of the terminal $\text{M}=\text{O}$ bonds that facilitates dissociation of MO_3 from the polyanion.

According to Pope and Muller, ^[51] it is convenient to discuss the variety of polyoxometalate structures starting from a few highly symmetrical 'parent' polyanions; then many other polyoxometalate structures may be considered as their 'derivatives'. There are three such parent structures, with a tetrahedron, an octahedron, and an icosahedrons as their central polyhedron XO_n ($n=4,6$ or 12) that determines the symmetry of the whole polyanion. These structures are mentioned in (Table 1.3) : ^[53-56] .

Table 1.3 : The different heteropolyanions families .

Type	Molecular formula	Unit	Type of Bond	Central Group
Keggin	$\text{X}^{n+}\text{M}_{12}\text{O}_{40}^{(8-n)-}$	M_3O_{13}	Edge	XO_4
Dawson	$\text{X}_2^{n+}\text{M}_{18}\text{O}_{62}^{(16-2n)-}$	M_3O_{13}	Edge	XO_4
Andeson	$\text{X}^{n+}\text{M}_6\text{O}_{24}^{(12-n)-}$	M_2O_{10}	Edge	XO_6
Waugh	$\text{X}^{n+}\text{M}_9\text{O}_{32}^{(10-n)-}$	M_3O_{13}	Edge	XO_6
Silverton	$\text{X}^{n+}\text{M}_{12}\text{O}_{42}^{(12-n)-}$	M_2O_9	Face	XO_{12}
Lindqvist	$\text{M}_6\text{O}_{19}^{\text{r}-}$			

I.3.1 - The Keggin Structure :

This is the first characterized ^[57] and the best-known structure that is adopted by many polyoxometalate. Among a wide variety of heteropoly compounds, the Keggin are the most stable and more easily available. These, together with some of their derivatives, are the most important for catalysis.

The Keggin type of heteropoly compound is an assembly of three kinds of structures. It is very important to distinguish between the primary, secondary and tertiary structure which are the building blocks of the complex .

I.3.1.1- Primary Structure

The heteropoly acids in the solid state are ionic crystals (sometimes amorphous) which consist of large polyanions that are linked together. This polyanionic Keggin structure specially the primary type has T_d symmetry and consists of a centrally located XO_4 tetrahedron (X = heteroatom or central atom) surrounded by twelve edge and corner sharing MO_6 octahedron (M = addenda atom) (**Figure 1.5**). The octahedron are arranged in four M_3O_{13} groups. Each group is formed by three octahedron sharing edges and having a common oxygen atom which is also shared with the central tetrahedron XO_4 . The oxygen atoms in the Keggin structure are classified into four classes of symmetry equivalent oxygens: $X-O_a-M$, $M-O_b-M$ ("inter" bridges between corner sharing octahedron), $M-O_c-M$ ("intra bridges between edge sharing, i.e., within a M_3O_{13} set) and $M-O_t$ (the terminal oxygens) where M is the addenda atom and X is the heteroatom.

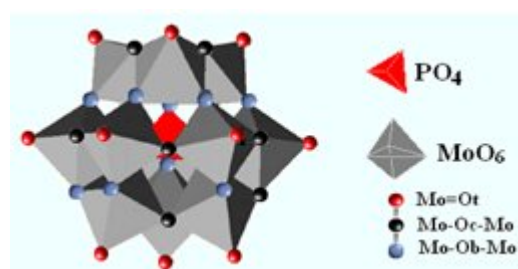


Fig. I. 5: Keggin Anion Structure.

The anion contains twelve quasilinear M-O-M linkages between the octahedra forming part of different M_3O_{13} triads, twelve angular M-O-M bonds between the octahedra within a single triad, four X-O-M bonds where the triads are joined to the central atom and twelve terminal $M = O$ bonds **figure 1.6** .

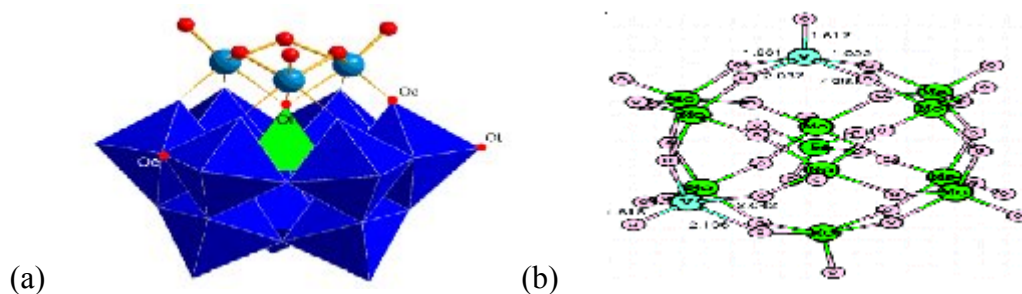


Fig. 1.6: Ball/stick and polyhedral representation of the alpha isomer of the Keggin structure with different types of oxygen. Color codes: The blue polyhedra represent the tungsten and the red balls represent oxygen. (b) Ball and stick representation of $H_4PMo_{10}V_2O_{40}$ Keggin type cluster

I.3.1.2 - Secondary Structure :

The three dimensional arrangement consisting of the large polyanions, cations, water of crystallization and other molecules constitute the secondary structure of heteropoly compounds, **Figure I.7(a).**

At low temperature ($4^{\circ}C$), heteropolyacids crystallize with a number of hydration water molecules between 29 and 31. At room temperature hydrates effloresce to form a network with 13 water molecules are more stable under these conditions. The protons are associated with two water molecules to form $H_5O_2^+$ dihydroxonium bridge between Keggin units (**Figure I.7(b,c)**). When replacing protons by small cations (Na^+ , Li^+ ), the crystal structure is similar to that of the heteropolyacid. On the other hand, when the cation is large (Cs^+ , K^+ ...), the crystal lattice is more compact and often cubic.^[58]

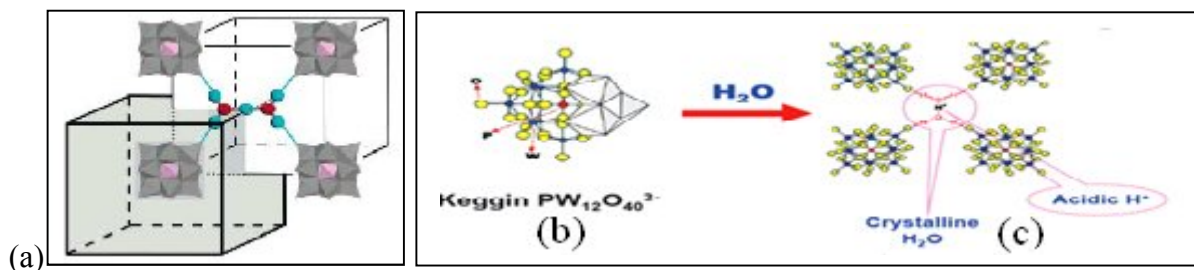


Figure I. 7: (a) Schematic diagram illustrating the structure of the hexahydrate $H_3P_{12}O_{40}.6H_2O$ As two interpenetrating simple cubic structures. The H^+ of an $H_5O_2^{+3}$ species coordinated to the body centered Keggin Unit is located at the midpoint of an edge of the conventional cubic cell. The KUs are shown in polyhedral representation. (b) Polyhedral representation of Keggin anion $[PW_{12}O_{40}]^{3-}$ (c) secondary structure of heteropolyacids.

I.3.1.3 - Tertiary Structure

Structure of the solid heteropolyacid as assembled constitutes the tertiary component of the complex. The size of the particles, pore structure and distribution of protons in particles are the elements of the tertiary structure.

I.3.2 - The Wells-Dawson Anions Structure : $[X_2M_{18}O_{62}]^{6-}$

They are formed from an acid solution containing Keggin anions $[XM_{12}O_{40}]^{3-}$ where X: P, As; and M: Mo, W. Under these conditions, each of Keggin anion loses three octahedrons (M_9 unit). Thereafter, two species trivacantes condense to form a molybdenum complex. These are known as Dawson or Wells – Dawson structures (**Figure I.8**). Their structure was characterized for the first time in 1953 [59] but had been proposed previously by Wells in 1945 [60].

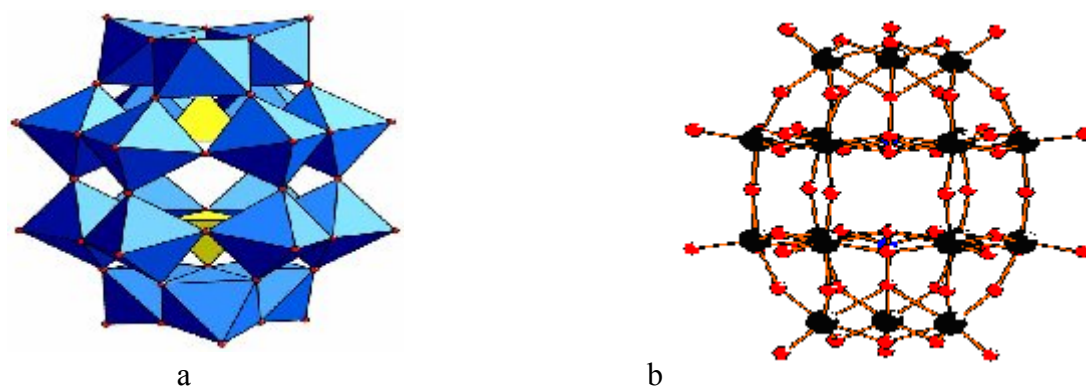


Figure I.8 Wells-Dawson Structure $[X_2M_{18}O_{62}]^{3-}$

In **Figure 1.8** the complete anion consists of two identical “half-units” related by a plane of symmetry perpendicular to the trigonal axis. The “half-units” are linked together by six oxygen atoms situated in the plane of symmetry so that these atoms are shared equally by the two halves. The two heteroatoms ‘X’ are tetrahedrally coordinated and surrounded by nine WO_6 octahedra linked together by edge sharing and corner sharing.

I.3.3 - The Anderson Structure : $[XM_6O_{24}]^{n-}$:

Anderson structures are formed from large heteroatoms as Te^{IV} , I^{VII} , Al^{III} , and Co^{III} obtained from aqueous solutions at pH 4 -5. They adopt the so-called Anderson structure (**Figure I.9**) in which the polyanion is based on an arrangement of seven edge shared octahedra where the heteroatom "X" is surrounded by six-oxo ligands in a pseudo-octahedral symmetry and it occupies the central position.

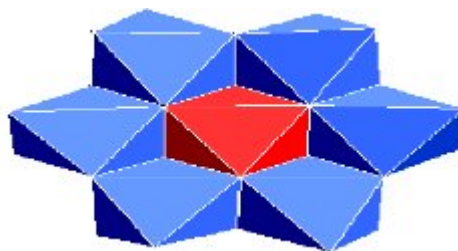


Fig. I.9: Polyhedron representation of the Anderson structure

This planar structure was originally proposed by Anderson for the heptamolybdate anion, $[\text{Mo}_7\text{O}_{24}]^{6-}$, but it was observed for the first time when Evans reported the structure of $[\text{TeMo}_6\text{O}_{24}]^{6-}$, which was isostructural to that of the 6-molybdo-anion $[\text{IMo}_6\text{O}_{24}]^{5-}$. It is generally known as 'Anderson-Evans' structure (Figure 10) [61].

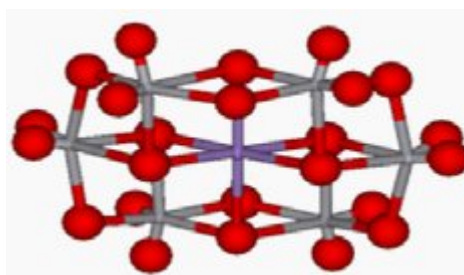


Figure I.10 Anderson Structure $[\text{XM}_6\text{O}_{24}]^{n-}$

There are two types of Anderson structure: with or without protonation of the central octahedron XO_6 . These structures are more frequently observed in the case of molybdenum.

I.3.4 : The Lindqvist Type Structure :

The $[\text{M}_6\text{O}_{19}]^{n-}$ isopolyanion representative of the Lindqvist type structure [62] is characterized by the presence of one terminal M-O bond at each metal center and thus, they belong to the type-I category in Pope's classification scheme. Each metal center is octahedrally coordinated and the structure consists of a compact assemblage of edgesharing octahedra, leading to an overall octahedral cluster, with full O_h symmetry. The pronounced distortion of each MO_6 unit and the three different oxygen coordination sites are shown in Figure 1.11. One can see that the metals occupy equivalent octahedral sites, so that they make one short terminal

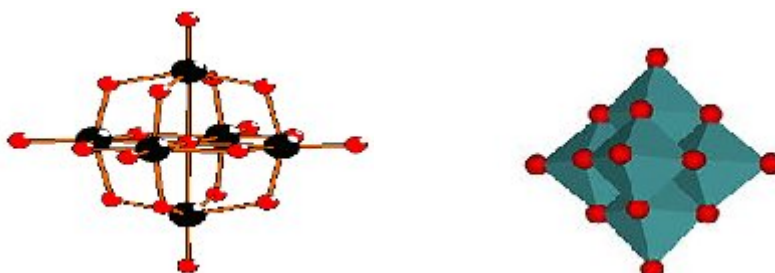


Figure I.11: Lindqvist structure .

M-O bond and a rather long M-O bond to the translocated high-coordinate oxygen site. This cluster is known as the Lindqvist type structure, e.g. $[M_6O_{19}]^{n-}$ ($n=8$ for $M= Nb, Ta$) and ($n=2$ for $M= Mo, W$).

I.3.5 - Lacunary Species

Although all polyoxoanions are ultimately decomposed to monomeric species in basic solution, controlling the pH can lead to the formation and isolation of 'defect' or 'lacunary' structures. These are best illustrated with the α isomers of the Keggin-type polyanion, the Keggin anion has five different rotational isomers known as 'Baker-Figgis' ($\alpha, \beta, \gamma, \delta, \epsilon$). β, γ, δ and ϵ are derived from the α -isomer, by rotation of 60° of 1, 2, 3, and 4 respectively. which can form $[XM_{11}O_{39}]^{n-}$ and $[XM_9O_{34}]^{n-}$ species by the 'removal' of one or three adjacent MO_6 octahedra respectively.

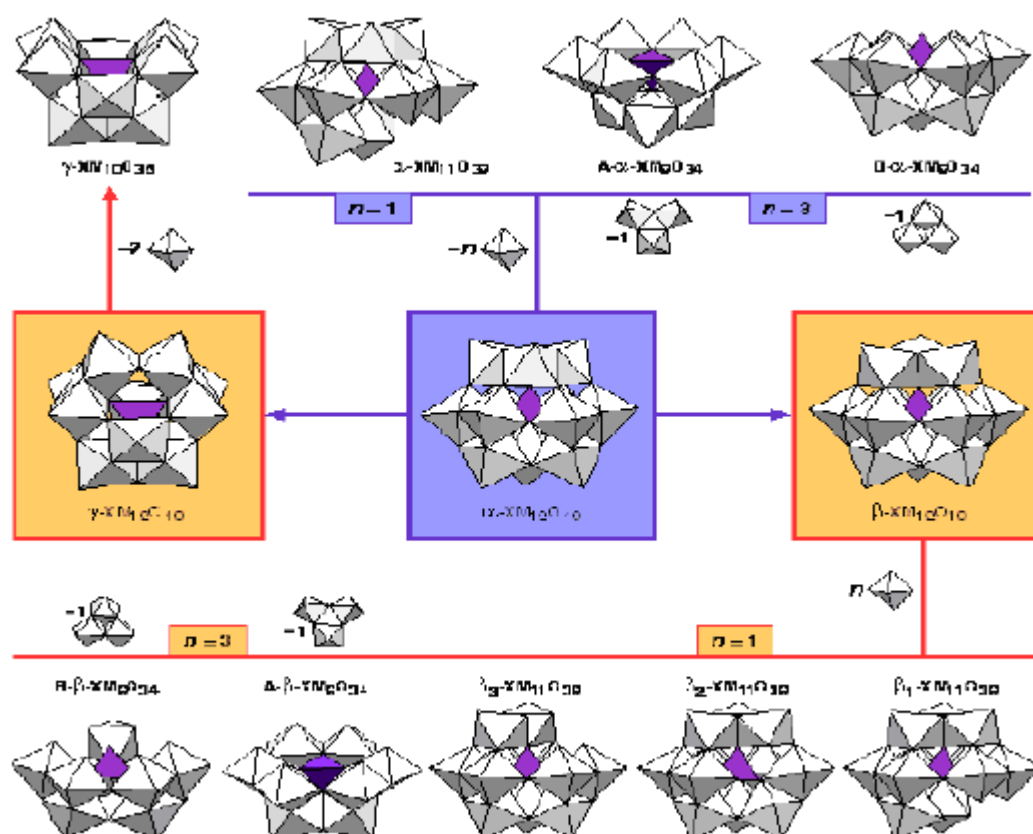


Figure 1.12: Schematic representation of the formation of lacunary Keggin-type.

An intermediate structure in which two adjacent octahedra have been removed has not been observed for the α and β isomers but observed only for the γ isomer; in the former two cases the structure would contain an MO_6 octahedron with three terminal face oxygen atoms and is therefore expected to be quite reactive.

These lacunary species derived from the Keggin type structure, are obtained from the three Baker-Figgis (α , β , γ) isomers by means of the elimination of a variable number of octahedra, so that a total of nine species are known whose structures are shown in **Figure 1.12** In the case of the phospho-tungstate system, the reaction patterns are similar to those of the silico-tungstates, but a series of remarkable differences exists, which can be visualized from **Figure 1.13**

The β -isomers are much more unstable and they isomerize to the α -isomers, with the exception of the trivacant species β - $[\text{PW}_9\text{O}_{34}]^{9-}$, which forms on acidifying solutions of tungstate and phosphate at pH around 9. When the reaction is carried out at 0 °C, the α -isomer is obtained but it isomerizes to the β -isomer at room temperature. In addition, the dilacunary species γ - $[\text{PW}_{10}\text{O}_{36}]^{7-}$ is not synthesized directly, but by overnight refluxing of polyanion $[\text{P}_2\text{W}_5\text{O}_{23}]^{6-}$, overnight at pH = 7 and it is only isolated with a cesium counterion.

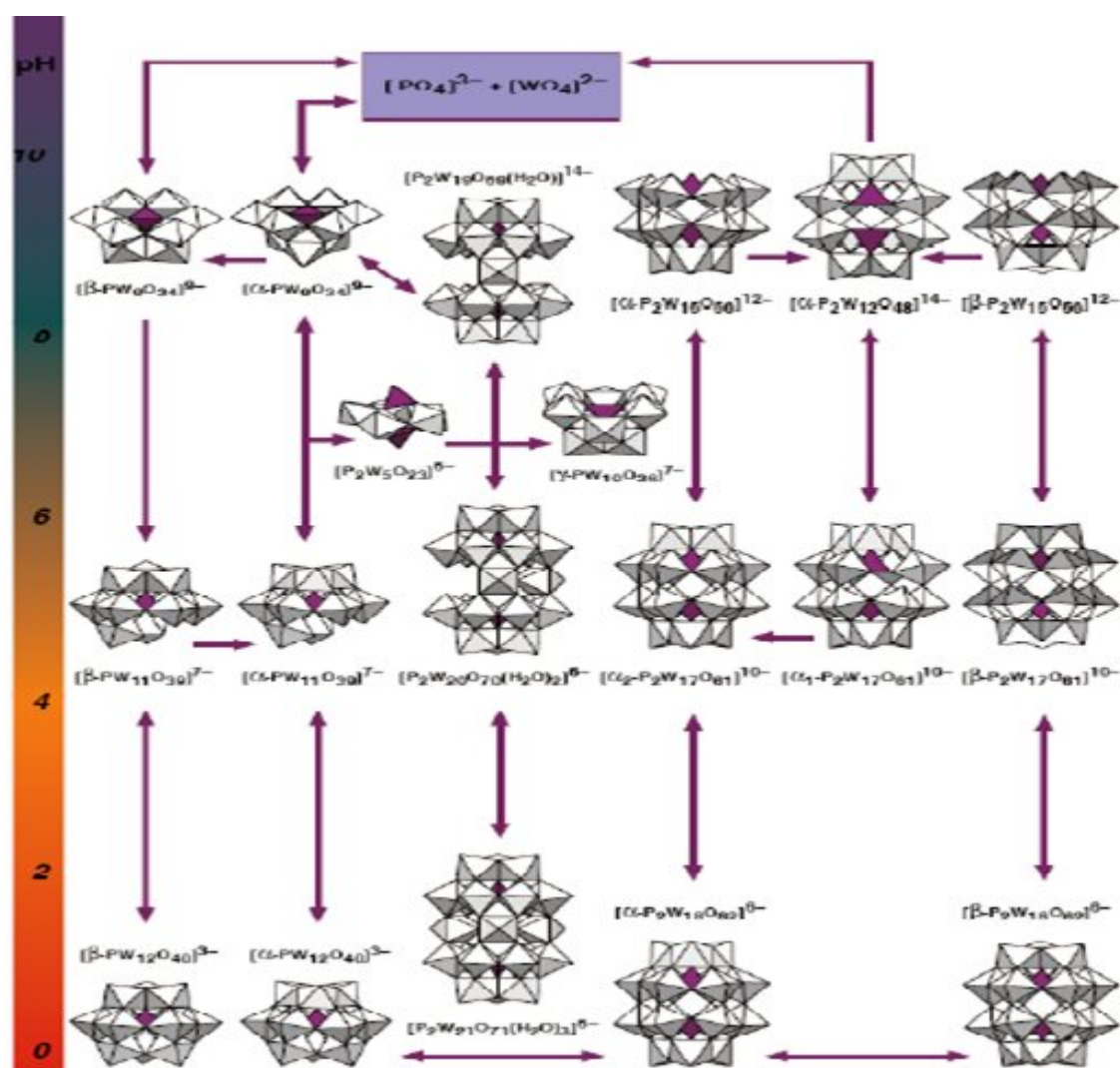


Figure 1.13: Schematic representation of the formation of Keggin- and Wells-Dawson lacunary type species in tungsto-phosphate system with respect to pH.

On the other hand, a series of heteropolyanions can be obtained which has no equivalent in silico-tungstate system. Thus, when the trivacant species α -[PW₉O₃₄]⁹⁻ is acidified in excess of potassium counter-ion, instead of the Keggin ion formation, association of two trivacant species takes place by means of a bridging tungsten in the belt. If the pH is decreased, different heteropolyanions are obtained, like [P₂W₁₉O₆₈(HO)]¹⁴⁻, [P₂W₂₀O₇₀(H₂O)₂]⁶⁻ and [P₂W₂₁O₇₁(HO)₃]⁶⁻, which show one, two and three (WO(HO))⁴⁺ groups in the central belt, respectively. In addition, when a solution of tungstate is acidified until pH below 2 in the presence of an excess of phosphate, mixture of α and β -isomers of the Wells-Dawson [P₂W₁₈O₆₂]⁶⁻ heteropolyanion is obtained instead of the Keggin. The Wells-Dawson heteropolyanion shows a similar behaviour to that of the Keggin, since the basicity of its dissolution produces hydrolytic cleavage of the M-O bonds to give rise to monovacant [P₂W₁₇O₆₁]¹⁰⁻ lacunary species, only if the pH is in between 4 and 6, and to the trilacunary [P₂W₁₅O₅₆]¹²⁻ at pH around 10. These trivacant species undergo irreversible processes of transformation to form the hexa lacunary species [P₂W₁₂O₄₈]¹⁴⁻. Lacunary anions with more than one surface 'vacancy' may also be derivatized by cation complexation. Reaction of a stable lacunary polyoxometalate with transition metal ions usually leads to a product with the unchanged heteropolyanion framework, depending upon the coordination requirement and the size of a given transition metal ion. The geometry of the reaction product can therefore often be predicted. At the same time, it must be pointed out that the mechanism of formation of polyoxometales is not well understood and commonly described as self assembly.

Therefore, the synthesis of polyoxoanions with novel shapes and sizes is a very difficult task. But according to Muller and Pope, POM structures are governed by two general principles.

- 1- Polyanions are generated by linking MO_n polyhedra via corners and edges leading to different types of faces on the surfaces.
- 2-Each metal atom forms an MO_n coordination polyhedron (most commonly an octahedron or a square pyramid) in which the metal atoms are displaced, as a result of M-O π bonding towards the terminal polyhedral vertices forming the surface of the structure.

Transition metal substituted polyoxometales can also be of interest owing to their magnetic properties. Structures which contain more than one paramagnetic transition metal ion in close proximity may exhibit exchange-coupled spins leading to large ground states spin ^{163, 64}. The polyoxometalate matrix may be considered as a diamagnetic host encapsulating and thereby isolating a magnetic cluster of transition metals.

1.4 Properties of Heteropolyanions

1.4.1 - Acid and Base Properties.

The great interest of heteropolycompounds in recent years is based on the ease of controlling their acid-base and oxidation-reduction properties by changing their compositions. These variations may reflect either changes in the central atoms, or addenda atoms or the nature of counter ions [65].

1.4.1.1- Bronsted Acidity of Solution:

Most of the heteropolyacids behave as strong acids in aqueous solution. They are stronger than oxoacids ($\text{XO}_n(\text{OH})_m$) Corresponding to the heteroatom. They are also stronger than many mineral acids (HCl , HNO_3 , H_2SO_4 ...) (**Table1.4**) and give comparable results to those of zeolites [66].

The strength of the Keggin HPAs depends weakly on their composition. Yet the tungsten acids are markedly stronger than molybdenum ones. The strongest acid in the Keggin series is PW_{12} . The acidity of concentrated HPA solutions in terms of the Hammett acidity function also weakly depends on their composition and is stronger than that of equimolar solutions of H_2SO_4 . Although the acid strength and catalytic activity of Bronsted acids are best quantified in terms of their dissociation constants and Hammett acidity function,

Table 1.4 Dissociation Constants of Heteropoly Acids in Acetone at 25 °C

acid	pK_1	pK_2	pK_3
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	1.6	3.0	4.0
$\text{H}_4\text{PW}_{11}\text{VO}_{40}$	1.8	3.2	4.4
$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	2.0	3.6	5.3
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	2.0	3.6	5.3
$\text{H}_4\text{SiMo}_{12}\text{O}_{40}$	2.1	3.9	5.9
H_2SO_4	6.6		
HCl	4.3		
HNO_3	9.4		

protons can be directly counter-ions: it is in the case of heteropoly acid or mixed salts. They can also form during two phenomena :

1. The dissociation of water coordinated
2. Reduction of metal ions or oxometal by dihydrogen.

It is mainly Bronsted acidity. The latter is due to the M-O-M bonds (bridge) which are protonated sites that predominate in solution

The high acidity of these compounds is mainly due to the weak electrostatic attraction of protons by large anions, the latter is much lower than that of oxoacids due to the dispersion of the negative charge on all oxygen atoms of the polyanion leading to very low densities of electronic surfacials of about 0.6 Cm^{-2} Inches, in the case of the anion $\text{H}_3\text{PMo}_{12}\text{O}_{40}^{3-}$. This low electronic density on the surface of the polyanion is due to the double bond of the $\text{M}=\text{O}$ which polarizes the negative charge of O to the metal M [67]. Thus in aqueous solution, the protons of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ are completely separated. The degree of dissociation can be changed in non-aqueous (acetone, ethanol ...).

The acidic properties are based on the polyanion elements and are linked to the total charge of the ion [68]. Some authors have suggested that the acid strength decreases in the following order:



Y. Ono et al. [69] reported that the acid strength decreases in acetone according to the following scale :



However these comparisons are discussed to the extent that the solvation of ions is never taken into account and where unexpected inversions over the water, in the case of strong acids usually cast doubt on these determinations. Moreover, these scales are performed in solution and are strongly dependent on solvent difficulty in producing the rankings in the solid state.

Different methods were used to determine the acidity of heteropolycompounds, like the characterization of acid sites by adsorption and desorption of bases such as NH_3 or alkyl amines on heteropolycompounds, or the reaction of dehydration of alcohols and especially isopropanol, involving acid sites of catalyst [70].

I.4.1.2 - Bronsted Acidity of Solid State

Solid HPAs possess purely Bronsted acidity and are stronger than such conventional solid acids "superacid" [71] as $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{H}_3\text{PO}_4/\text{SiO}_2$, and HX and HY zeolites. The acid strength of crystalline HPAs decreases in the series $\text{PW}_{12} > \text{SiW}_{12} \geq \text{PMo}_{12} > \text{SiMo}_{12}$ which is identical to that in solutions [72] (Table 1.4). Usually, relative catalytic activities of HPAs are

consistent with this order both in homogeneous and in heterogeneous systems. In the solid state, the terminal oxygen atoms (O_t) are most accessible to protonation [73] .

It was shown that the acidity of solids depends on both the central atom, and the addenda atom. An order of the acidity of heteropolycompounds according to the central atom and the addenda atom was described by Pope in his book of heteropolycompounds : [74]



The partial substitution of Mo^{VI} by V^V increases the burden on Keggin anion, therefore the number of protons constitution available acidity priori become lower and therefore a decrease in acidity compared to $H_3PMo_{12}O_{40}$ [75] .

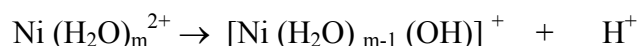
The nature and rate of substitution of the counter-ion in heteropoly salts also have an important influence on the acidity of the solid. Indeed, the replacement of solvated protons $H_5O_2^+$ in the strong Bronsted acid, a less acidic cation must reduce the acidity of the overall solid, at least in terms of accessible sites. The acidity of the salts is then determined in two ways: by the degree of protons replacement by the metal cation (number of sites), and the degree of acidity intrinsic hydrated metal cation (strong sites).

In the solid state, the acidity of heteropolyanions has several origins:

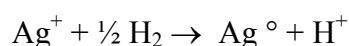
- Proton acidity of the unsubstituted cation;
- Partial hydrolysis during synthesis



- Dissociation of water of crystallization or physisorbed water;



- Protons formed by the reduction of metal cations;



- Lewis acidity of metal cations

1.4.1.3 - Lewis Acidity

The metal cations are Lewis acid type sites. There is a relationship between the acidity and the polarizing power of the cation: it is more electropositive, more stronger acidity .

A study of absorption of pyridine on $H_3PMo_{12}O_{40}$ [74] has shown the existence of two types of protons :

* hydrated protons which exchange readily with those of water molecules of hydration.

** Fixed protons linked to MOM of bridging oxygen O_b and O_c [76] .

The Lewis acid sites were identified in addition to the Bronsted heteropolycompounds container ($\text{Cu}_{1.5}\text{PW}_{12}\text{O}_{40}$) transition metals as counter ions ^[77] .

The acidic properties of polyoxometalates can be controlled by:

- * The choice of elements constituting the polyanion.
- * The partial neutralization of the proton acid salts.
- * The choice of counter-cations .

I.4.2 - Heteropolycompounds Oxidation-Reduction Properties :

I.4.2.1- In Solution

In solution, the HPA species are capable of exchanging electrons in several multielectronic reversible steps in which the metal atoms have oxidation rates (MO^{VI} , W^{VI} , V^{V}). They accept up to 6 electrons without decomposing. In the liquid state, as in the solid state, they are easily reduced to give compounds called blue "heteropoly blue", all retain their structure ^[78,79] .

The oxidation-reduction properties of heteropolycompounds depend as their acidic properties on both the central atom, and the addenda atom, as well as on the counter- ions. The oxidation potential of these strong oxidants decreases in the order : $\text{V} > \text{Mo} > \text{W}$ for addenda atom, and $\text{P} > \text{Ge} > \text{Si}$ for the central atom ^[74,77] .

I.4.2 - In Solid State:

The reduced HPA in the solid state can be obtained by direct electrochemical reduction of the solid or by a reducing agent. ^[80,81] Misono ^[82,83] studied the reduction of 12-molybdophosphoric acid by hydrogen. The proposed mechanism has nothing to do with the behavior of HPA in solution. It is shown in **Figure 1.14** :

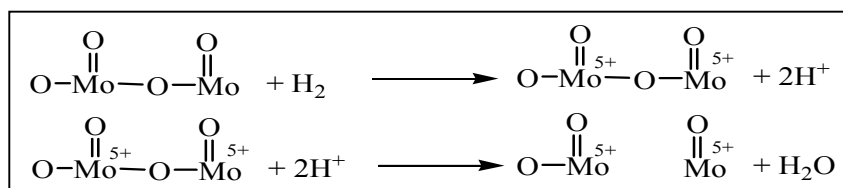


Figure I.14: Mechanism of acid reduction by dihydrogen $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ proposed by Misono .

The programmed thermoreduction showed that the reducibility of the solid decreases^[84] in the following order : $\text{SiMo}_{12} > \text{PMo}_{12} > \text{SiW}_{12} \sim \text{PW}_{12}$.

The counter-ion also has an influence on the redox properties of HPA and a correlation was proposed between the electronegativity of the cations and the reducibility of the solid state heteropoly salts equivalent^[85]. Substitution of the counter-cations or the central heteroatom with more electronegative atoms increased reduction potentials of the HPAs. However, substitution of more electronegative metals into the Keggin framework decreased reduction potentials. A map of reduction potentials of HPA catalysts is established to provide a design basis in searching for catalytic oxidation^[86]. The redox potentials of some Keggin type HPA are shown on **Figure I. 15**^[87].

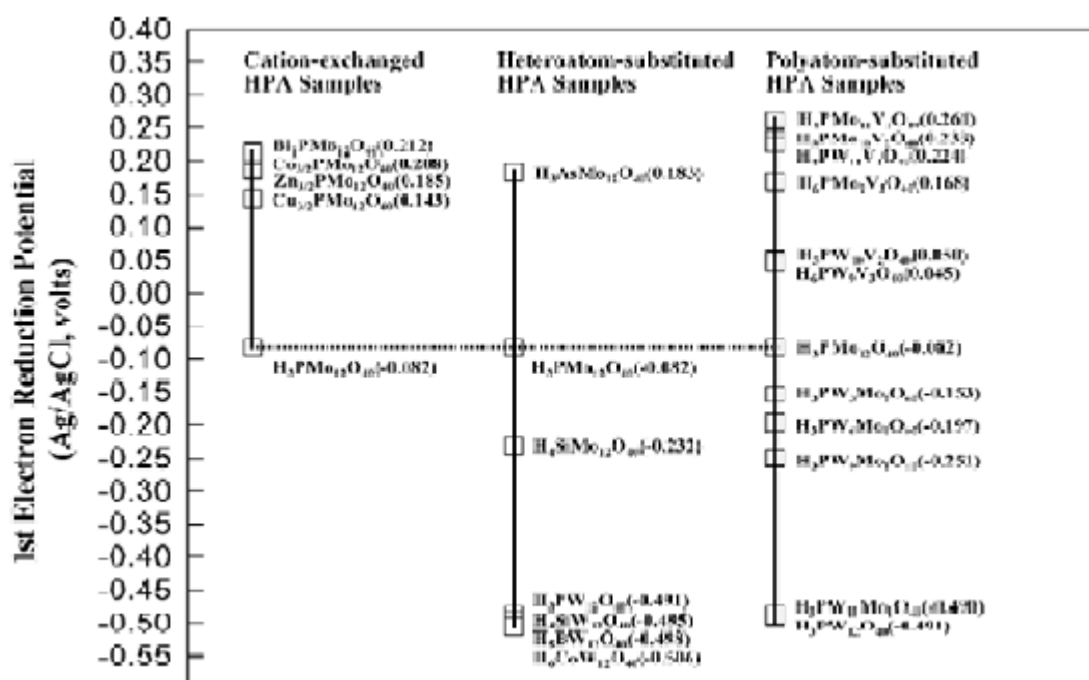
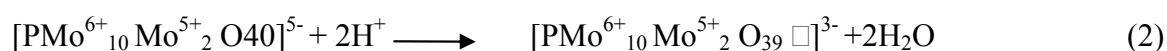
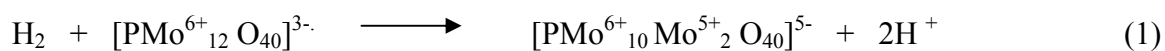


Figure I. 15 : Potential reduction of Keggin type HPA determined by electrochemical method.

To reduce $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ acid by hydrogen in the gas phase, redox mechanisms have been proposed^[88,89]. The latter would be in two stages:

- 1- the heteropolycompounds activated with formation of two reduced sites (2Mo^{+5}) and two protons.
- 2- the formation and starting of a water molecule from two protons and an oxygen trained network, leaving a deficiency of oxygen ($\square$).



Misono gives an explanation about the mechanism of the heteropolycompounds reduction in the solid state. Depending on the nature of the gearbox, he suggested the involvement of either the surface or heart of the solid. For example, oxidation of CO is one of the conventional surface reactions, while the H₂ uses a reaction of the heart in the sense that the charge-carriers electrons and protons migrate to the heart of solid .

I.4.3 - Stability of Heteropolyanions:

I.4.3.1 - Thermodynamic Stability of Heteropolyanions in Solution :

The nature of Heteropolyanions present in aqueous solution depends on pH and concentration of different constituents. The heteropolyacids and their salts formed with small cations (Li⁺, Na⁺, Cu²⁺ ...) are very soluble in polar solvents. The heteropolyacids have high affinity for oxygenated solvents and in particular to the ether which allows to extract a large number of compounds. In contrast, large cations (NH₄⁺, Cs⁺, Rb⁺ ...) give sparingly soluble or insoluble salts in water. The stability of polyoxometalates of keggin structure in solution depends on the solvent, acidity of the media and concentration. They are, in fact, a stable solution at acidic pH. But in dilute aqueous solution and high pH, they tend to decompose. Their stability is enhanced in organic medium, where the counter-ion is alkylammonium cation. The stability of these compounds also depends on the nature of the central atom and the nature of the constituent metal atoms .

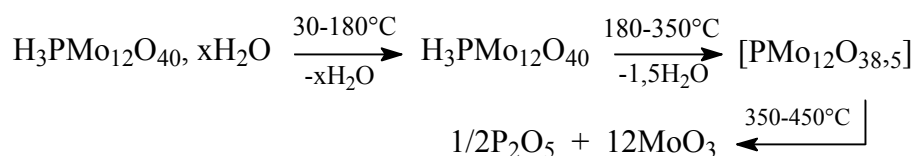
I.4.3.2 - Thermal Stability of Heteropolyanions:

The decomposition temperature of Heteropolyanions is one of the greater responsiveness characteristics. Indeed, an active and selective catalyst can be developed in an industrial catalytic process if its performance is stable over time. In solution, this stability depends on the acidity of the medium and the concentration of heteropolyanions. While in solid state, it depends on the composition and nature of the metal ion and heteroatoms. Indeed, molybdonmic compounds are less stable than tungstonic compounds. The latter decompose beyond 400 C⁰ [90,91] .

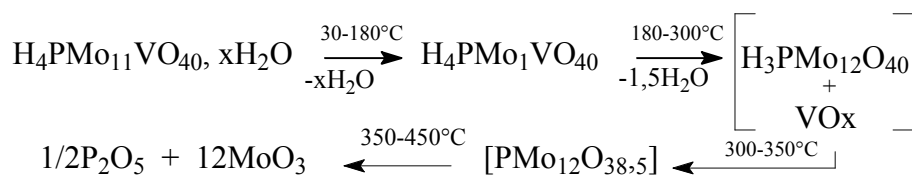
The difficulty facing industrial and academic researchers is to explain the deactivation of $H_{3+x}PMo_{12-x}V_xO_{40}$ catalysts type and their derivatives, as well as the structural instability in solids reaction conditions (especially temperature of 340 °C) that is close to the decomposition temperature of these compounds ^[92,93]. Therefore, the thermal properties and particularly the strong textural changes are key factors to consider.

Thermal study of POM in the solid state was followed by many methods: thermogravimetric analysis (TGA), differential thermal analysis (DTA), associated with the X-ray diffraction (XRD) and / or infra red spectroscopy (IR). The study by XRD of heteropolyacids at different temperatures showed that the crystalline structure depends on the number of water molecules of hydration which are 13 to 15 at room temperature for heteropolyacids and salts with small size counter-cation . The highly hydrated compounds with a high crystalline structure are not stable at room temperature, they evolve into more stable hydrates, generally 13 or 14 H₂O. For low or zero hydration levels, there is again a high crystalline structure (either cubic or quadratic).

Thermogravimetric analysis of the $H_3PMo_{12}O_{40}$ acid shows a first mass loss between 40 and 140 ° C corresponding to the departure of crystallization or hydration water. A second mass loss at temperatures between 250 and 350 ° C is attributed to the water content from the combination of H⁺ ions and oxygen network which leads to a reversible modification of polyanion ^[94,95]. In differential thermal analysis, the loss of water corresponds to endothermic peaks. An exothermic peak is observed beyond 350 ° C and is attributed to the decomposition of the acid to P₂O₅ and MoO₃ oxides ^[96,97]. $H_3PMo_{12}O_{40}$ acid thermally decomposes according to the following :



For $H_4PMo_{11}VO_{40}$ heteropolyacids, DTA profile shows two mass losses at around 145 and 350 ° C, respectively, interpreted as the departure of physisorbed water and constitution water ^[98].

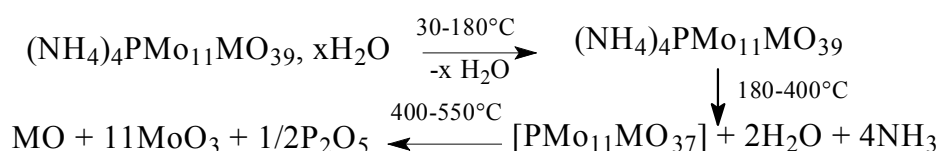


S. Hocine et al ^[99] have studied the type of salt $(\text{NH}_4)_4\text{HPMo}_{11}\text{MO}_{39}$ with $\text{M} = \text{Ni}, \text{Co}$ in order to evaluate qualitatively the thermodynamic phenomena occurring during the heat treatment of these solids.

Thermogravimetric analysis of the salts $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$ and $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$ is conducted ^[100] by heating 100 mg of each finely ground solid under nitrogen flow (50 ml / min) from room temperature up to 500 ° C by increasing the temperature at 5 ° C per minute. Three mass losses were observed

- * A first mass loss around 100 ° C is interpreted as the start of water physisorbed.
- * A second departure is around 240 to 300 ° C. It may be due to the molecules of water content related to nickel and cobalt.
- * Finally, a loss around 300 to 400 ° C, which corresponds to a departure of ammonia in the form of ammonia gas ^[101] or the state of molecular nitrogen. ^[102]

The three losses on the two salts can be summarized as follows:



When the HPA is processed at 200 ° C for 2h, the decomposition of ammonium is not observed ^[103]. The structure and parameters of stitch depend strongly on the hydration status of the HPA and on the temperature as shown in **Tables I.5** and **I.6**.

Table. I. 5: Structure and parameters of Heteropolyacids Unit.

Heteropolyacides	Elementary unit	Reference
$\text{H}_3\text{PMo}_{12}\text{O}_{40}, 30\text{H}_2\text{O}$	$a = 23,255\text{\AA}$ cubic	[104]
$\text{H}_3\text{PMo}_{12}\text{O}_{40} (13-14) \text{H}_2\text{O}$	$a = 14.10\text{\AA}$ $\alpha = 112.1^\circ$ $b = 14.13\text{\AA}$ $\beta = 109.8^\circ$ triclinic $c = 13.55\text{\AA}$ $\gamma = 60.7^\circ$	[105]
$\text{H}_3\text{PWO}_{12}\text{O}_{40}, 21\text{H}_2\text{O}$	$a = 20.788\text{\AA}$ $b = 13.086\text{\AA}$ orthorhombic $c = 18.879\text{\AA}$	[106]
$\text{H}_3\text{PWO}_{12}\text{O}_{40}, 14\text{H}_2\text{O}$	$a = 14.11\text{\AA}$ $\alpha = 112.04^\circ$ $b = 14.12\text{\AA}$ $\beta = 109.88^\circ$ triclinic $c = 13.55\text{\AA}$ $\gamma = 60.65^\circ$	[107]
$\text{H}_3\text{PWO}_{12}\text{O}_{40}, 6\text{H}_2\text{O}$	$a = 23,255\text{\AA}$ cubic	[108]
$\text{H}_4\text{PMo}_{11}\text{VO}_{40}, 13\text{H}_2\text{O}$	$a = 14.040\text{\AA}$ $\alpha = 112.10^\circ$ $b = 14.006\text{\AA}$ $\beta = 109.58^\circ$ triclinic $c = 13.39\text{\AA}$ $\gamma = 60.72^\circ$	[107]
$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ anhydre	$a = 13.759\text{\AA}$ $c = 15.906\text{\AA}$ quadratic	[107]

Table. I. 6: Symmetry crystalline hydrates during heat treatment of Heteropolyacids.

$\text{H}_4\text{SiMo}_{12}\text{O}_{40}, 29\text{H}_2\text{O}$ (cubic) $\downarrow 25^\circ\text{C}$ $\text{H}_4\text{SiMo}_{12}\text{O}_{40}, 13\text{H}_2\text{O}$ (triclinic) $\downarrow 60-80^\circ\text{C}$ $\text{H}_4\text{SiMo}_{12}\text{O}_{40}, 6\text{H}_2\text{O}$ (unstable) $\downarrow 100-350^\circ\text{C}$ $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ (quadratic) $\downarrow 360^\circ\text{C}$ $\text{SiO}_2 + 12\text{MoO}_3$	$\text{H}_4\text{SiW}_{12}\text{O}_{40}, 29\text{H}_2\text{O}$ (cubic) $\downarrow 25^\circ\text{C}$ $\text{H}_4\text{SiW}_{12}\text{O}_{40}, 13\text{H}_2\text{O}$ (triclinic) $\downarrow 60-80^\circ\text{C}$ $\text{H}_4\text{SiW}_{12}\text{O}_{40}, 6\text{H}_2\text{O}$ (unstable) $\downarrow 180-400^\circ\text{C}$ $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (quadratic) $\downarrow 520^\circ\text{C}$ $\text{SiO}_2 + 12\text{WO}_3$
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The importance of kinetic factors appears since the thermal measurements are usually made by thermogravimetric analysis (TGA) through temperature rise. It will then distinguish the thermodynamic stability and the kinetic stability of compounds. Indeed, the results depend on the process used: static (thermodynamic stability) or dynamic (kinetic stability) and on experimental conditions.

In the case of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, for example, the departure of the content water, strongly affects vanadium environment and its coordination sphere is affected. Initially, the Keggin $\text{PMo}_{11}\text{VO}_{40}$ leaves the structure at 200°C ^[109,110]. It is generally suggested for $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}, n\text{H}_2\text{O}$ acid type that vanadium would leave the anionic structure from 200°C leading to mixtures containing mainly : $\text{PMo}_{12}\text{O}_{40}^{3-}$ ion, vanadophosphates species and polymolybdates. The resulting incomplete structures are not yet understood. It seems they are recomposed to form the $\text{PMo}_{12}\text{O}_{40}^{3-}$ ion. It should be noted that the large alkali cations present in heteropolyanion salts often behave differently from that of the corresponding acids, they have better stability than their counterparts acids ^[111]. Remember that these salts are obtained by partial or complete substitution of protons from the acid by cations, and therefore, not crystallize water of hydration or water content. Their lattice crystal is then compact and anhydrous, their secondary structure is stabilized and their degradation in the form of oxides is retarded.

I.4.3.3 - Structural Stability of Heteropolyanions:

The structural decomposition is a major problem in heteropolycompounds catalysis. In some cases it has prevented the commercialization process based on these catalysts because of their short lifespan. This applies, for example, to oxydehydrogenation of isobutyric acid to methacrylic acid, where excellent initial performance of the catalyst deteriorates gradually over time ^[112]. A $\text{Cu}_{0.5}\text{H}_3\text{PMo}_{11}\text{VO}_{40}$ catalyst was the exception in retaining its performance catalyst for nearly a year ^[113].

Under oxidizing atmosphere, the decomposition temperature is a function of the heteroatom, the metal atom of polyanion and the nature of counter-cation ^[114]. With acids decomposition occurs at temperatures below 350 ° C.

In reaction conditions structural stability can be compromised either by high temperature needed to enable a stable molecule such as alkanes, or through the atmosphere reaction which is generally simplistic especially for high hydrocarbon / oxygen reports .

I.4.3.4 - Improvement of Structural Stability by Acting on the Process :

Structural stability can be improved by :

- * Operating under conditions that lower the reaction temperature in increasing the contact time as example.
- * Feeding MoO_3 as a volatile compound ^[112]. Indeed, it has been observed at high temperature and the presence of water in the reaction flow where $\text{PMo}_{12}\text{O}_{40}$ heteropolycompound type lose molybdenum as oxides form reduced to the vapor state. The supply of MoO_3 encourages reconstruction surface and reduces the effects of structural decomposition of the catalyst.
- * Acting on the environment of the catalyst, which is also important in the degradation process. It is faster in reducing conditions. Coexistence of water and oxygen in the gas phase enhances thermal stability of HPA at high temperature and can even sometimes regenerate the Keggin structure previously decomposed ^[115].

I.4.3.5 - Improvement of Structural Stability by Acting on the Catalyst:

- * The substitution of molybdenum by vanadium or tungsten can form more stable heteropolycompounds. It seems that monosubstitution leads to maximum stability. These include acids like $H_{3+x}PV_xMo_{12-x}O_{40}, nH_2O$ where heteropolycompound with $x = 1$ is the most stable ^[116].
- * Using heteropolyacids salts rather than the heteropolyacids themselves. Some of the heteropolyacids salts are more stable than the acids. In particular, the salts cation with ionic radius greater than 1Å form compounds remarkably stable ^[117]. An exceptional stability is obtained using heteropolycompounds substituted with potassium $K_3PMo_{12}O_{40}$ ^[118] or cesium $Cs_3PMo_{12}O_{40}$. It is claimed to be stable up to 500 °C; which mean, it is stable up to temperatures near the melting point (> 650 ° C). This suggests that the stability of HPA is associated with obtaining a cubic secondary structure type ^[119]. Unfortunately, some of the compounds completely neutralized are much less active than their acid.
- * By supporting the heteropolycompound on silica, silica doped with alkali metals or on activated carbon ^[120]. Because heteropoly acids and their transition metal salts usually have low surface areas (less than $10\text{ m}^2\text{ g}^{-1}$), heteropoly acid catalysts are usually supported on high surface area supports for improving the catalytic activity and stability.
- * Other authors propose the use of alkaline salts of heteropolyacids as supports. These compounds stabilize thermally neutral or basic, the heteropoly filed by the formation of an epitaxial layer of isostructural support (cubic lattice). Thus Brueckman et al. ^[121] studied various techniques to prepare supported HPA ($H_{3+x} PMo_{12}V_x / K_3PMo_{12}$) and their performance. They observed an increase in catalysts thermal stability and activity.

I.4.4 - Charastics of HPA Surface:

I.4.4.1- Surface Acidity:

The catalyst surface must be acidic in order to promote rapid desorption of the products formed in order to avoid excessive oxidation thrust in the adsorbed state. Water vapor can also promote the desorption of products ^[122]. The heteropoly compounds have a Bronsted acidity which is a function of position in the metal ions and anionic, cationic degree of neutralization (salification) and the degree of reduction. This can promote the desorption of products. They may also form a Lewis acidity type after oxo gap.

I.4.4.2 - Availability of Surface Mobile Oxygen Species:

The availability of mobile oxygen species on the surface of catalysts allows nucleophilic insertion into the hydrocarbon. However, for a catalyst process that is not limited by oxygen availability and to avoid a too much reduction which can cause disabling and may be structural decomposition, the catalyst must be reoxidized. This oxygen gas will replace the oxygen surface lost. The catalyst must also have the role for activation of oxygen gas the solid must possess elements capable of such activation. The heteropolycompounds P / Mo are predominant in the scientific literature. This is due to the greater reactivity of the Mo-O bond compared to the compounds P / W, Si / Mo or Si / W. Virtually all patents claim the use of vanadium and copper to modify the catalytic activity of 12-molybdophosphoric acid, but in some cases, arsenic is also claimed as an important element. Copper and vanadium are known to strongly influence the redox properties of the Departure compound ^[123] and thus alter the interactions with the hydrocarbon which implies change in oxidation state. Furthermore, excessive mobility of O⁻² species from the heteropolycompounds can lead to irreversible evolution of polyoxo or too oxidizing or inactive species. Therefore, it is necessary to reach a compromise in the availability of oxygen. For example, in the synthesis of maleic anhydride from n-butane, and probably in all oxidation reactions, the average degree of oxidation must be sufficiently high to ensure the catalyst surface rapid oxidation in all intermediarie. But, it must also be sufficiently low to avoid further oxidation of reagents or some intermediate or burning maleic anhydride. ^[124] This concept is supported by patents ^[125] claiming the need for partially reduced catalyst (for whom oxo mobility is necessarily reduced) to get the right level of activity and selectivity compared to methacrylic acid.

I.4.5 - Solubility

Since both the lattice energies of heteropoly compound and the salvation energies of heteropoly anions are low, the solubility of heteropoly compounds largely depends on the salvation energy of the cation. Heteropoly acids are extremely soluble in water and oxygen-containing organic solvents such as lower alcohols, ethers, etc, but not in nonpolar solvents such as benzene or petroleum ether. For example, the solubility (wt%) of the acid H₄[SiMo₁₂O₄₀].8H₂O is 88 in water, 86 in ethyl acetate, and 85 in diethyl ether at 25 °C . ^[126]

However, the solubility drops sharply when dried anhydrous heteropoly acids and thoroughly nonaqueous solvents are used. Salts with small cations such as Li^+ or Na^+ are readily soluble. In contrast, salts of large cations, e.g. K^+ , Cs^+ , NH_4^+ , etc., are insoluble in water.

Salts of large organic cation such as tetrabutylammonium are insoluble in water but soluble in organic solvents,^[127] which is frequently used for the isolation of polyoxometalates as well as for catalysis in organic media

I.5 - Catalysis in the Heteropolyanions:

I.5.1 - What is the Catalyst ?

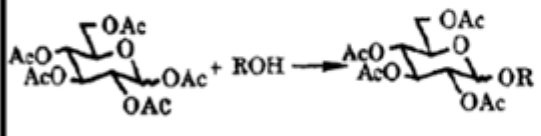
Catalysis plays a vital role in our society. And while some catalyst phenomena such as fermentation were known for centuries, the establishment of a theory was faced with the ignorance of causes and conditions of chemical reactions. Berzelius is generally credited with formalizing the theory in 1835, some results of experiments have recognized the phenomenon and have proposed the name of catalysis. He said that "Catalytic force appears in the fact that bodies by their mere presence and not by their affinities, affinities can awaken dormant at this temperature. The term "tsoo mei" used by the Chinese for a catalyst and means "Marriage broker", reflects a more appropriate perception of the term by a profane. The terms "الوساطة" (alwaqaata) and التحفيز (attahfiz) "used in the Arabic language for catalysis have different meaning. The first "alwaqaata means into the middle. The second "attahfiz means to encourage, to move, pushing from behind ... These terms reflect different aspects of catalysis, with emphasis on its dynamic character. Through their properties, polyoxometalates are excellent candidates for catalysis. They have the advantage of being used in redox catalysis and acid catalysis, both in homogeneous and heterogeneous phase catalysis. Therefore almost 80-85 % Of patents and publications addressing the application of HPAs belong to the catalysis field^[128].

I.5.2 - Homogeneous Catalysis :

I.5.2.1- Acidic Catalyzed Reactions:

In acid catalysis, the heteropolyanions have several industrial applications including: The hydration of propene to propane-2-ol,^[129] the hydration of n-butene^[130] and isobutene,^[131] polymerization of tetrahydrofuran (THF)^[132] and synthesis of vitamins E, C and K1^[133].

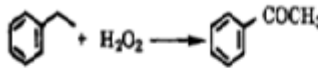
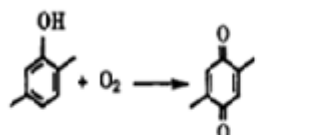
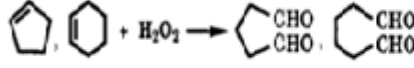
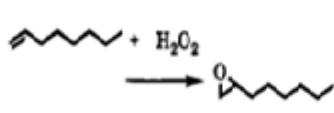
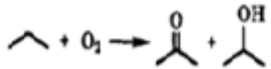
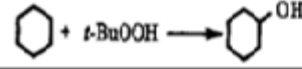
Table I. 7 : Reactions Catalyzed by acidic heteropolycompound ^[134].

Reactions	Catalyst	Notes
Hydration of olefines	$H_3PW_{12}O_{40}$	$T = 313-423\text{ K}$
$n \text{ } \text{C}_4\text{H}_8\text{O} \rightarrow \text{HO} \left[(\text{CH}_2)_4\text{-O} \right]_n \text{H}$ (PTMG)	$H_3PW_{12}O_{40} \cdot nH_2O$ ($n = 0-6$)	$T = 333\text{ K}$, MW ≈ 3000
	$H_3PW_{12}O_{40}$ $H_6P_2W_{18}O_{62}$	$T = 298\text{ K}$, rend = 60–98% (2h) $T = 315\text{ K}$, Selectivity $\approx 100\%$
$\text{C}_3\text{H}_6 + \text{CH}_3\text{OH} \rightarrow \text{C}_3\text{H}_8\text{O}$	$H_3PW_{12}O_{40}$ $H_3PMo_{12}O_{40}$	$T = 298\text{ K}$
$3 \text{ C}_2\text{H}_5\text{CHO} \rightarrow \text{Trimer}$		

I.5.2.2 - Redox Catalyzed Reactions :

Table I.8 shows the various oxidation reactions catalyzed by heteropolycompound as a homogeneous catalysts :

Table I.8 various oxidation reactions catalyzed by heteropolycompound as a homogeneous catalysts

Reactions	Catalysts	Notes
	$H_3PMo_{12}O_{40}$	reflux selectivity = 100%
	$H_3PMo_{10}V_2O_{40}$	$T = 333\text{ K}$, $O_2 = 1\text{ atm}$, Conv = 80%
	$H_3PMo_6W_6O_{40}$	$T = 303\text{ K}$
	$H^+ / WO_4^{2-} / PO_4^{3-} / QX$ $(CP)_3PW_{12}O_{40}$ CP = cetylpyridinium ion	$T = 343\text{ K}$, Conv = 82% $T = 333\text{ K}$, Conv = 75%
	$H_3PW_9Fe_2NiO_{37}$	$T = 423\text{ K}$, turnover number = 9730 (3 h)
	$PW_{11}CoO_{39}^{5-}$	$T = 298\text{ K}$

I.5.3 - Heterogeneous Catalysis :

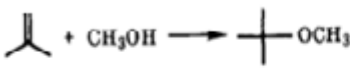
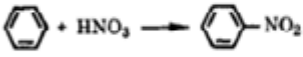
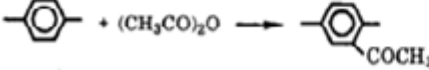
The heteropolycompounds are widely used in heterogeneous catalysis which had their redox and acidity properties. They have the advantage of being used both in homogeneous catalysis and heterogeneous catalysis. The nature of the chemical elements of heteropolycompounds determines the type of catalytic activity.^[135] In general, redox reactions and acid- reactions are competitive for this type of catalyst.

I.5.3.1 - Acidic Catalyzed Reactions :

The acidity of Heteropolyanions makes them potentially attractive candidates for acid-base catalyzed reactions (esterification, alkylation...). Although, they are more expensive than ordinary mineral acids, they have nevertheless the advantage of being non-volatile and slightly fragrant more easily conditioned ^[136].

Reactions in heterogeneous phase requiring acid sites, generally involve heteropolyacids containing tungsten or molybdenum. Indeed, their high acidity gives heteropolycompounds a special aptitude for the catalysis of dehydration, alkylation, isomerization and acylation. Thus, some examples can be found in the literature such as the dehydration of propan-2-propanol and alkylation of benzene ^[137]. (see Table I.9).

Table I. 9: Reactions catalyzed by heterogeneous heteropoly acid ^[134]

Reaction	Catalysts	Notes
$\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \longrightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	$T = 423 \text{ K}$, selectivity = 91% (90% Conv.)
Aromatic alkylation	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	$T = 303\text{--}373 \text{ K}$,
Alkane alkylation	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	$T = 293 \text{ K}$, $P = 5 \text{ kg cm}^{-2}$
Alkane isomerization	$\text{Pd}_{1.5}\text{PW}_{12}\text{O}_{40}$	$T = 483 \text{ K}$
$\text{CH}_3\text{OH} (\text{CH}_3\text{OCH}_3) \longrightarrow \text{C}_1\text{--C}_6 \text{ Hydrocarbons}$	$\text{H}_3\text{PW}_{12}\text{O}_{40}$ $\text{H}_3\text{PW}_{12}\text{O}_{40}$	$T = 348 \text{ K}$, $T = 573 \text{ K}$,
	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	$T = 563 \text{ K}$, selectivity ($\text{C}_2\text{--C}_4$ Alkene) = 74%
	$\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$	$T = 323 \text{ K}$
	$\text{Cs}_{1.5}\text{H}_{1.5}\text{PMo}_{12}\text{O}_{40}$ $\text{Cs}_{2.5}\text{H}_{0.5}\text{PMo}_{12}\text{O}_{40}$	$T = 413 \text{ K}$, selectivity = 97% (94% conv.) $T = 573 \text{ K}$

I.5.3.2 - Redox Catalyzed Reactions :

A major research areas of heterogeneous heteropolycompounds catalysis is the activation of light paraffins. Many oxidation reactions are also catalyzed by Heteropolyanions. This includes dehydrogenation reactions of alcohols and carboxylic acids ^[138], the oxidation of butene ^[139], n-butane ^[140] and n-pentane to dioxide maleic ^[141], the oxidation of isobutane to methacrylic acid, ^[142] and the oxidation of alkanes (ethane, propane) to alkenes and oxygenates acid, aldehyde ... etc. (see Table I.10, I.11).

Table I.10 : Oxidation reactions catalyzed by heterogeneous heteropoly ions [60]

Reaction	Catalysts	Notes
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO} + \text{O}_2 \longrightarrow \text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	$\text{CsH}_3\text{PVMo}_{11}\text{O}_{40}$	$T = 553 \text{ K}$, selectivity = 80-85%
 $+ \text{O}_2 \longrightarrow \text{C}(\text{CH}_3)_2\text{COOH}$	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$T = 623 \text{ K}$, selectivity = 45%
$\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH} \longrightarrow \text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	$\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$	$T = 573 \text{ K}$, selectivity = 72% (52% Conv.)
 $+ \text{O}_2 \longrightarrow \text{Maleic Anhydride}$	$\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$	$T = 583 \text{ K}$, selectivity = 55%

Table I.11 Different types of reactions catalyzed by heteropolyacids

Type of reaction	Common Catalysts	Solid Acidic Catalysts
Acylation	AlCl_3 , BF_3 , ZnCl_2	HPW
Cyclisation	AlCl_3 , ZnCl_2	HSiW
Alkylation	AlCl_3 , BF_3 ,	CsPW
Isomerisation	$\text{BF}_3 - \text{HF}$, $\text{BF}_3 - \text{SO}_3$,	HPW
Dealkylation	$\text{BF}_3 - \text{HSO}_3\text{H}$	HPW
Hydration	$\text{AlCl}_3 \cdot \text{H}_2\text{O}$, H_2SO_4	HPW
Dehydration	H_2SO_4	HPW
Esterification	PTSA , H_2SO_4	HPW
Trans-esterification	PTSA , H_2SO_4	HSiW
Etherification	HCl , PTSA , $\text{HF} \cdot \text{Et}_2\text{O}$	HPW
Condensation	H_2SO_4	HPW
Hydrolysis	H_2SO_4 , HCl	CsPW

I.5.4 - Classification of Catalytic Reactions

According to Misono et al ^[143-145], the reactions catalyzed by HPA can be classified into three types: Surface reaction, heart reaction type I, and heart reaction type II.

I.5.4.1- Surface Reaction (Surface-Type)

In such reactions, the molecules of the reactants are absorbed on the surface of the heteropoly ions (**Figure I.16**). In this case, the activity is proportional to the surface of the catalyst. Among the reactions belonging to this type of catalysis are:

- Oxidation of methacrolein;
- Oxidation of carbon monoxide;
- Isomerization of cis but-2-ene.

The catalysts used for this reaction are ammonium salts, potassium or cesium of phosphomolybdate because of their high specific surface areas ($> 200\text{m}^2 / \text{g}$).

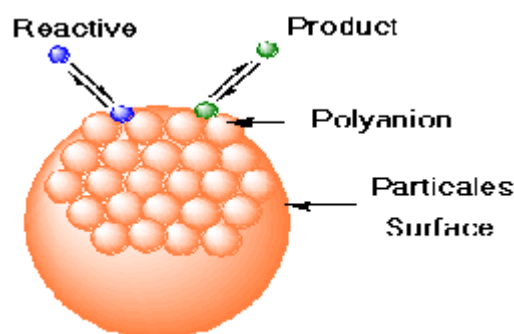


Figure I.16 : Schematic representation of the surface reaction on polyoxometalates

I.5.4.2 - Heart Reaction Type I (Bulk Type I)

In this type of reaction, the reactants diffuse into the network of the catalyst, by replacing the water of crystallization and by deforming the network of the polyanion. They react in pseudo-liquid phase (**Figure I. 17**). This is observed in acidic catalysis in the dehydrogenation reaction of alcohols at low temperatures ^[146]. In this case, the activity is connected to the acidity of the heart, and the reaction rate is proportional to the mass of the catalyst.

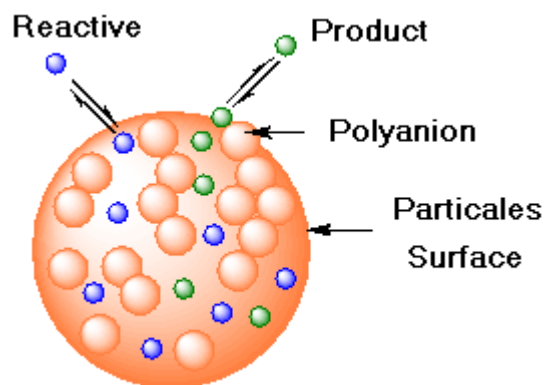


Figure I. 17: Schematic representation of reaction type I heart on polyoxometalates

I.5.4.3 - Heart Reaction Type II (Bulk Type II)

In such reactions, the molecules of the reactants remain on the surface, but there is migration of protons and electrons to the heart of the catalyst (**Figure I.18**). The reactions of this type are called redox. The activity does not depend on the specific surface area but depends on the amount of the catalyst. Such reactions include the oxidative dehydrogenation of isobutyric acid, cyclohexene and the oxidation of hydrogen ^[147].

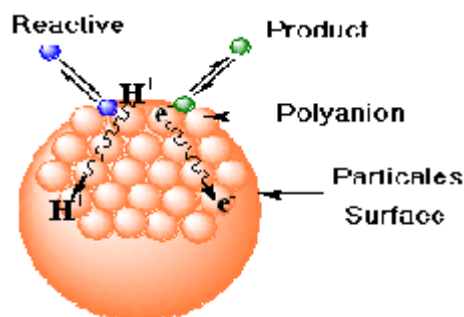


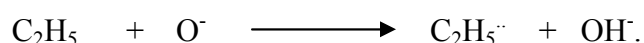
Figure I. 18: Schematic representation of reaction of heart type II on polyoxometalates.

I.6 - Transformation of Alkanes by Heteropolycompounds

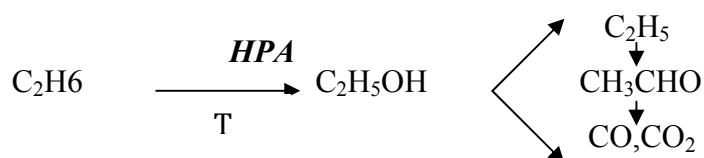
Much research has been developed in the catalytic transformation of saturated hydrocarbons on heteropolycompounds. The role of these solids is to rupture the CH link ^[148], which today remains to be a challenge in order to improve the activity and selectivity of certain products requested ^[149,150]. Studies on the use of these compounds for the recovery of natural gas and the activation of light alkanes C₂ to C₅ are increasing ^[151,152]. In contrast Mizuno et al ^[153] have shown that methane is not running on these systems (0.2% conversion).

I.6.1 - Transformation of Ethane by Heteropolycompounds :

The first work dealing with the conversion of ethane by heteropolycompounds was published in 1994 ^[154]. Ethane is converted to 55% ethylene, and acetaldehyde by heteropolycompounds supported on silica at 450 ° C and 570 ° C using N₂O. By analogy to the activation of methane, it can be assumed that the transformation process of ethane is through a radical mechanism ^[155].



Theoretical calculations by the Huckel method indicate that the terminal oxygen of the molybdenum HPA are more labile than tungstic compounds ^[156], which explains the difference of catalytic properties of these two types of solids. The mechanism of transformation of ethane assuming ethanol as an intermediate is :



A similar mechanism is proposed in the transformation of ethane on B₂O₃/Al₂O₃ and B₂O₃/P₂O₅ ^[157]. Recently the conversion of ethane was studied in the mixed salts of potassium and ammonium 12-molybdophosphoric acid H₃PMo₁₂O₄₀ ^[158]. A selectivity of 34 to 56% for ethylene conversion of 1 to 7% was observed ^[159].

I.6.2 - Transformation of Propane by Heteropolycompounds

It is found in literature ^[160,161,162] that several systems are capable of activating the CH bond of propane, but the difficulty lies in the functionalization and control of degradation reactions. However heteropolycompound can be considered as a very economically interesting catalyst. H. Krieger, Coll, Rohm and Hass ^[163] have patented in 1981 a heteropolyanion catalysts system able to selectively activate propane to propene. In another type of heteropolyanion system (H₃PMo₁₀V₂O₄₀), G. Centi and F. Trifiro ^[164] obtained the propene yield of 20% in 1990.

I.6.3 - Transformation of n-C₄ on Heteropolycompounds

The studies dealing with the transformation of n-butane and iso butane are much more numerous than those of other alkanes ^[165], King noted that the butane oxydeshydrogenation is

more studied than those of ethane or propane and viewed its industrial interest. The isomerization of n-butane to produce isobutane, tertibutyl of precursor used in place of tetraethyl in diesel ^[166].

The heteropoly salt $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is used in the isomerization of n-butane to isobutane. At 300 ° C the conversion is 20% and isobutane selectivity is 83% ^[167]. Recemmant synthesized several Cesium heteropoly salts, characterized and tested in the isomerization reaction of n-butane, where a better conversion is observed in the case of two cations heteropoly salts (mixed salts) ^[168].

I.6.4 - Transformation of Isobutane on Heteropolycompounds

The conversion of isobutane to methyl methacrylate (MMA) was studied on the heteropolyanionic compounds ^[169]. The oxidation of isobutane in the mixed salt of ammonium potassium 12-molybdophosphoric acid, (and some of heteropoly salts with iron as a third counter ions) increase isobutane conversion at 350 ° C from 4% to 6% for a composition of iron from 0 to 1.5% with a yield of methacrylic acid increasing from 1 to 3% ^[170].

The conversion of isobutane to (MAA) and metacroleine is studied on Cesium salts of 12-molybdophosphoric acid ^[171] with nickel, manganese or iron as the second cation. By using $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ at 340 ° C the conversion increases with increasing x, untill it reaches a maximum at $x = 2.85$. However at this value of x the selectivities of MAA and metacroleine (MAL) are respectively 5 and 10%.

The maximum selectivities of (MAA) and MAL are 34 and 18% respectively for the values of $x = 2$ and 0. A maximum selectivity of CO_2 is observed for $x = 2.85$ and is (81%). The introduction of a transition ion as a counter second ion with $x = 2.5$ and an appropriate amount of protons in the salt of the 12 -molybdophosphoric acid gradually improve the conversion and the selectivities of products ^[164].

I.7- Hydroisomerization of n-Paraffins

Crude oil is a highly variable mixture in which there are paraffins or alkanes (18 to 65%), naphthalene (25 to 90%) and aromatics (up to 15%). Sulfur, nitrogen and metals are also present in varying proportions depending on the origin of raw and fractions considered. There are no alkenes (olefins) or alkynes in the crude oil.

The objective of refining is firstly to separate the molecules constituting the oil according to their volatility (distillation). Each fraction is then converted (either by catalytisis or thermally) to lead mainly to fuel (gasoline, kerosene, diesel) spreading to more stringent standards. The consequence of these stringent standards is that to maintain a high octane, while reducing the olefin content, aromatic process done by providing the refiner paraffins with high octane number (number of connections on the skeleton hydrocarbon) will be increasingly necessary. The two main processes are the hydroisomerization of light gasoline (C₅-C₇) and alkylation of isobutane / butene.

I.7.1 - The Purpose of the Hydroisomerization of n-Paraffins

The oil fraction collected at 70 ° C during the distillation under atmospheric pressure or catalytic reformer contains n-C₅-C₆ paraffins and aromatics. These n-alkanes are hydroisomerized ^[172], then converted into isoparaffins or aromatics with a higher octane number ^[173].

The octane number, which characterizes the properties of Anti-species, is expressed on a scale established by mixing 2 hydrocarbons stallions: 0 for n-heptane and 100 for isooctane (2,2,4-trimethylpentane). The motor octane number (MON) is representative of the behavior of fuel in on-road driving at high speed while the research octane number (RON) best expresses the performance of urban driving at low speeds. The table gives the values adopted for the pure pentanes and hexanes ^[174]. We see that the degree of branching is essential : the more isoparaffins are connected, the higher the octane number is.

Table I.12 octane number of different hydrocarbons.

Hydrocarbon	RON	MON
Isopentane	93	90
n-pentane	62	61
2,2-diméthylbutane	94	95
2,3-diméthylbutane	105	104
2-méthylpentane	74	75
3- méthylpentane	75	76
n-hexane	31	30
Méthylcyclopentane	96	85
Cyclohexane	84	77

I.7.2 - Industrial Processes for the Isomerization of n-Paraffins

There are many industrial processes for the isomerization of n-paraffins ^[175-180] and cycloparaffins ^[181,182]. Industrial isomerization species units comprise a fixed catalytic bed unit that converts n-paraffins to isoparaffins, and a separation unit which enables the recycling of the n-paraffins to non-transformed catalyst unit and a substantial increase in the octane number of the isomerate .

The catalytic unit generally consists of two reactors in series: the downstream reactor corrects the upstream isomerization reactor when the catalytic upstream is off. The state of the bed catalyst is known by the fall in the rate of isomerization itself correlated with the fraction of the deactivated catalyst. The catalyst contained in the upstream reactor can be removed by gravity or by suction while the load is processed by the second reactor ^[183]. More adding of a fluid (a mixture of methane, ethane, propane and butane) gas in the upstream area at 40 ° C can handle loads with more than 8% of benzene because it allows moderate exothermicity due to the hydrogenation of aromatics ^[184]. The separation of normal attached hydrocarbons can be done by passing over molecular sieve absorbent pores of 5A ^[185].

I.7.3 - Generations of n-Paraffins Isomerization Catalysts:

Several generations of the catalysts have been used successively to perform the isomerization of n-paraffins.

a- First-Catalysts Generation : Friedel-Crafts catalysts.

The first generation (in 1940) consists of the Friedel-Crafts catalysts type, such as AlCl_3 . They are used in homogeneous liquid phase or supported on porous solids, and work at low temperature, between 30 and 180 ° C with hydrogen chloride as co-catalyst (1 to 3 bars) ^[186,187]. The isomerization is carried out under hydrogen pressure (0.1 to 30 bar), which plays the role of promoter. But the higher pressures of hydrogen play an inhibitory role ^[188]. These catalysts are very active, however, lead to a significant cracking, and they can be disabled fast enough.

b-Second Generation of Catalysts : Reforming Catalysts.

The second generation (in 1960) is based on the catalytic reformer such as Pt/Al₂O₃ working between 350 and 500 °C. These solids contain about 1%W of Pt and 1% W of Cl [189,190] where at these temperatures they cause the dehydrocyclisation of n-hexane in benzene at the same time as the isomerization of hexanes. The addition of chlorine increases their isomerizing power. Today, these catalysts are no longer used.

c- Third Generation of Catalysts : Chlorinated Aluminas

The third generation (the 1970s) consists of halogenated alumina, preferably chlorine (10% w Cl). These catalysts also contain 0.5-1% of a Group VII metal (mainly Pt), which are used between 80 and 150 ° C and also catalyze the isomerization of cycloparaffins [191]. The consumption of these catalysts is very low, where the HOT (Hydrogen Once - thought) process was developed in which hydrogen output unit is recycled [192]. This mode of operation allows a significant reduction of operational cost of the units. In addition, a dope is introduced into the charges.

d- Fourth Generation of Catalysts: Zeolites.

The zeolites catalysts [193-195] of the protonated mordenite type are the fourth generation (in 1980). The mordenite is treated with an acid wash that provides a dealuminated and protonated mordenite (H-MOR) by molar ratio SiO₂/Al₂O₃ = 20 the catalyst obtained after depositing 0.5% Pt (given by (NH₃)₄PtCl₂) converts the n-hexane between 250 and 350 ° C [196]. The mole ratio of SiO₂/Al₂O₃ is optimized for maximum activity [197] and we can increase this ratio by alternating treatments with water vapor at 540 °C and washes with concentrated hydrochloric acid [198].

These catalysts are less active than the chlorinated aluminas but they are more resistant to poisons such as sulfur and water because the micropores is buried in the plate.

e- Last-Catalysts Generation: Sulfated Zirconia

The sulfated zirconia supported on alumina containing a little platinum [199-202] are the latest generation of catalysts used in the hydroisomerization of paraffins. They are activated

and regenerated in situ by calcination in air at 480 ° C, followed by reduction under hydrogen. Their catalytic performance is markedly inferior to those of halogenated catalysts but higher than the zeolites. It appears that UOP has already replaced certain zeolites charges by sulfated zirconia. Their large hydrogen consumption and rapid inhibition by naphthenes limit their use, for the time being.

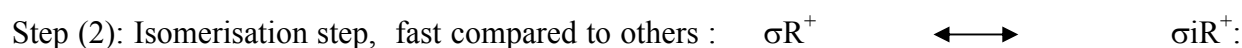
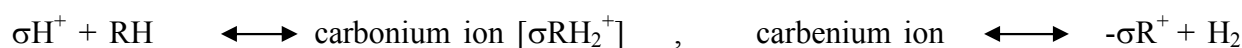
I.8 - Reactions Mechanism

The hydroisomerization is generally considered to operate by a monofunctional acid mechanism since it uses Friedel-Crafts catalysts type. The bifunctional mechanism is amorphous or zeolite due to the presence of metal sites which may have a hydrogenating / dehydrogenating function in the reaction conditions as in the following mechanisms:

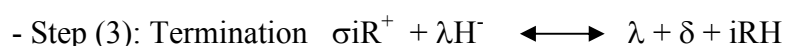
- σH^+ : Bronsted acid sites ; λ : Lewis acid sites; δ : Lewis basic sites.
- RH: n-alkane; IRH: iso-alkane, R = n-alkenes; iR = iso-alkenes.
- R + linear carbenium ion ; R + branched carbenium ion.

I.8.1 - Monofunctional mechanism on Bronsted acid sites ^[203,204]

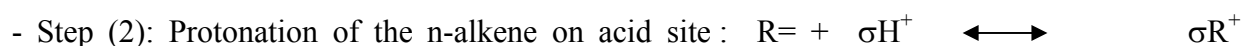
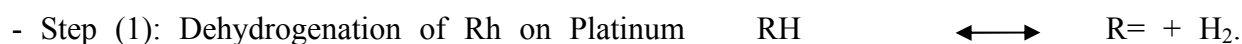
- Step (1) Initiation by protonation of n-paraffin using superacids site:

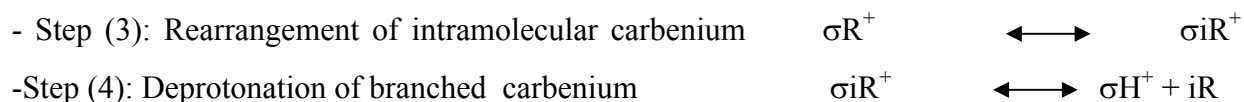


I.8.2 - Monofunctional mechanism on Lewis acid sites ^[205-206]



I.8.3 - Bifunctional Mechanism ^[207]





I.9 - Transformation of n-Hexane

The reaction of catalytic reforming of n-hexane on heteropolycompounds has been not been reported in the literature. The catalytic systems addressing the transformation of n-hexane systems are all cited in the preceding paragraphs (isomerization of n-paraffins). They can also be classified according to the product obtained:

a- cracking catalysts b- isomerization catalysts c- aromatization catalysts .

a-Cracking Catalysts:

Zeolites of aluminocelicates type are often used because of their acidity. ^[209,210] These catalysts are represented by H-[Al]-ZMS-5 in which Si atoms in the zeolite are substituted by Al atoms. Concentration of acid sites in these catalysts is directly related to the amount of substituted Al₃Si₄ which generates a negative charge and allows the creation of a Bronsted acid site, which is responsible for the catalytic phenomenon. Systems H-[Al], [Ga], [Fe]-ZMS-5, where we study the effect of trivalent element on their catalytic performance appear very active in the catalytic cracking of n-hexane ^[111 , 212] .

Recently it was shown that the catalytic activity of these solids can be correlated linearly with the concentration of Bronsted acid sites ^[213 , 214]. For example, the catalytic cracking of n-hexane is proportional to the number of Bronsted acid sites in ZSM-5 ^[215] .

b-Isomerisation Catalysts

The system WO₃/ZrO₂ is heavily investigated for the isomerization of n-hexane ^[216,217] . These systems are less acidic than the system SO₄²⁻/ ZrO₂ , but more stable. In practice, WO_x systems are synthesized by co-precipitation of zirconium hydroxide and tungsten or by impregnation of zirconium hydroxide with a solution of ammonium meta-tungstates followed by calcination at 700-800 ° C ^[218]. However, the catalysts are obtained with low specific surfaces. Recently V.V. Brei et al ^[219] described a method of preparation by co-precipitation to

obtain catalysts for specific surfaces of 40 to 250 cm²/g. They are very active in the isomerisation of n-hexane.

c- Catalysts for Aromatization

The supported platinum is one of the oldest materials used in the activation of n-hexane for its flavor. It is found that Pt / Zeolite is active and selective in the reaction of aromatization of n-hexane ^[220]: the catalyst is bound in this case to the interaction of metal particles and support, ^[221,222] specially the support structure ^[223,224]. Recently, Melczarshi et al ^[225] have shown that the aromatization of n-hexane is not related to the two reasons mentioned above but to the ability to maximize the stability of platinum on this type of particle.

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CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF HETEROPOLYACIDS , ISOMERIZATION OF n-HEXANE

II. 1 – Introduction :

The goal of a catalyst manufacturer is to produce and reproduce a commercial product which can be used as a stable, active, and selective catalysts. To achieve this goal, the best preparative solution is sought which results in sufficiently high surface area, good porosity, and suitable mechanical strength. The first of these surface area is an essential requirement in that reactants should be accessible to a maximum number of active sites. The properties of a good catalysts for industrial use may be divided at least for the purpose of easy classification, into two categories:

(1) properties which determine directly catalytic activity and selectivity, such factors as bulk and surface chemical composition. Local microstructure, and phase composition are important.

(2) properties which ensure their successful implementation in the catalytic process, here thermal and mechanical stability, porosity, shape, and dimension of catalyst particles. The requirements which are fundamental for catalyst performance generally require a compromise in order to produce a material which meets the contradictory demands imposed by industrial processes. An acceptable solution is typically ascertained by a trial-and-error route. Catalytic materials become catalysts when they are used in industrial processes. A way this can be realized occurs when the variety of methods used to prepare catalytic materials are viewed in relation to their successful implementation in commercial applications.

In general, it is well established that the essential properties of a catalyst such activity, selectivity and thermal stability are strongly related to the conditions and the method of synthesis. In order to obtain a catalyst with maximum efficiency, we prefer to have the original catalytic system as pure as possible; it requires a lot of rigor and expertise.

Obtaining a given heteropolyanion species depends on the nature of the reactants, their stoichiometry, and their sequence of addition, pH and reaction temperature.

The synthesis of heteropolyanion catalysts requires three steps:^[1]

Preparation of heteropoly acid in acid solution.

- Isolation of the heteropoly acid by evaporation or ether extraction.
- Synthesis of substituted catalysts, by reacting the solution of the heteropoly acid with a metal salt.

II.2 - Synthesis of Heteropolyacids :

There is different methods using for preparing of Heteropoly acid catalysts such as : Tsigdinos method ^[2], hydrothermal method ^[3], sol-gel method ^[4],

II.2.1 - Synthesis of H₃PMo₁₂O₄₀, 13 H₂O:

H₃PMo₁₂O₄₀ sample was synthesized in two methods: hydrothermal method, tsigdinos method

II.2.1.1 - Hydrothermal Methods :

A- Presentation :

H₃PMo₁₂O₄₀ acid is prepared according to the methods described in the literature ^[3]. A desired amounts of MoO₃ and H₃PO₄ (85 wt.%) were added in a round bottom flask, until the desired stoichiometry was achieved. The solution was maintained at reflux for 24 h. evaporated at 50°C. The powder sample was collected and dried in vacuum overnight at 120°C

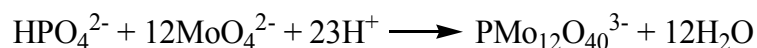
B- Procedure:

In a 1000 cm³ round bottom flask, 650 cm³ of distilled water was added. Then (18.58g) of MoO₃ and phosphoric acid H₃PO₄ (85 vol.%, 0.011 mol) were added in the solution, The solution was maintained at reflux for 24 h. The mixture was converted to a clear green solution and was evaporated for the removal of water until dryness at 50 °C. The powder sample was collected and dried in vacuum overnight at 120 °C.

II.2.1.2 - Tsigdinos method :

A. Presentation:

H₃PMo₁₂O₄₀ acid is prepared according to the methods described in the literature ^[5-7] the disodium salt Na₂HPMo₁₂O₄₀ which synthesized by reacting sodium molybdate and orthophosphoric acid. The reaction of formation of Keggin anion is:



H₃PMo₁₂O₄₀ synthesis involves two steps. The first is the preparation of the disodium salt Na₂HPMo₁₂O₄₀, x H₂O, once dried, cooled to room temperature, filtered and then dried again in air, then the second stage which consists of isolating the heteropolyacid by extraction with ether.

B. Procedure:

First stage: Synthesis of $\text{Na}_2\text{HPMo}_{12}\text{O}_{40} \cdot x \text{H}_2\text{O}$.

- Dissolve 290.5 g (1.2 mol) of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$) in 420 ml of distilled water.
- Add to the previous solution: 6.8 ml of phosphoric acid (H_3PO_4), (85%, 14.8 M) and 284 ml of perchloric acid, HClO_4 (70%, 11.7 M). The precipitated $\text{Na}_2\text{HPMo}_{12}\text{O}_{40} \cdot x \text{H}_2\text{O}$ salt then cooled to room temperature, filtered and dried in air.

Second stage: Extraction with ether.

- Dissolve 250g (or 0.13 mol) of $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}$ in 300 ml of distilled water acidified by 75 ml of (2M) hydrochloric acid (HCl).

- Add 400 ml of ether to the obtained solution .

After separation, the heavy phase of ether-acid-water complex is recovered, and half of its volume added in water.

- Shake at room temperature, it will lead to evaporation of the ether.
- Let the solution crystallize at 4 ° C.
- Collect the formed crystals after a few days by filtration and let them to dry in air.

A yellow-green crystals then obtained .

II.2.2 - Synthesis of $\text{H}_4\text{PVMo}_{11}\text{VO}_{40} \cdot x \text{H}_2\text{O}$:

$\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ sample was synthesized in two methods .

II.2.2.1 - Hydrothermal Methods :

A. Presentation :

$\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ acid is prepared according to the methods described in the literature ^[3]

A desired amounts of V_2O_5 , MoO_3 and H_3PO_4 (85 wt.%) were added in a round bottom flask, until the desired stoichiometry was achieved. The solution was maintained at reflux for 24 h. evaporated at 50 °C. The powder sample was collected and dried in vacuum overnight at 120 °C.

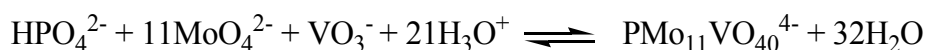
B. Procedure:

In a 1000 cm³ round bottom flask, 650 cm³ of distilled water was added. Then (18.58g) of MoO_3 and (1.067g) of V_2O_5 and phosphoric acid H_3PO_4 (85 vol.%, 0.011 mol) were added in the solution, The solution was maintained at reflux for 24 h. The mixture was converted to a clear orange-red solution and was evaporated for the removal of water until dryness at 50 °C. The powder sample was collected and dried in vacuum overnight at 120 °C.

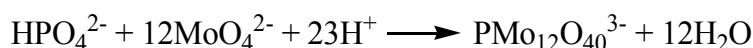
II.2.2.2 - Tsigdinos method :

A. presentation:

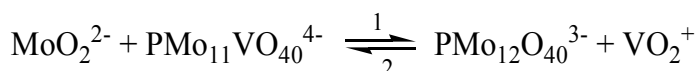
1-vanado 11-molybdophosphoric acid is synthesized by the method described by P. Courtin ^[8, 9] and developed in the laboratory of Professor Herve Paris (VI) ^[10]. It consists of acidification with a strong acid with a stoichiometric mixture vanadate / molybdate / phosphate. The overall reaction is:



This reaction is competed by formation of $\text{PMo}_{12}\text{O}_{40}^{3-}$:



After cooling, the acid was extracted as etherate (heavy layer). The use of ether in the extraction enriches the mixture species $\text{PMo}_{11}\text{VO}_{40}^{4-}$, the overall balance is strongly shifted in the direction 1:



Crystallization of the acid by cooling at (4 ° C) after evaporation of ether was reported as a modification to previous work ^[11,12]. In these conditions, a pure product is obtained 95% against 75% with the method of Tsigdinos ^[11,13].

B. Procedure:

In this procedure a three solutions will be prepared in parallel (Solution 1,2 and 3) ^[1, 14, 9].

Solution 1: It is prepared as :

- * 12.2g of sodium metavanadate (NaVO_3) was dissolved in 500 ml of boiling distilled water.
- * After dissolving, 17.8 g of sodium monohydrogenophosphate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) was added .

The solution obtained solution was cooled to room temperature.

Solution 2: The solution prepared as :

246 g of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was Dissolved in 500 ml of distilled water at room temperature.

Solution 3: A solution of 400 to 410 ml of concentrated hydrochloric acid (32%, 12 M) was prepared . Once these three solutions are prepared:

- Solution (1) was quickly Acidified by a fraction of the solution (3) until a purple color was appeared .
- Then solution (2) was added dropwise to the previous solution.

- It was allowed to cool to room temperature.
- $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ acid was isolated by the addition of 400ml of ether to the mixture of three solutions.
- The obtained solution was decanted. It gets three phases :
 - * A heavy phase which corresponds to a complex of acid-ether-water called "etherate", it is very dark red.
 - * A middle aqueous phase of light yellow, it corresponds to molybdates.
 - * An upper phase for excess present ether .
- Recovered etherate was add to half of its volume in water.

By shaking at room temperature, excess ether was evaporated for about ten hours. the cold solution Left to crystallize at (4 ° C). After a few days, red crystals were deposited, they are then collected on sintered glass.

By letting to dry by air, red crystals effloresce and by hydrate with 13 water molecules a yellow- orange crystals appears .

II.2.3 - Synthesis of Heteropoly salts :

II.2.3.1- $(\text{NH}_4)_4\text{HPMo}_{11}\text{MO}_{39}, x\text{H}_2\text{O}$ salts with $\text{M} = \text{Ni}^{2+}$, Cu^{+2} and Co^{2+}

A. Presentation:

Ions of mixed type $(\text{PMo}_{11}\text{MO}_{40})^{7-}$ have been prepared by the method described in the literature ^[14]. This method involves preparing a mixture of acids (H_2SO_4 and H_3PO_4) and MSO_4 and place it in a solution of ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ then heteropolyanion salts precipitate by the addition of NH_4NO_3 .

B. Procedure:

- * Dissolve 48.75 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in 250ml of distilled water at 50 ° C, to avoid the formation of 6-Molybdometalate, the synthesis of mixed-type ions $(\text{PMo}_{11}\text{MO}_{40})^{7-}$ was performed at about 0 ° C.
- * Prepare a mixture of H_3PO_4 (1M), H_2SO_4 (0.5 M) and MSO_4 (1M) ($\text{M} = \text{Co}$, Cu , Ni).
- * Place the mixture in the aqueous solution of ammonium paramolybdate.
- * Add NH_4NO_3 , this will lead to the immediate precipitation of $(\text{NH}_4)_4\text{HPMo}_{11}\text{MO}_{39}$ salts.

II.2.3.2 - $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}, x\text{H}_2\text{O}$ Salt :

A. Presentation:

The heteropoly salts type $(\text{PMo}_{11}\text{FeO}_{39})^{4-}$ was prepared by the method described in the literature ^[14]. This method involves adding a mixture of iron nitrates, H_3PO_4 (1M) and HNO_3 (0.5 M) to a solution of ammonium molybdates at 0 ° C. The salt immediately precipitated by the addition of NH_4NO_3 .

C. Procedure :

- * Dissolve 48.75 g of ammonium molybdate in 250 ml of distilled water at 50 ° C, in order to avoid the formation of 6-molybdoferate, the synthesis is carried out at 0 ° C.
- * Prepare a mixture of H_3PO_4 (1M), HNO_3 (0.5 M) and $\text{Fe}(\text{NO}_3)_3$ (1M).
- * Place the mixture in the prepared solution of ammonium paramolybdate at 0 ° C.
- * Add NH_4NO_3 , the desired salt precipitates immediately.

III.2. 3.3 - $(\text{NH}_4)_4\text{H SiMo}_{11}\text{FeO}_{39}, x\text{H}_2\text{O}$ Salt :

A. Presentation:

The synthesis method of of salt type $(\text{SiMo}_{11}\text{FeO}_{39})^{4-}$ is to prepare a solution of ammonium molybdate at 0° C ^[14], a mixture of H_4SiO_4 (1M), HNO_3 (0.5M) and $\text{Fe}(\text{NO}_3)_3$ (xM), then stir at 0 ° C. The salt immediately precipitated by the addition of NH_4NO_3 .

Procedure:

- * Dissolve 48.75 g of ammonium molybdate in 250 ml of distilled water at 50 ° C, in order to avoid the formation of 6-molybdoferate, the synthesis is carried out at 0 ° C.
- * Prepare a mixture of H_4SiO_4 (1M), HNO_3 (0.5 M) and $\text{Fe}(\text{NO}_3)_3$ (xM).
- * Place the mixture in the prepared solution of ammonium molybdate at 0 ° C.
- * Add NH_4NO_3 , the desired salt precipitates immediately.

II.2.3.4 - Synthesis of $(\text{NH}_4)_{3-x}\text{Fe}_x\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ Salts :

The method of preparation of iron-doped samples is described by Mizuno et al ^[15]. The transition metal (iron) is added in the form of an aqueous solution of nitrate (mol.l^{-1}) to the acidic solution $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (0.06 mol.l^{-1}) at room temperature, and (0.08 mol.l^{-1}) of NH_4Cl , are slowly added to the stoichiometric ratio at 50°C . The precipitate formed is dried using a rotary evaporator at 50°C under vacuum. It is then recovered as such without further washing.

II.2.3.5 - Synthesis of $(\text{NH}_4)_{3-x}\text{Ni}_x\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ Salts :

The method of preparation of nickel-doped samples is described by Mizuno et al ^[15]. The transition metal (nickel) is added in the form of an aqueous solution of nitrate (mol.l^{-1}) to the acidic solution $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (0.06 mol.l^{-1}) at room temperature, and (0.08 mol.l^{-1}) of NH_4Cl , are slowly added to the stoichiometric ratio at 50°C . The precipitate formed is dried using a rotary evaporator at 50°C under vacuum. It is then recovered as such without further washing.

II.2.3.6 - Synthesis of $(\text{NH}_4)_4\text{H PMo}_{11}\text{MnO}_{39}$ Salt :

$(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{39}$ salt were prepared ^[16] by :

- *dissolving 48.25 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 250ml of bi-distilled water at 40°C , then the temperature of the solution was fixed at 0°C using ice .
- * a solution of (25.2ml of 1M H_3PO_4 and 50 ml of 0.5M HNO_3 and 25 ml of 1M $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 6.25 ml of H_2O) was added to the first solution drop by drop .
- *PH was adjusted at 4 to 5 by adding NH_4NO_3 .
- *the precipitation was filtrated then but in the freeze at 4°C .

II.2.3.7 - Synthesis of mixed salts: $\text{KFe PMo}_{12}\text{O}_{40}$:

$\text{KFePMo}_{12}\text{O}_{40}$ were prepared by mixing 4 g of $\text{Na}_3\text{PMo}_{12}\text{O}_{40}$ and 0.0678 g of $\text{Fe}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and 0.256 g of KCl . After the precipitation was formed, it was filtrated and dried.

II.2.3. 8 - Synthesis of $\text{KFePW}_{12}\text{O}_{40}$ Salts:

$\text{KFePW}_{12}\text{O}_{40}$ were prepared by mixing 6 g of $\text{Na}_3\text{PW}_{12}\text{O}_{40}$ and 0.0678 g of $\text{Fe}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and 0.256 g of KCl . after the precipitation was formed , it was filtrated and dried .

II.2.3.9 - Synthesis of $(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$ Salts :

$(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$ was prepared by the method described in the literature.^[17] A 15 g quantity of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ was dissolved in 20 mL of water; a 5 g quantity of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ (TBABr) was dissolved in 50 mL of CH_2Cl_2 and the mixture was poured into the molybdophosphate solution with vigorous stirring. Three phases were formed: a yellow solid one, a lower liquid one (CH_2Cl_2), yellow coloured and an aqueous upper one, poorly coloured. The solid was washed with Et_2O , providing 8.5 g of product. A further yield of 2.5 g was obtained by addition of Et_2O to the CH_2Cl_2 phase. Recrystallization was performed in CH_2Cl_2 .

II.3 - Technical Analysis

II.3.1 – Introduction

The characterization of our catalysts was carried out in the solid state by infrared spectroscopy (FTIR) , X-ray diffraction (XRD), MEB and ^{31}P NMR. Thermal analysis using DSC,TGA was also done in order to investigate the thermal behavior for the catalysts. The good solubility of these solids in hydroorganic acetonitrile / water has also allowed us to characterize in solution by UV-V spectroscopy and voltamperometer. The interpretation of the performance of a catalyst and approach to the mechanism of the catalytic act requires the study of physicochemical characteristics of solid intrinsic and the establishment of a correlation between some of these characteristics and catalytic performance.

II.3.2- Solid State Characterization :

II.3.2.1- Analysis by infrared spectroscopy (FTIR) :

The Keggin type of heteropolyanions show bands vibration characteristics that appear in the spectral domain 1200 - 400 cm^{-1} .

We found two bands characteristic of the presence of hydration of water or the support (KBr): A very large one at around 3400 cm^{-1} (ν_{OH}) and a finer one at 1620 cm^{-1} ($\delta_{\text{H}_2\text{O}}$). According to the literature ^[18 - 21] there are two groups of vibrations: the first, located in the range 750 to 1100 cm^{-1} corresponds to the asymmetric valence vibrations between the heteroatom and oxygen which forming the tetrahedron (PO_4^{3-} or SiO_4^{4-}) represent by P-Oa, between the metal ion and the terminal oxygen (M-Ot) and between metal ions via the oxygen octahedrons junction between two of the same trimetallic group (M -Oc-M) or two different groups trimetallic (M-Ob-M). The second group of vibration in the range of about 280 to 600 cm^{-1} , it corresponds to deformation vibrations of the skeleton.

The most important characteristics bands attributed to the Keggin polyanion are those of the metal-oxygen vibrations:

- ν P-Oa at 1060-1080 cm^{-1} .
- ν Mo = Ot at 960-990 cm^{-1} .
- ν Mo-Ob-Mo at 870-900 cm^{-1} .
- ν Mo-Oc-Mo at 760-810 cm^{-1} .

The IR spectra of the prepared catalysts have a look identical to that of the Keggin type heteropolyanions (**Figures II. 1 to II.10**). The bands around 962 cm^{-1} , 871 cm^{-1} and 786 cm^{-1} are assigned to metal-oxygen vibrations respectively ν Mo = Ot, ν Mo-Ob-Mo and ν Mo-Oc-Mo ^[21]. The frequency of vibration of Mo-Ob-Mo is higher than that of Mo-Oc-Mo, because it is more tense (the angle of binding Mo-Ob-Mo is 150 ° while that of Mo-Oc-Mo 120 °) ^[22]. The substitution of molybdenum by (V) slightly modifies the vibration spectrum by lowering the Td symmetry of homometallic polyanion, which explains the partial lifting of degeneracy of the vibrator PO_4 ^[23]. There are, however, for the ion- $\text{PMo}_{11}\text{VO}_{40}^{-4}$ a very small frequency shift and very slight shoulders on bands P-Oa (1060 cm^{-1}) and Mo = Ot (960 cm^{-1}) respectively 1063 and 962 cm^{-1} ^[24] (**figure II.2**), these shoulders are not present in the spectrum of the ion $\text{PMo}_{12}\text{O}_{40}^{3-}$. This shift in vibration frequency type ν M-O is mainly due to the increase in the

total negative charge of the Keggin ion. This load is distributed almost evenly over all the atoms of oxygen devices. In the cases that ($M=Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}$) is introduced as a coordination metal in $H(NH_4)_4PMo_{11}MO_{39}$ compound, the vibration frequency ν P-O is moved from 1060 to 1045 cm^{-1} (**Table II.1**). This is due to the decrease in anion-anion interaction [22] and to increase the total negative charge of anion spread over the terminal oxygen [20].

The general appearance of the infrared spectra of the mixed salts $(NH_4)_{2.5}Fe_{0.1}H_{0.4}PMo_{12}O_{40} \cdot xH_2O$ is identical to that of the corresponding acid (**Figures II.8**). The presence of ammonium ion and the metal ion Fe^{3+} in place of hydroxonium ions in the crystal lattice does not change the characteristics vibration bands of Keggin structure. The band observed at 1400 cm^{-1} is attributed to the ether in the case of $H_4PMo_{11}VO_{40}$ and ammonium in the case of salts .

The polyoxotungstates have characteristic bands in the region 700-1000 cm^{-1} , these bands are related to the vibrations of W = O bonds and W-O-W [25,26] The infrared spectra are shown in **Figure II.1** and frequencies of these bands are assigned in **Table II.1** .

The tape position $sW = Od$ is displaced towards lower frequencies compared to that of the saturated acid dodecaphosphotungstates $H_3PW_{12}O_{40}$ which is due to the negative charge augmentation of the polyanion passing from -3 to -7, $H_3PW_{12}O_{40}$, and $K_7PW_{11}O_{39}$.

phosphorus-oxygen linked vibration ν (P-O) is the most informative in a spectrum of a tungstophosphate. In the case of the saturated anion of Keggin $[PW_{12}O_{40}]^{-3}$, the vibration of P-Oa in the central of PO_4 tetrahedron gives a single band at 1096 cm^{-1} , this band is exploded in the case of incomplete $PW_{11}O_{39}^{7-}$.

According to the literature [5], the characteristic bands of the Keggin anion of $(SiMo_{12}O_{40})^{4-}$ are the following:

- ν Si-Oa at 907 cm^{-1} - ν Mo = Ot at 958 cm^{-1} .
- ν Mo-Ob-Mo at 850 cm^{-1} - ν Mo-Oc-Mo at 776 cm^{-1} .

In the case of $(NH_4)_4HSiMo_{11}FeO_{39}$ salt (**Figure II.10**), Si-Oa band is observed at 897 cm^{-1} , those of metal-oxygen bands Mo = Ot, Mo-Ob-Mo and Mo-Oc-Mo at 941, 780 and 727 cm^{-1} respectively. The change in the order of bands is explained by the effect of the size of the heteroatom, while the frequency shift is justified by the increase in negative charge of the Keggin ion by the introduction of ions Fe^{3+}

Table II. 1: The main IR bands of HPA.

Catalyst	ν P-O _a	ν M-O _t	ν M-O _b -M	ν M-O _c -M
H ₃ PMo ₁₂ O ₄₀	1060	962	879	789
H ₄ PMo ₁₁ VO ₄₀	1063	962	872	781
(NH ₄) _{2.5} Fe _{0.1} PMo ₁₂ O ₄₀	1064	962	871	790
(NH ₄) ₄ HPMo ₁₁ CoO ₃₉	1045	943	872	808
(NH ₄) ₄ HPMo ₁₁ NiO ₃₉	1045	943	820	745
(NH ₄) ₄ PMo ₁₁ FeO ₃₉	1045	980	904	744
(NH ₄) ₄ HPMo ₁₁ MnO ₃₉	1108	933	900	725
(NH ₄) ₄ HPMo ₁₁ CuO ₃₉	1049	977	830	744
H ₃ PW ₁₂ O ₄₀	1096	989	902	777
KFe PW ₁₂ O ₄₀	1064	962	868	789
(TBA) ₇ PW ₁₁ O ₃₉	1059	962	884	797
(NH ₄) ₄ H SiMo ₁₁ FeO ₃₉	897	941	780	727

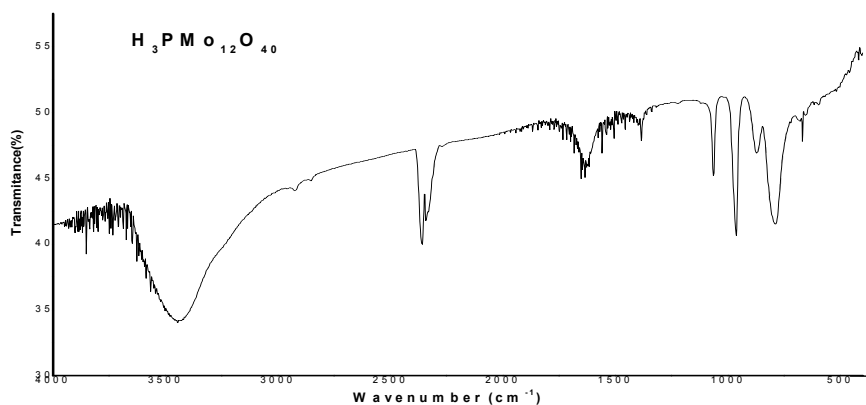


Figure II.1: IR Spectrum for H₃PMo₁₂O₄₀

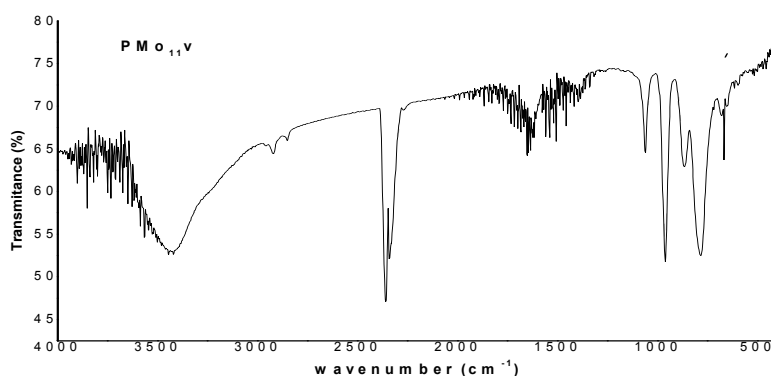


Figure II.2 : IR Spectrum for H₄PMo₁₁VO₄₀

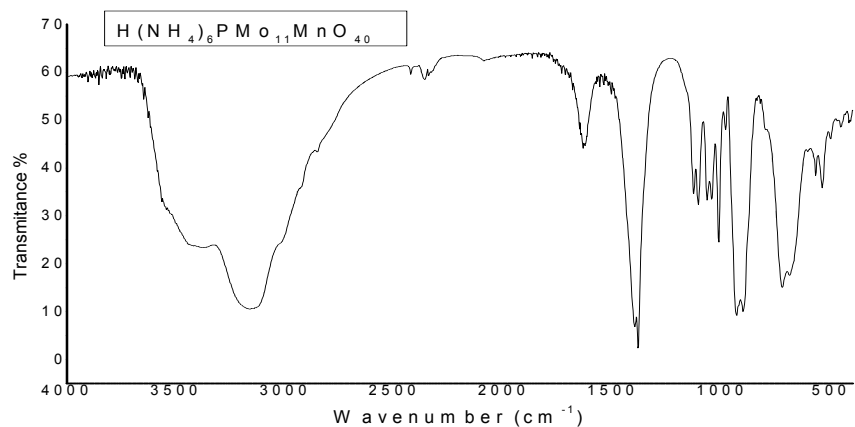


Figure II.3 : IR Spectrum for $\text{H}(\text{NH}_3)_4\text{PMo}_{11}\text{MnO}_{39}$.

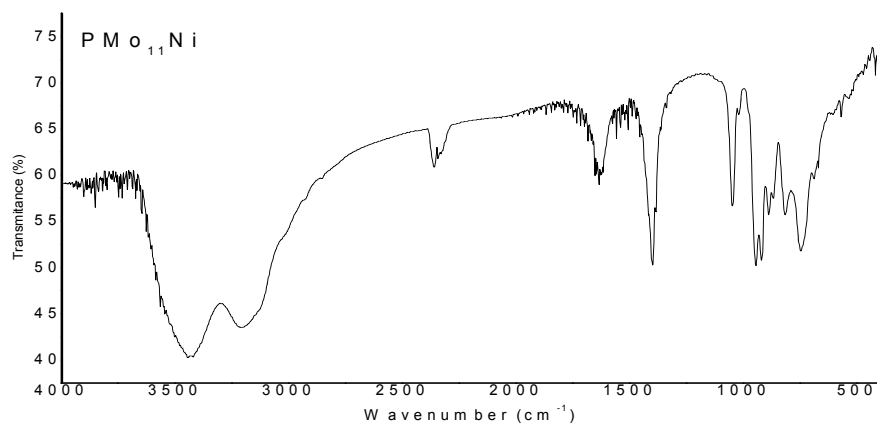


Figure II.4 : IR Spectrum $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$

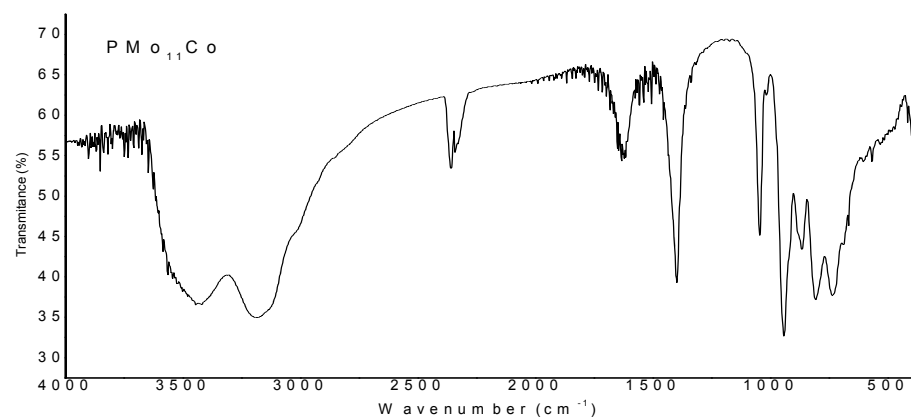


Figure II. 5: IR Spectrum for $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$

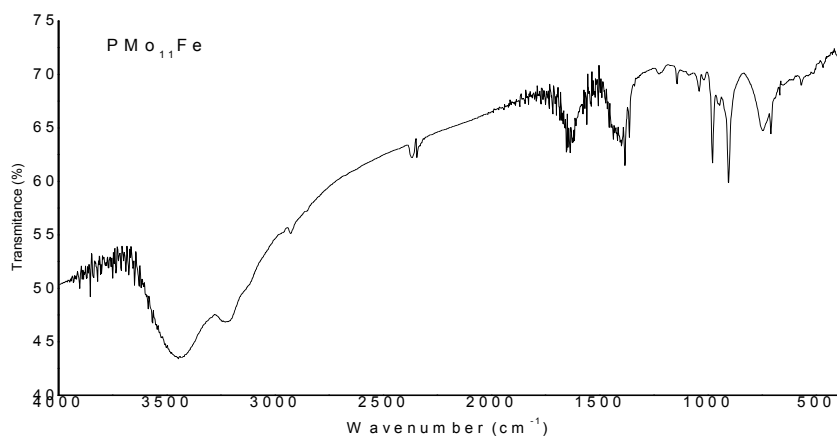


Figure. II.6 : IR Spectrum for $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$

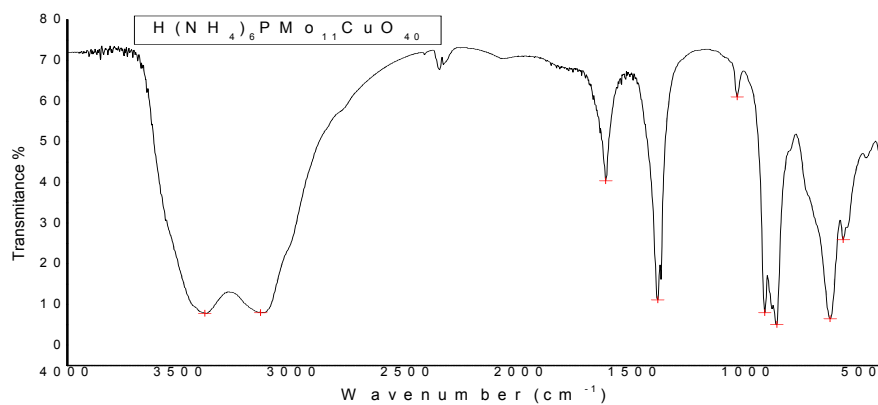


Figure II.7 : IR Spectrum for $\text{H}(\text{NH}_4)_4\text{PMo}_{11}\text{CuO}_{39}$

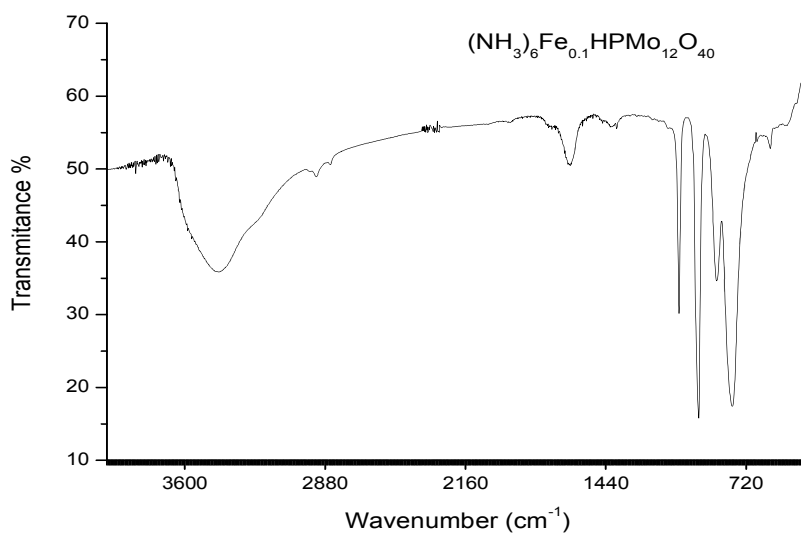


Figure II.8 : IR Spectrum for $(\text{NH}_4)_{2.5}\text{Fe}_{0.1}\text{H}_{0.4}\text{PMo}_{12}\text{O}_{40}$

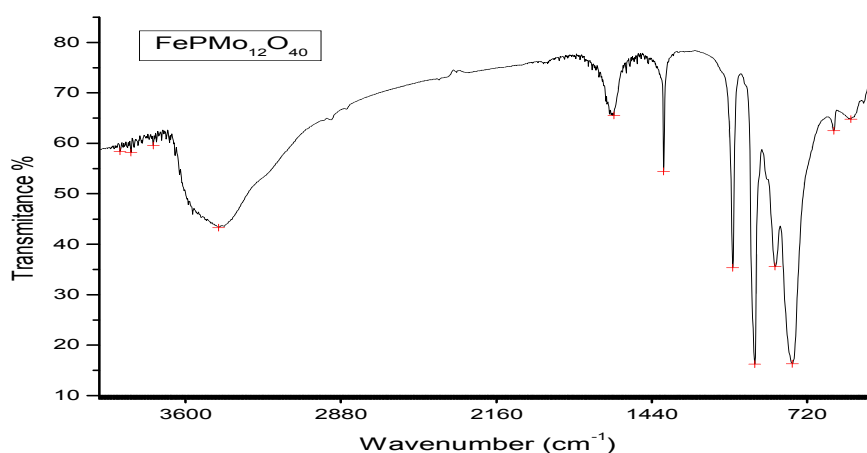


Figure II.9 : IR Spectrum for $\text{KFe}_{0.1}\text{PMo}_{12}\text{O}_{40}$

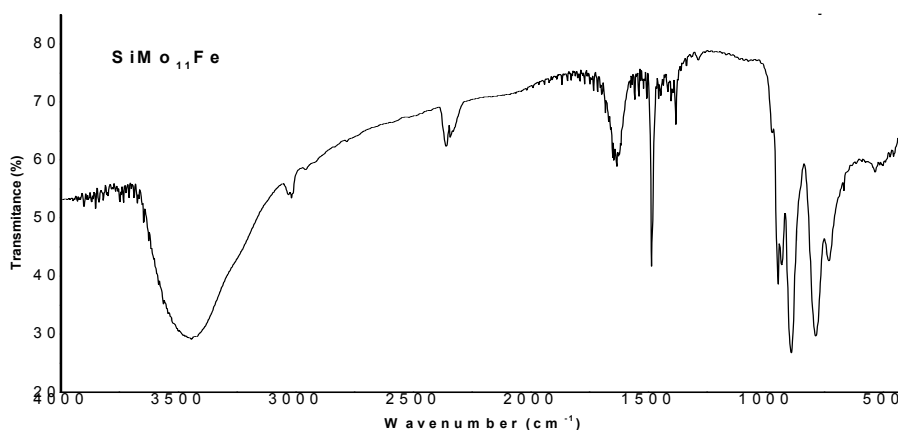


Figure II.10: IR Spectrum for $(\text{NH}_4)_4\text{HSiMo}_{11}\text{FeO}_{39}$

II. 3.2.2 - Analysis by X-ray Diffraction (XRD) :

It is clear from our study that at room temperature, the heteropolyacid is hydrated by 13 or 14 water molecules and crystallizes in a triclinic system (**Fig. II.11**). However, the symmetry of the lattice depends strongly on the degree of hydration. Indeed, phosphomolybdic acid with 29 H_2O is cubic symmetry, the lattice parameter a is 24Å . The spectrum of X-ray diffraction of the anhydrous ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $1.5\text{H}_2\text{O}$) acid as presented in the literature corresponds to a hexagonal ($a = 15.884\text{ Å}$ and $c = 20.715\text{ Å}$) ^[27]. $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ acid has the same crystal symmetry (triclinic) (**Fig. II. 12**).

Highly hydrated compounds ($30 \text{ H}_2\text{O}$) with a high crystal symmetry is not stable at room temperature, then they evolve into more stable hydrates, usually 13 or 14 H_2O . This dehydration is accompanied by a loss of crystallinity [28] and we obtain structures of lower symmetry and smaller lattice volume. For degree of hydration low or zero, a crystal structure of higher symmetry (quadratic or cubic) is observed again. Anhydrous $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ acid has quadratic symmetry. [29]

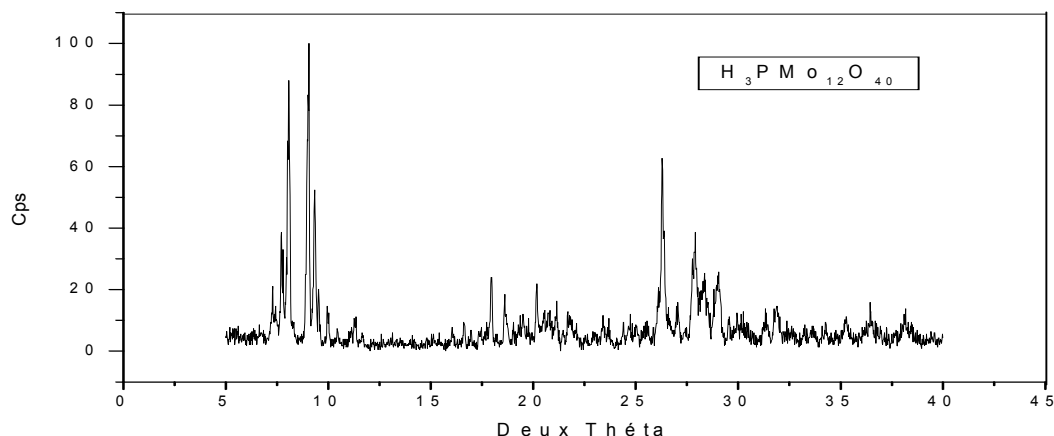


Figure II.11 : XRD spectrum of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ Heteropolyacids .

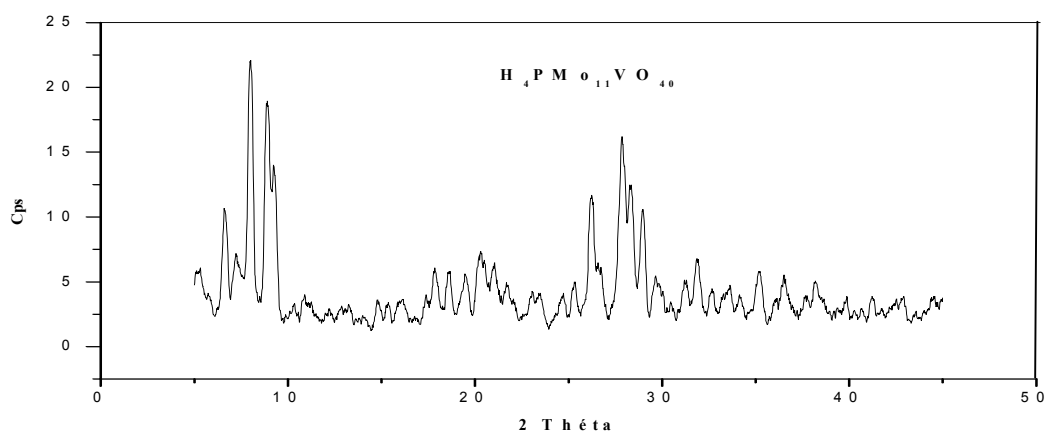


Figure II.12 : XRD spectrum of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ Heteropolyacids .

Figures II.13-II.16. shows XRD spectrum for $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$, $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$, $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$, $(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{39}$ and $(\text{NH}_4)_4\text{HSiMo}_{11}\text{FeO}_{39}$ salts, it show a monoclinic structure .

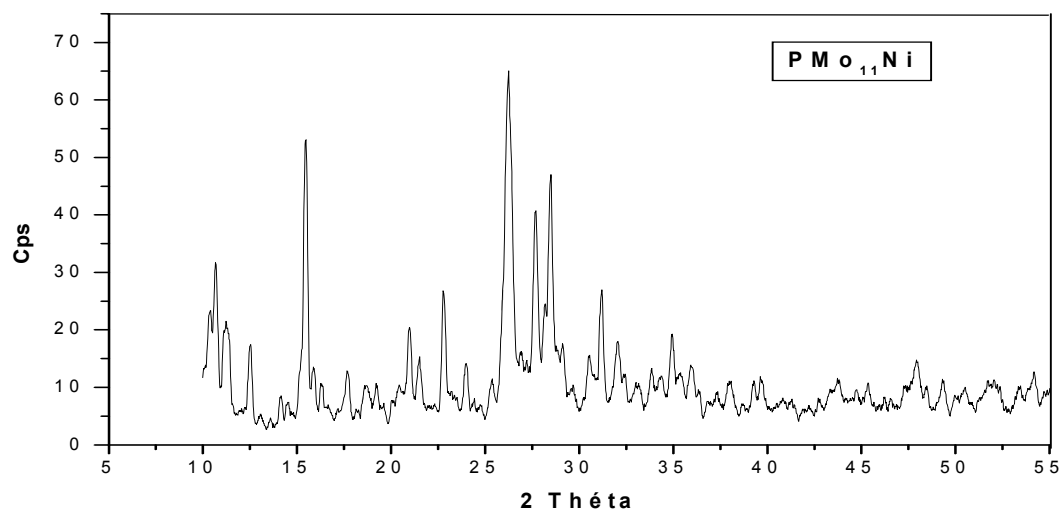


Figure II.13 XRD spectrum of $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$.

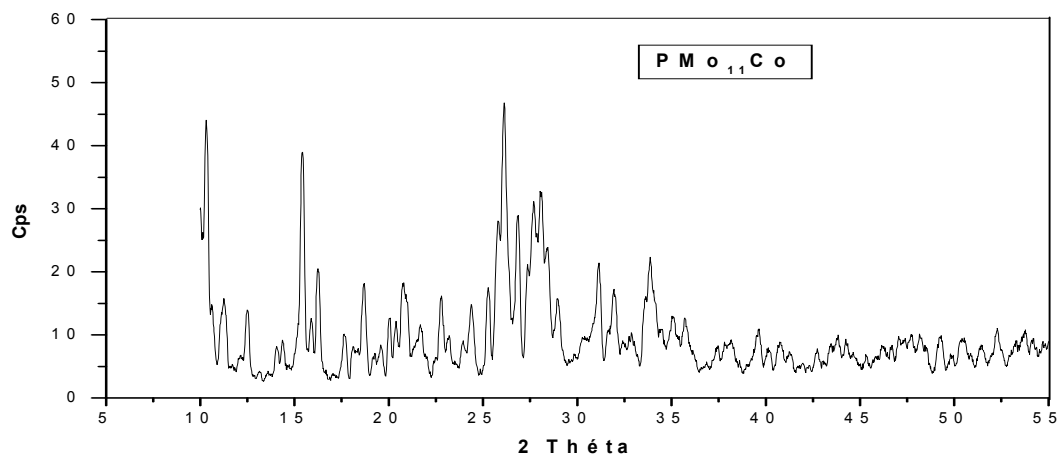


Figure II.14 : XRD spectrum of $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$.

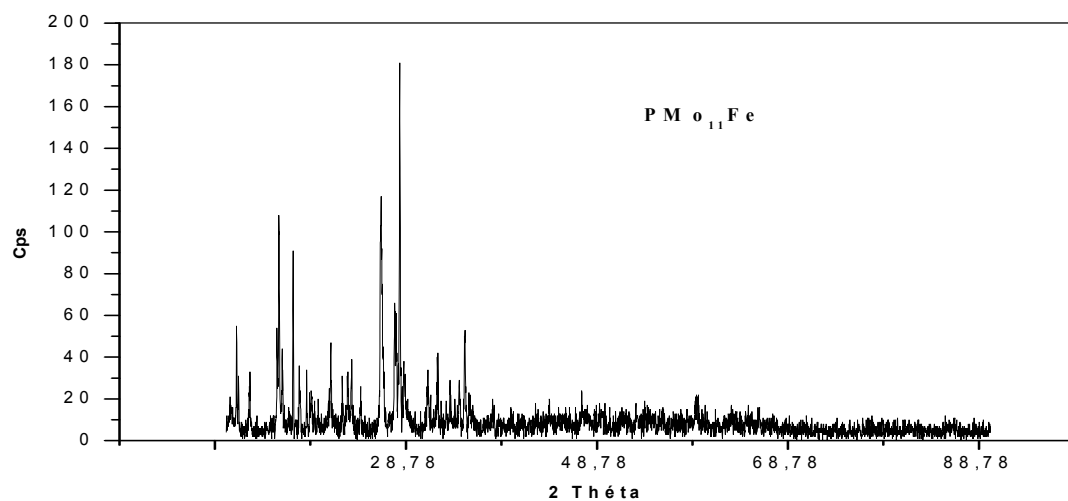


Figure II. 15 : XRD spectrum of $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$

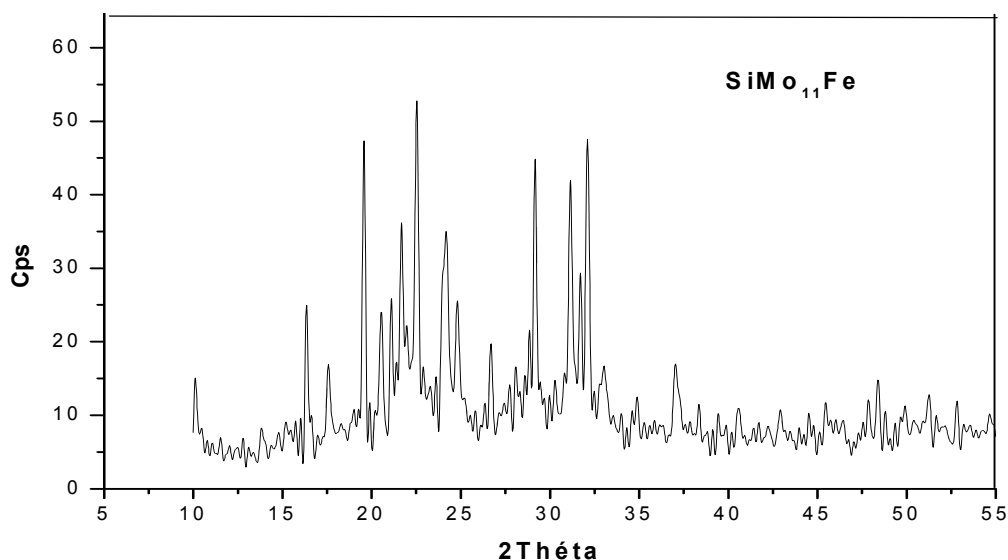


Figure II.16 : XRD spectrum of $(\text{NH}_4)_4\text{HSiMo}_{11}\text{FeO}_{39}$

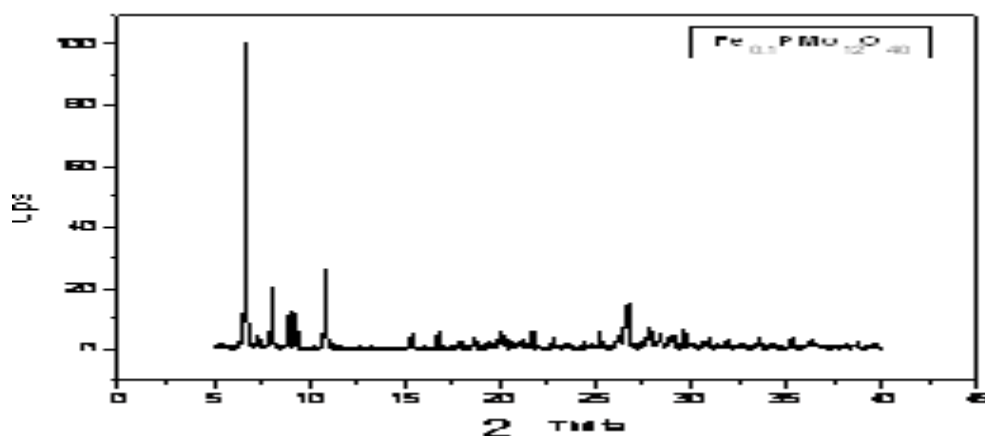


Figure II.17 : XRD spectrum of $(\text{NH}_4)_{2.5}\text{Fe}_{0.1}\text{PMo}_{12}\text{O}_{40}$

The lattice parameters of solids studied are reported in **Table II.2**. The lines were indexed according to the literature ^[30,31]. They are generally large, the more intense is the index line 222. The salts lattice parameters are of the same order of magnitude as acids and we can see that the addition of iron, nickel, manganese or cobalt does not change significantly these parameters.

Our results are comparable to those in the literature ^[32]. At room temperature, the size of the against-ion is responsible for the structure of the salt.

Table II.2: Lattice parameters (Å) measured for different catalyst systems .

Heteropolycompounds	Parameters (Å °)	Ref.
H ₃ PMo ₁₂ O ₄₀ , 13H ₂ O	a= 14,10 α= 112,1° b= 14,13 β= 109,8° triclinic c= 13,39 γ= 60,73°	[33]
H ₃ PW ₁₂ O ₄₀ , 14H ₂ O	a = 14.11Å α = 112.04° b = 14.12Å β = 109.88° triclinic c = 13.55Å γ = 60.65°	[34]
H ₄ PMo ₁₁ VO ₄₀ , 13H ₂ O	a= 14,04 α= 112,1° b= 10,006 β= 109,58° triclinic c= 13,55 γ= 60,72°	[34]
(NH ₄) ₄ HPMo ₁₁ NiO ₃₉	a= 20,07210 b= 11,55938 monoclinic c= 18,77828 β= 109,58°	[35]
(NH ₄) ₄ HPMo ₁₁ CoO ₃₉	a= 21,01022 b=7,84688 monoclinic c= 17,00056 β= 97,539°	[35]
(NH ₄) ₄ PMo ₁₁ FeO ₃₉	a= 21,12322 b=7,19688 monoclinic c= 17,00056 β= 97,653°	[35]
(NH ₄) ₄ HPMo ₁₁ MnO ₃₉	a=21,12322 b=7,19688 c= 17,00056 β = 97,653° monoclinic	[35]

II.3.2.3 - Analysis by ^{31}P NMR Spectroscopy

^{31}P NMR spectra were measured for only Three catalyst types, as shown in **Figure II.18 - II.20**. **Figure II.18** shows a single peak at -3.47 ppm for salt $\text{Fe}_{0.1}\text{PMo}_{12}\text{O}_{40}$, which indicates purity of the sample. **Figure II.19** shows a main peak at 7.1 ppm for PMo_{11}Fe . The KPW_{11} heteropolyanion showed a signal at 10.35 ppm, **Figure II.20**.

The signal is characteristic for the lacunary species $\text{K}_7[\alpha\text{-PW}_{11}\text{O}_{39}]$ [36,37].

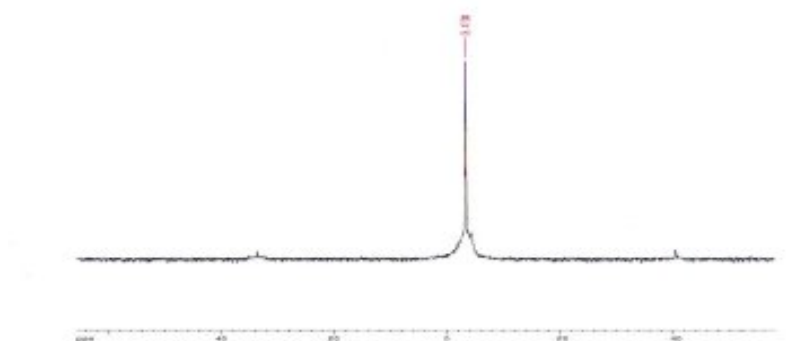


Figure II.18 : ^{31}P NMR spectra for FePMo_{12}

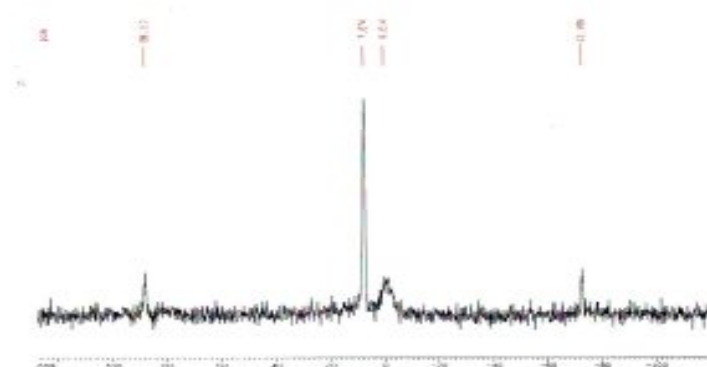


Figure II.19 : ^{31}P NMR spectra for PMo_{11}Fe

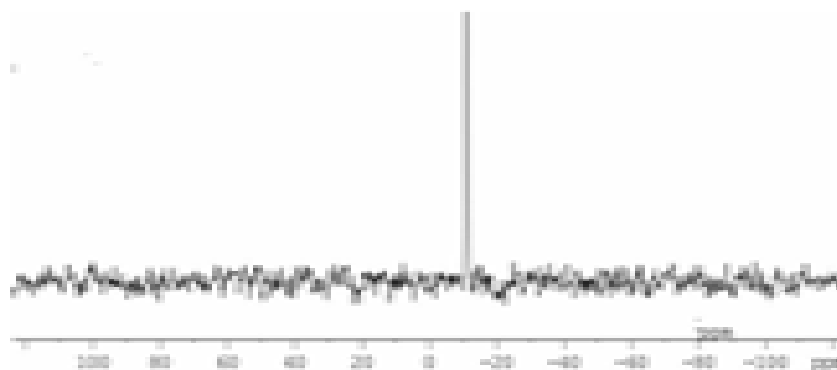


Figure II.20 : ^{31}P NMR spectra for PW_{11}

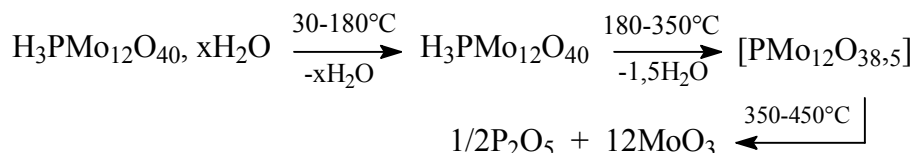
^{31}P NMR measured and literature data are summarized in **Table II.3**.

Table II.3: ^{31}P NMR measured and literature data for different catalyst systems.

No.	Catalysts	Chemical shift ppm	Ref.
1	PMo_{12}	-3.7	[38]
2	PMo_{12}Ni	-1.1551	[35]
3	PMo_{11}Co	-4,826	[35]
4	PW11	-10.35	This work
5	FePMo_{12}	-3.47	This work

II.3.2.4 - Thermogravimetric Analysis

Thermogravimetric (TGA) analysis of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ acid shows two mass loss **Figure II.21**, the first signals between 40 and 140°C corresponding to the departure of water of crystallization or hydration. A second mass loss at temperatures between 250 and 350°C, was attributed to water content resulting from combination of H^+ ions and network oxygen. This mass loss leads to a reversible modification of the polyanion :



In differential thermal (DT) analysis, the loss of water corresponds to endothermic peaks. An exothermic peak was observed above 350°C and was attributed to acid decomposition into P_2O_5 and MoO_3 oxides.

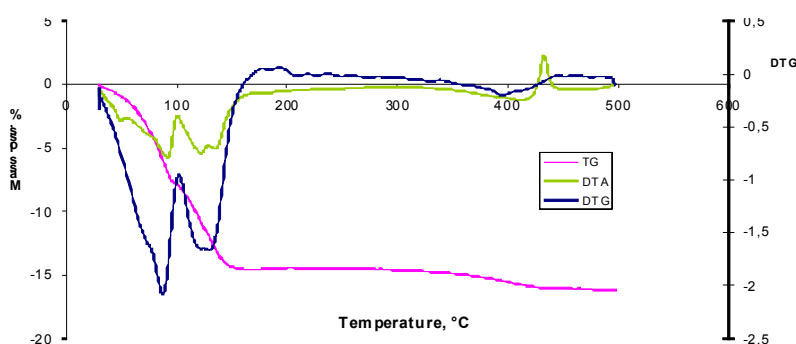
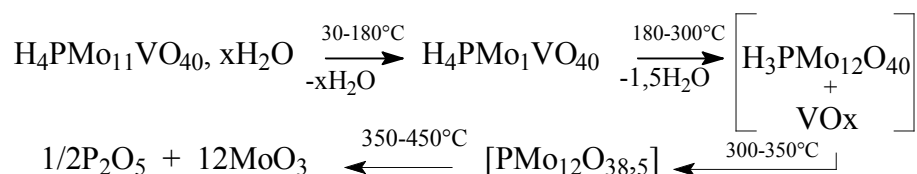


Figure II.21 : Differential scanning calorimetry (DSC) of $\text{PMo}_{12}\text{O}_{40}$

PMo_{11}V acid also has two mass loss ^[37]: the first mass loss observed between 20 and 160 ° C corresponding to the start of water hydration. The second loss of weight between 300 and 430 ° C corresponding to the departure of water molecules formed from the protons and

oxygen of the heteropolyacid, called water content and results in anhydride structure according to the reaction.



On the DTA curve of PMo_{11}V acid an exothermic peak is observed around 440°C , attributed to the decomposition of the compound in a mixture of anhydride oxide (91% MoO_3 , 5% V_2O_5 , 4% P_2O_5).

The thermogram of the mixed $(\text{NH}_4)_{2.5}\text{Fe}_{0.1}\text{H}_{0.2}\text{PMo}_{12}\text{O}_{40}, x\text{H}_2\text{O}$ salt (**Figure II.22**) has three endothermic peaks, the first at around 100°C which corresponds to the start of the water of crystallization. A change in crystal system is often observed during the departure of water [39,40]. At 250°C another endothermic peak is observed, it is attributed to the loss of water of constitution and the formation of anhydrous Keggin structure [41,42]. A final peak at 300°C corresponds to the departure of gaseous ammonia [43] or the state of molecular nitrogen [44]. No exothermic peak is observed, which is explained by the thermal stability of the mixed salt $(\text{NH}_4)_{2.5}\text{Fe}_{0.1}\text{H}_{0.2}\text{PMo}_{12}\text{O}_{40}$ and non decomposition of a oxides mixture.

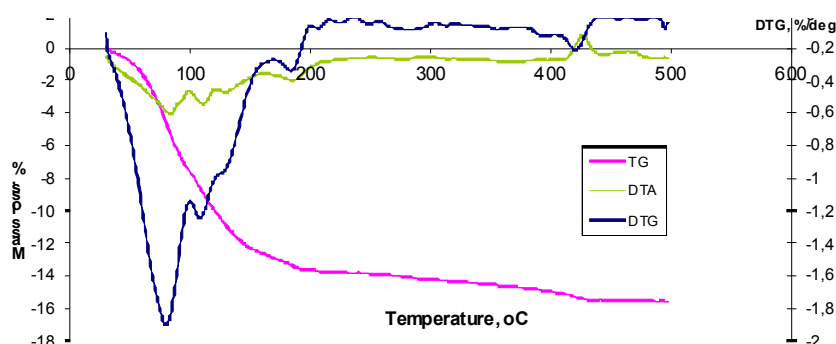
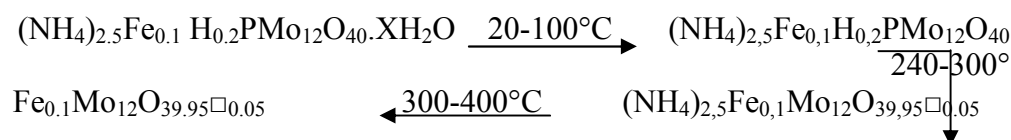


Figure II.22 : Differential scanning calorimetry (DSC) of FePMo_{12}

The three observed transitions can be summarized as follows:



The DSC thermogram of $(\text{NH}_4)_{2.5}\text{Fe}_{0.1}\text{H}_{0.2}\text{PMo}_{12}\text{O}_{40}$ shows three distinct areas of change of energy resulted in endothermic peak, attributed the departure of water of hydration at 100°C , water content of heteropolycompound at 300°C and the departure of ammonia 380°C .

TGA analysis for the salts PMo_{11}Ni , PMo_{11}Co , PMo_{11}Mn , PMo_{11}Fe , PMo_{11}Cu , PW_{11} shows three mass losses **Figure II.23**. A first mass loss occurred around 100°C , which is

interpreted as the start of physisorbed water loss. A second departure is at around 240 to 300°C, which is due to loss of constitution water molecule. Water molecules coordinated to nickel and cobalt ions are involved here. Finally, a loss around 300 to 400°C, corresponding to departure of molecular ammonia or molecular nitrogen, was observed.

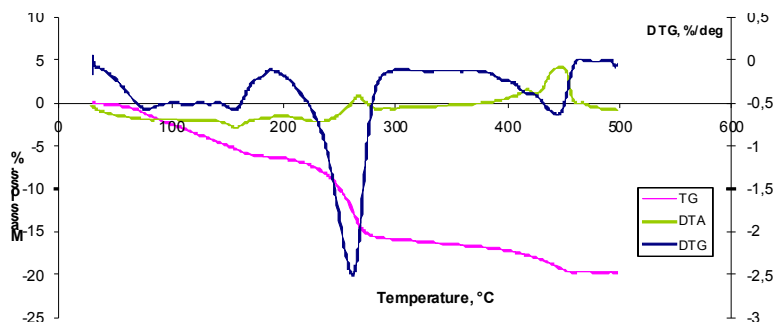
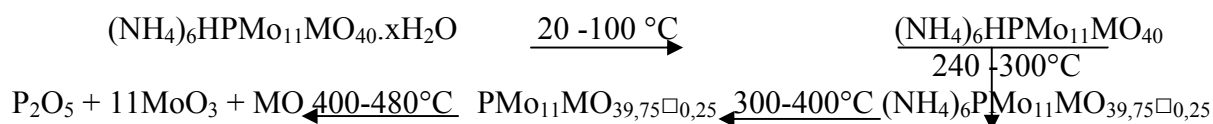


Figure II.23 : Differential scanning calorimetry (DSC) of PMo_{11}Ni

Salt catalysts exhibit higher thermal stability than $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. The temperature at which their degradation starts depends on the position of the ion M^{3+} . When the counter ion involved metal ionic species, the decomposition temperature exceeded 500°C. On the other hand, the heteropolyacid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is less thermally stable than the salt, and its decomposition started at 350°C.

The exothermic peak observed at 500 ° C corresponds to the oxides from the decomposition of heteropolyanion, who is also a criterion of thermal stability of the HPA from 500 °C. The three transitions observed in the $(\text{NH}_4)_6\text{HPMo}_{11}\text{MO}_{40} \cdot x\text{H}_2\text{O}$ can be summarized as follows [44]:



For $\text{SiMo}_{11}\text{Fe}$ compound the departure of water is carried out below 190 ° C, a corresponding level to the anhydrous compound is observed between 190 and 400 ° C, before the formation of crystallized oxides. On the DTA curve we observed the existence of several large endothermic peaks between 92 ° C and 184 ° C. The exothermic peak above 400 ° C to 434 ° C is attributed in the literature to a formation of oxide complex [45 - 47].

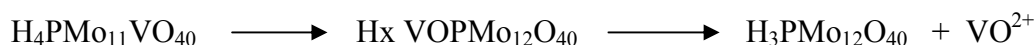
II.3.2.5 - Characterization of residues by IFTR after thermogravimetric analysis

To monitor the thermal behavior of solids, they were treated in air at different temperatures (150, 250, 350 and 450 ° C) on a mass of 0.2 g of catalyst introduced in a tubular reactor placed in Pyrex glass cylindrical furnace with a thermocouple.

The IR spectra of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$ and $(\text{TBA})_7\text{PMo}_{11}\text{O}_{39}$ after heat treatment in air for 6 hours in each of the following temperatures: 150, 250, 350 and 450 ° C are shown in **Figure II.24-II.26**. We note that the characteristics vibration frequencies of the Keggin structure is retained up to 450 ° C for $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$, $(\text{TBA})_7\text{PMo}_{11}\text{O}_{39}$ and up to 350 ° C for $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$.

The band 1400cm^{-1} attributed to the ether in the case of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ and ammonium in the case of $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$ disappears at 450 ° C.

Our catalysts were systematically green or blue after heat treatment. This indicates the presence of Mo^{5+} and a reduction catalyst. Vibration frequencies P-O and Mo-O are identical to those of the spectra of these compounds before testing. The Keggin structure is retained up to temperatures below 350 ° C. The IR spectrum of acid $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ after testing at 350 ° C shows that the shoulder of the P-O band at $1079\text{-}1080\text{ cm}^{-1}$, this spectrum is identical to that of acid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. This may be due to the removal of vanadium from the Keggin unit ^[14] as follows:



Deltcheff and Fournier ^[48], when heat treated $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ acid in dry air at 300 ° C, also observed a band at 1030 cm^{-1} . They suggest attributed to the vibration ν P-Oa of a PO_4 tetrahedron vanadophosphate species.

If we refer to the work of Eguchi et al ^[49] and Fournier et al ^[50] on the reduced compounds of the anion $\text{PMo}_{12}\text{O}_{40}$, the amount of molybdenum in our catalysts after treatment is too low to significantly affect the shape of the IR spectra. The absorbance bands P-Oa, Mo-Ob-Mo and Mo-Oc-Mo highlights the presence of Mo reduced. Eguchi et al ^[49] showed that the absorbance of the bands decreases linearly with the degree of reduction of the polyanion that is to say, the amount of Mo reduced.

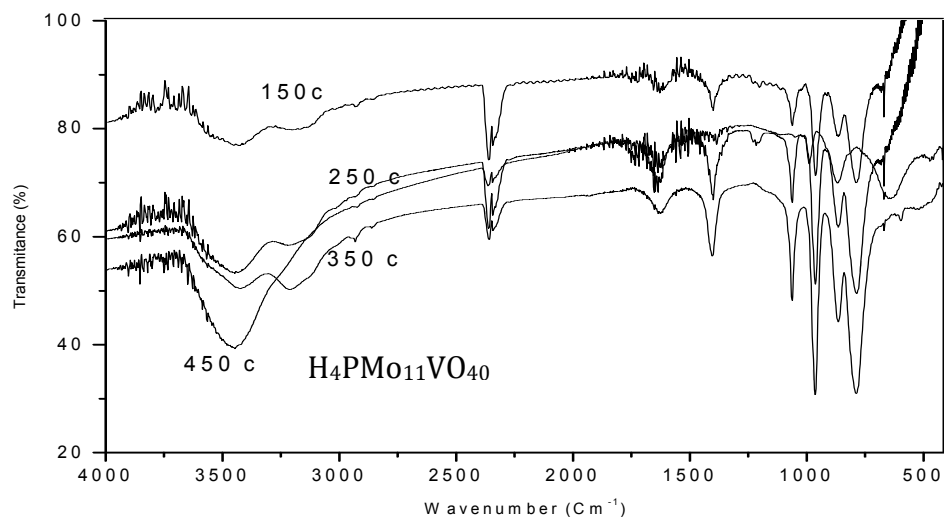


Figure II.24: IR spectra of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ acid after heat treatment.

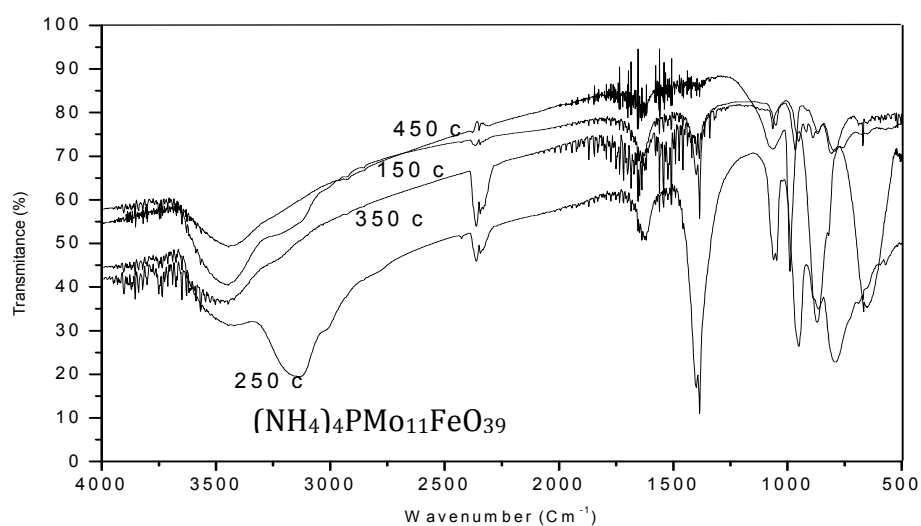


Figure II.25 : IR spectra of $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$ salt after heat treatment.

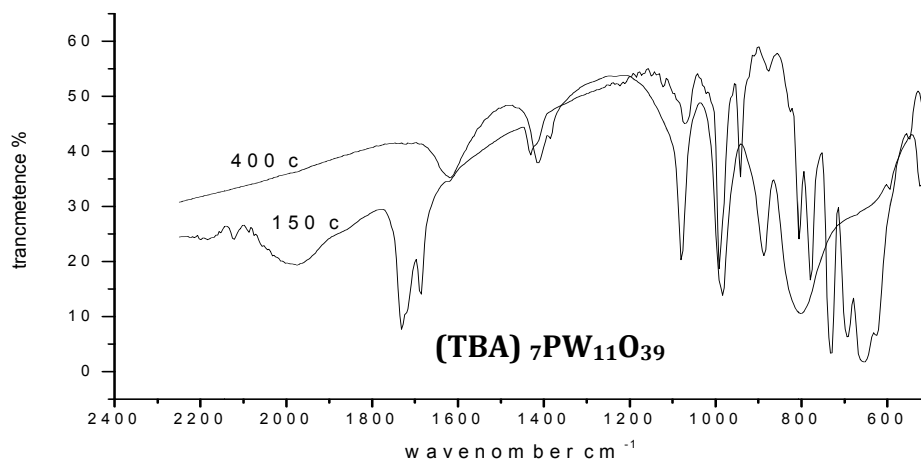


Figure II.26 : IR spectra of $(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$ salt after heat treatment.

II.3.2.6 - Characterization by scanning electron microscopy

The figures (II.27 – II.51) show the morphology of different studded catalytic powders $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ powder has the shape of "cabbage flower" (Figure II.27), the grains are of various sizes. The latter have a compact appearance due to the presence of water. Indeed in the literature postulating the low specific surface of this acid which is about $3\text{M}^2/\text{g}$ which is due to the presence of water of hydration. The magnification of a single pattern (Figure II.28) indicates that these grains have micropores.

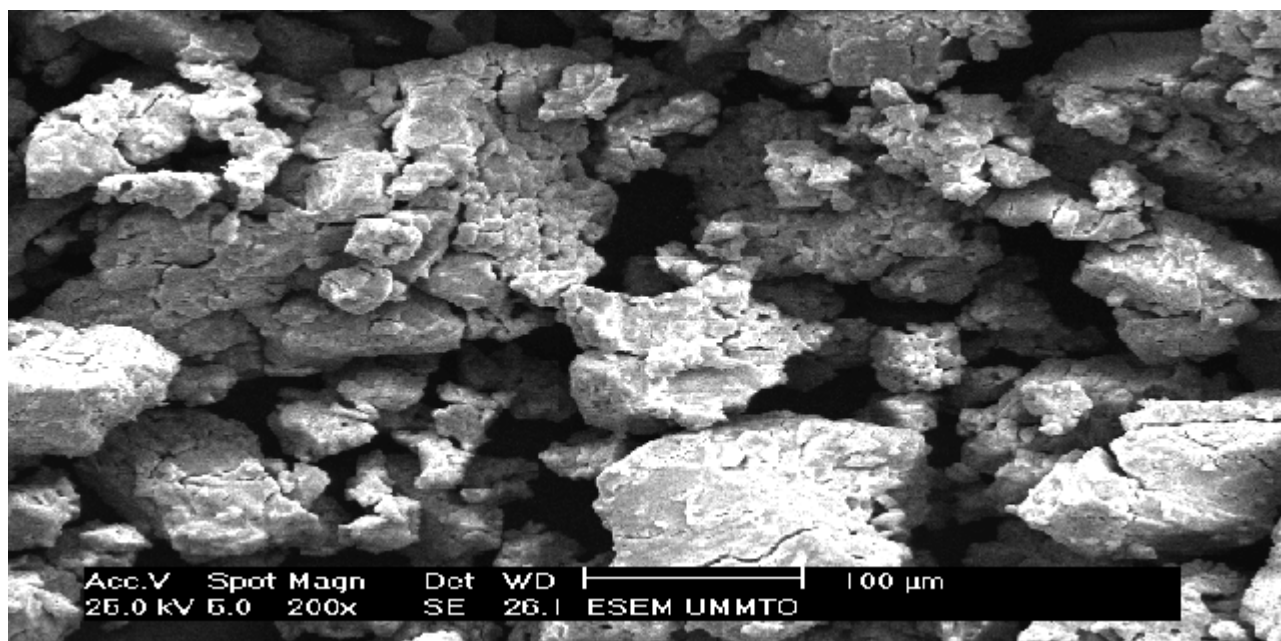


Figure II.27 Grain Morphology $\text{H}_3\text{PMo}_{12}\text{O}_{40}$

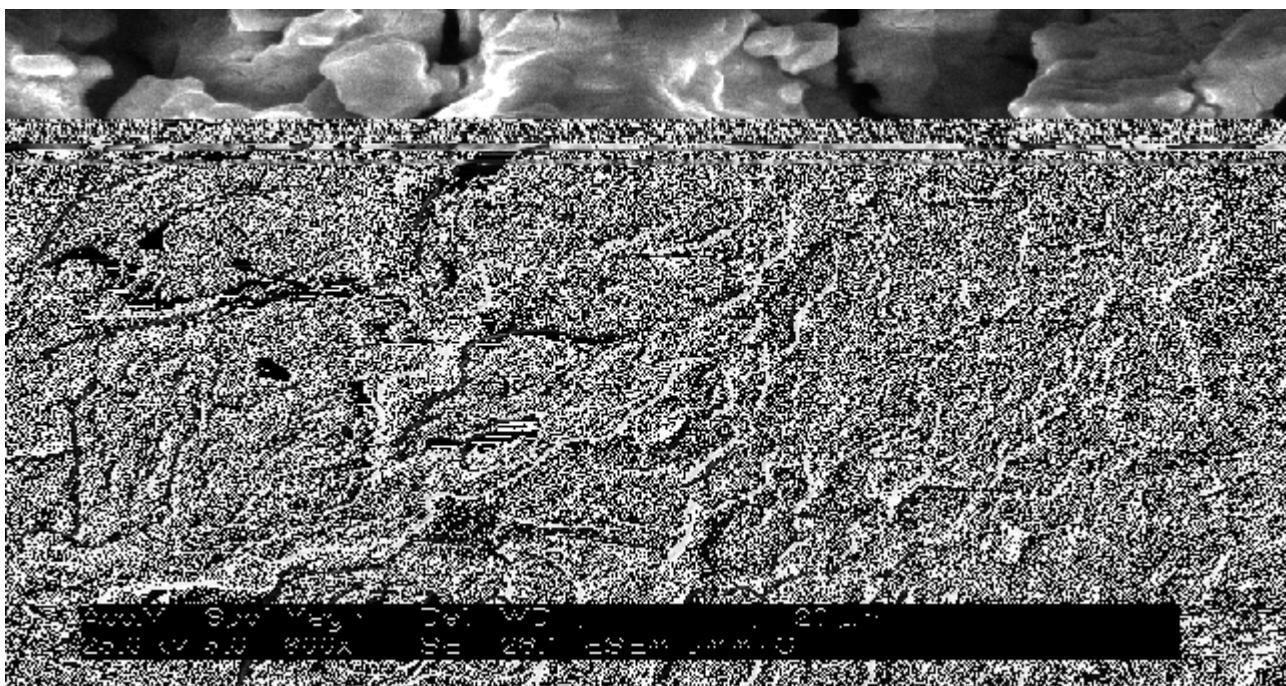


Figure II.28 Magnification of a single aggregate $\text{H}_3\text{PMo}_{12}\text{O}_{40}$

In the photograph of $(\text{NH}_4)_{2.5}\text{Fe}_{0.5}\text{HPMo}_{12}\text{O}_{40}$ (Figure II.29) we distinguish two different structures: a form of "cabbage flower" majority and minority in another form of "needles" (Figures II.30), probably attributed to iron in position against the ion of heteropolyacompounds. In literature it is reported that the specific surface area of mixed salts is higher than the corresponding acid, it is about $215 \text{ m}^2/\text{g}$ for the mixed salt $(\text{NH}_4)_{2.5}\text{Fe}_{0.5}\text{HPMo}_{12}\text{O}_{40}$ which suspect the existence of a microporos within the heteropoly salts .

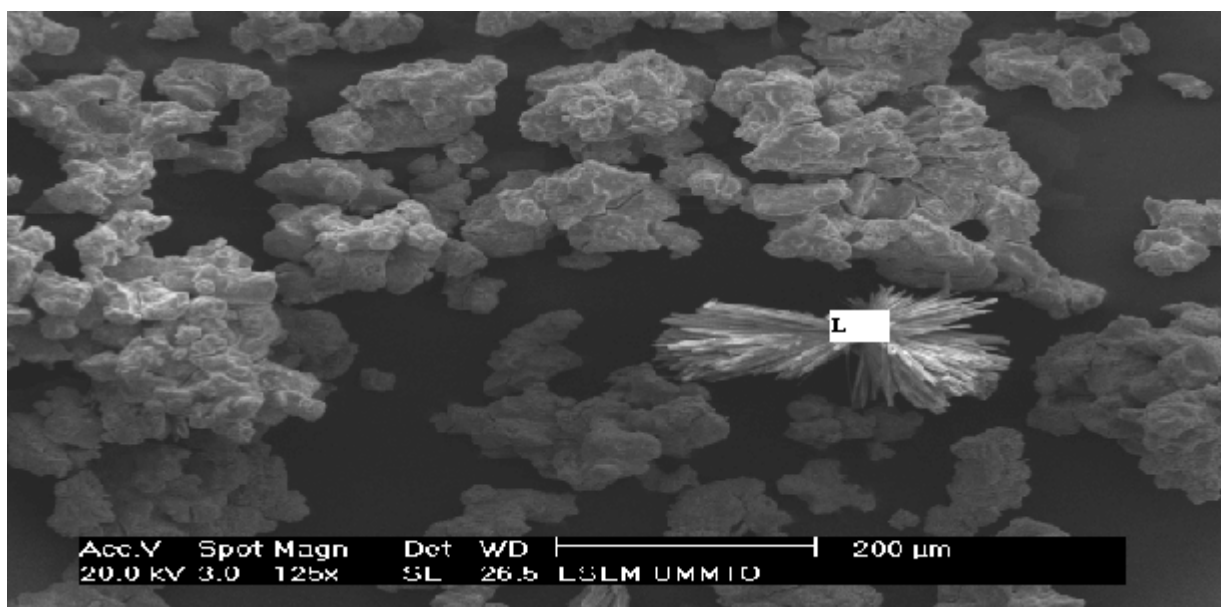


Figure II.29 Grain Morphology of $(\text{NH}_4)_{2.5}\text{Fe}_{0.5}\text{HPMo}_{12}\text{O}_{40}$

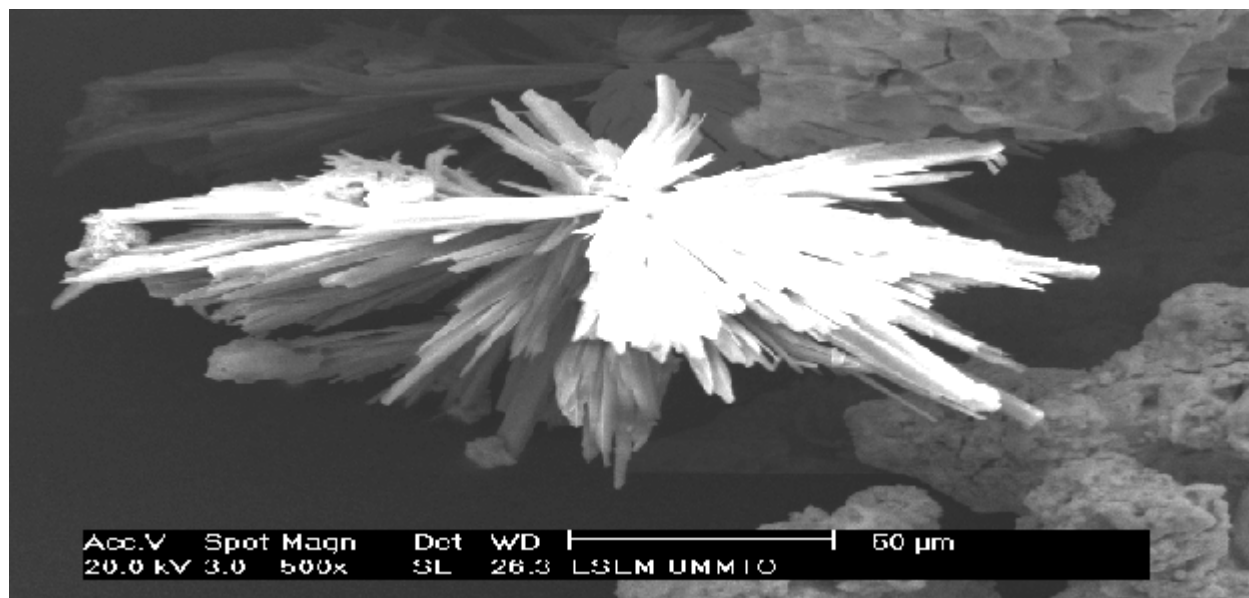


Figure II.30 Magnification of $(\text{NH}_4)_{2.5}\text{Fe}_{0.1}\text{H}_{0.2}\text{PMo}_{12}\text{O}_{40}$

As for the grains of salt $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$ (**Figure II.31**) are rounded in shape and size neighbor. It should be noted that all crystals are in the form of aggregates. The expansion of a zone (**Figure II.32**) informs us that it is the combination of grains welded them forming interstitial voids. These compounds were classified as solid $5 \text{ m}^2 / \text{g}$.<misoporeux, because of their low specific surface .

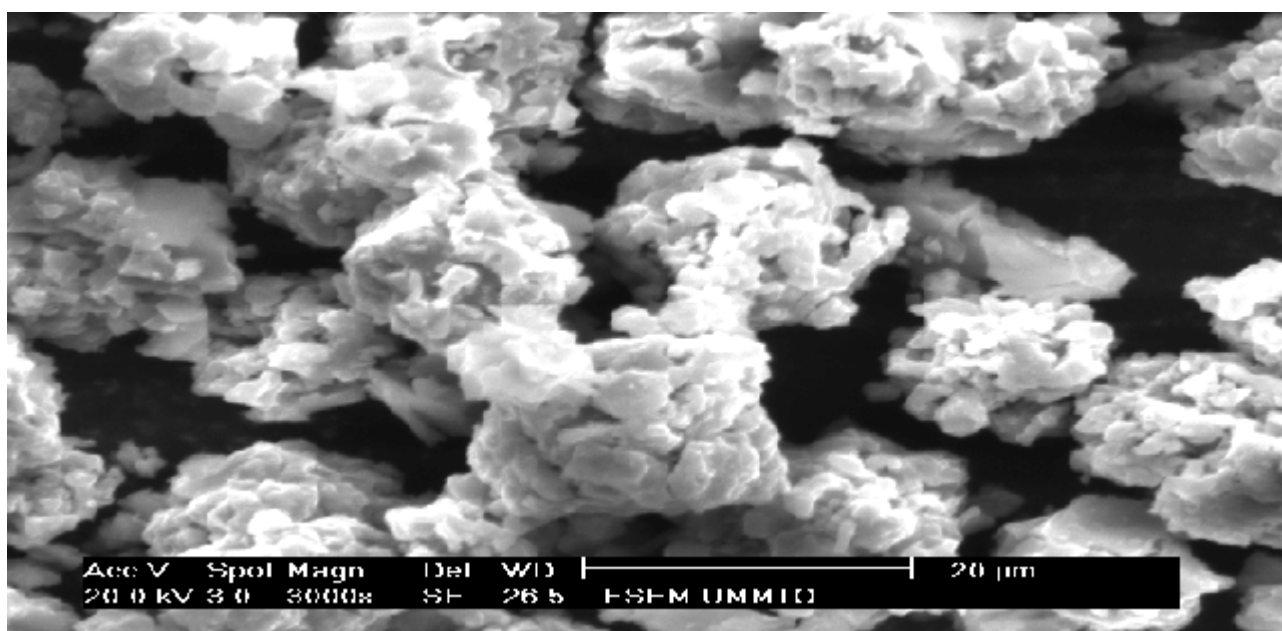


Figure II.31 Grain Morphology of $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$

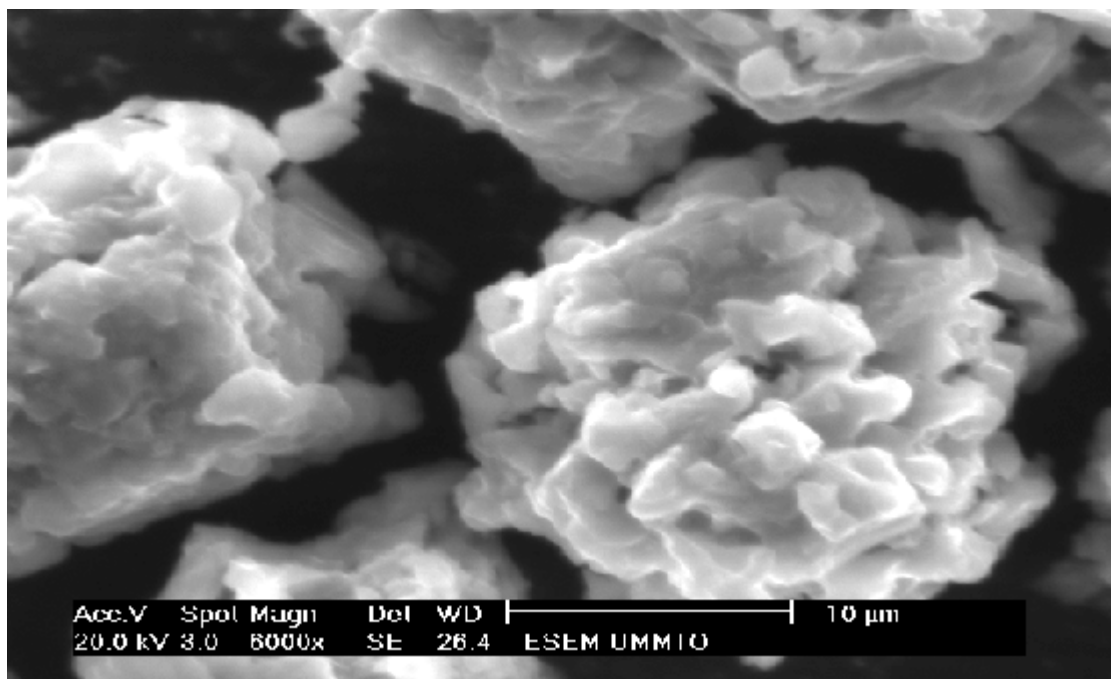


Figure II.32 Magnification of aggregate of (NH₄)₄PMo₁₁FeO₃₉

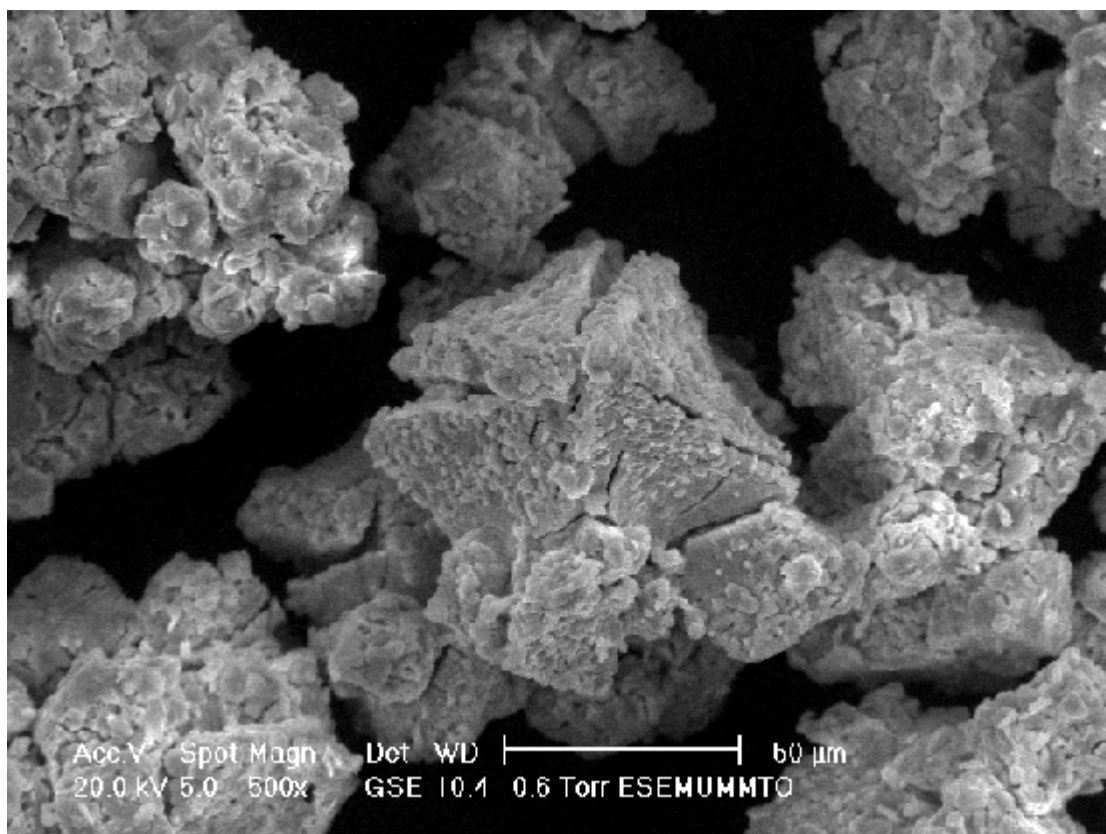


Figure II.33 Magnification of aggregate of 50μm (NH₄)₄HPMo₁₁CoO₃₉



Figure II.34 Magnification of aggregate of 20 μm $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$

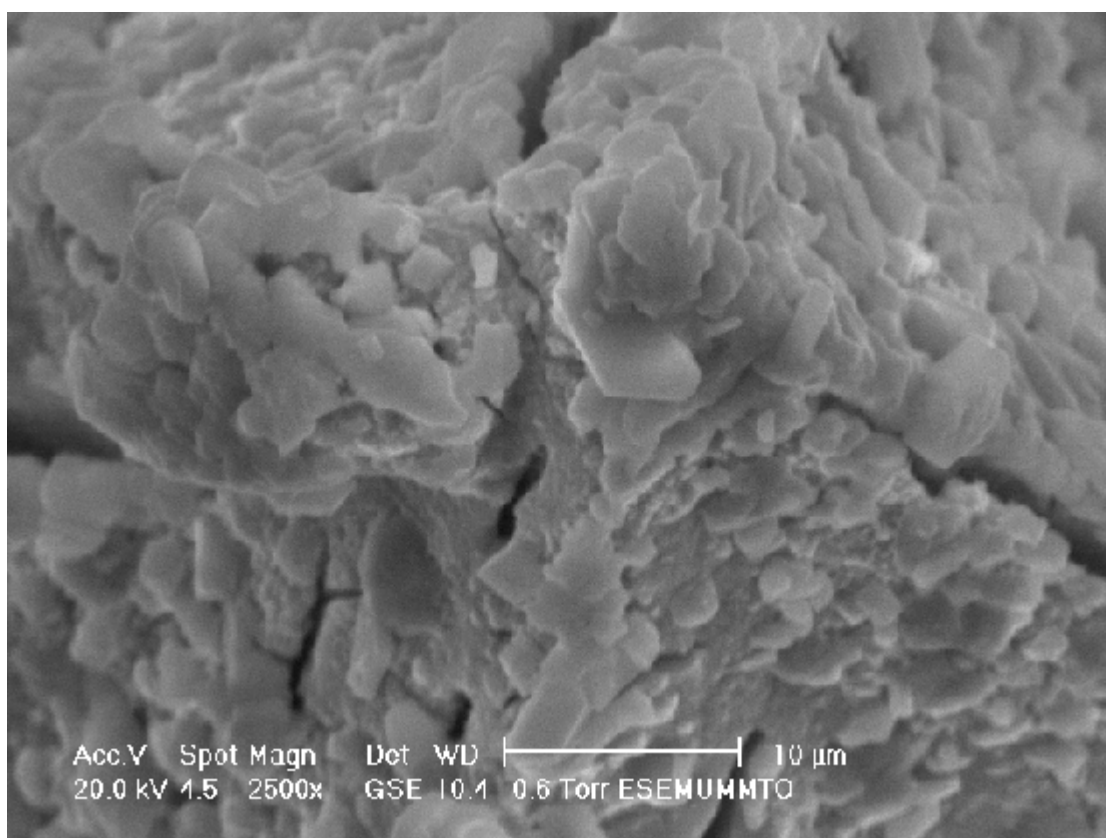


Figure II.35 Magnification of aggregate of 10 μm $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$

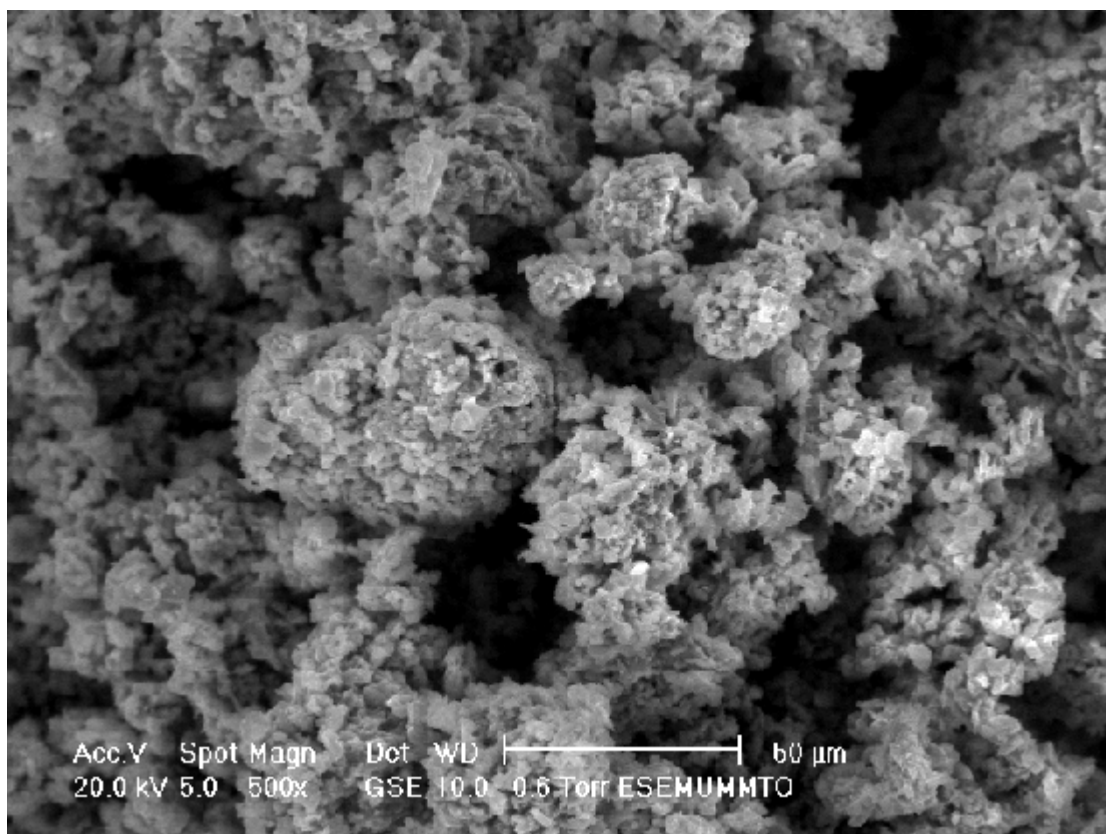


Figure II.36 Magnification of aggregate of 50 μm $(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{39}$

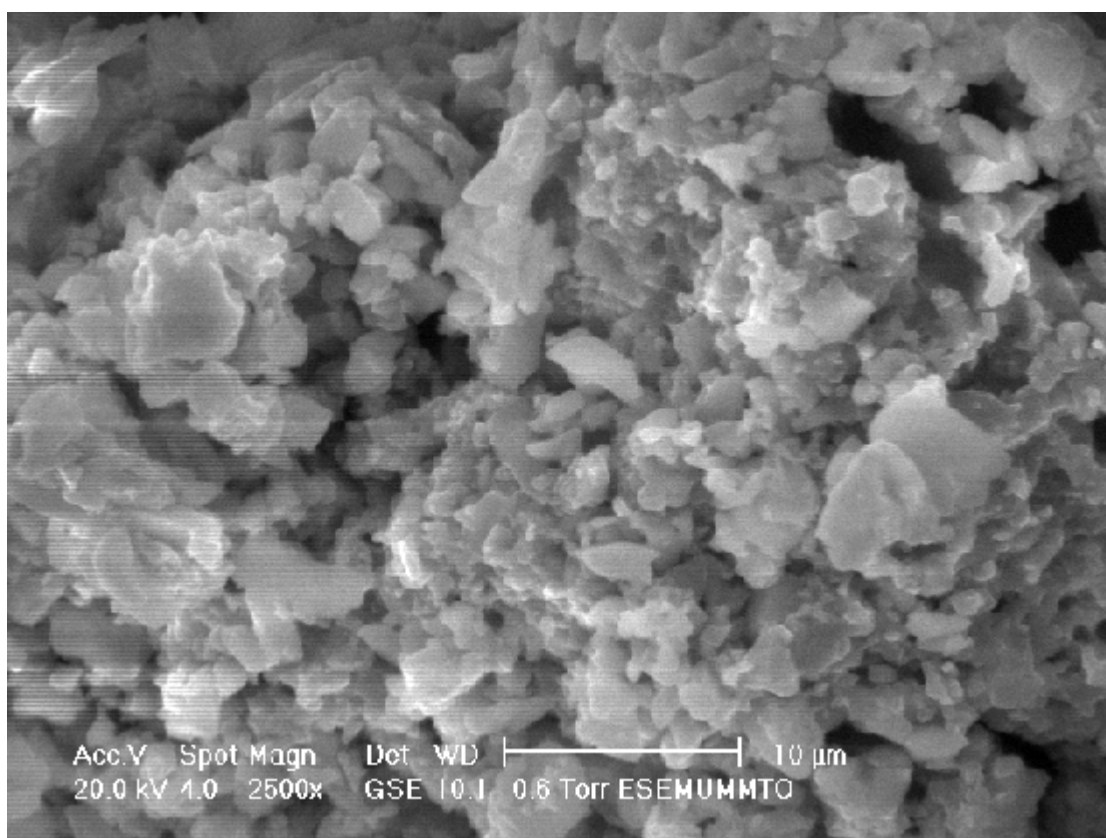


Figure II.37 Magnification of aggregate of 20 μm $(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{39}$

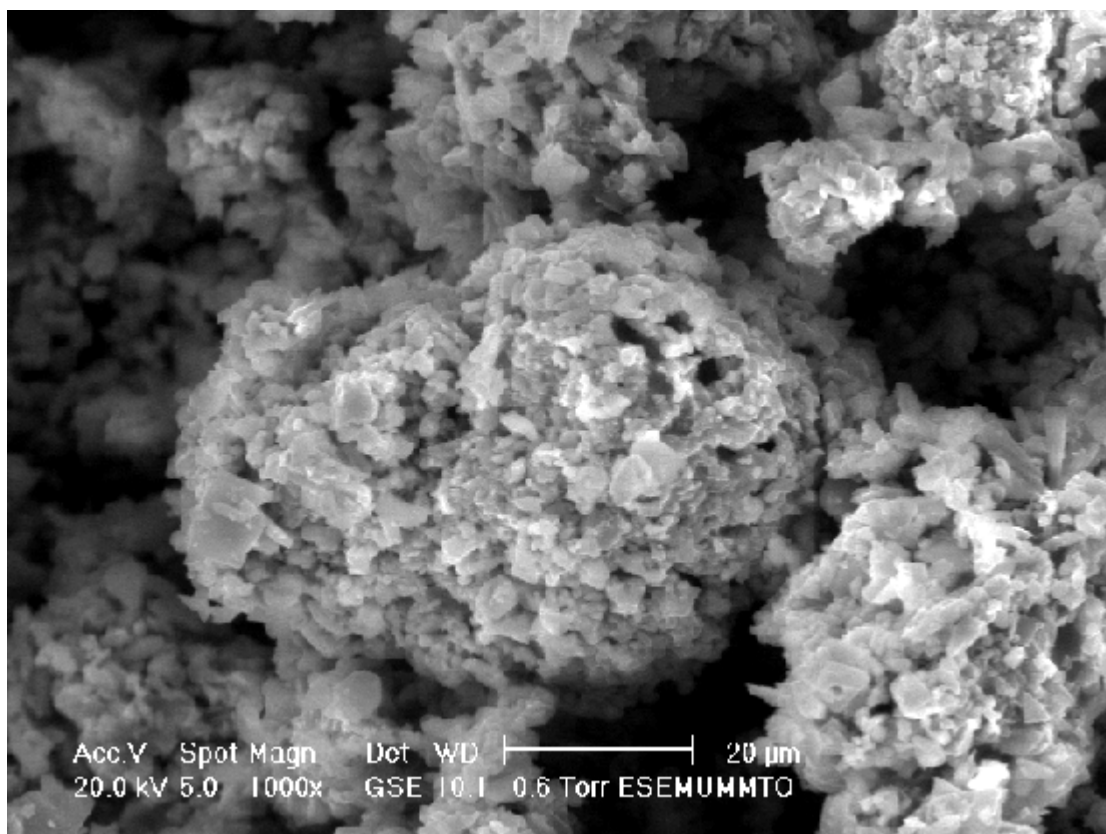


Figure II.38 Magnification of aggregate of 10μm $(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{39}$

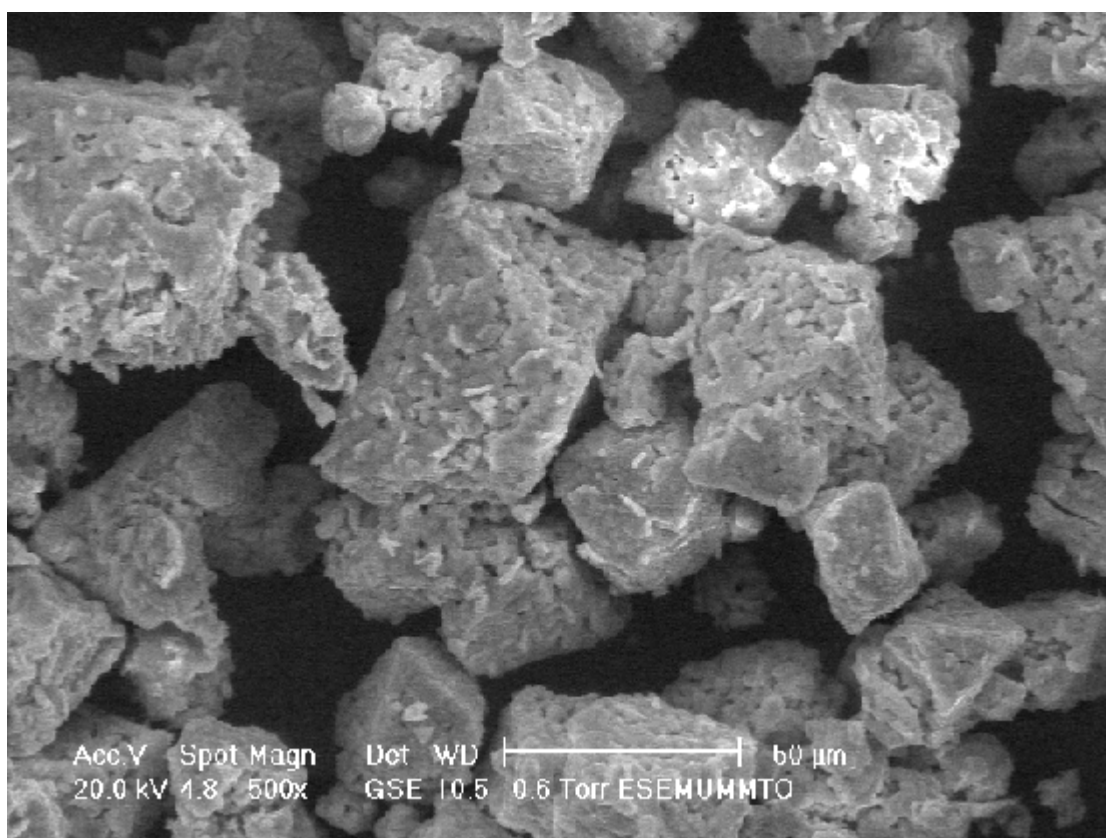


Figure II.39 Magnification of aggregate of 50μm $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$

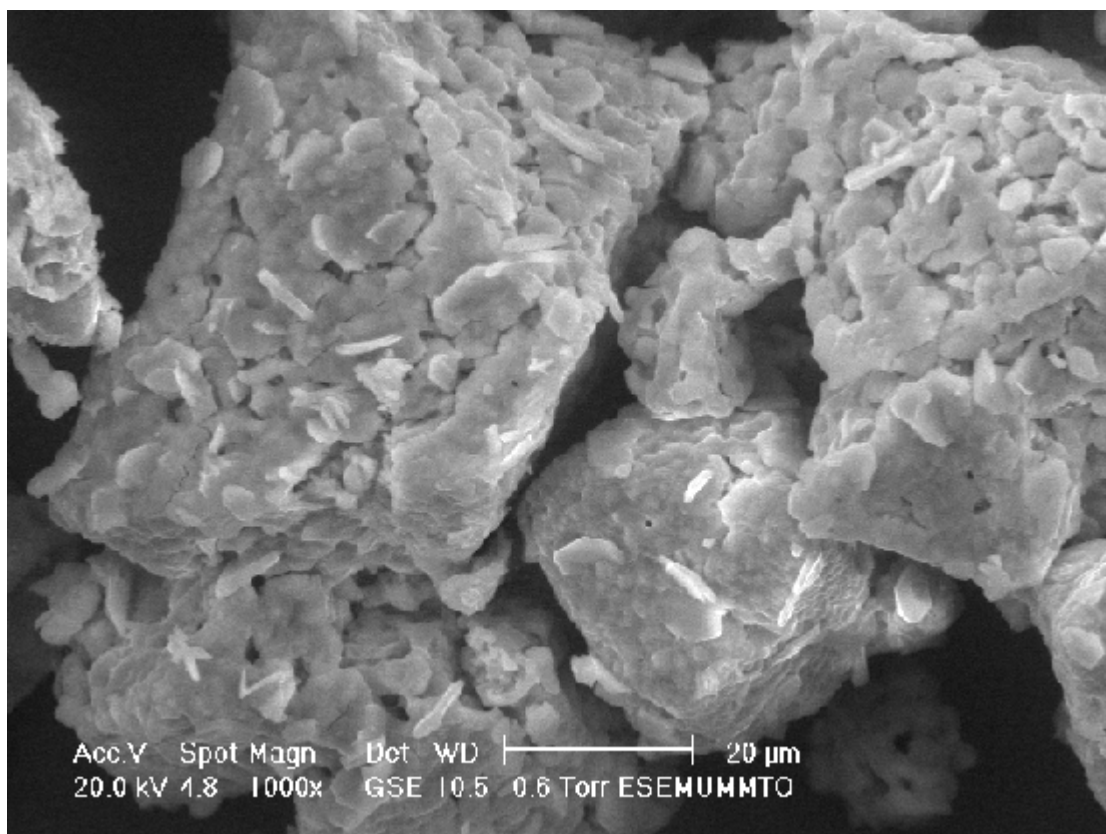


Figure II.40 Magnification of aggregate of 20 μm $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$

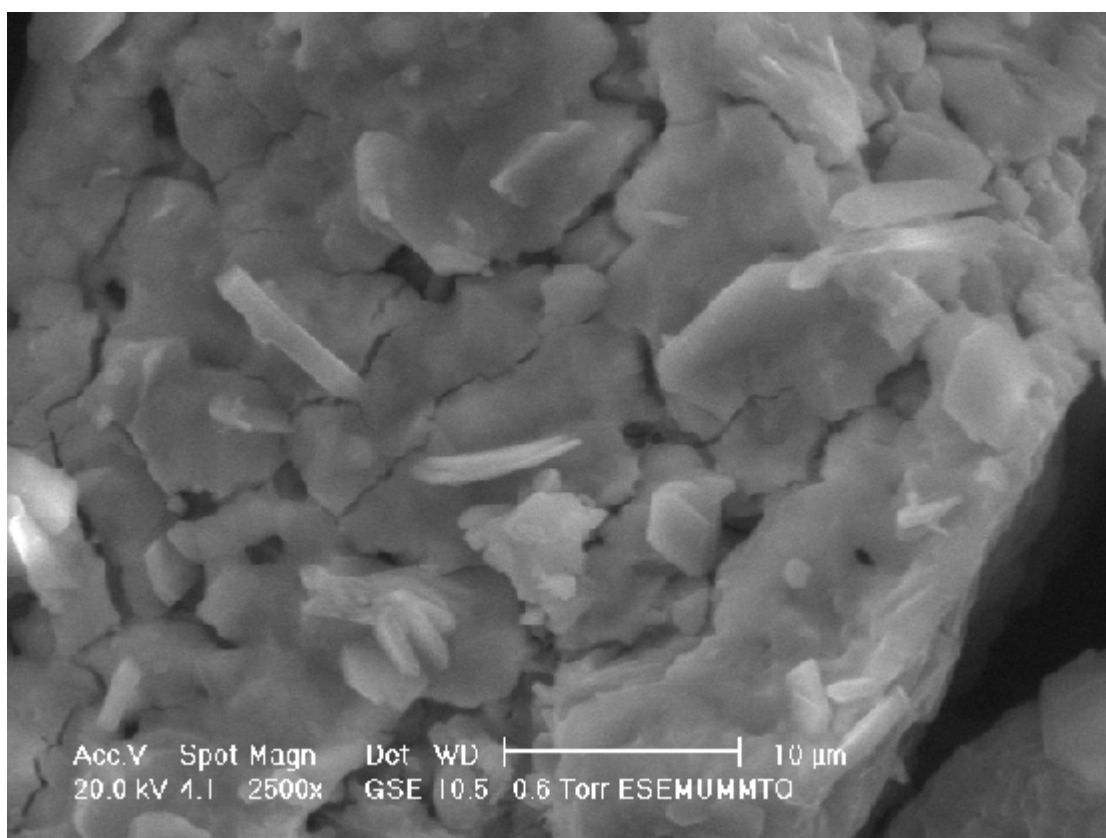


Figure II.41 Magnification of aggregate of 10 μm $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$

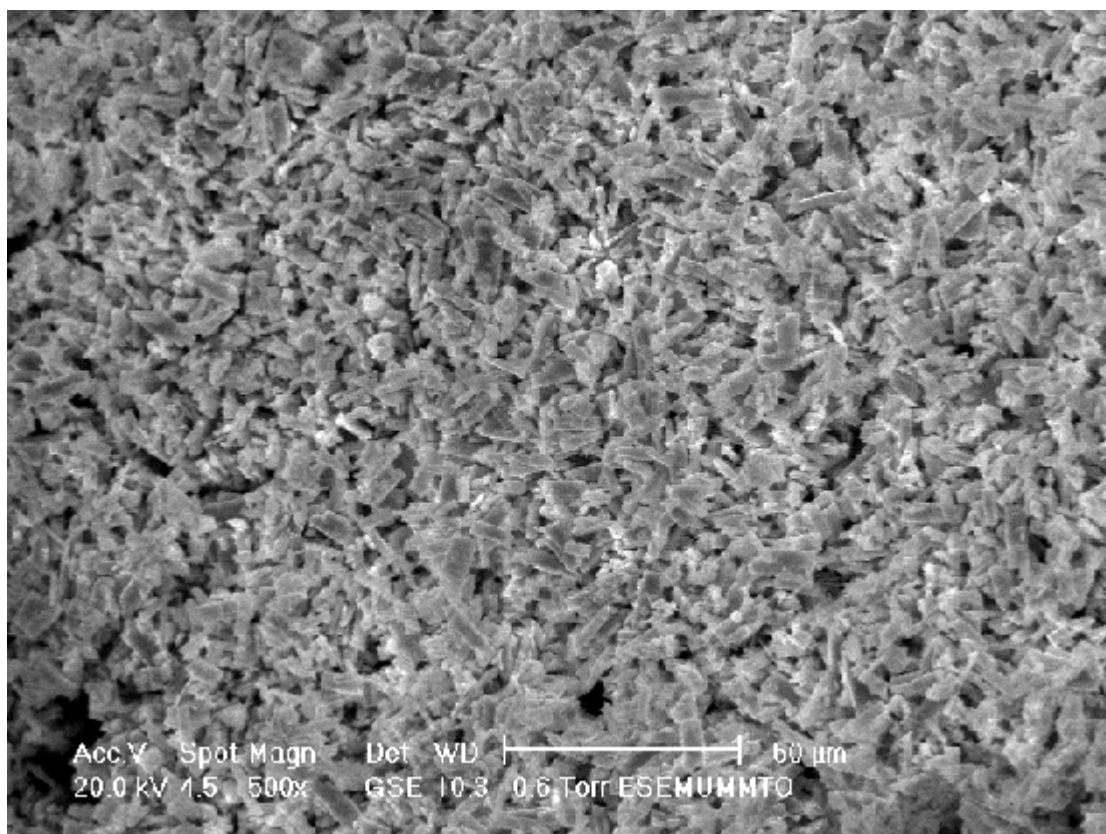


Figure II.42 Magnification of aggregate of 50 μm $(\text{NH}_4)_4\text{HSiMo}_{11}\text{NiO}_{39}$

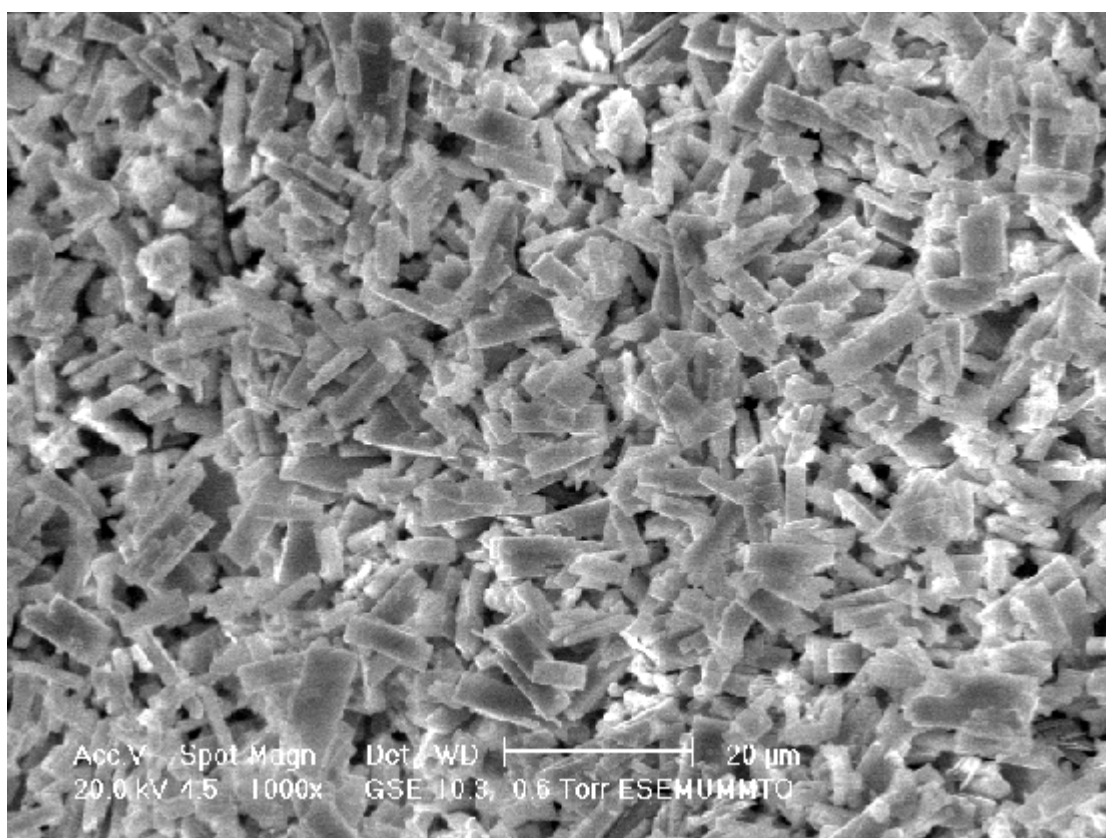


Figure II.43 Magnification of aggregate of 20 μm $(\text{NH}_4)_4\text{HSiMo}_{11}\text{NiO}_{39}$

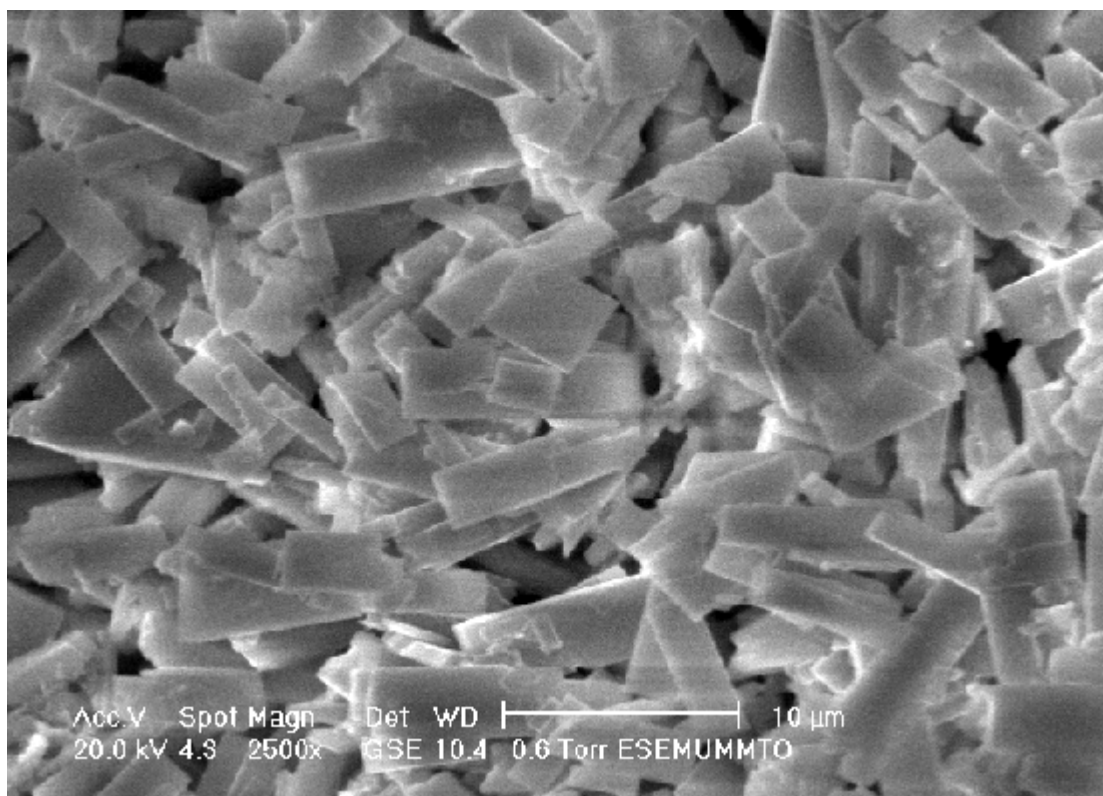


Figure II.44 Magnification of aggregate of 10 μm (NH₄)₄HSiMo₁₁NiO₃₉

The SEM image of pure phosphotungstic acid (HPW) reveals the presence of a (Fig. 25A) mixture of small (micro size) crystals together with few larger crystals. [51,52] .

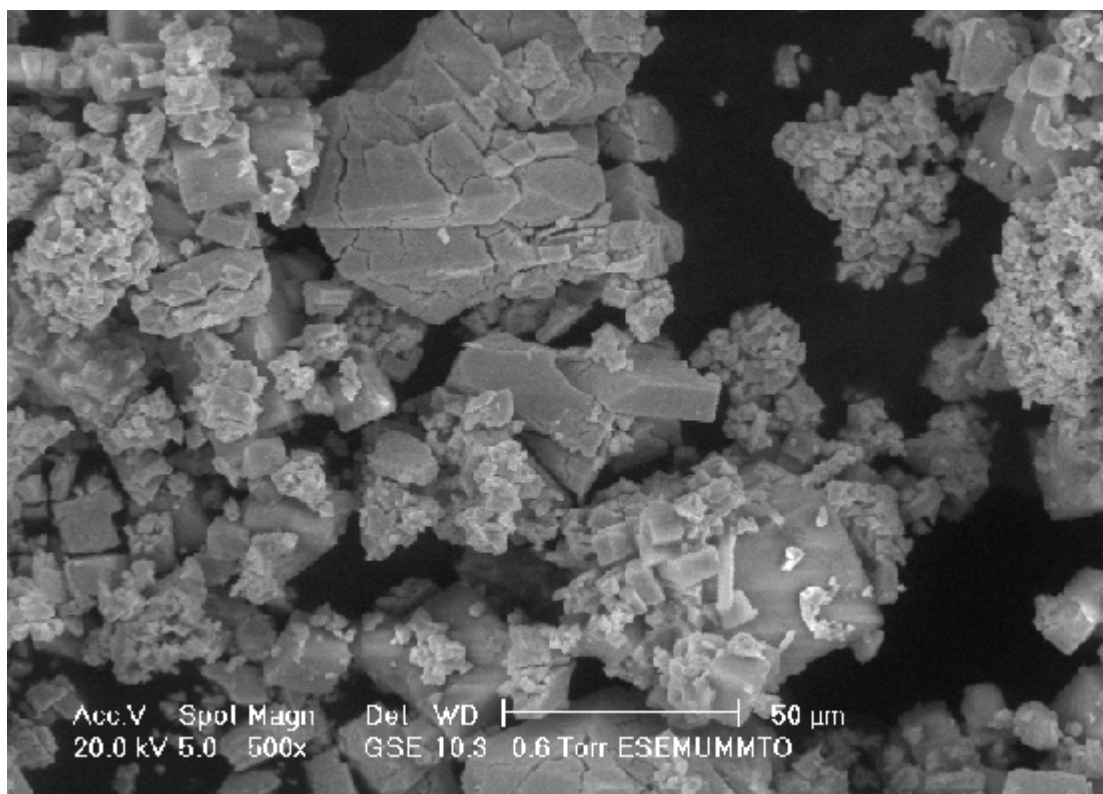


Figure II.45 Magnification of aggregate of 50 μm H₃PW₁₂O₄₀

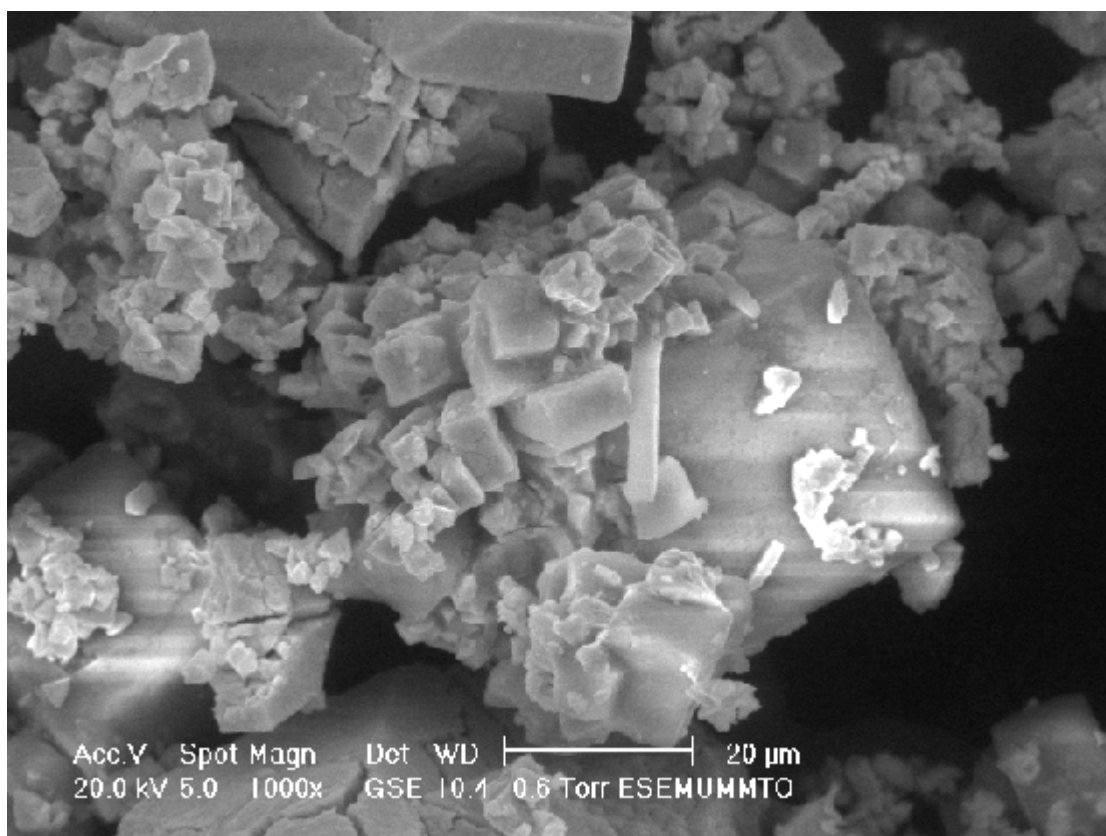


Figure II.46 Magnification of aggregate of 20 μm $\text{H}_3\text{PW}_{12}\text{O}_{40}$

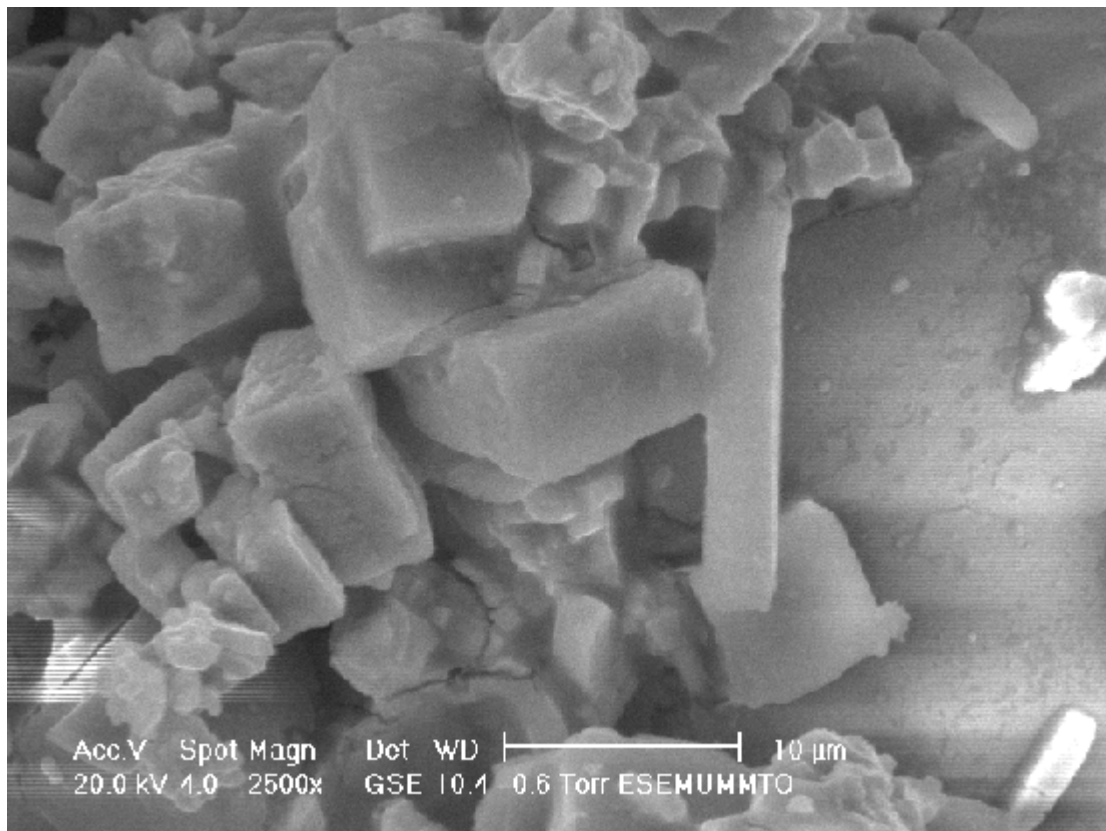


Figure II.47 Magnification of aggregate of 10 μm $\text{H}_3\text{PW}_{12}\text{O}_{40}$

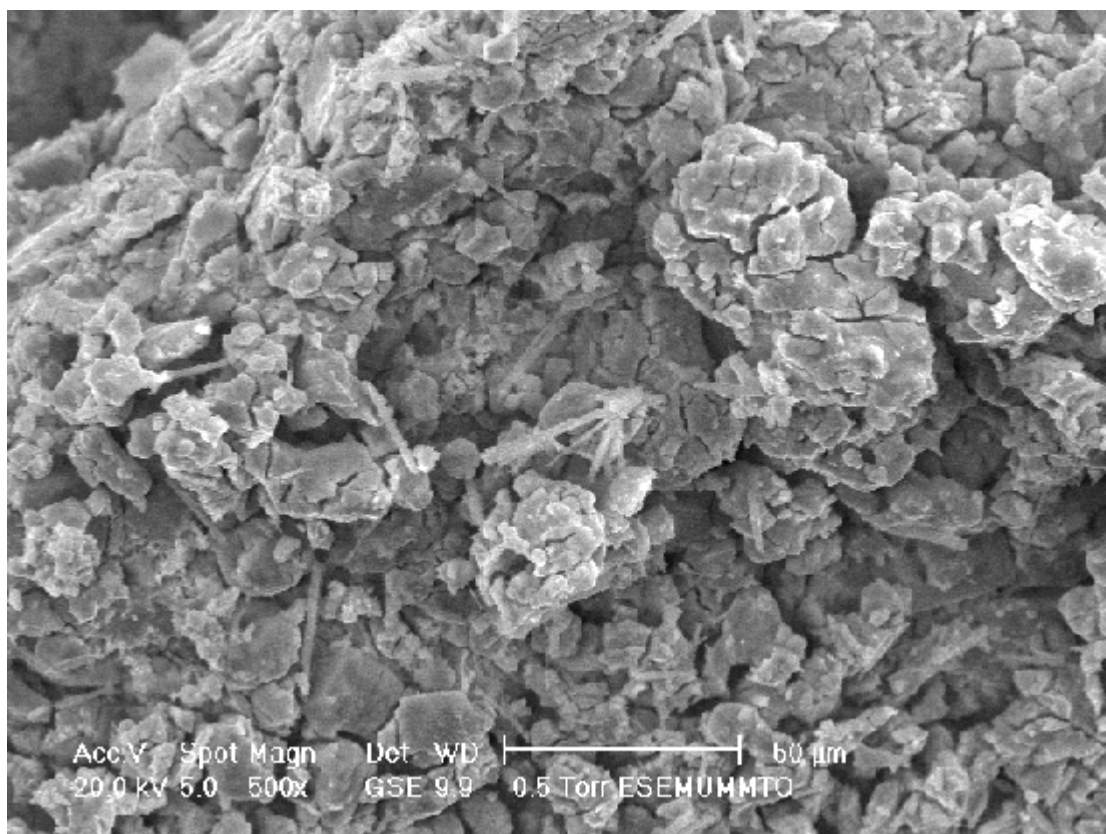


Figure II.48 Magnification of aggregate of 50 μm $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$

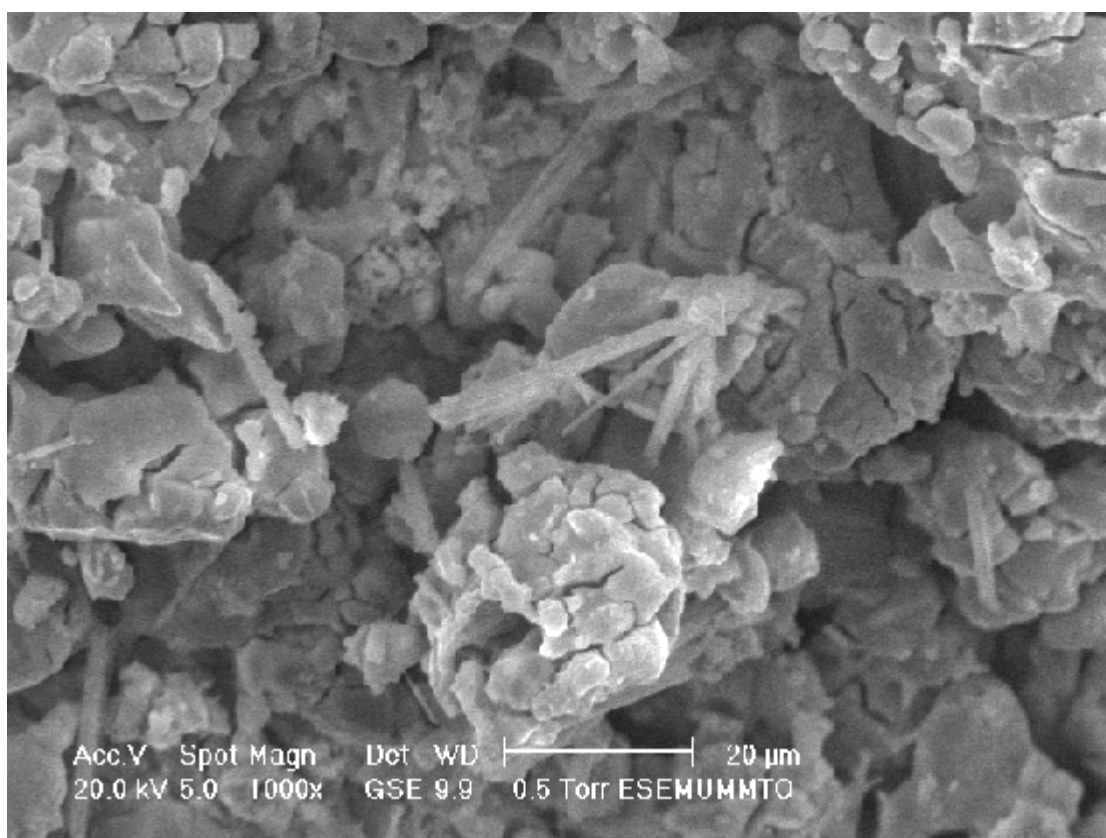


Figure II.49 Magnification of aggregate of 50 μm $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$



Figure II.50 Magnification of aggregate of 10 μm $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$

II.3. 3 - Solution Characterization :

II.3.3.1 - Analysis by ultraviolet-visible spectroscopy :

In the near UV, the Keggin type heteropolyanions show two absorption bands around 200 nm and another around 280 nm, These bands attributed to metal oxygen charge transfer. According to the literature [53], these bands are assigned respectively to the vibrations of Mo = Ot bonds and Mo-Ob / Oc. This result shows that the oxidation state of molybdenum VI ^[54].

When the concentration decreases, these bands gradually disappear indicating that the polyanion decomposed with dilution ^[55] (Figures II.51 to II.57).

Table II.4 Shows the absorption bands of different studied catalysts .

Table II.4: Main UV bands observed for different HPA catalyst systems.

Catalyst	λ max (nm)	
	Mo= Ot	Mo- Ob
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	237	310
$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$	237	311

$(\text{NH}_4)_6\text{FePMo}_{12}\text{O}_{40}$	237	310
$(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$	232	306
$(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$	236	306
$(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{39}$	237	311
$(\text{NH}_4)_4\text{HPMo}_{11}\text{CuO}_{39}$	234	306
$(\text{NH}_4)_4\text{HPMo}_{11}\text{FeO}_{39}$	237	311
$\text{KFePMo}_{12}\text{O}_{40}$	235	306
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	260	310
$\text{KFePW}_{12}\text{O}_{40}$	257	308
$(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$	260	311
$(\text{NH}_4)_4\text{HSiMo}_{11}\text{NiO}_{39}$	235	306

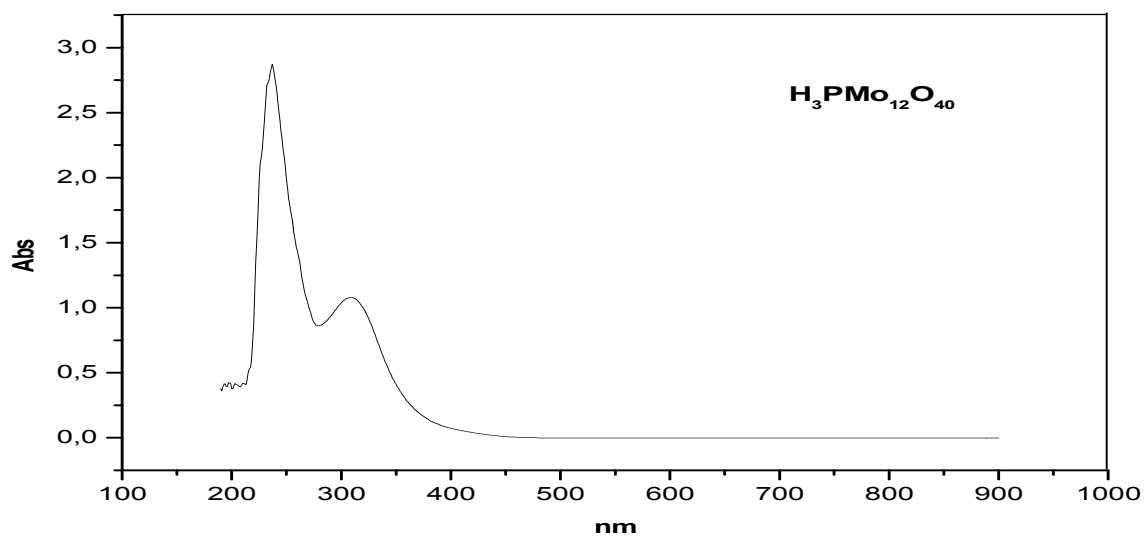


Figure II.51 : UV Spectrum of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$

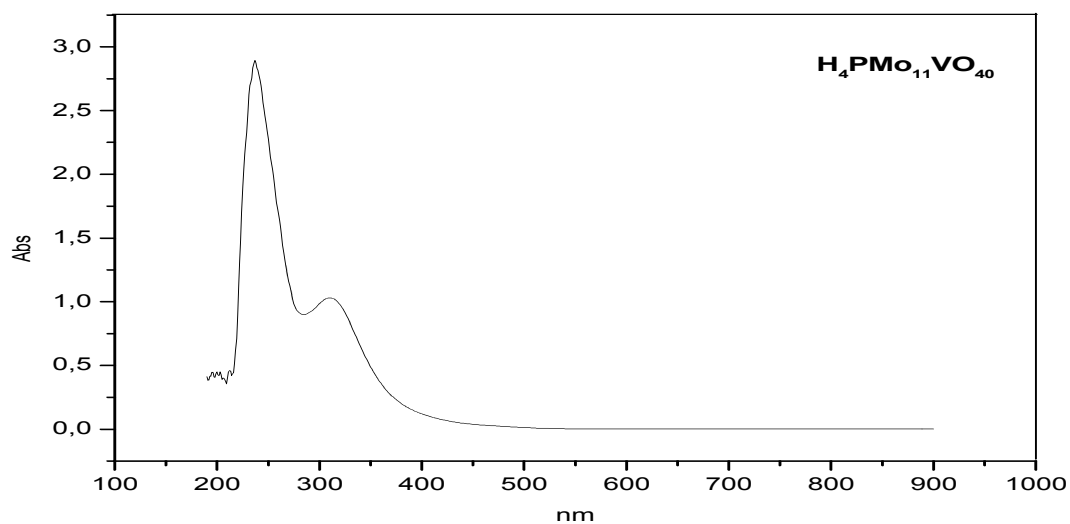


Figure II.52 : UV Spectrum of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$

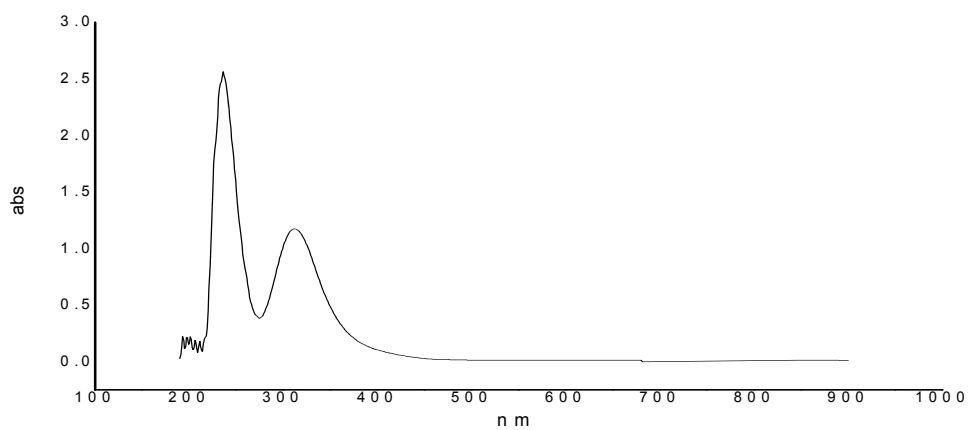


Figure II.53 : UV Spectrum of $\text{FePMo}_{12}\text{O}_{40}$

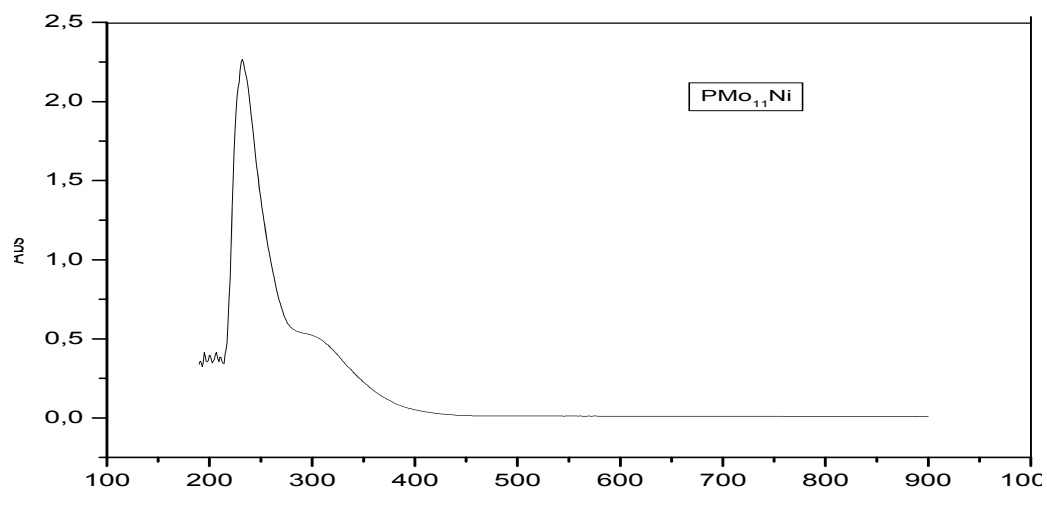


Figure II.54 : UV Spectrum of $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$

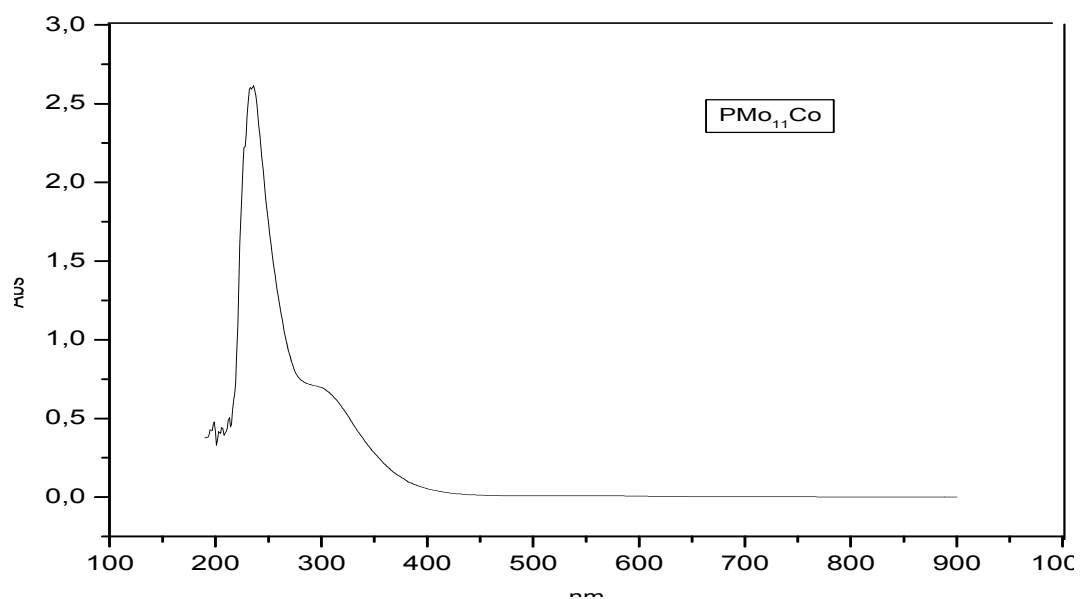


Figure II.55 : UV Spectrum of $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$

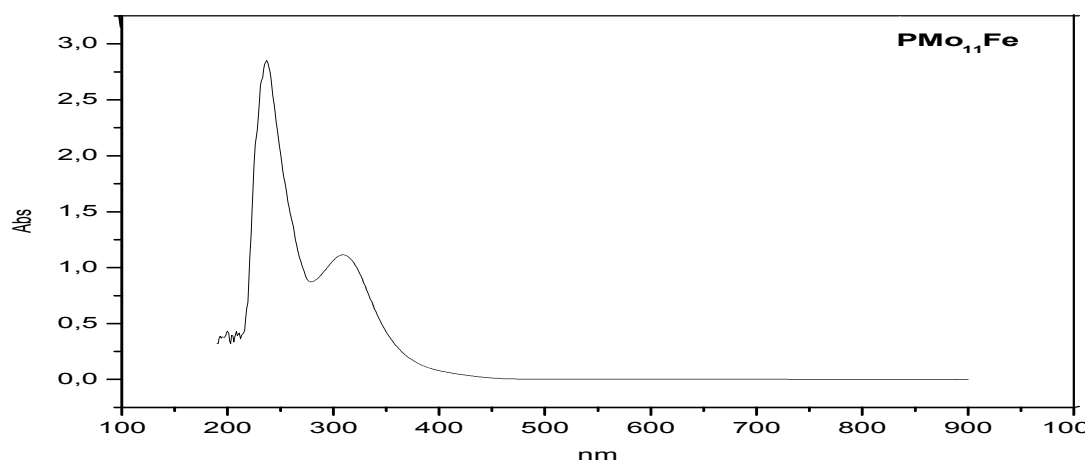


Figure II.56: UV Spectrum of $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$

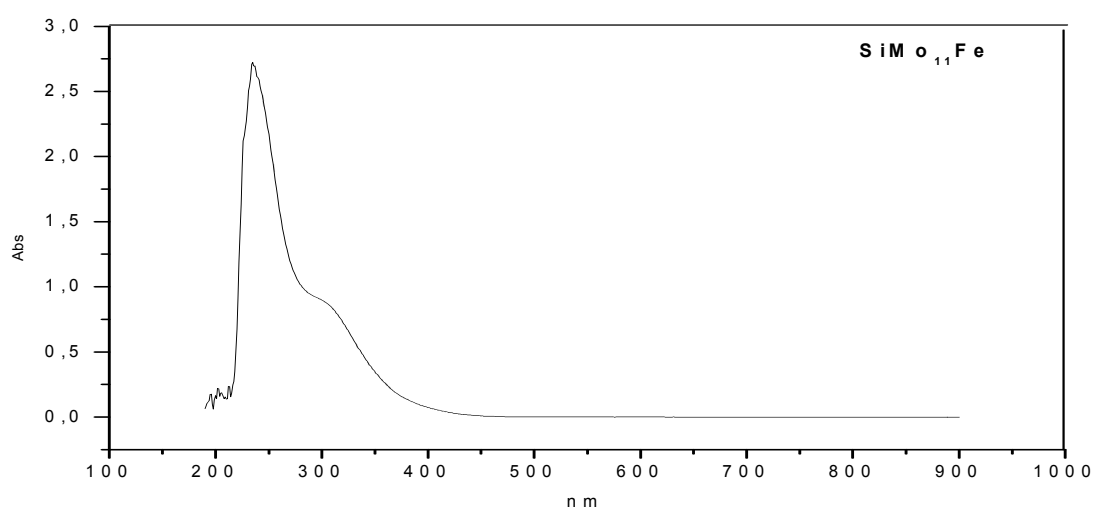
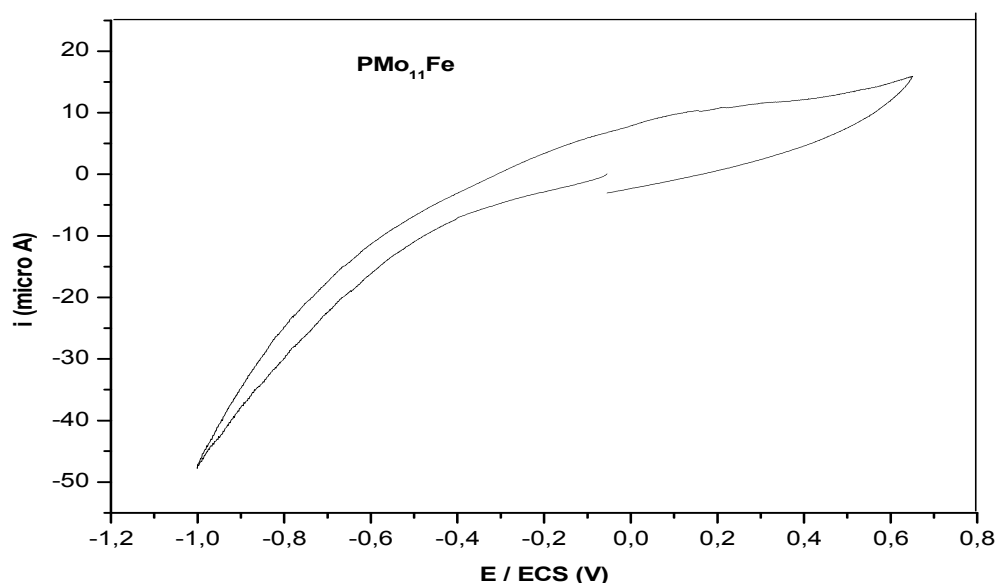


Figure II.57 : UV Spectrum of $(\text{NH}_4)_4\text{SiMo}_{11}\text{NiO}_{39}$

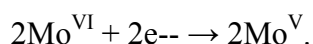
II.3.3.2 - Electrochemical Analysis :

The voltamperometric is a technique for studying the properties of oxido-reducing heteropolyanions. In the Keggin structure, the $\text{Mo}^{\text{VI}} / \text{Mo}^{\text{V}}$ is a reversible system.

The catalysts voltamperometric analysis studied is performed on glassy carbon rotating electrode. The potential of half-wave reduction are compared to a saturated calomel electrode (SCE). The concentration of our compounds is always taken equal to $3 \cdot 10^{-3}$ M in a acetonitrile / water (ratio 1 / 1 by volume).



The voltamperogram of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ acid is represented in **Figure II.58**. We found two reduction waves at -0.05 and -0.4 V / SCE, because they correspond closely to the reduction of a molybdenum atoms pair.



These waves are characteristic of $\text{PMo}_{12}\text{O}_{40}^{3-}$ ion. The potential of half-wave reduction for all of our catalysts is $E_{1/2} = -0.075$ V.

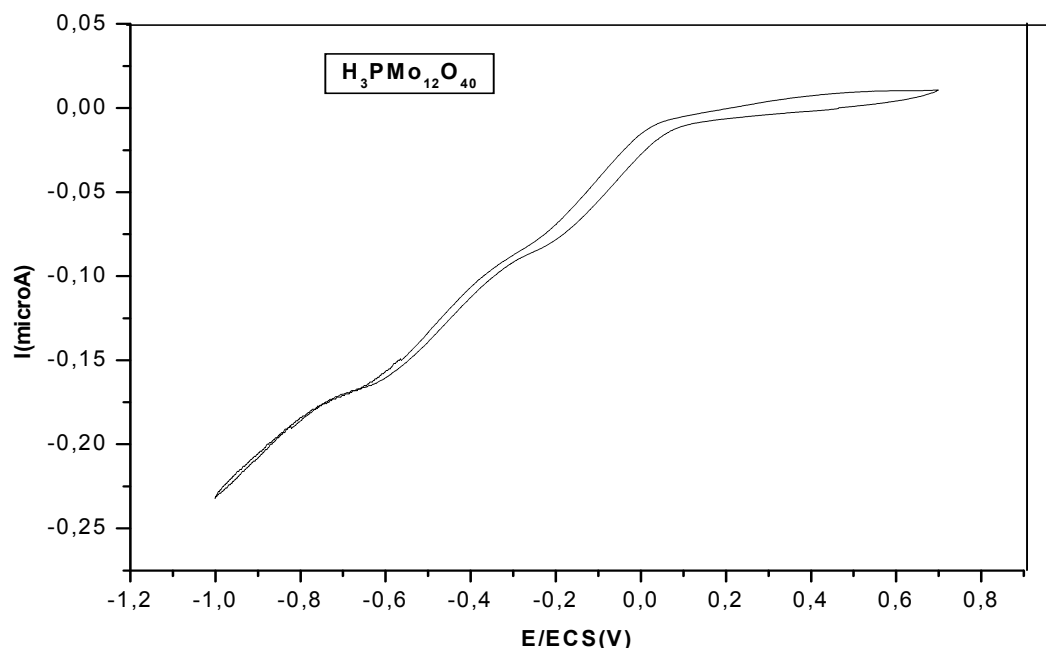
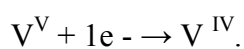


Figure.II.58: voltamperogram of Heteropolyacids $\text{H}_3\text{PMo}_{12}\text{O}_{40}$.

This method allows to highlight the difference between $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ acid. Indeed, the latter shows off additional monoelectronic wave $-0,017 \text{ V} / \text{ECS}$, which can be attributed to the reduction of vanadium (Figure II.59).



In the literature, voltamperometric analysis of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ acid is carried out in hydroorganic HClO_4 (0.5 M) / DMSO (1 / 1 by volume), this environment will ensure the stability of the Keggin entity at low concentrations [14].

The voltamperogram obtained has four waves whose reduction potential of half-waves are 0,420, 0,180, 0,110 and $-0,070 \text{ V} / \text{ECS}$.

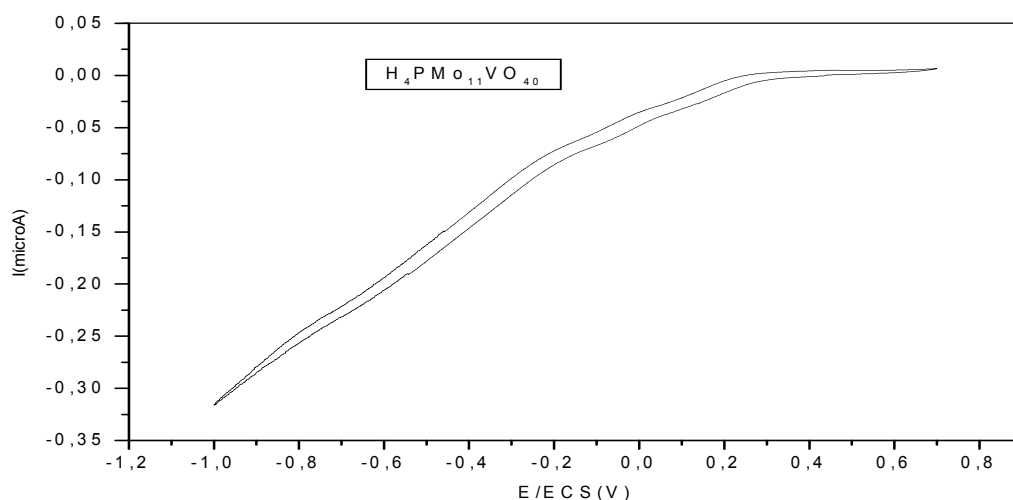


Figure.II.59: voltamperogram of Heteropolyacids $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$.

The bielectronic wave characterizing the reduction of Mo^{VI} ions observed in the case of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ acid and not observed in the case of $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$ salt (**Figure II.60**), which is explained by the low reducibility of molybdenum ions in this entity because of the strong interaction between Mo^{6+} and Fe^{3+} ions [35].

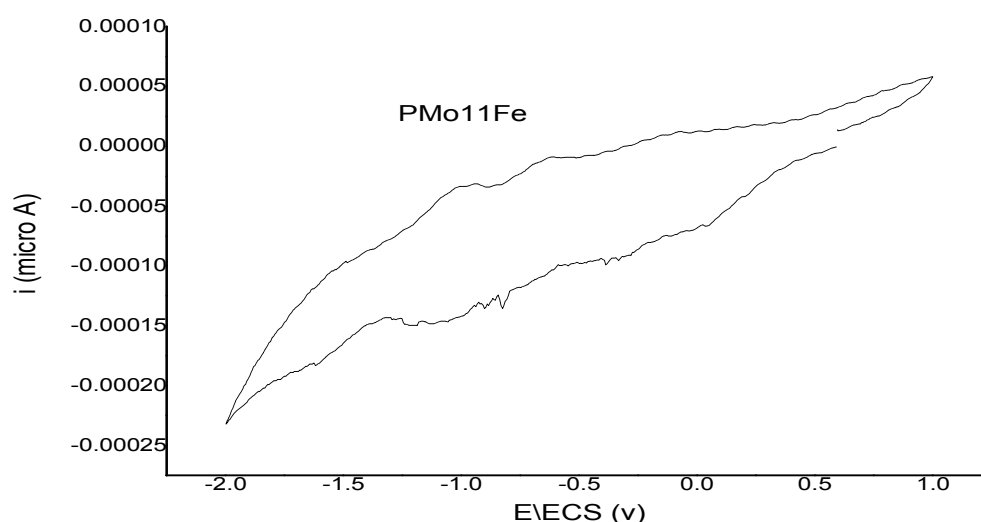


Figure.II.60 : Voltamperogram of $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$ heteropoly salt.

The general voltamperograms catalysts of $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$, $(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{39}$, $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$ and $(\text{NH}_4)_4\text{HSiMo}_{11}\text{FeO}_{39}$ is identical to that of the $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$ salt.

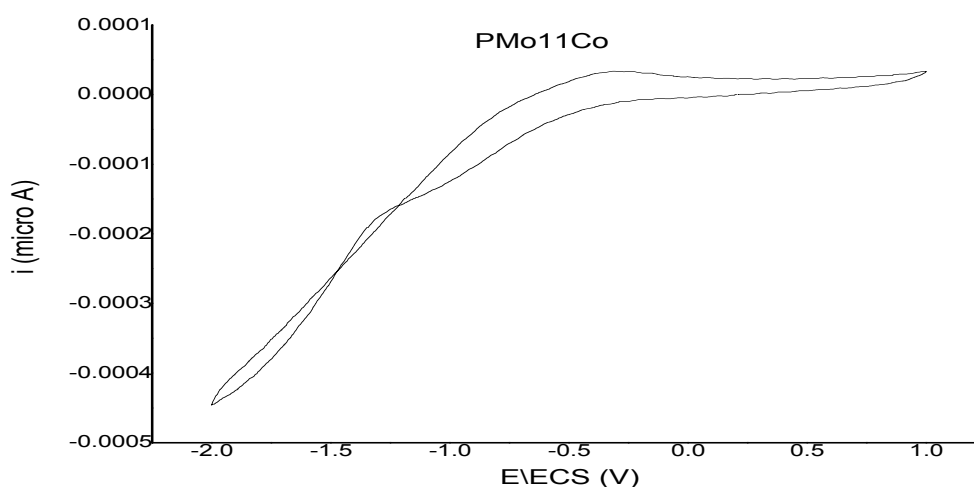


Figure.II.61: Voltamperogram of $\text{PMo}_{11}\text{CoO}_{40}$ heteropoly salt.

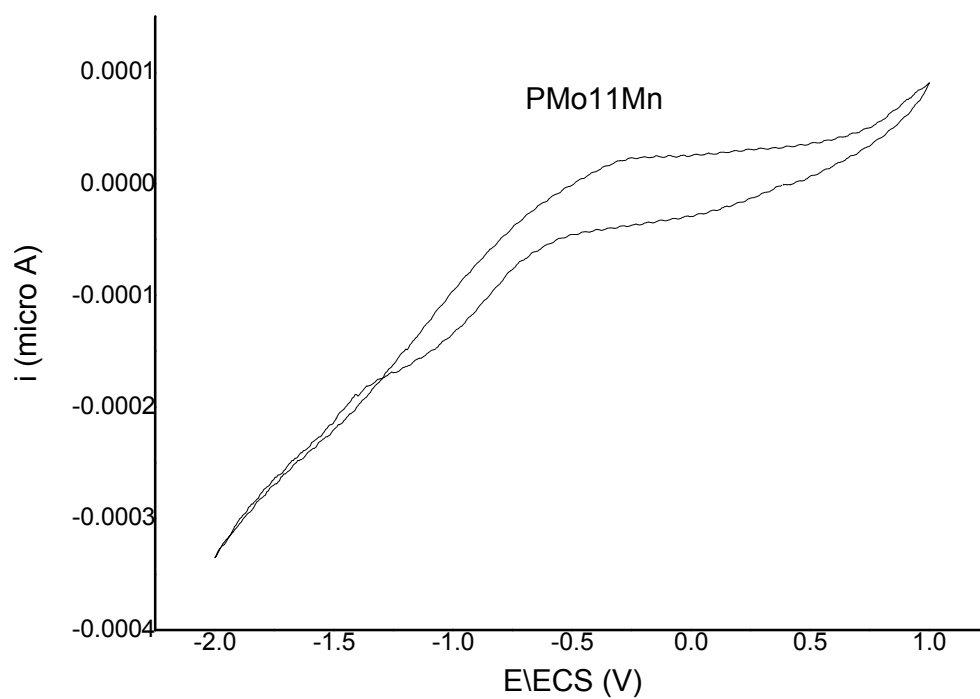


Figure.II.62: Voltamperogram of $\text{PMo}_{11}\text{MnO}_{40}$ heteropoly salt.

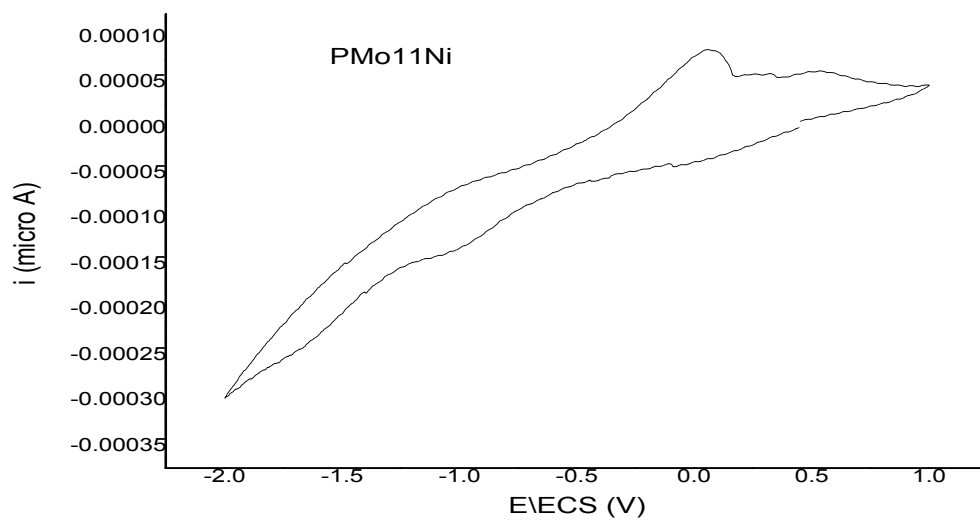


Figure.II.63: Voltamperogram of $\text{PMo}_{11}\text{NiO}_{40}$ heteropoly salt.

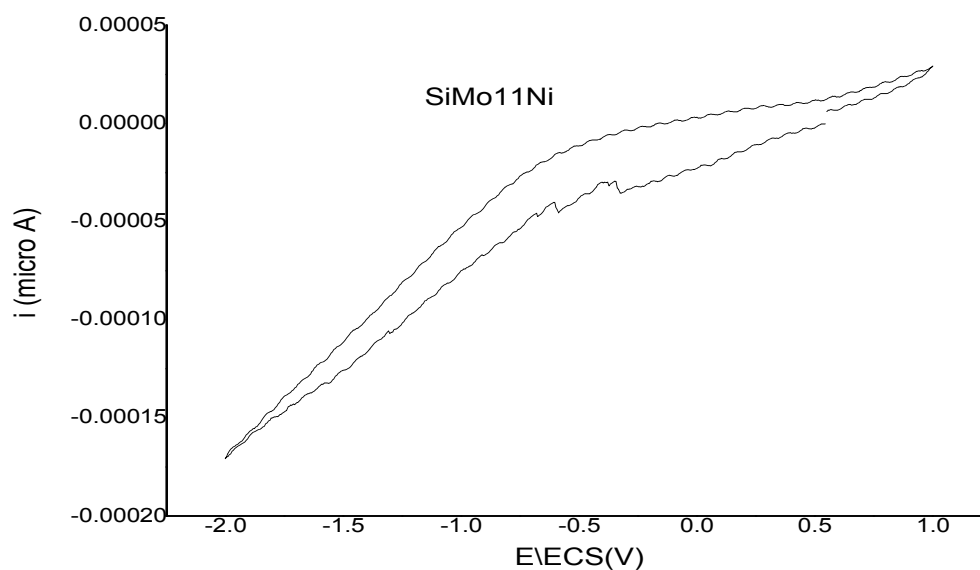
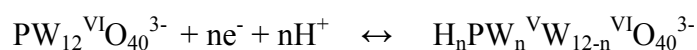


Figure.II.64: Voltamperogram of $\text{SiMo}_{11}\text{NiO}_{40}$ heteropoly salt.

Figure II.65 shows typical cyclic voltammogram for Keggin-type 12-phosphotungstic acid. The two couples of peaks at potentials -0.027 V and 0.24 V correspond to two redox reactions and can be described in terms of two consecutive reversible one-electron processes [56 - 58].



where n is equal to 1 or 2

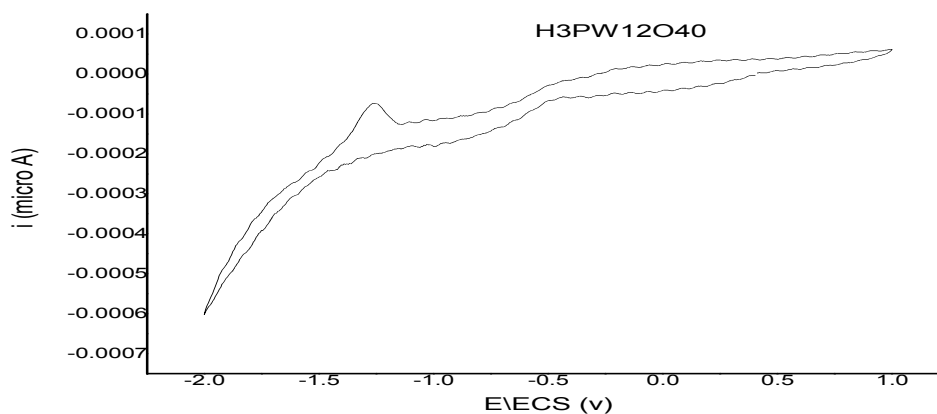


Figure.II.65: Voltamperogram of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropoly acid.

In **Figure II.66** we observe three waves and quasi-reversible one-electron potentials which are attributed to the successive reduction centers tungsten (VI) tungsten (V).

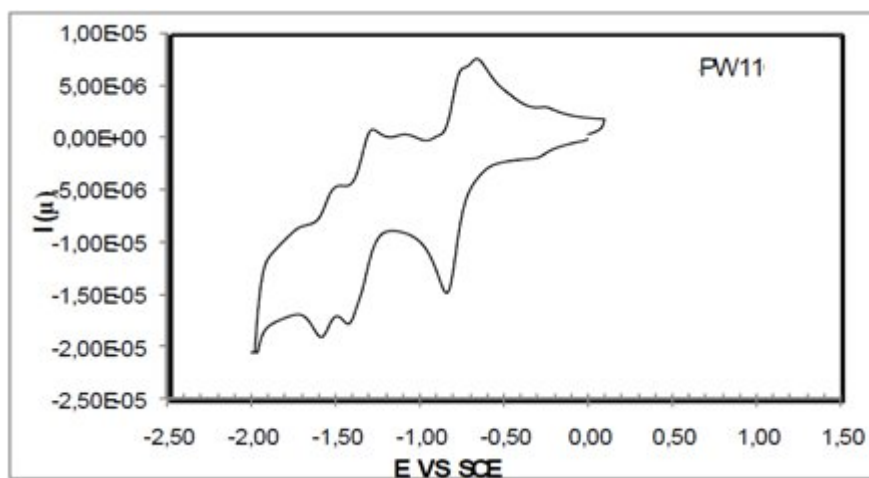


Figure.II.66: Voltamperogram of PW_{11} heteropoly salt.

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CHAPTER III

REACTIVITY OF HETEROPOLYCOMPOUNDS

III.1 Introduction

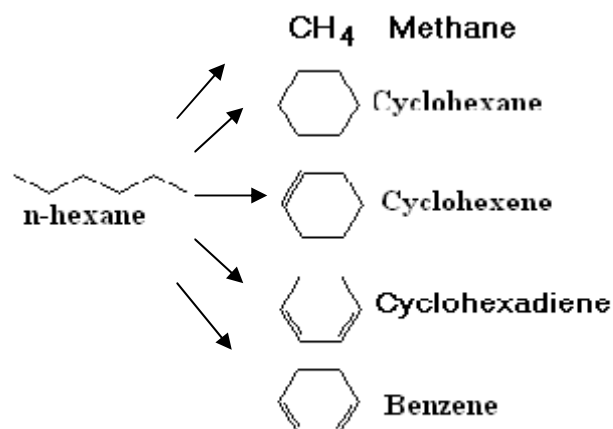
We used catalytic test to characterize the catalytic properties of heteropolycompounds by testing the conversion of n-hexane to identify the influence of some parameters on the recovery of the hydrocarbon .

Enhancement of n-hexane by its direct conversion depends on the composition of the solid catalysts and operating conditions. Thus the platinum deposited on gamma alumina ^[1], rhenium, germanium or tin associated with platinum ^[2], or using mixed carbides such as (W / Mo) or bimetallic (W / Ni) deposited on alumina ^[3], the observed products are those which correspond to the different reactions:

- * Hydrogenolysis reaction whose products are methane, ethane, propane, butane and pentane
- * Isomerization reaction whose products are isobutane, isopentane, 2.2 dimethyl butane, 2.3 dimethyl butane, 2-methyl pentane, 3 methyl pentane.
- * dehydrocyclisation reaction whose products are : methyl cyclopentane, cyclohexane cyclohexene, cyclohexadiene and benzene.

In the present work we studied the transformation of n-hexane in the presence of molecular hydrogen on $H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$ Heteropolyacids, and mixed salts ($H(NH_4)_4PMo_{11}NiO_{39}$, $(NH_4)_4PMo_{11}FeO_{40}$ $H(NH_4)_4PMo_{11}CoO_{39}$, $H(NH_4)_4PMo_{11}CuO_{39}$, $H(NH_4)_4PMo_{11}MnO_{39}$, $(NH_4)_{2.5}Fe_{0.1}PMo_{11}O_{40}$, $(NH_4)_{3-x}Ni_xPMo_{12}O_{40}$, $(TBA)_7PW_{11}O_{39}$, $KFePW_{12}O_{40}$ at different reaction temperatures.

The products of the catalytic transformation of n-hexane are: cyclohexane, cyclohexene, cyclohexadiene , benzene and methane .



III.2 n-Hexane Reaction using H₂ as Carrier Gas

III. 2.1 Effect of time on the Catalytic Activity of Heteropolycompounds

The transformation of n-hexane was studied at atmospheric pressure and a temperature range between 200 and 400 ° C on the prepared heteropolycompounds catalysts. **Figure III.1** shows the evolution of catalytic activity of some studied heteropolycompounds at 250 ° C over time. Initially PMo₁₁Mn is the most active catalyst and PMo₁₂ is the least one. The catalytic activity of all catalysts increases during the first four hours of reaction, and then remains constant with slightly decrease. The great activity of (PMo₁₁Mn, PMo₁₁Ni, FePMo₁₂ ...) is linked to their bifunctional catalyst since it has both acidic properties by the presence of protons and oxido-reductive by the transition metal (Mo and / or Mn, Ni, Fe ...). The position of metal in the polyanionic body plays a considerable role in the catalytic performance.

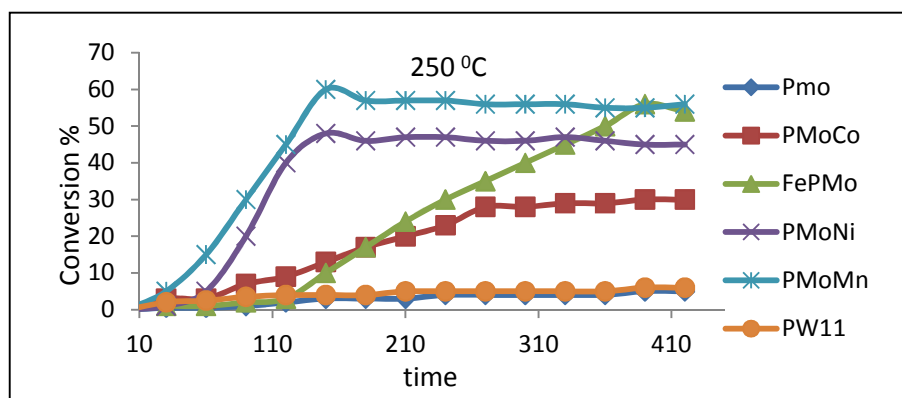


Figure III.1 : Evolution of the activity of catalysts as a function of time at 250 ° C
total flow (H₂ + n-hexane) = 0.1 l / h

Figure III.2 shows that (PMo_{11}Mn , PMo_{11}Ni , FePMo_{12} , ...) salts still has higher activity compared to PMo_{12} acid at 300 ° C. Activity increases during the first four hours of reaction, and then stabilizes. At this temperature. The major activity is linked to the strength and numbers of Bronsted acid sites present in catalysts .

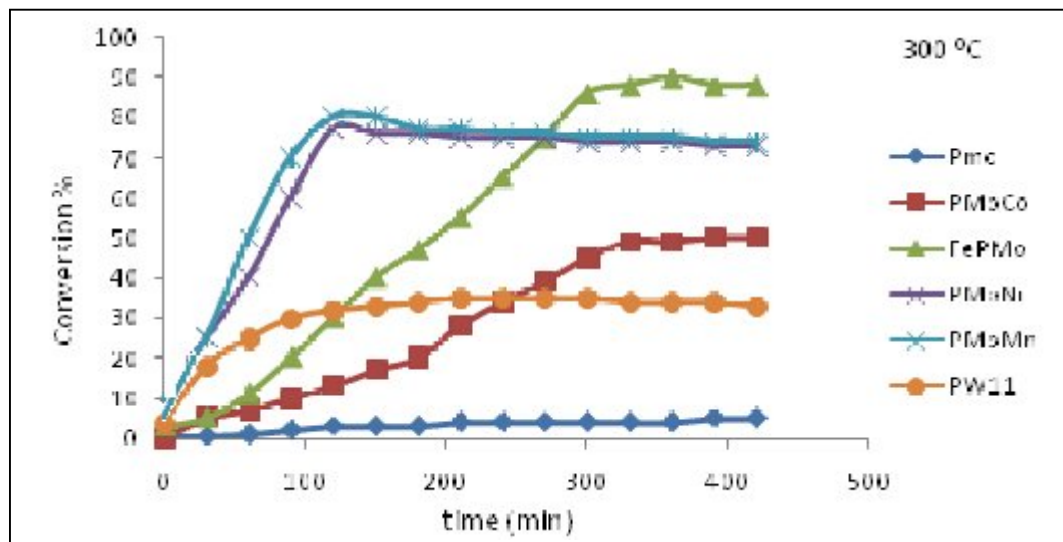


Figure III.2 : Evolution of the activity of catalysts as a function of time at 300 ° C
total flow (H_2 + n-hexane) = 0.1 l / h

Figure III.3 shows the evolution of catalytic activity at 350 ° C for some of studied HPA. At this temperature the PMo_{12} acid presents in a patchy structure,^[4] the loss of water content leads to the decline in Brönsted acidity and thus the decrease in catalytic activity. The great activity of (FePMo_{12} , PMo_{11}Mn , PMo_{11}Ni , ...) salts results due to the presence of Bronsted and Lewis acid sites which are generated by the departure of ammonia as shown in thermogravimetric analysis^[5].

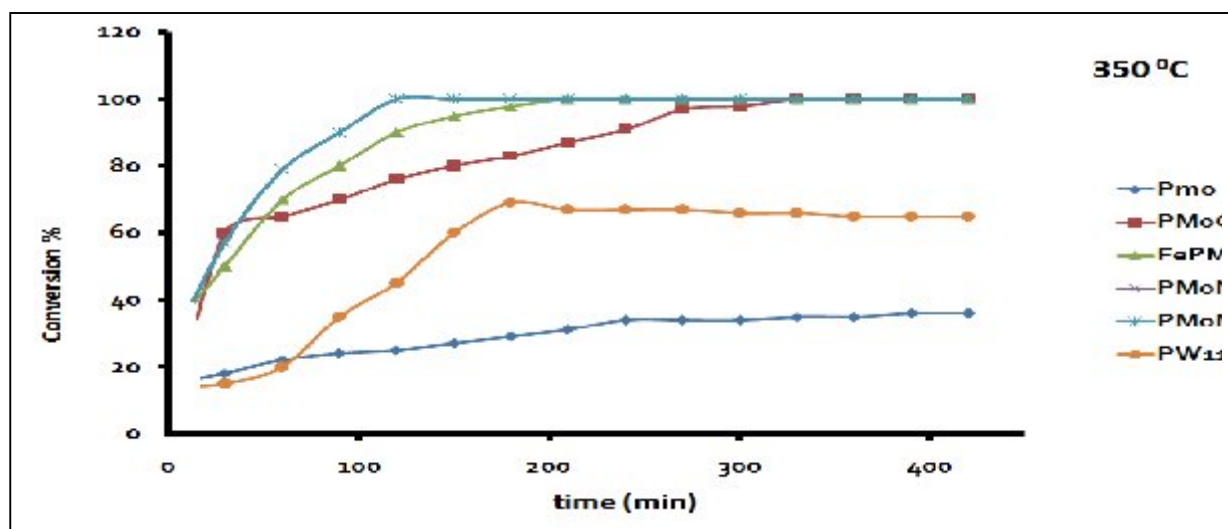


Figure III.3 : Evolution of the activity of catalysts as a function of time at 350 ° C
total flow (H_2 + n-hexane) = 0.1 l / h

The evolution of catalytic activity at 400 ° C for PMo_{12} acid is comparable to that of the corresponding heteropolyanions catalysts (**figure III.4**). This high activity could be Related to the change in the structure of acid. At this temperature the Keggin structure of the PMo_{12} acid is destroyed, it takes the form of a mixed oxide (MoO_3 and P_2O_5) as confirmed by the results of X-ray diffraction ^[6]. The activity of the reaction increases in the first three hours, then it is stable .

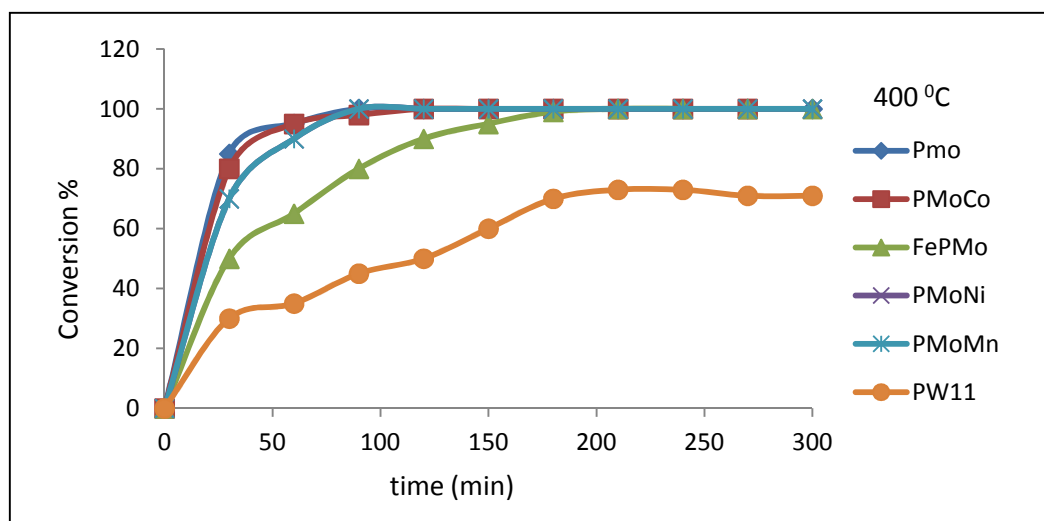


Figure III.4 : Evolution of the activity of catalysts as a function of time at 350 ° C
total flow (H_2 + n-hexane) = 0.1 l / h

The selectivity of benzene slightly decreased with time on all catalysts as shown in **Figure.III.5**, when keeping temperature constant at 350°C. This due to high thermodynamic stability of benzene.

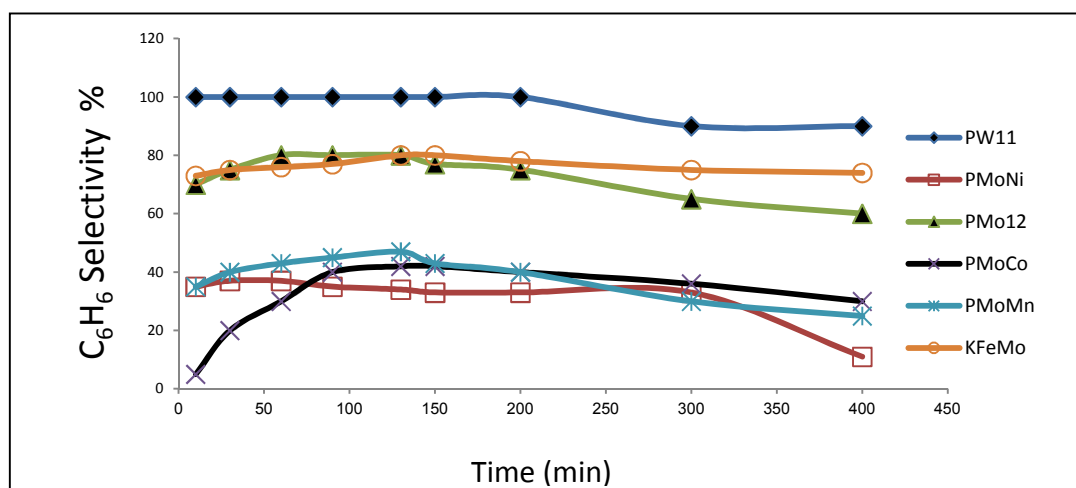


Figure III.5: Selectivity of benzene as function of time at 350°C, (using H_2 as carrier gas).

Selectivity of n-Hexane reactions products is depend on the time. Methane selectivity increased by time in the first 8 hours then slightly decreased , while the other products (

benzene, cyclohexane, cyclohexene, cyclohexadiene) slightly decrease at different temperature, as shown in **Figures III.6** and **Figure III.7** for PMo_{11}Ni catalyst as example .

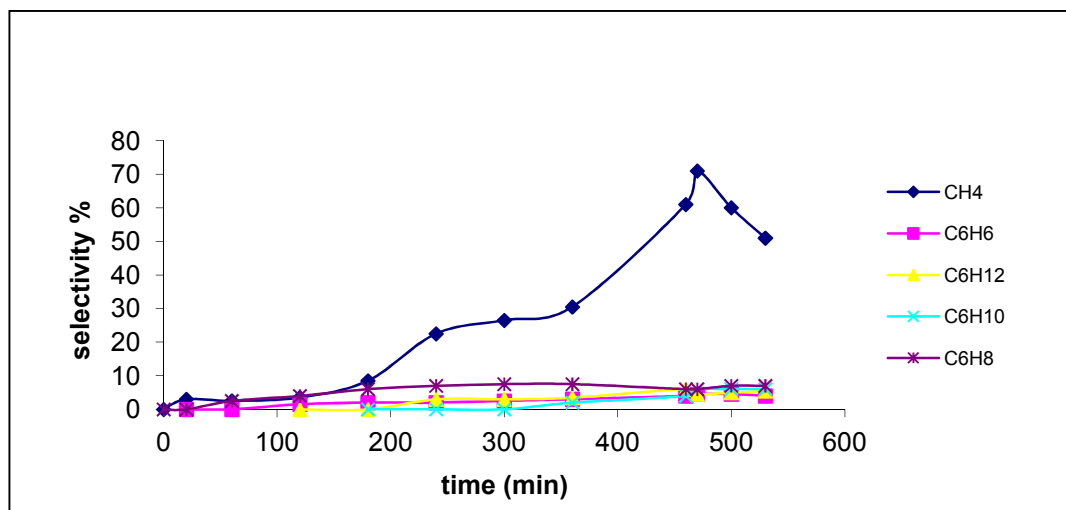


Figure III.6: Selectivity of different products as function of time at 300°C,(using H_2 as carrier gas , PMo_{11}Ni).

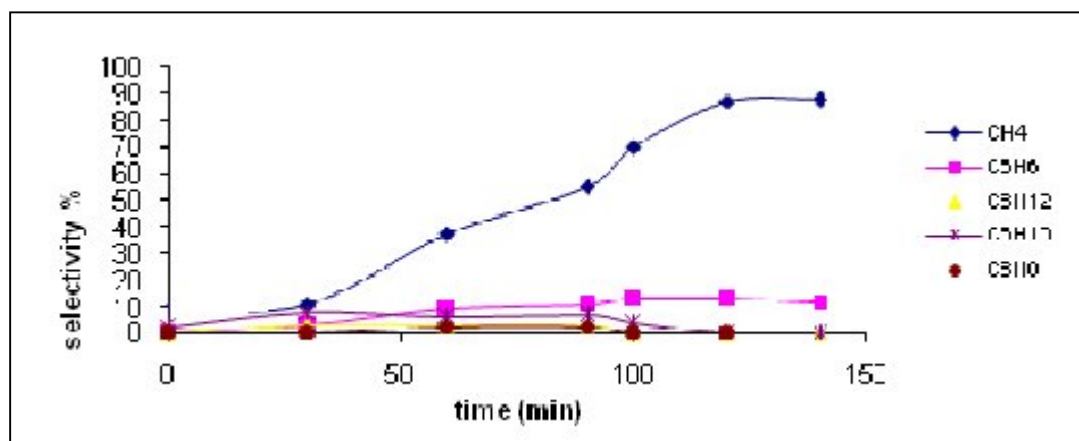


Fig.III.7. Selectivity of different products as function of time at 350°C,(using H_2 as carrier gas , PMo_{11}Ni).

Figure III.8 shows the relation between n-hexane conversion and the products selectivity. Methane selectivity is increased and reached up to 100% when n-hexane completely converted, while selectivity of other products decreased by increasing n-hexane conversion , and disappeared at high conversion of n-hexane (90% - 100%) .

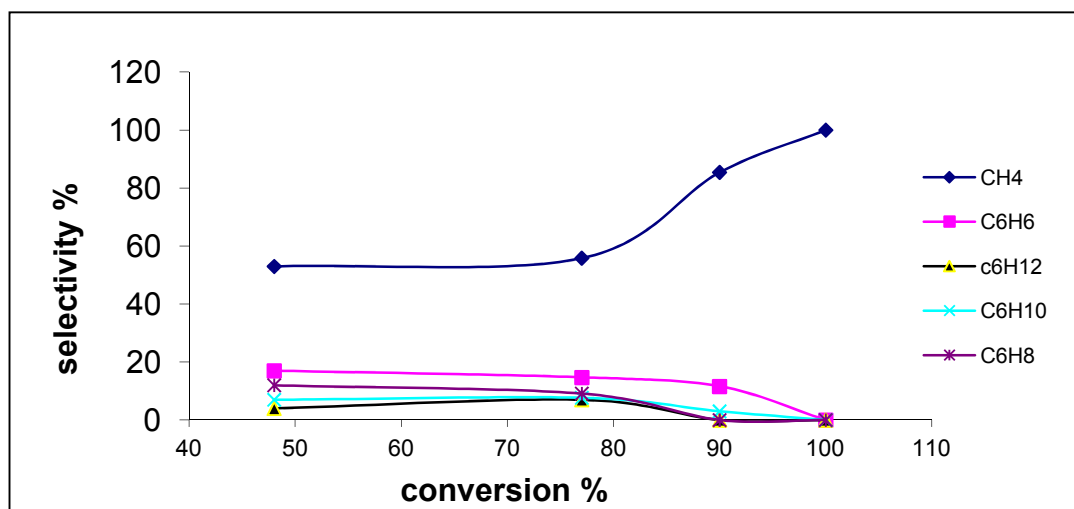


Figure III.8 : Selectivity of different products as a function of n-hexane conversion (using H_2 as carrier gas , $PMo_{11}Ni$).

III.2.2 Effect of chemical composition of heteropolycompounds on catalytic activity

The reaction of dehydrocyclization and aromatization of n-hexane was studied on heteropolycompounds catalysts under a temperature range between 200 and 400 ° C. The n-hexane is added with a saturator maintained at 0 ° C. The partial pressure of n-hexane is adjusted from the flow of hydrogen passing through the saturation. The reaction mixture (H_2 + n-hexane) passes through a mass of 0.5 g of catalyst with a flow rate of 0.1 l / h. Transformation rates of n-hexane and formation of reaction products correspond to those of the steady state.

Steady-state activity for catalytic n-hexane dehydrocyclization was reached within about 4 hours. The observed products were benzene, (one most preferred product), cyclohexane, cyclohexene, cycloheadiene and methane(least preferred product). As expected, the catalytic activity and selectivity were dependent on the nature of the catalyst.

Figures (III.1- III.4) shows the conversion of n-hexane using different catalysts. The conversion of the solid catalyst was sensitive to the nature of the coordination ion (Mo^{6+} , W^{6+} , Ni^{+2} , Co^{+2} , Mn^{+2} , V^{+3} , Fe^{+3} , Cu^{+2}) and counter ion H_3O^+ , NH_4^+ , Ni^{+2} , Fe^{3+}). The replacement of mobile M (Ni^{+2} , Co^{+2} , Mn^{+2} , V^{+3} , Fe^{+3} , Cu^{+2}) ions in the HPA framework increased the activity of the catalyst. Also replacing H^+ ion with (Fe^{+3} , Ni^{+2}) increase the activity. PW_{11} exhibited relatively higher activity than PMo_{12} . In general, the heteropolysalts were higher activity than the heteropolyacids.

Detailed studies on n-hexane isomerization catalysis with HPC are summarized in (Tables.III.1,III.2) The results show that benzene was the major product at low conversion level while using different catalysts. Cyclohexane, cyclohexene, cyclohexadiene, benzene and methane were also observed. As the conversion level increased benzene product ratio was lowered in ratio of methane product. The 30% activity for PMo_{12} (or even 100% for other catalysts) shows that the protons in anhydrous HPA are accessible to the reactant molecules. The high catalytic activity of HPA may thus be related to high acid strength and high mobility of protons, as reported earlier [7]. The resulting protons are responsible of the aromatization of n-hexane. Cyclohexane , cyclohexene cyclohexadiene were also obtained, with variable ratios depending on type of catalyst. An important selectivity (when use N_2 as carrier gas, **Table III.4**) obtained by PMo_{11}Ni catalyst involved cyclohexane 14%, cyclohexene 2%, cyclohexadiene 40%. A lower selectivity with PMo_{11}Co and PMo_{11}Mn catalysts was observed. The results indicate that both relatively strong acidity and metallic propriety are responsible for catalyst efficiency at lower temperature (lower than 350°C).

The PW_{11} catalyst showed specially high efficiency, selectivity and stability towards benzene formation. For example, PW_{11} showed high activity (69%)conversion and high selectivity (100%) at 350°C compared to PMo_{12} (30% conversion and 17% selectivity), PMo_{11}Ni (100% and 11.5%), and PMo_{11}Co and PMo_{11}Mn (100% and 0%). Such behaviour should be ascribed to the Lewis acid properties of the TBA cations, Also, we may conclude that Lewis acid species should be important components of the active site in the isomerization of n-hexane reaction over HPAs, in agreement with other studies [8,9].

Table III.1 : Catalytic performances of studied Heteropoly compound (carrier gas H_2 ,flow rate : 0.1 L/h)

Catalyst	T $^\circ\text{C}$	Conversion %	Selectivity				
			CH_4	C_6H_6	C_6H_{12}	C_6H_{10}	C_6H_8
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	300	5	79	21			
	350	30	83	17			
	380	100	100				
$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$	300	0					
	350	15	75	25			
	350	38	80	20			
	400	100	100	0			
$\text{H}(\text{NH}_4)_4\text{PMo}_{11}\text{NiO}_{39}$	250	48	53	21	7	12	7
	300	77	56	21	8	9	6
	350	100	85	12	3		
	380	100	100				
$\text{H}(\text{NH}_4)_4\text{PMo}_{11}\text{CoO}_{39}$	250	35	57	23	20		
	300	50	86	8	6		
	350	100	98		2		
	380	100	100				

	250	60	90	7	3		
	300	80	98		2		
H(NH ₄) ₄ PMo ₁₁ MnO ₃₉	350	100	100				
	380	100	100				
	250	56	52	20		12	12
(NH ₄) _{2.5} Fe _{0.1} PMo ₁₂ O ₄₀	300	90	89	11			
	350	100	100				
	380	100	100				
(TBA) ₇ PW ₁₁ O ₃₉	300	3	0	100			
	350	69	0	100			
	250	56	56	20	0	12	
KFe _{0.1} PW ₁₂ O ₄₀	300	90	77	11	0	6	
	350	100	100	0	0	0	
	380	100	100	0	0	0	
	300	3	6	0	1	61	12
H(NH ₄) ₄ PMo ₁₁ CuO ₃₉	350	22	19	0	3	48	6
	380	52	40	0	7	33	0
	400	62	55	0	7	23	0
	250	31	62	20	4	6	32
(NH ₄) _{4-x} Ni _x PMo ₁₂ O ₄₀	275	36	77	14	7	3	30
	300	60	90	8	2	0	20
	325	95	98	2	0	0	15
	350	100	100	0			0
	300	22	78	6	4	6	6
H(NH ₄) ₄ SiMo ₁₁ FeO ₃₉	350	33	81.8	3.6	5.4	6.2	4
	380	51.5	92	2	2	2	2
	400	100	100	0	0	0	0

III.2.3 Effect of Temperature

The effect of temperature on efficiency and benzene selectivity has been studied for different catalysts. Figure III.9 shows how conversion varies with reaction temperature. The temperature curves exhibit linear character. For different catalysts, overall hexane conversion increased with temperature. The transformation of n-hexane on the tested catalysts started only above 250⁰C and the conversion reached 100% at 350-400C .

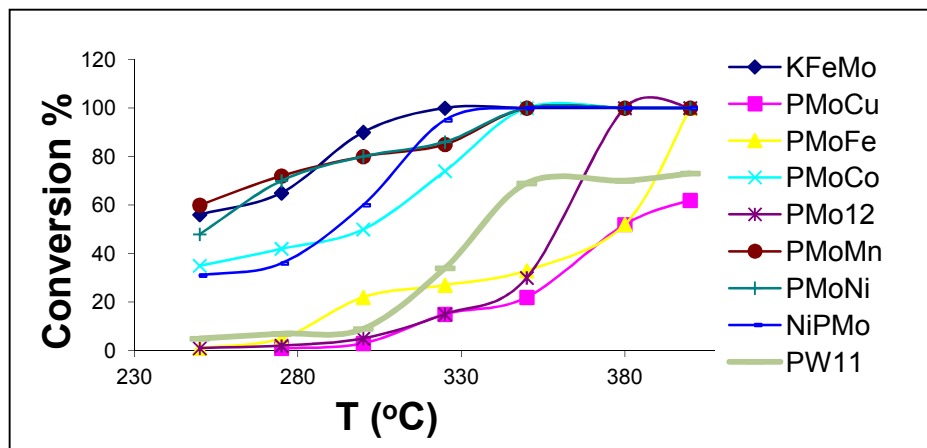


Figure III.9 : Conversion of n-hexane as function of temperature,(using H₂ as carrier gas).

Products selectivity was affected with reaction temperature and type of catalysts

A- Formation of benzene

Until 300°C, benzene was the unique or major product. The selectivity to benzene decreased with increasing temperature (**Table III.1**). The conversion increased from 2 up to 30%, whereas benzene selectivity decreased from 100 to 80% when the reaction temperature was increased from 300°C to 350°C when using PMo₁₂ heteropolyacid catalyst

Figure III.10 shows the evolution of the selectivity of benzene as a function of temperature on different catalysts studied. The general shape of these curves are identical. The selectivity of benzene appears to be related to both temperature and composition of the catalyst.

The decrease of the selectivity of benzene could be explained by the decrease in strength and number of Brønsted acid sites. From the reaction temperature of 350 °C HPA are deficient structures resulting from the departure of the water content as shown by the results of the DSC. This structure does not promote aromatization of n-hexane earlier but its cyclization.

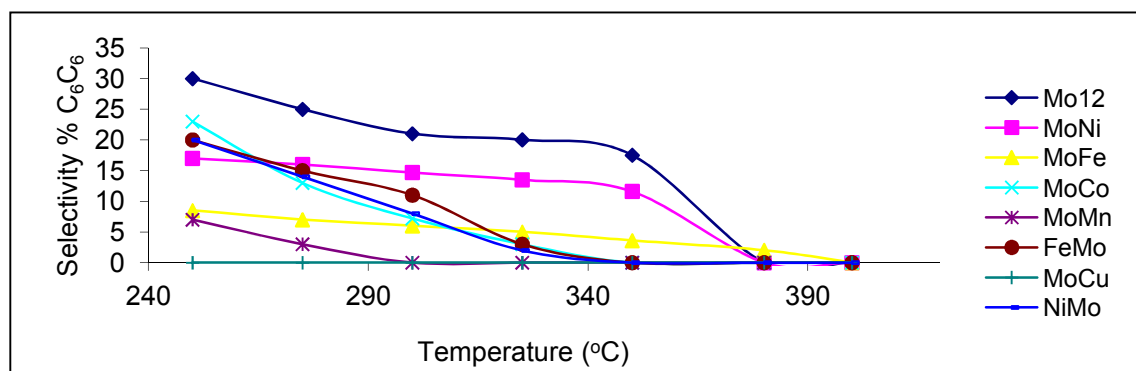


Figure III.10 : Evolution of selectivity in benzene according to the reaction temperature, total flow (H₂ + n-hexane) = 0.1 l / h

B- Formation of cyclohexane

Cyclohexane appears at 250 - 330 ° C on PMoNi, NiPMo catalysts, and at 300 – 400 on PMo₁₁Fe, PMo₁₁Cu catalysts . The evolution of selectivity of cyclohexane as a function of temperature is shown in **Figure III.11** .

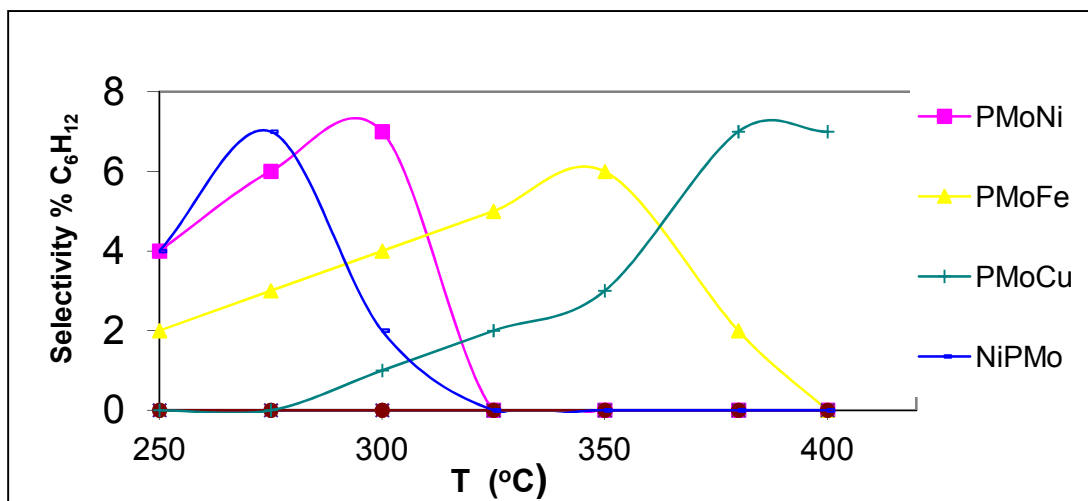


Figure III.11. Evolution of selectivity in cyclohexane according to the reaction temperature, total flow ($H_2 + n\text{-hexane}$) = 0.1 l / h.

C- Formation of cyclohexene

Selectivity in cyclohexene passes through a maximum near 300 °C to 350 ° C on the catalysts NiPMo₁₂, PMo₁₁Ni, PMo₁₁Mn, PMo₁₁Fe. This temperature corresponds to the departure of ammonia, which generates a strong Brönsted acidity ^[10] which promotes the formation of benzene at the expense of cyclohexene. While selectivity on PMo₁₁Co catalyst decrease by increase temperature. (**Figure III .12**).

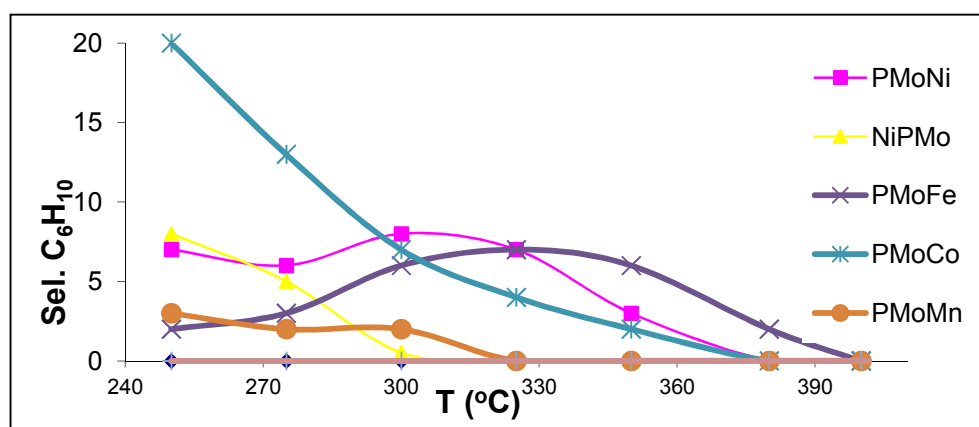


Figure III.12 : Evolution of selectivity in cyclohexene according to the reaction temperature, total flow ($H_2 + n\text{-hexane}$) = 0.1 l / h

D- Cyclohexadiene

Cyclohexadiene appeared only when use PMo_{11}Ni , PMo_{11}Cu , KFeW catalysts and it is selectivity decreased by increasing the temperature

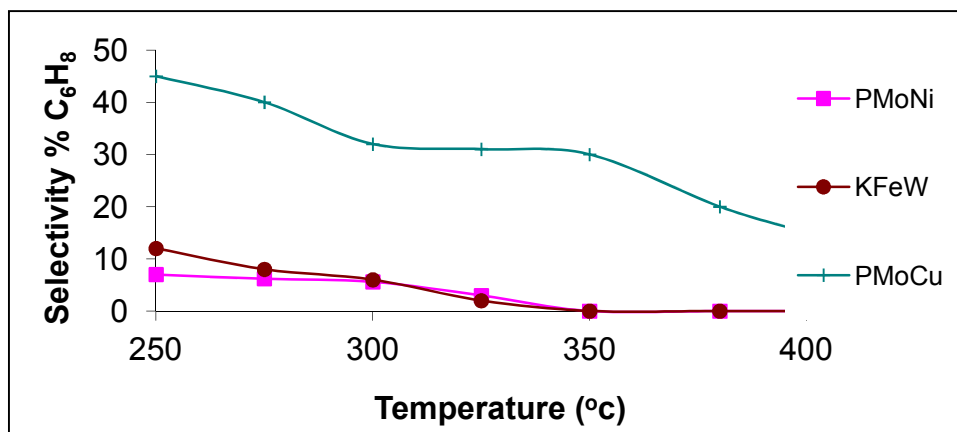


Figure III.13. Evolution of selectivity in cyclohexadiene according to the reaction temperature, total flow (H_2 + n-hexane) = 0.1 l / h

Methane was obtained with all catalysts at temperature above 300 °C. Methane production selectivity increased with temperature at the expense of benzene. At 400 °C n-hexane was converted completely to methane with all catalysts. The high methane selectivity was with PMo_{11}Mn catalysts.

At 400°C the $\text{H}_3\text{PMo}_{12}$ heteropolyacid was decomposed into MoO_3 and P_2O_5 . This result agrees with literature ^[11] which showed that the isomerization of n-hexane was due to surface Bronsted acid sites.

III.3 n-Hexane Reaction using N_2 as Carrier Gas

The type of carrier gas affected both conversion and selectivity of the reaction. The overall conversion increased by using H_2 as a carrier gas, while benzene selectivity increased when using N_2 as a carrier gas. This applied to all catalytic systems, as shown in **Tables (III.1-III.2)**. Comparison between the Tables shows that for each catalyst system, using H_2 gas gives higher conversion than using N_2 . On the other hand, the Tables show using N_2 gave higher benzene selectivity than using H_2 , for each catalyst.

The effect of temperature on efficiency and benzene selectivity using N_2 as carrier gas has been studied for different catalysts. **Figure III.14** shows how conversion varies with reaction temperature. The temperature curves exhibit linear character. For different catalysts, overall hexane conversion increased with temperature. The transformation of n-hexane on the tested catalysts started only above 250 °C with low conversion (1% - 5%) and the conversion increase by temperature for all catalysts and reached up to 60% at 350 °C and 100% at 400 °C for $PMo_{11}Mn$, $PMo_{11}Co$, $PMo_{11}Ni$, PMo_{12} .

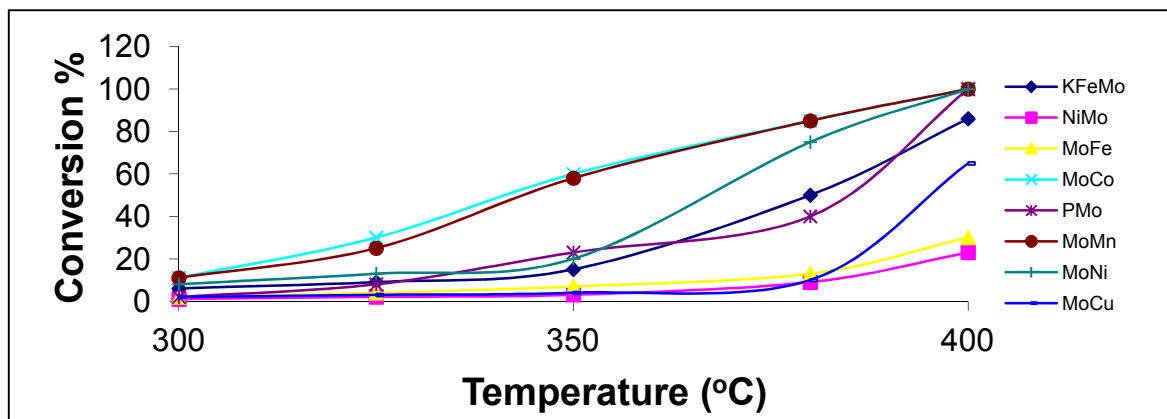


Figure III.14 Conversion of n-hexane as function of temperature,(using N_2 as carrier gas).

At low temperature (250 °C – 300 °C) benzene is the unique product by using most of the catalysts , by increasing the temperature benzene selectivity decreased until reached 0% for most of the catalysts, in the other hand , benzene is the only product at all temperatures in the range (250 °C – 400 °C) when using PW_{11} catalyst in the reaction, as shown in **Figure III.15** .

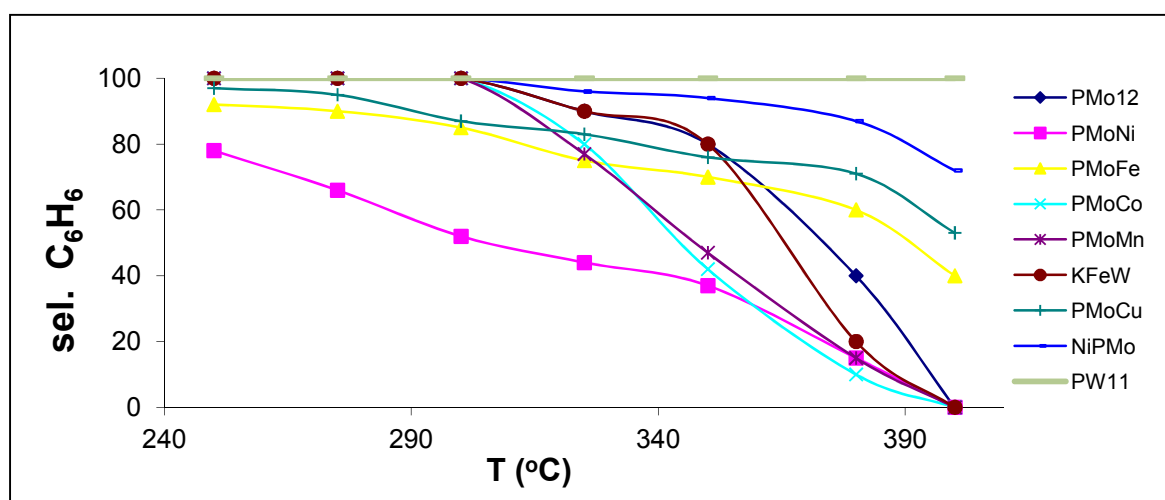


Figure III.15. Evolution of selectivity in benzene according to the reaction temperature, total low $(N_2 + n\text{-hexane}) = 0.1 \text{ l/h}$

Figure III.16 shows the relation between the conversion of n-hexane and the selectivity of different products, selectivity of methane increased by increasing the conversion and reached 100% at 100% conversion of n-hexane .selectivity of benzene decreased by increasing the conversion and reached 0% at 100% of n-hexane conversion , while the selectivity of cyclohexane, cyclohexene and cyclohexadiene increased by increasing the conversion until 15% - 20% , then decreased by increasing the conversion until the selectivity reached 0% at 100% of n-hexane conversion .

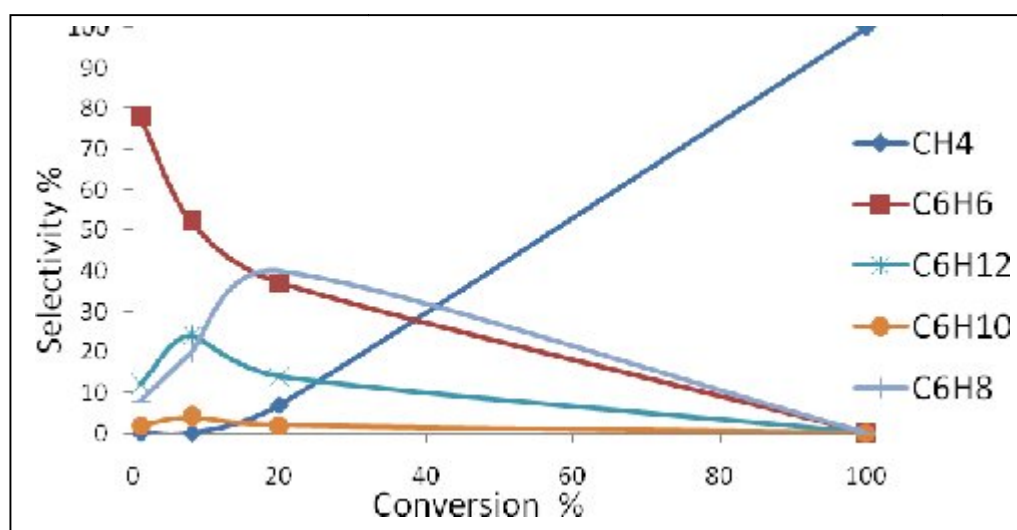


Figure III.16. Selectivity of products as function of conversion (using N_2 as carrier gas , $PMo_{11}Ni$).

Table III. 2 : Catalytic performances of Studied heteropoly acids (carrier gas N_2 ,flow rate : 0.1 L/h)

Catalyst	T °C	Conversion %	Selectivity				
			CH ₄	C ₆ H ₆	C ₆ H ₁₂	C ₆ H ₁₀	C ₆ H ₈
H ₃ PMo ₁₂ O ₄₀	300	2	0	100			
	350	23	20	80			
	380	100	60	40			
H ₄ PMo ₁₁ VO ₄₀	300	2	0	100			
	350	10	21	79			
	380	15	30	70			
	400	25	35	65			
H(NH ₄) ₄ PMo ₁₁ CoO ₃₉	250	4	0	100			
	300	11	0	100			
	350	60	58	42			
	400	100	100	0			
H(NH ₄) ₄ PMo ₁₁ MnO ₃₉	250	3	100	0			
	300	11	0	100			
	350	58	53	47			
	400	100	100	0			
H(NH ₄) ₄ PMo ₁₁ NiO ₃₉	250	2					100
	300	5		52		24	24
	350	9		37		14	49
	400	100	100				

(NH ₄) _{2.5} Fe _{0.1} PMo ₁₂ O ₄₀	300	6	0	100		
	350	15	20	80		
	380	50	80	20		
	400	86	100	0		
(TBA) ₇ PW ₁₁ O ₃₉	300	3	0	100		
	350	57	0	100		
	400	67	0	100		
KFe _{0.1} PW ₁₂ O ₄₀	300	6	0	100		
	350	15	20	80		
	380	50	80	20		
	400	86	100	0		
H(NH ₄) ₄ PMo ₁₁ CuO ₃₉	300	2	10	87		3
	350	4	20	76		6
	380	10	25	71		4
	400	65	47	53		
(NH ₄) _{3-x} Ni _x PMo ₁₂ O ₄₀	300	1	0	100	0	
	350	3	6	94		
	380	9	13	84	2	
	400	23	19	72	6	
H(NH ₄) ₄ SiMo ₁₁ FeO ₃₉	300	2	15	85	8	3
	350	7	19	70	10	4
	380	13	26	60		
	400	30	40	40	12	8

III.4 Activation Energy

Reaction rates (r) were calculated from the following equation:

$$r(\text{mol.h}^{-1}\text{g}^{-1}) = F/22.4 \times 273/T \times p/760 \times 1/m \quad (1)$$

where F is the flow rate of the vector gas (l/h), T the reaction temperature (K), p the partial pressure of the products (torr) and m the mass of the catalyst (g).

The activation energy (Ea) was obtained from the Arrhenius plot according to:

$$r = k^{\circ} \times \exp(-E_a/RT) \quad (2)$$

where R is the perfect gas constant and k° the pre-exponential factor..

n-hexane conversion rate were determined over the temperature range 200 °C - 400 °C for different catalysts. From (Figures III.17- III.22),

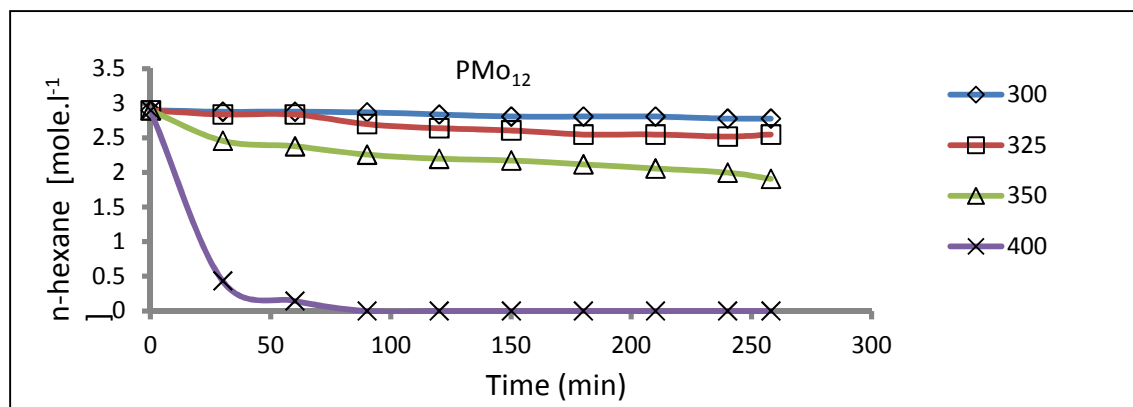


Figure III.17. n-hexane conversion as a function of time for PMo₁₂ catalyst .

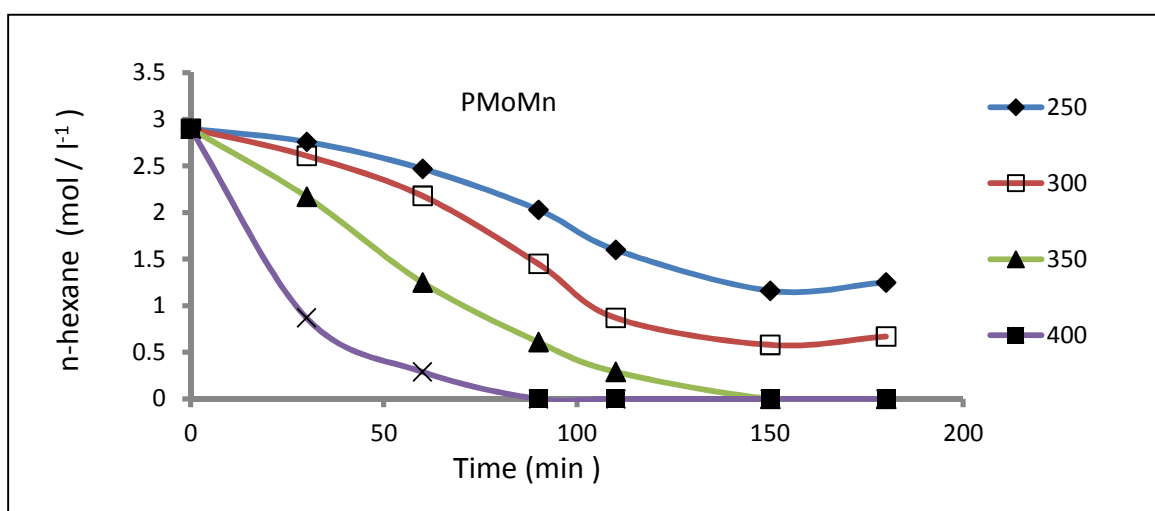


Figure III.18. n-hexane conversion as a function of time for PMo₁₁Mn catalyst .

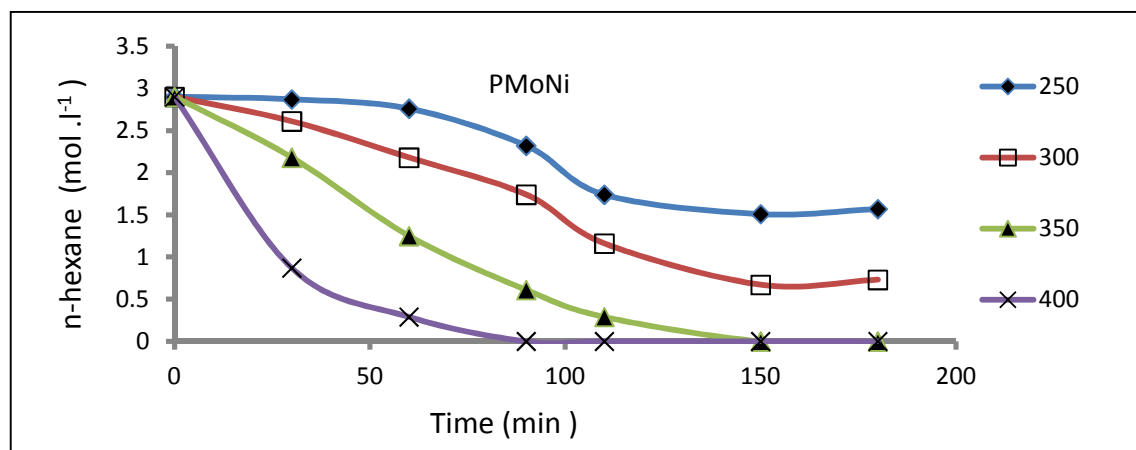


Figure III.19. n-hexane conversion as a function of time for PMo₁₁Ni catalyst .

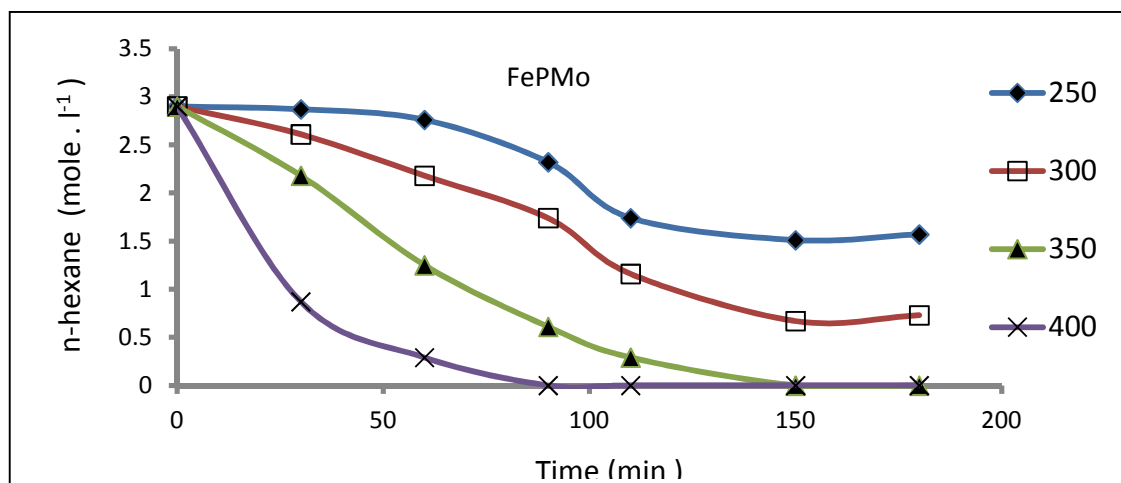


Figure III.20. n-hexane conversion as a function of time for PMo₁₁Ni catalyst .

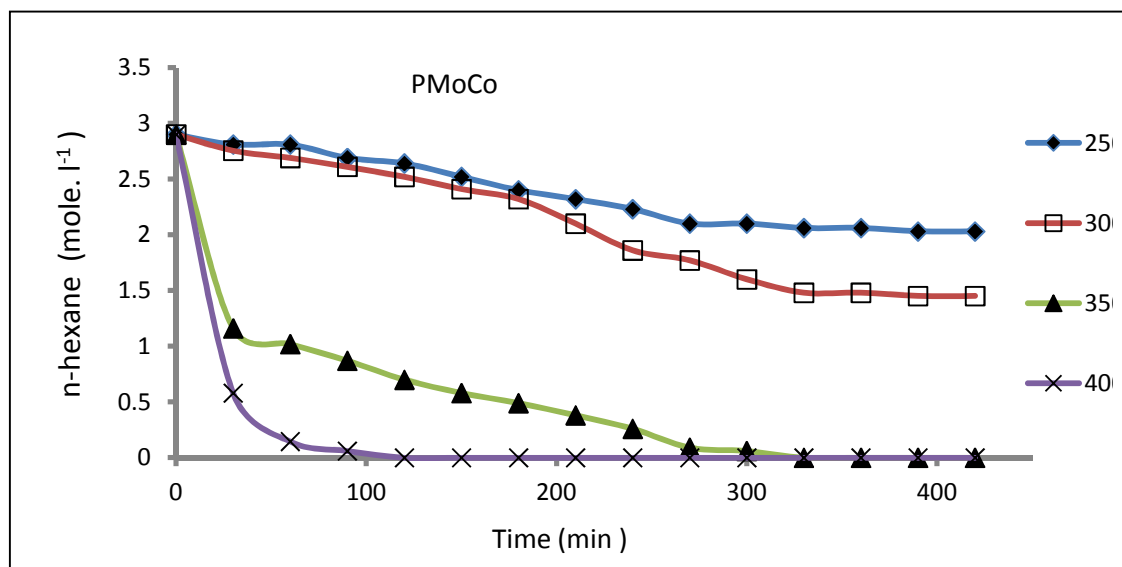


Figure III.21. n-hexane conversion as a function of time for FePMo₁₂ catalyst .

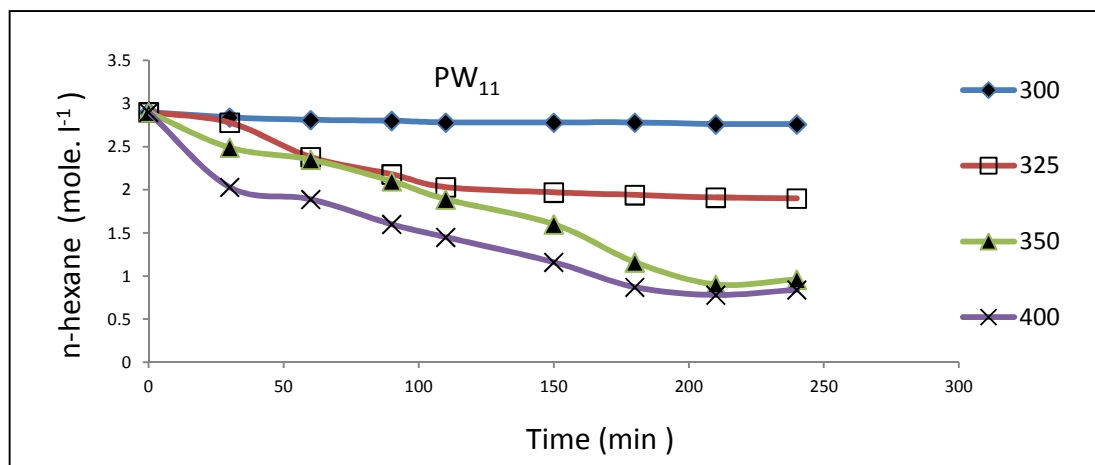


Figure III.22. n-hexane conversion as a function of time for PW₁₁ catalyst .

n-hexane dehydrocyclization rate constants were determined over the temperature range 200 °C – 450 °C. From Arrhenius plots (**Figure III.23**),

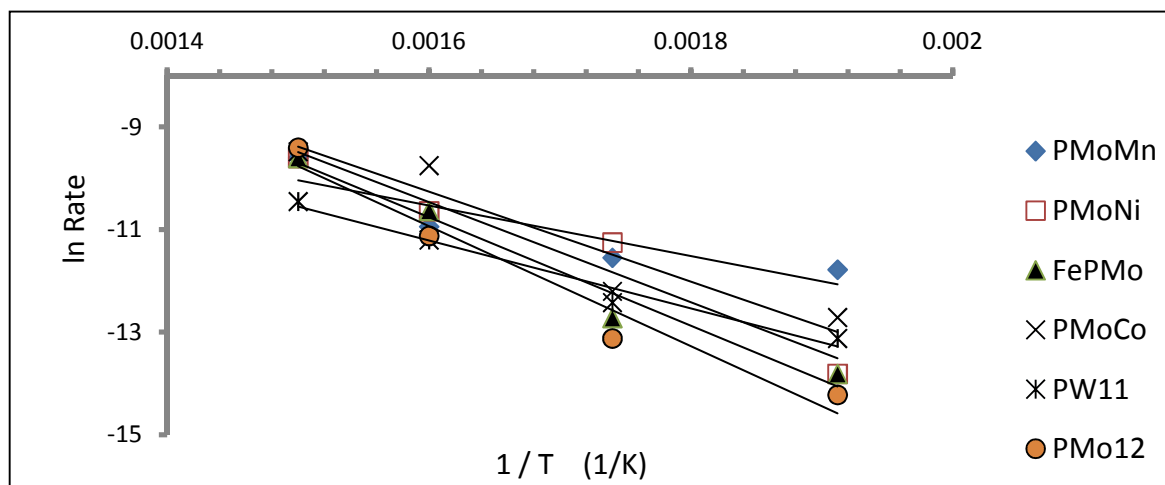


Figure III.23 : Arrhenius plots for different catalyst systems (using N₂ as carrier gas)

Activation energies for the transformation of n-hexane over acidic catalysts were calculated as shown in **Table III.3**.

Table III.3 : Reaction activation energy for different catalyst systems measured based on amount of n-hexane consumption.

No	Catalysts	<u>Ea (KJ/mol) : H₂</u>	Ea (KJ/mol) : N ₂
		0.1 l/h	0.1 l/h
1	H ₃ PMo ₁₂ O ₄₀	88.4	95.2
2	H(NH ₄) ₆ PMo ₁₁ NiO ₄₀	38	83.2
3	H(NH ₄) ₆ PMo ₁₁ CoO ₄₀	26.8	63.7
4	H(NH ₄) ₆ PMo ₁₁ MnO ₄₀	11.4	43
5	KFe _{0.1} PMo ₁₂ O ₄₀	35.1	83.2
6	(TBA) ₇ PW ₁₁ O ₃₉	45.3	52.7

Values of activation energies for the overall process of dehydrocyclization and aromatization of n-hexane using the acidic catalyst systems (11.4 to 95.2 kJ.mol⁻¹) are much lower than those known for metal type catalysts (typically 230 to 293 kJ.mol⁻¹) [12]. Acidic catalytic activity is expected to occur by the highly acidic heteropoly compounds. Actually the activation energies are comparable to those found for the transformation of the n-hexane in benzene using acidic catalysts. [13].

Furthermore the selectivity of the benzene decreases, while the conversion increases, with higher temperatures or longer retention times. In case of all catalysts, the benzene is the secondary product of the reaction.

These results show that all the catalysts convert the n-hexane with the same mechanism.

III .5 Mechanisms of transformation of n-hexane on heteropolyoxometallates

On a bifunctional catalyst metal-acid reaction the three modes (acid, metallic or bifunctional) can coexist. These reaction modes give apparent activation energies very different [14]. The selectivities and the nature of the reaction products also depend on the reaction mode. Thus conversion of n-hexane [15]:

- if the mechanism is monofunctional metal, we observe the formation of methylcyclopentane as intermediary between the n-hexane and methylpentane.
- if the mechanism is typically acid, n-hexane is transformed into giving the mixture of products, namely cyclohexane, cyclohexene, benzene.
- if the mechanism is bifunctional, the only primary products are the methylpentane.

Heteropolyanionic catalysts have two types of sites: sites with metal hydrogenation and dehydrogenation properties and acids sites whose function is isomerized and / or dehydrocycliser. In addition to participating in bifunctional catalysis, each of these types of sites may be an activity for conversion of alkanes. These catalysts do not work only by a bifunctional mechanism but also by an acid mechanism.

A plausible mechanism has been suggested to explain the observations discussed above. As shown in Scheme I, two possible products can be expected by the HPA catalyst systems. The Scheme shows that with excess H_2 (carrier gas, as discussed above) the carbonium ion formed by super-acid activation of hexane will be cracked into CH_4 [16]. Such a process involves complete saturation of all carbon atoms with hydrogen, via complete cracking of the hydrocarbon chain. On the other hand, in case of nitrogen carrier gas (with no hydrogen) dehydrocyclization process is favored to dominate, with no significant carbon chain cracking, as shown in the Scheme. The process is multi-stage involving β -H elimination in each step. This explains the production of cyclohexane, cyclohexene and cyclohexadiene as accompanying products to benzene.

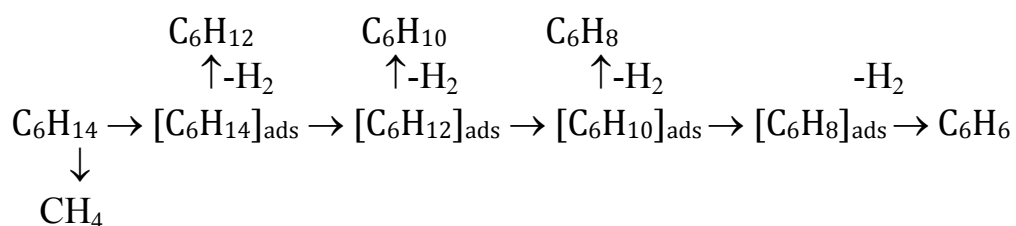
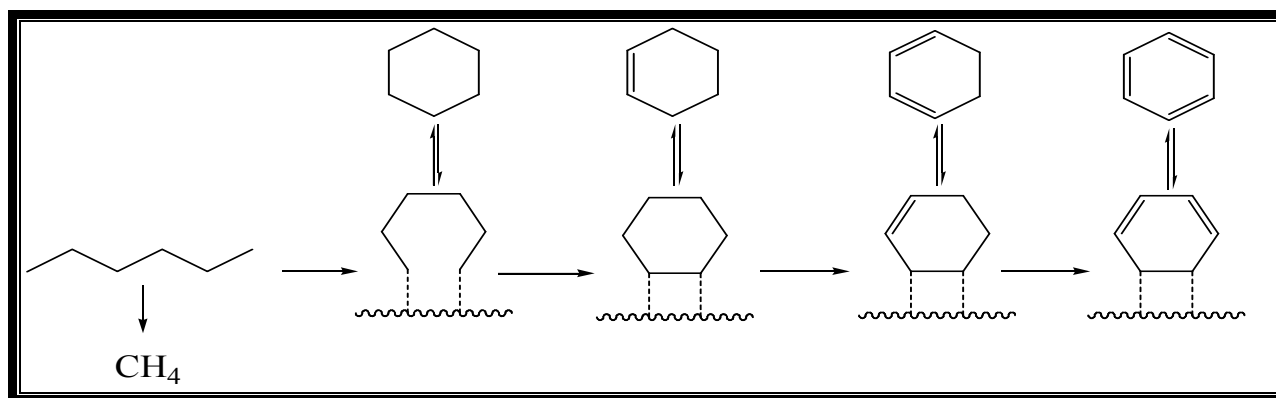


Figure III.11: Reaction Scheme of n-hexane dehydrocyclization over heteropolycompounds catalysts

It should also be noted that this logic does not fully work under higher temperatures, where CH_4 production dominates even in the absence of hydrogen gas. In such a case, high temperature experiments without hydrogen yielded high molecular weight aromatics and tars, in parallel to CH_4 formation, which caused some technical difficulties such as reactor blockage during experiments. Therefore, If benzene is the desired product from n-hexane, hydrogen gas should not be used, and the reaction must be conducted under mild temperatures (350 °C or lower) .

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GENERAL CONCLUSION

The aim of this thesis was to study the influence of structural and textural properties of the catalytic performance of polyoxomolybdates, polyoxotungstates catalysts in the dehydrocyclization reaction of n-hexane .

A number of heteropoly acids $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{11}\text{VO}_{40}$ and heteropoly salts $(\text{NH}_4)_4\text{HPMo}_{11}\text{CoO}_{39}$, $(\text{NH}_4)_4\text{HPMo}_{11}\text{NiO}_{39}$, $(\text{NH}_4)_4\text{HPMo}_{11}\text{MnO}_{39}$, $(\text{NH}_4)_4\text{HPMo}_{11}\text{CuO}_{39}$, $(\text{NH}_4)_4\text{PMo}_{11}\text{FeO}_{39}$, $(\text{NH}_4)_{3-x}\text{Ni}_x\text{PMo}_{12}\text{O}_{40}$, $(\text{NH}_4)_{2.5}\text{Fe}_{0.1}\text{PMo}_{12}\text{O}_{40}$, $\text{KFePMo}_{12}\text{O}_{40}$, $(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$ have been prepared using different methods and characterized by UV, IR, ^{31}P NMR , XRD, TGA, SEM, and Voltamperometer .

UV, IR, X-ray analysis showed that the compounds were of Keggin type structure. The X-ray diffraction showed that the studied heteropoly acids, crystallize in a triclinic structure. While the studied heteropoly salts crystallize in a monoclinic structure .

Thermal analyses (TGA and DTA) showed that the heteropoly acids are stable until $350\text{--}400^\circ\text{C}$, where the heteropoly salts are stable until $400\text{--}450^\circ\text{C}$.

IR spectra after testing showed that heteropoly compounds were begin decomposing into oxide mixture at $(400\text{--}450^\circ\text{C})$.

Due to their superacidic nature, the heteropoly compounds showed catalytic efficiency in the dehydrocyclization of n-hexane. The product distribution (benzene, cyclohexane, cyclohexene, cyclohexadiene and methane) strongly depends on :

- the nature of the catalyst, in general, heteropoly salts showed more activity than heteropoly acids, The conversion of the solid catalyst was sensitive to the nature of the coordination ion (Mo^{6+} , W^{6+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Cu^{2+} , Fe^{3+}) and counter ion (H_3O^+ , NH_4^+ , Fe^{3+} , Ni^{2+}). The replacement of mobile M (Ni^{2+} , Co^{2+} , Mn^{2+} , Cu^{2+} , Fe^{3+}) ions in the HPA framework increased the activity of the catalyst.

- the type of carrier gas, the type of carrier gas affected both conversion and selectivity of the reaction. The overall conversion increased by using H_2 as a carrier gas, while benzene selectivity increased when using N_2 as a carrier gas. This applied to all catalytic systems .
- the reaction temperature. The overall conversion of n-hexane increased by increasing the reaction temperature, over all tested catalysts ,

Benzene was the unique or major product at low temperature (250 – 300) and it's selectivity decreased by increasing the temperature, at high temperature (380 - 400) n-hexane was completely converted to methane .

The observed differences in the behaviour of the studied catalysts should be firstly ascribed to the superacidic nature of the catalysts, which can activate saturated alkanes.

Appendix

Technical Study and Characterization

I- Characterization Techniques

I.1- Solid Characterization

I.1 .1- Characterization by infrared spectroscopy:

Our samples were analyzed by infrared spectroscopy using a spectrometer of Fourier transform-type FTIR-8400 - SHIMADZU and Bio Rad Win - IR FTS 165 between 4000 and 250 cm⁻¹. The digital resolution of 4 cm⁻¹. The samples analyzed were ground in KBr and pelletized

I.1.2 Analysis by X-ray diffraction (XRD):

Crystallographic analysis of the various samples was performed using reflection diffractometer D8 ADVANCE-- SIMENS whose role is to irradiate the sample in powder form placed on the flat surface of a sample holder.

The operating mechanism comprises

- * A generator operating at 40 kw, feeds a copper anticathode producing X-ray
- * A monochromator located before the sample Cu K α radiation selects strictly monochromatic with $\lambda = 1.506$. Å. The sample plane is at the center of a goniometer.

The diffractometer is associated with a whole computer. The atoms of the material undergo reflection, which does not occur as in a mirror. Only certain values of λ (wavelength of X-rays) are known and are related to the plan and the distance by reticular Bragg relationship :

$$\lambda = 2 d \sin\theta \quad \text{where}$$

λ : wavelength of X-ray

θ : diffraction angle

d: distance between two atoms

I.1.3 Characterization by ^{31}P NMR Spectroscopy

The ^{31}P NMR analysis of solid phase samples was performed on a spectrometer Avance DSX 400 Bruker, using a sample holder (rotor) 4mm diameter and a speed of 6000 rev / sec. $\text{Al}(\text{PO}_3)_3$ is used as reference.

I.1.4 Thermal Analysis

Differential thermal analysis and thermogravimetric analysis measures were performed on a TA instrument SDT Q 600. The sample (approximately 15 mg) was placed in a drilled platinum, a platinum crucible second vacuum as a reference. The system was placed under an argon (100 mL / min). The sample was heated up to 650 ° C with a heating rate of 10 °C / min.

I.1.5 Characterization of residues by IFTR after thermogravimetric analysis

To monitor the thermal behavior of solids, they were treated in air at different temperatures (150, 250, 350 and 450 ° C) on a mass of 0.2 g of catalyst introduced in a tubular reactor placed in Pyrex glass cylindrical furnace with a thermocouple. Then the catalysts samples analyzed as in I.1.1 .

I.1.6 Characterization by scanning electron microscopy (SEM)

The SEM analysis of the samples was performed using an environmental scanning electron microscope ESEM XL 30 type digital (Figure Appendix) Philips brand with tungsten filament.

The principle of the analysis sample is bombarded by electrons causing several phenomena. Five of them are put to use in a current SEM: A. The sample itself emits secondary electrons. B. Part of the primary electrons is reflected (backscatter). C. The electrons are absorbed by the sample. D. The sample emits X-rays E. The sample emits sometimes photons (light). All these phenomena are interconnected and all dependent, to some extent, topography and atomic number of the chemical state of the sample. The amount of secondary backscattered electrons, at each point of the sample depends on the topography of the sample,

I.2 Characterization in solution

I.2.1 Analysis by UV-Visible spectroscopy

The analysis of our samples by UV-Visible spectroscopy was performed using a spectrophotometer UV-1601PC SHIMADZU on dilute solutions (10^{-5} to 10^{-3} M) as a solvent with a mixture acetonitrile / water in the ratio 1:1. This method is based on the interaction of electromagnetic radiation with energy between 555-35 Kcal with our sample. This radiation can cause transitions of the less bound electrons of atoms. The passage of a UV-Vis through a substance makes it possible to obtain a spectrum of absorption mail: residual intensity depending on the wavelength. The absorption is expressed by the law of Beer-Lambert:

$$I = I_0 10^{-\epsilon c l}$$

with:

ϵ : molar extinction coefficient.

l : thickness of the substance in solution.

c : concentration in mol / l.

I.2.2 Electrochemical Analysis

The voltamperometric is a technique for studying the properties of oxido-reducing heteropolyanions. In the Keggin structure, the $\text{Mo}^{\text{VI}} / \text{Mo}^{\text{V}}$ is a reversible system. The voltamperometric analysis of our solid was performed on a Potentiostat / Galvanostat model 273a. using a conventional three electrodes.

The measuring electrode is a rotating disk electrode of glassy carbon having undergone a mechanical polishing. The potentials are identified in relation to a reference saturated calomel electrode (SCE). Against electrode is a platinum wire. The recording of intensity-potential curves is carried out on diluted solutions (10^{-3} M) in a hydroorganic: acetonitrile / water (ratio 1 / 1 by volume) to avoid decomposition of the polyanion

II n-Hexane Isomerization Catalytic Test :

The catalytic test of the different solids investigated was carried out using an experimental design at the Laboratory of Applied Chemistry and Chemical Engineering (LCAGC). The general pattern of the circuit is presented in **figure II.1**. The dehydrocyclization reaction of n-hexane on heteropolyanions was carried out in a U-shaped reactor made of stainless steel with a powder. A mass of about 0.5 g of powder catalyst placed in the reactor and heated to the reaction temperature (250 - 450° C). The reactor is placed vertically inside a cylindrical furnace directly connected to a temperature regulator reader that allows to know the temperature inside the oven. The flow of the reaction mixture (n-hexane , H₂) is 0.1 l / h. The remaining reactive products formed are analyzed using a chromatograph of GC-14 B brand SHIMADZU (FID, TCD). The chromatograms were recorded with an integrator C-R8 A. SHIMADZU Chromatopac brand.

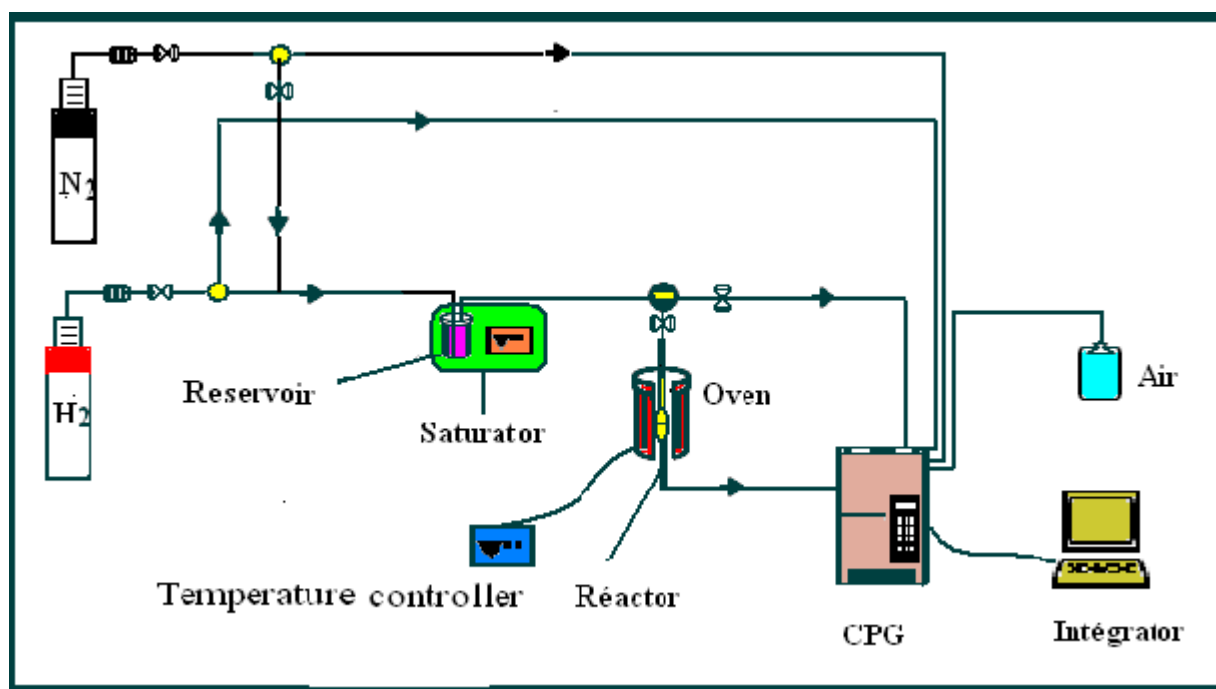


Figure II.1: Experimental mounting test used in the catalytic reaction of dehydrocyclization of n-hexane

Table II.1 shows the products detected with retention time. The chromatograms of reactants and products of the reaction of partial oxidation of methane are reported in Figure II.2.

II.4 Experimental Procedure

After connecting the experimental equipment, the reaction mixture with a total flow rate of 0.1 l / h was introduced in the system. The exit of compound from the reactor were separated and analyzed by gas chromatography (FID). The conditions of analysis are:

Stationary phase: Porapak Q 80/100.

Column: stainless steel Length: 6m.

Diameter: 2mm.

Injector temperature: 180 ° C

Detector temperature: 180 ° C

Column temperature: 70 ° C

Flow of reaction mixture: 0.1 l / h

Flow of carrier gas (N₂): 0.1 l / h.

Table II.1: Retention time of n-hexane dehydrocyclization products in FID Chromatogram

Compound	n-Hexane	CH ₄	C ₆ H ₁₄	C ₆ H ₁₂	C ₆ H ₈	C ₆ H ₆
t _R (min)	0.83	0.28	0.34	0.48	0.64	1.14

II. 5 Chromatographic Calibration

The identification of reaction products was established by comparing the retention times obtained after the analysis of pure products directly injected into the column.

II.5.1 Calculation of response factors K_f :

The response factor of a compound "i" is by definition the response of the chromatograph in respect of this compound. This coefficient was determined experimentally by injecting standards (reagents and products). It is defined by:

$$K_f = (X_i / S_i) * 10^6$$

With:

X_i : % of the compound "i" in the standard mixture.

S_i : surface peak of the compound "i" given by the integrator.

II.5.2 Determination of response factors of products of the reaction of dehydrocyclization of n-hexane .

Calibration of methane has been achieved by direct injection of the bottle. To analyse the reaction products the same conditions of analysis used for the reagent still used .

Table II. 2: response factor Kf (i) of methane and reaction products of dehydrocyclization of n-hexane .

Composed	n-Hexane	Methane	C ₆ H ₁₂	C ₆ H ₁₀	C ₆ H ₈	C ₆ H ₆
Kf (i)	1.94	1.7	3,5	3.3	3.7	1.8

II. 6 Calculation Methods :

To evaluate the results of catalytic tests, we used the following definitions:

II.6.1 conversion rate:

The conversion rate or rate of global transformation TTG noted is defined by the ratio between the number of moles of converted reactant and the number of moles of introduced reagent into the engine.

$$\text{TTG (\%)} = \frac{\text{Number of moles of n-hexane transformed}}{\text{Number of moles of n-hexane introduced}} \times 100$$

II.6.2 rate processing product "i":

The rate of conversion into compound "i" (denoted TTI) is the ratio between the number of moles of converted reactant to compound "i" and the number of moles of introduced reagent.

$$\text{TTG (\%)} = \frac{\text{Number of moles of product i formed}}{\text{Number of moles of n-hexane introduced}} \times 100$$

II.6.3 Selectivity:

The selectivity of a catalyst, for a product "i" is defined as the ratio between the number of moles of converted reactant to compound "i" and the number of moles of reactant converted to products.

$$S_i (\%) = \frac{TT_i}{TTG} \times 100$$

Abstract

The catalytic dehydrocyclization of n-hexane was studied here for the first time using a number of compounds based on $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. The described catalysts were prepared by either replacing the acidic proton by with counter-ions such as ammonium or transition metal cations (NH_4^+ , Fe^{3+} , Ni^{2+} , K^+), or by replacing Mo^{6+} with (Ni^{2+} , Cu^{2+} , Fe^{3+} , Co^{2+} , Mn^{2+}) in the polyoxometalate framework, as reported earlier. For comparison purposes, the known $(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$ catalyst system was used. All reactions were conducted at different temperatures in the range 200-450°C.

The Keggin structure of these heteropolycompounds was ascertained by XRD, UV, SEM and IR measurements. ^{31}P NMR measurements, Electrochemical measurements and thermal behaviour of the prepared catalysts were also studied. These modified polyoxometalates exhibited heterogeneous super-acidic catalytic activities in dehydrocyclization of n-hexane into benzene, cyclohexane, cyclohexene and cyclohexadiene. The catalysts obtained by substituting the acidic proton or coordination atom exhibited higher selectivity and stability than the parent compound $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. Catalytic activity and selectivity were heavily dependent on the composition of the catalyst and on the reaction conditions. At higher temperatures, the catalyst exhibited higher conversion efficiency at the expense of selectivity. Using higher temperatures (>400°C) in the presence of hydrogen carrier gas, selectivity towards dehydrocyclization ceased and methane dominated. To explain the results, a plausible mechanism is presented, based on super-acidic nature of the catalyst systems.

Résumé

La déshydrocyclisation catalytique du n-hexane a été étudiée ici pour la première fois en utilisant un certain nombre de composés à base de $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. Les catalyseurs décrits ont été préparés soit par le remplacement du proton acide par des contre-ions tels que les cations de sels d'ammonium ou métaux de transition (NH_4^+ , Fe^{3+} , K^+), ou par substitution Mo^{6+} avec (Ni^{2+} , Co^{2+} , Mn^{2+}) dans le cadre polyoxométallate, comme signalé précédemment. Aux fins de comparaison, les plus connus $(\text{TBA})_7\text{PW}_{11}\text{O}_{39}$ système de catalyseur a été utilisé. Toutes les réactions ont été effectuées à différentes températures dans la gamme 200-450 ° C.

La structure de Keggin de ces hétéropolycomposés a été déterminée par diffraction des rayons X, UV et IR mesures. Mesures de RMN ^{31}P et le comportement thermique des catalyseurs préparés ont également été étudiés. Ces polyoxométallates jour présentaient hétérogènes super-acides activités catalytiques en déshydrocyclisation du n-hexane en benzène, cyclohexane, cyclohexène et le cyclohexadiène. Les catalyseurs obtenus par la substitution du proton acide ou un atome de coordination exposé plus haut que la sélectivité et la stabilité du composé mère $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ parent. L'activité catalytique et la sélectivité ont été fortement dépendante de la composition du catalyseur et des conditions réactionnelles. A des températures plus élevées, le catalyseur exposé efficacité de conversion plus élevé au détriment de la sélectivité. Utiliser des températures plus élevées (> 400 ° C) en présence d'un gaz porteur hydrogène, la sélectivité en méthane et de déshydrocyclisation cessé dominé. Pour expliquer ces résultats, un mécanisme plausible est présentée, basée sur les super-acides nature des systèmes catalytiques.

ملخص

لقد تم دراسة اثر الحفازات على تفاعل الهكسان لاعطاء مركبات حلقيه من خلال نزع الهيدروجين و ذلك باستخدام عدد من المركبات المشتقة من H_3PMo_{12}

لقد تم تحضير الحفازات المشروحة من خلال استبدال البروتون الحمضي بايونات مضادة مثل ايونات الامونيوم او ايونات الفلزات الانتقالية (NH_4^+ , Ni^{2+} , Fe^{3+} , K^+) ، او من خلال استبدال Mo^{6+} بـ (Ni^{2+} , Co^{2+} , Fe^{3+} , Cu^{2+} , Mn^{2+}) في مركبات عديد اكسجين الفلزات كما ذكرت سابقا . تم استخدام المركب المحضر سابقا $(TBA)_7PW_{11}O_{39}$ من اجل المقارنة. تم تنفيذ جميع التفاعلات عند درجات حرارة مختلفة ما بين 200 الى 450 درجة مئوية .

لقد تم التأكد من امتلاك الحفازات المحضرة لشكل كيجن من خلال استخدام تقنيات التحليل التالية : SEM ، DTA ، TGA ، ^{31}P NMR ، IR ، UV ، XRD

اظهرت الحفازات المحضرة فعالية عالية توازي فعالية الحموض القوية عند استخدامها في تفاعل الهكسان العادي لانتاج البنزين و السيكلوهكسان و السيكلوهكسين، و السيكلو هكساديين، و الميثان. كذلك اظهرت الحفازات التي تم استبدال البروتون الحمضي و ايون المولبدينيوم فيها بايونات الفلزات الانتقالية فعالية و ثباتية و انتقائية اعلى من الحفاز الذي حضرت منه $H_3PMo_{12}O_{40}$.

تعتمد فعالية الحفازات و انتقائيتها تجاه التفاعل على تركيب الحفاز و ظروف التفاعل عند درجات حرارة مرتفعة أظهرت الحفازات فعالية عالية في تفاعل الهكسان على حساب انتقائية التفاعل، و كذلك لوحظ عند درجات حرارة عالية (اعلى من 400 م) و بوجود الهيدروجين كغاز ناقل ان الميثان هو المركب الذي ينتج بشكل عام .

بالنسبة لانتقائية التفاعل تجاه إنتاج البنزين (المادة التي نرغب في انتاجها) لوحظ انها تكون عالية عند درجات حرارة منخفضة (قريب من 300 م) و تقل بزيادة درجة الحرارة . لتفسير النتائج السابقة تم اقتراح آلية تفاعل تعتمد على ان الحفازات المستخدمة تمتلك خواص الحموض القوية خلال تفاعلها مع الالكانات .