

IN THE NAME OF GOD



**Razi University
Faculty of Chemistry
Department of Inorganic Chemistry**

M.Sc. Thesis

Title of the Thesis:

Investigation of the activity of 12-tungstocobaltate supported on nano silica from rice husk, its potassium salt and cesium 12-tungstophosphoric acid as nano catalysts in the synthesis of β -keto enol ethers and some organic reactions

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This Thesis Dedicated to:

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Abstract

Polyoxometalates (POMs) are a class of well known molecularly defined, discrete and anionic metal-oxygen clusters of early transition metals in their highest oxidation states (most commonly V^V, Mo^{VI}, and W^{VI}). In the past decades, POMs have attracted considerable interest because of their widespread use in many fields including biological applications, magnetism, medicinal chemistry, materials science and catalysis. In recent years, the catalytic activity of POMs have been increasingly recognized, and their applications as an efficient catalyst in organic transformations are becoming a key topic.

Among the all of type of POMs Keggin type POMs in bulk and salts or supported forms have been extensively investigated because of their high structural stability, strong Brönsted acidity, exhibiting fast reversible multi electron redox transformations under mild conditions and etc.

In this study, catalytic activity of 12-tungstocobaltate supported on nano silica from rice husk and its potassium salt and also cesium 12-tungstophosphoric acid as nano catalysts have been investigated for some organic reactions like synthesis of β -keto enol ethers, synthesis of β -amino ketones via three component Mannich type reactions, Hantzsch Three Component Condensation, Synthesis of β -Enaminones, Biginelli Reaction, Synthesis of β -Acetamido Ketones and some other organic reactions.

In summary, the present methodologies offers several advantages such as catalyst recyclability, inexpensive catalyst, environmental friendly procedure, short reaction time, high yields and easy isolation.

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Abbreviations and Symbols

1,4-DHP	1,4-dihydropyridines
BET	Braunauer, Emmet and Teller
CAN	Cerium Ammonium Nitrate
CoW	$H_5CoW_{12}O_{40}$
CoW/NSiO ₂	Nano Silica Supported $H_5CoW_{12}O_{40}$
Cs ₁ PW	$Cs_1H_2PW_{12}O_{40}$
Cs ₂ PW	$Cs_2H_1PW_{12}O_{40}$
Cs _{2.5} PW	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
Cs ₃ PW	$Cs_3PW_{12}O_{40}$
Cs _x PW	$Cs_xH_{3-x}PW_{12}O_{40}$
DHPM	3,4-Dihydropyrimidin-2(1H)-one
DTA	Diffraction Thermal Analysis
FT-IR	Fourier-Transform Infrared
GeW	$H_4GeW_{12}O_{40}$
HPA	Heteropoly anion
HPC	Heteropoly Compound
IPA	Isopoly anion
K ₅ Co	$K_5CoW_{12}O_{40}$
NMR	Nuclear Magnetic Resonance
PA	Polyanion
PMo	$H_3PMo_{12}O_{40}$
POM	Polyoxometalate
PW	$H_3PW_{12}O_{40}$
RHA	Rice Husk Ash
SEM	Scanning Electron Microscopy
SiMo	$H_4SiMo_{12}O_{40}$
SiW	$H_4SiW_{12}O_{40}$
TEM	Transmission Electron Microscopy
TGA	Thermo Gravimetric Analysis
THF	Tetra Hydro Furane
TLC	Thin Layer Chromatography
XRD	X-Ray Diffraction

Chapter One

Introduction

1.1. Nanotechnology and Catalysis

In 1836 the famous Swedish chemist J.J. Berzelius introduced the concept of catalysis. In the Edinburgh New Philosophical Journal, he proclaimed: “I hence will name it the catalytic force of the substances, and I will name decomposition by this force catalysis. The catalytic force is reflected in the capacity that some substances have, by their mere presence and not by their own reactivity, to awaken activities that are slumbering in molecules at a given temperature” [1]. At the beginning of the 20th century, W. Ostwald presented the generally accepted definition of a catalyst as a species which increases the rate of a chemical reaction through the formation of intermediate compounds and which is restored at the end of the reaction. In 1909, Ostwald was awarded the Nobel Prize in Chemistry for his work on catalysis chemical equilibrium and reaction velocities [2].

Catalysis is perhaps one of the most important technologies available, since it plays a critical role in the development of efficient production methods for a wide range of materials, from fuels to polymers, and in the development of more effective and safer pharmaceuticals. Catalysis is the occurrence by which certain chemicals (catalysts) can promote a chemical reaction without undergoing any permanent chemical transformation themselves. Thus, theoretically, recovery of the catalyst is possible after the reaction is completed, enabling it to be recycled. Without the proper catalyst, many reactions proceed infinitely slowly or not at all. Moreover, because of its effects on the kinetics of the reaction, which can lead to different chemical entities, the chemical nature of the catalyst can have a decisive impact on the selection of reaction manifolds. Over the last few decades, there has been rapid progress in the understanding of the molecular events (micro-steps) leading to the final products in some of these reactions. Subsequently, there has been a striking effect on the number of new catalyst systems currently under development. Combinatorial methods have recently been introduced in the catalyst discovery process for rapid screening of potential homogeneous and heterogeneous catalysts [3].

Nowadays, nanotechnology has been widely used in chemical industries especially in nanocatalysis industries. The emergence of the term “nanotechnology” and its increasing use in the scientific and popular scientific literature reflects the expanding interest in the

ability to gain control over the organisation of material, in order to fabricate and exploit entities with dimensions of less than 100 nm. This fascinating field opens up many new exciting possibilities for example in materials science, biomolecular transport systems, bio-sensor technologies and nanocatalysis.

Nanocatalysis is a rapidly growing field which involves the use of nanomaterials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. Heterogeneous catalysis represents one of the oldest commercial practices of nanoscience; nanoparticles of zeolites [4], oxides [5], heteropoly acids [6,7], and other compounds have been widely used for important chemical reactions. A key objective of nanocatalysis research is to produce catalysts with 100% selectivity, extremely high activity, low energy consumption, and long lifetime. This can be achieved only by precisely controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nanocomponents.

Among various type of nanocatalysts, heteropoly acids (HPAs) are most attractive, because of their unique properties such as well defined structure, Brönsted acidity, possibility to modify their acid–base and redox properties by changing their chemical composition (substituted HPAs), ability to accept and release electrons, high proton mobility, etc [8-10]. Several new industrial processes based on HPAs catalysis have been developed and commercialized in the last two decades, which are considered to be the efficient measure to resolve the environment problems.

1.2. Polyoxometalate: Scope and Definitions

Polyoxometalates (POMs) are generally soluble metal-oxygen clusters composed of high atomic proportions of one kind of atom in a positive oxidation state (‘addenda atoms’) and much smaller proportion(s) of the other kind(s) of atom(s) in positive oxidation state(s) (‘heteroatom’) and normally oxygen (-2) atoms . The group of V and VI transition metal centers function as addenda atoms in high oxidation states (mainly Mo, W and V and also Nb and Ta). The atoms that can function as addenda are those that: 1) change their coordination with oxygen from 4 to 6 as they polymerize in solution upon acidification and 2) have high positive charges and are among the smaller atoms that fall within the radius range for octahedral packing with oxygen. The ability to act as addenda is greatly enhanced if the atoms are able to form double bonds with unshared oxygens, by pp-dp interaction. The heteroatom could be from the p-block elements (e.g. Al^{3+} , Si^{4+} , P^{5+} , Ge^{4+} ,

I⁷⁺, Se⁴⁺, Te²⁺, Bi²⁺ etc.), or transition metals, although some derivatives with S, F, and Br are known [11].

POMs are composed of MO_n units, where ‘n’ indicates the coordination number of M (n = 4, 5, 6 or 7). Usually, distorted octahedral coordination (n = 6) is observed. Apart from M and O, other elements (heteroatoms), which are usually labeled as ‘X’, can be part of the POM framework. As a general rule, they are tetra- or hexa- coordinate and they lie in the center of the M_xO_y shell.

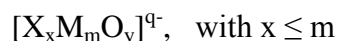
According to their chemical composition they can be classified in two groups:

- 1) The isopoly compounds (isopolyanions or isopolyoxometalates) contain only d⁰ metal cations and oxide anions.
- 2) The heteropoly compounds (called heteropolyanions, heteropolyoxometalates, or heteropolyacids, when contain in the structure H⁺, H₃O⁺, H₅O₂⁺) contain one or more p-, d- or f-block “heteroatom” in addition the other ions.

Isopolyanions (IPAs):



Heteropolyanions (HPAs):



Where ‘X’ is the heteroatom which located in the centre of the polyanion and ‘M’ is the metallic element which act as an addenda atoms. There is no restriction for the heteroatom ‘X’ and it can be either tetrahedrally coordinated (as in the Keggin and Wells-Dawson’s type polyanions) or octahedrally coordinated (as in Anderson-Evans type polyanions). Almost 70 elements from most groups of the Periodic Table (except noble gases) are known to be able to play this role [12,13].

The HPAs are environmentally benign solid catalysts, which offer several advantages in terms of catalytic performance, strong acidic, redox sites and selectivity to particular reaction products by selective stabilization of reaction intermediates [14,15]. These compounds by virtue of their strong acid sites and redox characteristics have been used as catalysts under homogeneous as well as heterogeneous conditions [14,15]. They are green catalysts that function in a variety of reaction fields and are efficient harmless to the environment with respect to corrosiveness, safety, quantity of waste and separability [16]. Furthermore they are inorganic polymer complexes with oxygen bridge, which can form donor-acceptor complexes with various kinds of electron donors as electron acceptors.

1.3. Historical Conspectus

In 1826, Berzelius [17] first observed a ‘yellow precipitate’ after mixing ammonium molybdate and ortho-phosphoric acid. This yellow precipitate was originally formulated as

$3(\text{NH}_4)_2\text{O}\cdot\text{P}_2\text{O}_5\cdot 24\text{MoO}_3$.aq which now we call ammonium 12-molybdophosphate, the first synthetic heteropoly salt or POM isolated. In 1854, Struve [18] reported polymolybdates based on some metal heteroatoms, including 6-molybdates of Al^{3+} , Cr^{3+} and Cu^{2+} . The study of polyoxoanion chemistry was accelerated by Marignac [19] in 1862, when two isomeric forms of a silicotungstate $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ were identified by analytical techniques. After that, the field developed rapidly, so that over 700 heteropoly compounds were reported by the first decade of the twentieth century and analyzed by several scientists.

Among the most active were P. Chretien, H. Copaux, W. Gibbs, R. D. Hall, A. Rosenheim, E. F. Smith and H. Struve. In 1929, Linus Pauling [20] made a major breakthrough in the structural chemistry of HPAs. Pauling proposed a structure of 12:1 heteropoly complexes based on the arrangements of central tetrahedron hetero atoms XO_4 surrounded by twelve addenda MO_6 corners sharing octahedral and their isomers; and also structures of 9-heteropoly and a structure of 18:2 heteropoly complexes based on eighteen MO_6 octahedral surrounding, two central XO_4 tetrahedron. It was Keggin [21,22] who in 1933 solved the structure of the most important of the 12:1 type of HPAs, $[\text{H}_3\text{PW}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$, by powder X-ray diffraction. This structure involves four 3-fold W_3O_{13} groups, and each WO_6 octahedron shares two edges with other WO_6 groups; and the four W_3O_{13} groups are attached to one another by corner sharing, which partially confirmed the Pauling proposal. In 1948, Evans [23] determined the structure of another type Anderson's HPA (6:1) by single-crystal X-ray analysis of $[\text{TeMo}_6\text{O}_{24}]^{6-}$ salts. This structure is often referred to as the Anderson-Evans structure. In 1953, Dawson [24] reported the structure of a 18:2 HPA, $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$. The use of X-ray crystallography was the turning point for the determination of structure in POM chemistry and in the past fifty years, hundreds of structures have been reported.

1.4. Structural Characteristic

There are several reports, [25] books [26] and reviews [27,28] published on POMs, showing an enormous molecular diversity in this inorganic family of molecules. Many authors state that POMs can be regarded as packed arrays of pyramidal MO_5 and octahedral MO_6 units. These entities are analogous to the $-\text{CH}_2-$ building block in organic chemistry.

All POM clusters included in this classification contain MO_n units and the frameworks are built with the MO_6 unit. The MO_6 units are then packed to form different shapes but there are some rules to connect the each unit. The molecule as a whole is built

by edge- and/or corner-sharing MO_6 octahedral (Fig. 1.1). The most stable unions between two octahedral are the corner- and edge-sharing models, in which the M^{n+} ions are far enough from each other, and their mutual repulsion is modest. In case C of Fig. 1.1, the metallic centers are closer than A and B.

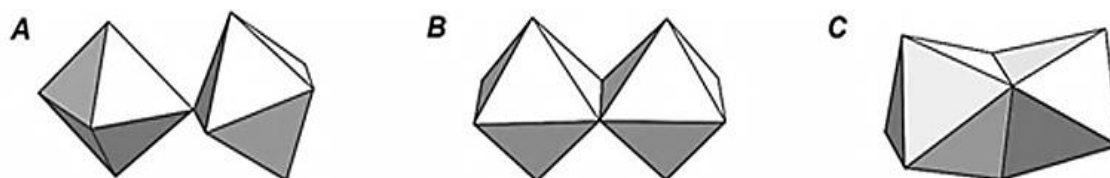


Fig. 1.1. The polyhedral models represent the three possible unions between two MO_6 octahedral units. A) corner-sharing, B) edge-sharing and C) face-sharing. Each corner represents an oxygen position.

The polyanion structures are governed by electrostatic and ionic radius (charge/radius) of the metal centers and the addendum atom should have the ability to form metal-oxygen π -bonds [29].

1.4.1. Isopoly Anions

Traditionally, IPAs are polyanions containing only transition metals. Main group elements may appear but they are considered as ligands only, not as a part of the framework.

Many IPAs are known today and the number of published structures increases rapidly with synthesis in nonaqueous solvents and with the use of ligands other than oxo ligands. IPAs may be based upon various metallic frameworks with a number of metal centers varying from 2 up to over 150. Involved metals are vanadium, niobium, tantalum, molybdenum, tungsten, and more seldomly some others.

There are mixed species involving several types of metal atoms. It is also possible to have polyoxometalates in which other ligands having incorporated, for instance thio, or nitrosyl, or various organic moieties, all of them replacing oxo ligand(s) of a parent structure. Finally mixed species in which the same metal species occurs under various oxidation states are known [30].

1.4.2. Heteropoly Anions

HPAs are those polyanions and their derivatives made of an assembly of fused MO_6 octahedrons more or less completely wrapped around a tetrahedron containing traditionally a main group element, more seldomly a transition metal [30].

1.4.2.1. Keggin Structure

As mentioned previously, Berzelius is credited for the discovery and documentation of the first fully recognized POM; $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]$. However structure resolution is credited to Keggin, thus HPAs of the $[\text{XM}_{12}\text{O}_{40}]^{n-}$ type are often described as a ‘Keggin type’ (Fig. 1.2) [31]. Keggin HPAs, with general formula $\text{X}^{n+}\text{M}_{12}\text{O}_{40}^{n-8}$ where “X” is the central atom (Si^{4+} , Ge^{4+} , P^{5+} , As^{5+} , Co^{3+} , etc.), “n” the degree of its oxidation, and “M” is molybdenum, tungsten or vanadium which can be partly replaced by other metals [32].

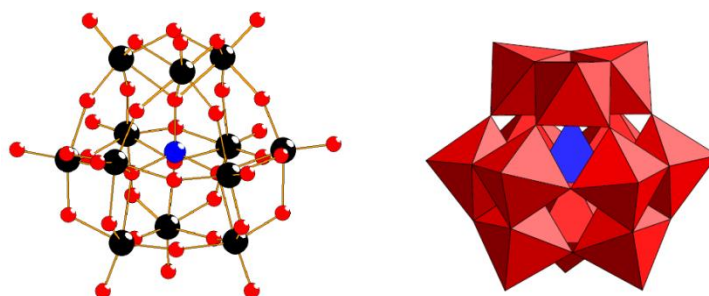


Fig. 1.2. Keggin $\alpha\text{-XM}_{12}\text{O}_{40}^{n-}$.

Keggin POMs overall exhibit virtual tetrahedral (T_d) symmetry, with a central XO_4 tetrahedral unit surrounded by 12 MoO_6 octahedral units which are arranged into four groups of three edge sharing Mo_3O_{13} units. Each of the four Mo_3O_{13} groups are linked to the central PO_4 unit and to each other by their corresponding edges [33].

1.4.2.1.1. Primary, Secondary and Tertiary Structures

It should be noted that the hierarchical structure of solid HPAs was important for the understanding of the heterogeneous HPA catalysis, and we denoted the substructures as primary, secondary and tertiary [34]. This may appear a very simple idea, but enormously helped the progress of our research.

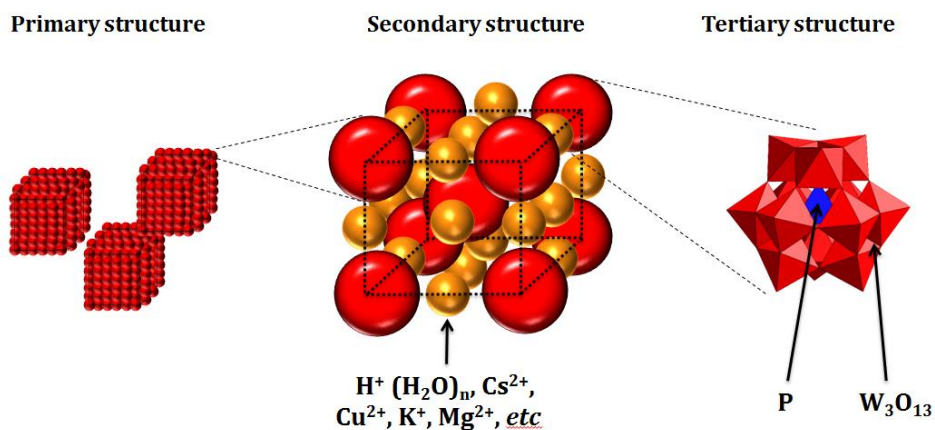


Fig. 1.3. Primary, secondary and tertiary structures; hierarchical structure of heteropoly compounds (HPCs) in the solid state.