GENERAL INTRODUCTION

In 21st century, the key challenge of modern chemistry is to achieve 100% selectivity in the desired product in multipath reactions (designated as "green chemistry") and to develop renewable energy-based processes [1]. Since chemical sector is the leading consumer of supplied energy, significant progress in this area is essential to make it more sustainable and long-term viable. To achieve this, a thorough understanding of selectivity mechanism in the complex chemical transformations is necessary.

"90% of chemicals production relies on a catalytic process at some point in their manufacturing process. Catalysts are the philosopher's stone of chemist."

was narrated by Philippe Marion [2]. According to this statement, the designing of catalysts and catalytic systems must be done to achieve the dual goals of environmental protection and economic benefits together, i.e. reduced energy requirements, increased selectivity, reduced or eliminated use as well as generation of hazardous substances, and use of catalytic rather than stoichiometric amounts of ingredients [3]. An interdisciplinary strategy, including both experiment and theory are essential to gain a basic understanding of catalyst reactivity in order to build catalytic processes with high conversion and selectivity, hence boosting their sustainability. Optimizing reaction selectivity under catalytic conditions would (i) lead to new options to reduce energy consumption and (ii) produce more efficient and selective processes with benign by-products [4].

This knowledge will also help to advance some of the most significant scientific issues, such as the development of atom- and energy-efficient syntheses of revolutionary new type of catalytic systems with tailored features. New capabilities of advanced heterogeneous catalytic systems are feasible by the direct and controlled building of unique nanoscale and mesoscale structures, presenting prospects for more efficient, benign, durable, and/or 'sustainable' catalytic systems [4].

All chemical transformations, including bond-breaking and bond-forming steps, must be examined since they require certain surface properties such as acidity or basicity, as well as solid-states, electrical and especially redox properties, specific types of surface site, and so on [5]. In this context, we have selected Polyoxometalate (POMs), an inorganic class of metal oxide clusters. POMs-based materials as catalysts have become a very important filed of research, academically and industrially because of its unrivalled structural versatility and convergent properties [6-15]. They provide good basis for the molecular level designing of mixed oxide catalysts and have high capability in practical uses.

Polyoxometalates- an overview

POMs are a well-defined discrete class of inorganic complexes comprised of molecular level anionic transition metal-oxygen clusters with unique properties of topology, size, electronic versatility as well as structural diversity ranging from nano to micrometer scale [16]. POMs have enjoyed a wide range of applications [17] including catalysis [18-22], optics [23, 24], electronic and electrochemical [25-27], magnetic [28, 29] also in other fields like biology [30, 31], nano-materials [32-34] and surface sciences [35, 36] due to the combination of their value added properties such as redox, large sizes, high negative charge, nucleophilicity.

POMs have the general formula $[A_xB_mO_y]^{q-}$, in which A is the heteroatom, usually a main group element (e.g., P, Si, Ge and As), and B is the addenda atom, being a d-block element in high oxidation state, usually $V^{IV/V}$, Mo^{VI} or W^{VI} [14]. These compounds are always negatively charged although the negative density is widely variable depending on the elemental composition and the molecular structure.

History of POMs

In 1826, for the first time Berzelius reported the formation of a canary yellow colored precipitate of ammonium 12-phosphomolybdate on excess addition of ammonium molybdate to phosphoric acid [37]. Following the discovery of the first POM, significant advancement in POM chemistry was observed [38].

1. Nearly two decades later, in 1848, Svanberg and Struve demonstrated that the insoluble ammonium salt of this complex could be utilised for the gravimetric analysis of phosphate [39].
2. The discovery of the tungstosilicic acids and their salts by Marignac in 1862 provided a boost for POM chemistry research. The 12-tungstosilicic acid and 12-silicotungstic acid, also known as the α and β-isomers today, were successfully synthesised and analysed by him [40].
3. Subsequently, the field advanced significantly, and by the end of the first decade of this century, over 60 different types of polyoxometalates had been identified, giving rise to several hundred salts.
4. The central heteroatom was thought to have an octahedral coordination with MO_4^{2-} or $M_2O_7^{2-}$ ligands, according to the structural theory put forth by A. Miolati in 1908. In the 1930s, A. Rosenheim later added a laboratory perspective to this.
5. Linus Pauling made an attempt to clarify the structure of a polyoxometalate for the first time in 1929. He suggested a complex construction with a 12:1 ratio based on the positioning of 12 octahedra around an XO_4 tetrahedron in the centre. His structural theory states that one PO_4 or SiO_4 tetrahedron is surrounded by twelve WO_6 octahedra to produce 12-tungstoanions, and that all polyhedron links employ vertex sharing rather than edge sharing to reduce electrostatic repulsion. The molecular formula for the proposed structure would be $[(PO_4)W_{12}O_{18}(OH)_{36}]^{3-}$ [41], and it would contain 58 oxygen atoms.
6. Immediately after, in 1933, Keggin determined the structure of $H_3[PW_{12}O_{40}].5H_2O$ and discovered that it was in fact built on WO_6 octahedra that were connected by egdes as well as corners [42, 43]. The determination of polyoxometalate structures using X-ray

crystallography has further sped up the development of polyoxometalate chemistry.

7. The next year, Signer and Gross verified that Keggin's structure was structurally isomorphous with $H_4SiW_{12}O_{40}$, $H_5BW_{12}O_{40}$, and $H_6[H_2W_{12}O_{40}]$ [44].
8. Bradley and Illingworth added clarification to Keggin's elucidation of $H_3[PW_{12}O_{40}]$. After the development of single crystal X-Ray diffraction techniques [45], single crystal investigations of Brown and coworkers [46] provided more evidence in favour of their findings by analysing the crystal structure of $5H_2O$.

With the development of POMs chemistry, various types of structures were discovered [43, 47-52]. Ball and stick representations of various types of POMs are presented in Figure 1.

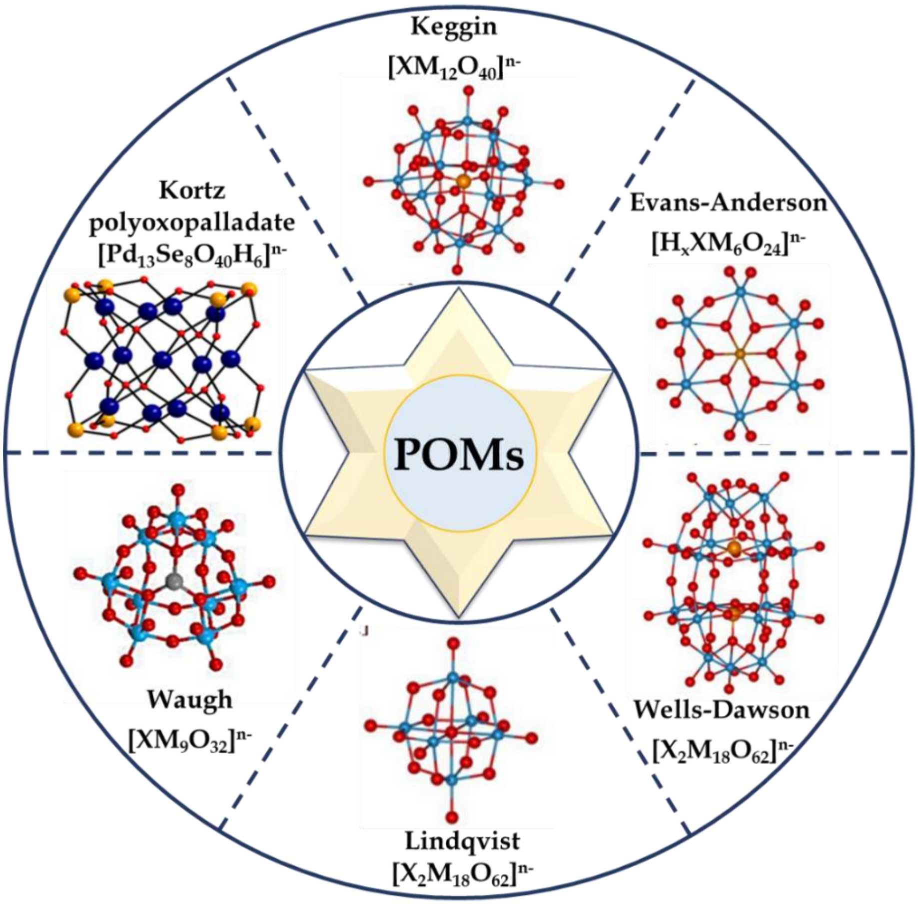


Figure 1. Ball and stick representation of different types of POMs.

Of all the different types of POMs, the most extensive research has been carried on Keggin type POMs as Mo- and W-based Keggin structures have thermal stability up to about 350 °C, making them catalytically attractive even at high temperatures [14, 53]. Since they are polynuclear superacid that are redox active, therefore, they offer a reactive surface for a number of catalytic processes [53].

Keggin type POMs

The Keggin type POMs have the general formula is $[XM_{12}O_{40}]^{n-}$, where X is the central heteroatom, usually a main group element like P, Si, Ge and As and M is the addenda atom, a d-block element in high oxidation state, usually V^{IV},V^{V}, Mo^{VI} or W^{VI} and formed by condensation of different mononuclear oxoanions at lower pH as shown in the following equation.

$$12MO_4^{m-} + HXO_4^{p-} + 23H^+ \rightarrow [XM_{12}O_{40}]^{n-} + 12H_2O \quad \text{.........(1)}$$

The acidic salts of POMs are known as Heteropoly acids (HPAs).

Structure

The ideal Keggin structure of POMs, $[XM_{12}O_{40}]^{3-}$ of α-type has T*d* symmetry and consists of a central XO_4 tetrahedron (X = central heteroatom) surrounded by twelve MO_6 octahedra (M = addenda atom). The twelve MO_6 octahedra form four groups of three edge-shared octahedra, the M_3O_{13} triplet [42, 43], which have a common oxygen vertex connected to the central heteroatom (Figure 2a). The oxygen atoms in this structure fall into four classes of symmetry-equivalent oxygen (Figure 2b): central oxygen atoms [X-O_a-$(M)_3$], terminal oxygen atoms ($M{=}O_d$) and two types of bridging oxygen atoms (connecting two M_3O_{13} units by corner sharing; M-O_b-M and connecting two M_3O_{13} units by edge sharing; M-O_c-M) where M is the addenda atom and X the heteroatom.

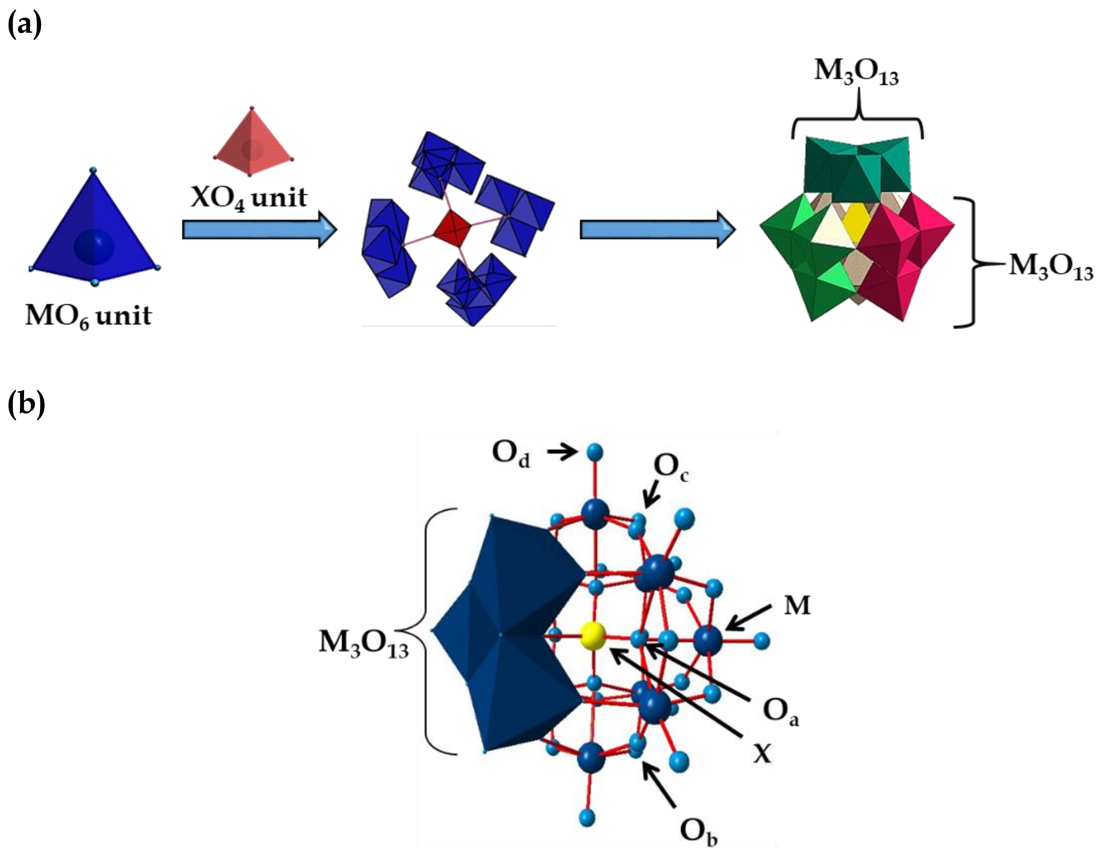


Figure 2. (a) Formation of Keggin ion structure (b) Ball and stick structure of Keggin ion

POMs compounds, in the solid state, are composed of polyoxoanions, cations such as protons, metals or onium ions and water of crystallization. Sometimes in additions they contain neutral organic molecules. From the view point of catalysis based on POMs, it is very important to distinguish between the primary, secondary and tertiary structure [6, 8, 54-56]. It has also been identified that in addition to these structures, tertiary and higher-order structures can also influence the catalytic function [56]**.** The different types of structures for the polyoxoanion are represented in Figure 3.

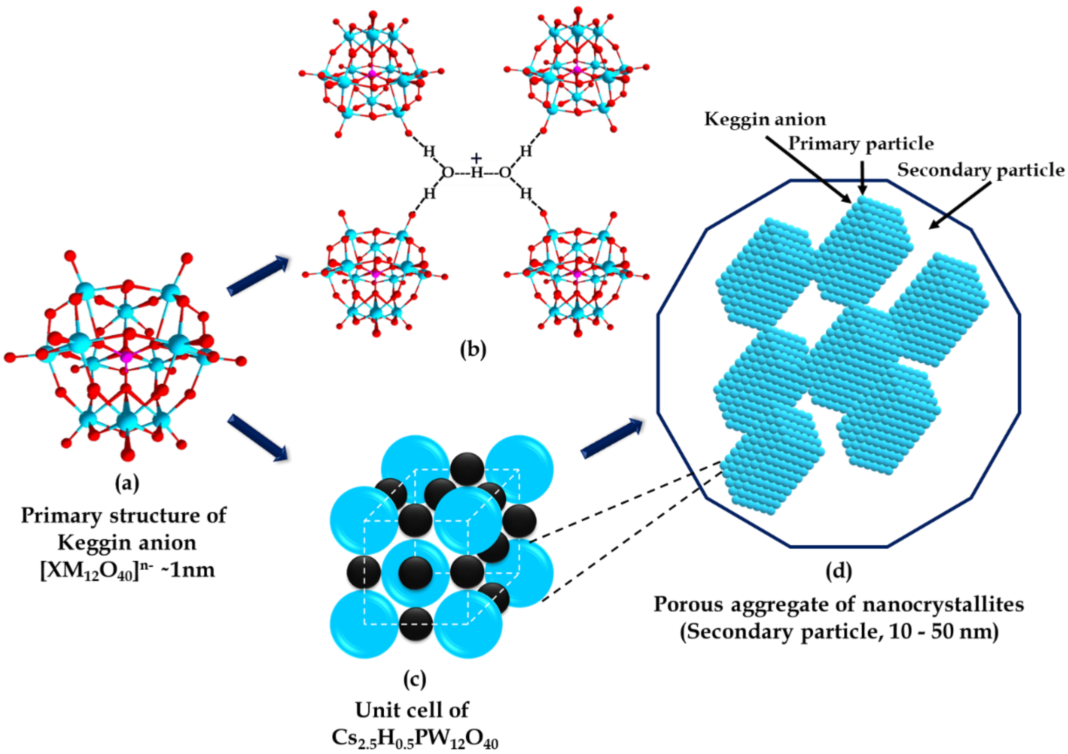


Figure 3. Primary, secondary, and tertiary structures of Keggin type POMs; (a) primary structure (Keggin structure, $XM_{12}O_{40}$); (b) secondary structure ($H_3PW_{12}O_{40}.6H_2O$); (c) secondary structure for unit cell of ($Cs_3PW_{12}O_{40}$); (d) tertiary structure with porous aggregates ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) [8, 10]

The basic structure of a polyoxoanion molecule itself is called a "primary structure" (Figure 3a), which is formed from the condensation of oxoanions. The secondary structure (Figure 3b) of the solid POM is formed from the coordination of the polyoxoanion with acidic protons, other cations and/or water molecules of hydration. A stable form contains six water molecules of hydration per Keggin unit, forming a body centered cubic (BCC) structure with Keggin units at the lattice points and $H_5O_2^+$ bridges along the faces. Each terminal oxygen atom is bound to a hydrogen atom of an $H_5O_2^+$ bridge. In this structure, the acidic protons are located in the $H_5O_2^+$ bridges between lattice points (Figure 3c). If less than six water molecules are present, acidic protons may be located in remaining $H_5O_2^+$ bridges, in H_3O^+ or may be directly coordinated to oxygen atoms of the Keggin unit. The tertiary structure is the structure of solid POMs as assembled. The size of the particles, pore structure, distributions of protons in the particle is the elements of the tertiary structure (Figure 3d).

Properties of POMs

The high aqueous solubility of POMs is attributed to their low surface area (about 1-10 m^2/g) while the pores are inter-particle and not intra-crystalline in nature. Considering the size (10 nm) and shape of the Keggin anion and the crystal structure, there is no open pore through which nitrogen molecule can penetrate. A list of their properties is presented below.

i. **Thermal stability:** The acidic salt of POMs are thermally stable. The thermal stability of different type of Kaggin POMs depend on the heteroatom, polyatom and polyanion structure, the stability trend is as followed: $PW_{12}O_{40}^{3-}$ > $PMo_{12}O_{40}^{3-}$ > $SiMo_{12}O_{40}^{4-}$ [8, 10, 22, 54, 55]
ii. **Acidic properties:** The acidic form POMs are pure Brønsted acids in solid state. Its acidic strength is much higher than the conventional acids i.e. SiO_2-Al_2O_3, H_3PO_4/SiO_2, HX and HY zeolites, oxoacids of constituent elements as well as mineral acids. [8, 10, 11] The strong acidic nature is attributed to the negative charge dispersion over a large number of polyanion atoms and due to the double bond character of M=Ot, negative charge polarization over the outer surface of polyanion. The order in acid strength is found to be: $H_3PW_{12}O_{40}$ > $H_4SiW_{12}O_{40}$ > $H_3AsW_{12}O_{40}$ > $H_4GeW_{12}O_{40}$ [8-11]
iii. **Redox properties:** In most of POMs, addenda atoms are present in their highest oxidation states (d^0) because of which they are capable to act as oxidizing agents. Many polyanions, particularly 12-molybdo Keggin type species tend to reduce to form blue species more commonly known as "heteropoly blues" or "molybdenum blues". The oxidation potential depends on the addenda atoms and is not influences by central heteroatom. The reported oxidative ability is: V^- > Mo^- > W^- [8-11].

The synthesis, structure, and properties of POMs over the years have been thoroughly surveyed and summarized in a number of books:

Title	Authors	Publisher and Year
Heteropoly and Isopoly Oxometalates	M. T. Pope, (Eds.) C. K. Jorgensen	Springer-Verlag, Berlin, (1983)
Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity	M. T. Pope, A. Muller	Springer Science & Business Media, (1994)
Polyoxometalate Chemistry From Topology via Self-Assembly to Applications	M. T. Pope, A. Muller	Springer Science & Business Media, (2001)
Polyoxometalate Molecular Science	M. T. Pope, A. Muller	Kluwer Academic publishers, (2003)
Polyoxometalate Chemistry for Nano-Composite Design	T. Yamase, M. T. Pope	Springer Science & Business Media, (2006)
Polyoxometalate Chemistry: Some Recent Trends	F. Secheresse	World Scientific Publishing Company, (2013)
New Synthetic Routes to Polyoxometalate Containing Ionic Liquids An Investigation of their Properties	S. Herrmann	Springer Spektrum, (2015)
Trends in Polyoxometalate Research	L. Ruhlmamm, D. Schaming	Nova Science Publishers, (2015)
Polyoxometalates: Properties, Structure and Synthesis	A. P. Roberts	Nova Science Publishers, (2016)

Co-assembly of Polyoxometalates and Zwitterionic Amphiphiles In to Supramolecular Hydrogels: From Crystalline Fibrillar to Amorphous Micellar Networks	A. Wu, X. Gao, P. Sun, F. Lu, L. Zheng	Wiley-VCH Verlag GmbH, (2018)
Polyoxometalate-Based Assemblies and Functional Materials	Y. F. Song	Springer International Publishing AG, Springer Cham, (2018)

Similarly, a number of reviews are also available showcasing the advancements in the synthetic procedures, structural characterizations and properties of POMs over the years:

Reviews		
Introduction: Polyoxometalates multicomponent molecular vehicles to probe fundamental issues and practical problems	C. L. Hill	Chem. Rev., 98, 1, (1998)
Tungsten-183 nuclear magnetic resonance spectroscopy in the study of Polyoxometalates	Y. G. Chen, J. Gong, L. Y. Qu	Coord. Chem. Rev., 248, 245, (2004)
Polyoxometalate complexes of layered double hydroxides	C. Hu, D. Li	Interface Sci. Technol., 1, 374, (2004)
From Scheele and Berzelius to Müller: polyoxometalates (POMs) revisited and the "missing link" between the bottom up and top down approaches	P. Gouzerh, M. Che	L’Actualité Chimique, 298, 9, (2006)

Polyoxometalate clusters, Nanostructures and Materials: From self-assembly to designer materials and devices	D. L. Long, E. Burkholder, L. Cronin	Chem. Soc. Rev., 36, 105, (2007)
Stabilization and Immobilization of Polyoxometalates in Porous coordination polymers through host-guest interactions	R. Yu, X. E. Kuang, W. Y. Wu, C. Z. Lu, J. P. Donahue	Coord. Chem Rev. 253, 2872, (2009)
Polyoxometalates containing late transition and noble metal atoms	P. Putaj, F. Lefebvre,	Coord. Chem. Rev., 255, 1642, (2011)
Pushing the frontiers in polyoxometalate and metal oxide cluster science	D. L Long, L. Cronin	Dalton Trans., 41, 9799, (2012)
The chemistry of organoimido derivatives of polyoxometalates	J. Zhang, F. Xiao, J. Hao, Y. Wei	Dalton Trans., 41, 3599, (2012)
Recent advances in paramagnetic-TM-substituted polyoxometalates (TM = Mn, Fe, Co, Ni, Cu)	S.-T. Zheng, G. Y. Yang	Chem. Soc. Rev., 41, 7623-7646, (2012)
Entangled structures in polyoxometalate-based coordination polymers	W.-W. He, S.-L. Li, H.-Y. Zang, G.-S.Yang, S.-R. Zhang, Z.-M. Su, Y.-Q. Lan	Coord. Chem. Rev., 279, 141, (2014)
Polyoxometalate based Open-Frameworks (POM-OFs)	H. N. Miras, L. Vila-Nadal, L. Cronin,	Chem. Soc. Rev., 43, 5679, (2014)
Environmentally Benign Polyoxometalate Materials	S. Omwomaa, C. T. Gorea, Y. Ji, C. Hub,	Coord. Chem. Rev. 286, 17, (2015)

	Y. -F. Song	
Architectural chemistry of polyoxometalate-based coordination frameworks constructed from flexible N-donor ligands	X. Wang, A. Tian, X. Wang	RSC Adv., 5, 41155, (2015)
Supramolecular architecture based on high lacunary sandwich-type building blocks: synthesis, characterization, and properties	Q. Wu, X. Miao, H. Wang, Y. Wu, J. Li, J. Lu, Q. Zhou, H. Ju	Z. Naturforsch., 71, 7, 783, (2016)
Tuning the topology of hybrid inorganic-organic materials based on the study of flexible ligands and negative charge of polyoxometalates: A crystal engineering perspective	S. Taleghania, M. Mirzaeia, H. Eshtiagh-Hosseinia, A. Frontera	Coord. Chem. Rev., 309, 84, (2016)
A brief review of the crucial progress on heterometallic polyoxotungstates in the past decade	J. Liu, Q. Han, L. Chen, J. Zhao	CrystEngComm., 18, 842, (2016)
Design and synthesis of polyoxometalate-framework materials from cluster precursors	L. Vilà-Nadal. L. Cronin	Nat. Rev. Mater., 2, 17054, (2017)
Rare Earth Polyoxometalates	C. Boskovic	Acc. Chem. Res., 50, 9, 2205, (2017)
Tailor–made Covalent Organic-Inorganic Polyoxometalate Hybrids: Versatile Platforms for the Elaboration of Functional Molecular Architectures	G. Izzet, F. Volatron, A. Proust	Chem. Rec., 17, 250, (2017)
Lacunar Keggin Heteropolyacid Salts: Soluble, Solid and Solid-Supported Catalysts	N. C. Coronel, M. J. da-Silva	J. Clust. Sci., 29, 195, (2018)

Synthetic strategies, diverse structures and tuneable properties of polyoxo-titanium clusters	W. H. Fang, L. Zhang, J. Zhang	Chem. Soc. Rev., 47, 404, (2018)
Metallopolymers from organically modified polyoxometalates (MOMPs): A review	J. Yan, X. Zheng, J. Yao, P. Xu, Z. Miao, J. Li, Z. Lv, Q. Zhang, Y. Yan	J. Organomet. Chem., 884, 1, (2019)
Recent advances in transition-metal-containing Keggin-type polyoxometalate-based coordination polymers	D. Li, P. Ma, J. Niu, J. Wang	Coord. Chem. Rev., 392, 49, (2019)
Metal-addenda substitution in plenary polyoxometalates and in their modular transition metal analogues	C. Simms, A. Kondinski, T. N. Parac-Vogt	Eur. J. Inorg. Chem., 2559, (2020)
Multiscale assembly of polyoxometalates: From clusters to materials	B. Yu, X.Zhao, J. Ni, F. Yang	ChemPhysMater, (2022)
Supramolecular assemblies of organofunctionalized hybrid polyoxometalates: from functional building blocks to hierarchical nanomaterials	J. M. Cameron, G. Guillemot, T. Galambos, S. S. Amin, E. Hampson, K. M. Haidaraly, G. N. Newton, G. Izzet	Chem. Soc. Rev., 51, 293, (2022).

Modifications in POMs

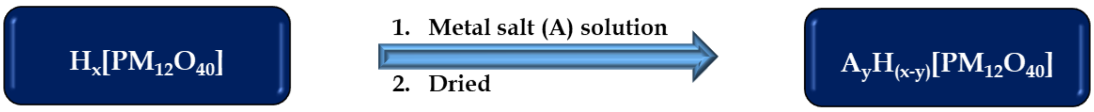
As previously discussed, the ability of tuning the redox and acidic properties of POMs at the molecular level has led to the development of a new class of materials with unique structural as well as electronic properties. One of the most important properties of modified precursors is their ability to accept and release specific numbers of electrons reversibly under marginal structural rearrangement [57-59]. Hence, the modification of parent POMs are likely to result in the development of new generation catalysts with enhanced electronic properties and stability.

The modification of parent POMs in terms of acidic/redox properties, can be accomplished by tuning the primary and secondary structure at the molecular level in four different ways; (1) by formation of metal salt of POMs (2) by creating the defect (lacuna) in parent POMs structures (i.e. Lacunary Polyoxometalates, LPOMs), (3) by inserting transition metal ions into the defected structures (i.e. Transition Metal Substituted Polyoxometalates, TMSPOMs) and (4) by supporting POMs (including 1, 2 and 3) on suitable supports as well as metal exchanged supported POMs.

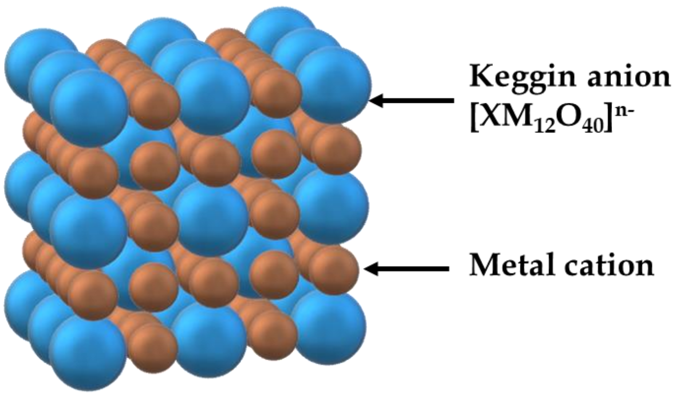
1. Metal Salts of POMs

In this method, metal salts of POMs are synthesized by the exchange of metals with available protons of POMs, in which alkali metals or transition metals such as V, Fe, Co, Ni, Cu, Zn and Pd are used. The saturated solutions of POMs and metal salts are mixed in stoichiometric amount to form metal salt of POMs (MSPOMs) by evaporation, followed by drying (Scheme 1a). The formation of body centered cubic (BCC) structure of metal salt of POMs shown in Scheme 1b.

(a)



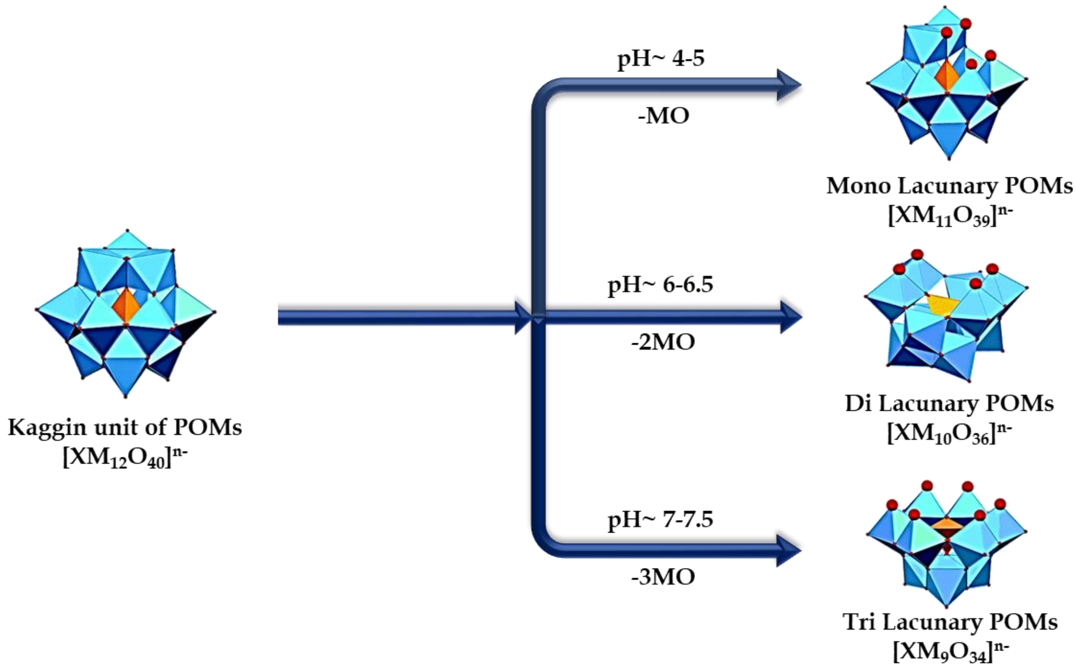
(b)



Scheme 1. (a) General synthetic route for metal salt of POMs and (b) BCC structure of Bulk metal salt of POMs

2. Lacunary POMs (LPOMs)

Controlled treatment of heteropoly/polyoxo species with base can produce “lacunary” heteropoly/polyoxo species wherein one or more addenda atoms can be eliminated from the structure along with the oxygens [13]. When solutions of parent POMs $[XM_{12}O_{40}]^{3-}$ are treated with base (pH~ 4-7), a series of hydrolysis reactions depending on pH, take place to remove one, two or three MO unit from parent POMs, producing mono-, di-, and tri-lacunary polyoxometalates having general formula $[XM_{11}O_{39}]^{7-}$, $[XM_{10}O_{36}]^{8-}$ and $[XM_9O_{34}]^{11-}$ respectively (Scheme 2).



Scheme 2. pH dependent formation of LPOMs

3. Transition metal substituted POMs (TMSPOMs)

The third method of POMs modification is the insertion of transition metal ions into lacunary polyoxometalates, resulting into a new class of compounds known as transition metal substituted polyoxometalates (TMSPOMs). TMSPOMs have attracted enormous attention in the world (field) of POMs chemistry because of their ability to be rationally modified at the molecular level including size, shape, charge density, acidity/redox, stability, and solubility [60-62], resulting in outstanding unique electrochemical, magnetic, medicinal, and catalytic properties [12, 60]. It provides convenient platforms for the stabilization of metal-oxo species with unusually high oxidation states. In addition, TMSPOMs have a number of advantages over organometallic complexes such as (i) the ability to tune their solubility by replacing one counter-cation with another (ii) their adjustable redox properties by replacing the central (hetero) atom and incorporating the transition metal and (iii) they are robust under oxidation conditions, under which most organic catalysts decompose [63]. This distinct family of metal oxygen clusters are remarkable inorganic building blocks due to their enormous unquestionable versatility and structural variation in both symmetry and size, opening up a wide range of scope for applications in many fields of science [12, 60].

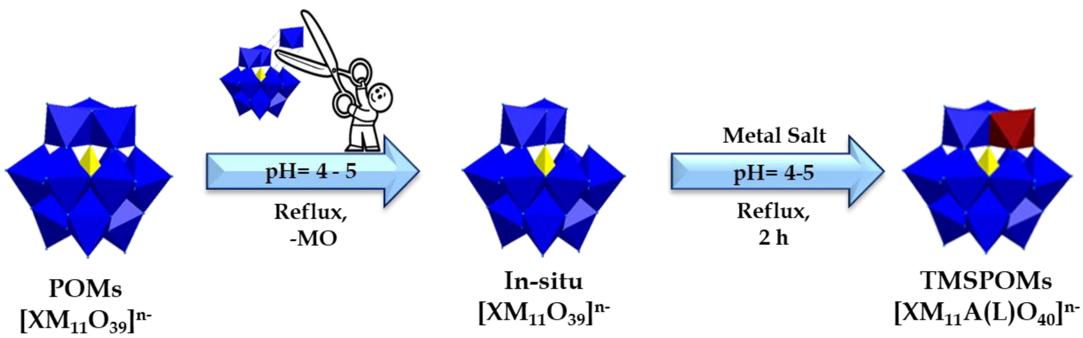
Depending upon mono-, di-, and tri-lacunary polyoxometalates (LPOMs), mono-, di-, and tri-/sandwich transition-metal-substituted polyoxometalates can be synthesized respectively.

In the present work, we have focused only on mono-transition metal substituted POMs.

i. Mono transition metal substituted polyoxometalates

Keggin type mono-TMSPOMs, recognized as inorganic analogues of metalloporphyrin complexes, offer a significant advantage over the metallophorphyrins and other organometallic complexes due to their rigidity, hydrolytic stability, and thermal robustness [64, 65]. Polyanions act as an inert, multi-dentate ligand that may accommodate a multitude of transition metal centres due to the non-oxidizable M-oxo framework [64-67].

The reaction involving in-situ formation of the mono lacunary $[XM_{11}O_{39}]^{n-}$ anion from parent POMs with transition-metal cations (A) in aqueous solution leads to the formation of mono transition-metal-substituted POMs (TMSPOMs) $[XM_{11}A(L)O_{39}]^{n-}$, (where A = transition metal and L = generally H_2O) (Scheme 3).

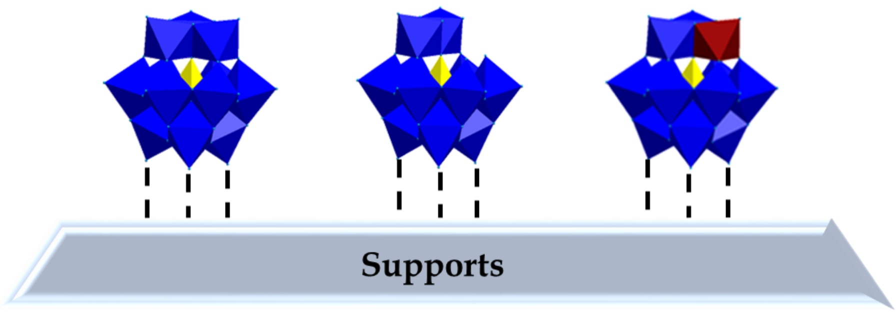


Scheme 3. General synthetic route for mono-transition metal substituted polyoxometalates

In the TMSPOMs, the environment surrounding the substituted transition metal is considered to be nearly octahedral, and such complexes exhibit many similarities to metalloporphyrins [58, 64].

4. Supported POMs

POMs and the different types of modified POMs, (1) metal salt of POMs (MSPOMs), (2) LPOMs and (3) TMSPOMs, can act as homogeneous catalysts which results in the traditional disadvantages including high solubility, low surface area, tedious isolation, and reusability. The above-mentioned disadvantages can be overcome by supporting/anchoring POMs based homogeneous catalysts on appropriate supports (Scheme 4).



Scheme 4. Different types of supported POMs

In case of supported parent POMs, the advantage of available exchangeable protons of POMs (counter cation as secondary structure of POMs) can be taken to design a new catalyst. In this technique, first POMs are supported on to appropriate supports and after that the available protons of POMs are exchanged with the transition metals by ion exchange method. This method consists of two steps for synthesis:

Step-I: Supporting of POMs on suitable supports

Step-II: Exchange of available protons of supported POMs by transition metals

Advantages of supported POMs

The following are the most significant advantages of supported POMs :

- Increase in surface area
- Enhanced thermal and chemical stability
- High catalytic activity and selectivity

- Ease of separation from reaction mixture
- Ease to recycle and reuse
- Process simplification under mild and sustainable reaction conditions
- Kinetically and thermodynamically difficult reactions can proceed with wide range of temperature, even in gas phase
- 'Tailoring' of catalysts for specific feedstock or for selective product synthesis is made possible.

Following are some common methods used for supporting/anchoring:

1. Co-precipitation
2. Deposition precipitation
3. Dry impregnation/incipient wet impregnation
4. Equilibrium adsorption/ion exchange

We are concentrating on impregnation because it is one of the most economic and widely used method for synthesizing supported catalysts.

Impregnation is a method of preparation in which a solution of the active phase's precursor is brought into contact with the support [68]. It can be carried out by the following two methods:

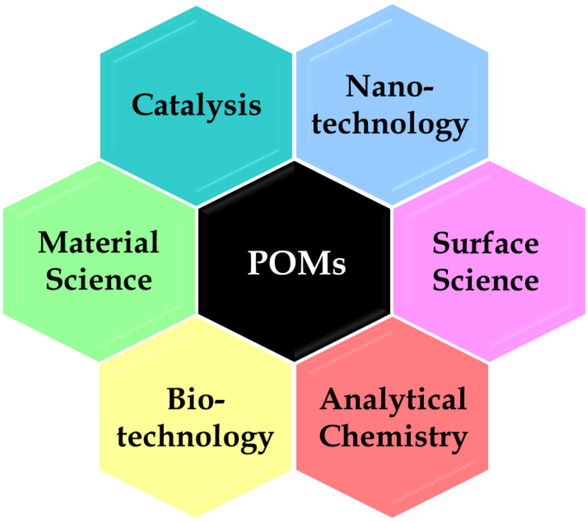
i. Dry impregnation: Also known as "pore volume impregnation," this method uses just enough liquid (precursor solution) to fill the pore volume of the support. The optimum loading available during each time of impregnation is determined by the solubility of the catalyst precursors and the pore volume of the support in dry impregnation. If a high loading is required, subsequent impregnation (and heat treatment) may be required. Three processes occur during the first step of impregnation:

   1. Transport of solute to the pore system of the support bodies
   2. Diffusion of solute within the pore system
   3. Uptake of solute by the pore wall

ii. Incipient wet impregnation: The support is immersed in an excess of solution containing the active phase precursor. A fourth process is operative, viz. transport of solute to the outer surface.

Applications of POMs

Even after being around two centuries old, the application areas of POMs in diverse fields of science and engineering have resulted in rapid and continuous growth of POMs chemistry. Catalysis, nanotechnology, surface science, analytical chemistry, bio-technology, material science, clinical analysis, food chemistry, solar cell, energy storage and colorant for pigmenting paints are just a few of the applications (Scheme 5) [44, 57, 69-79].



Scheme 5. Applications of POMs

POMs have an eminent Brønsted acidity, as well as the capacity to undergo relatively fast reversible multi-electron redox transformations under comparatively mild conditions, polarities, negative charge densities on surface oxygens and their inherent resistance to strong oxidants. Furthermore, they have excellent resistance to strong oxidants in addition to the ability to remain stable at high temperatures.

POMs as catalysts [8-11]

POMs have numerous practical advantages as catalysts due to their unique properties.

1. **Designing at molecular level**
   - *Acidic and redox properties:* By selecting proper elements (type of polyanion, heteroatom counter-cation etc.), these catalyst properties can be successfully controlled
   - *Multifunctionality:* Acid-Redox, Acid-Base, multielectron transfer etc.
   - Counter cations have good control over tertiary structure, bulk type behavior, and other aspects of solid-state behavior
2. **Molecular metal-oxide clusters**
   - Molecular designing of catalyst
   - Cluster models of mixed oxide catalyst and relationships between solution and solid catalyst
   - Description of catalytic processes at atomic/molecular level, spectroscopic study and stoichiometry are realistic [80]
3. **Unique reaction fields**

   POMs completely dissociate in solution, making them more potent than common mineral acids like HCl, HNO_3, and H_2SO_4. On the contrary side, POMs catalysts can generally behave in one of the three ways when exposed to heterogeneous conditions: (a) Surface type catalysts, (b) Bulk type (I) catalysts, and (c) Bulk type (II) catalysts are all examples of catalysts.

   (a) *Surface type catalysis:* The reaction occurs on the surface of the solid catalyst, making it the most common type of catalysis. Here, the surface area and the rate of reaction are inversely related (Figure 4a).

   (b) *Bulk type I catalysis:* As the reaction proceeds, the reactant molecules are adsorbed in the interpolyanion spaces of the ionic crystal, where the products are eventually released (Figure 4b). The acid-catalyzed reaction of polar molecules over group I salts at relatively low temperatures is the conceptual example of this type. The reaction surface becomes three-dimensional and the solid behaves somewhat like a solution; this is why "pseudoliquid" catalysis is used to describe it. Here, the volume of the catalyst affects the reaction rate; for example, the acidity of the catalyst's bulk would affect the rate of an acid-catalyzed reaction.

(c) *Bulk type II catalysis:* Although the reaction takes place on the surface, electrons and protons migrate quickly, and as a result, the bulk catalyst in theory also contributes to the reaction (Figure 4c). The rate of reaction is proportional to the bulk volume of the catalyst, and classic examples of this kind usually involve the dehydrogenation and oxidation of hydrogen at high temperatures. Because POMs exhibit "pseudoliquid" behavior and adhere to bulk type II catalysis, which creates a distinctive three-dimensional environment and enables practical and accurate spectroscopic and stoichiometric studies.

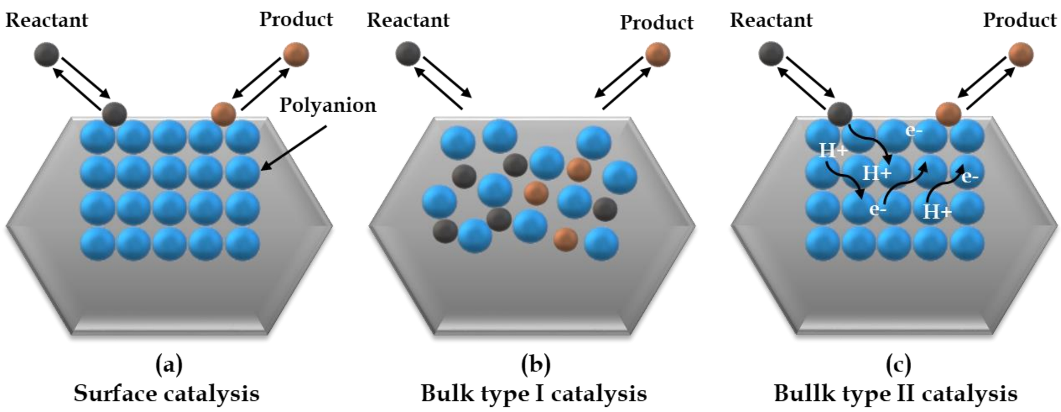


Figure 4. Types of catalyst by POMs

4. Unique basicity of polyoxoanions

- Basicity of polyoxoanions is crucial to their high catalytic activity because they aid in the stabilization of reactive intermediates in the solution, pseudoliquid, and solid phases as well as in selective coordination

In addition, they have following advantages: (i) Robust oxoanionic nature which greatly enhance the stability power [81-84], (ii) reducing capacity which favors the stability of metal into its most stable oxidation state (zero) and (iii) large relative sizes which sterically hinder metal particle and prevent them from agglomeration during the synthesis as well as its catalytic reactions [85-87].

A thorough investigation of POMs as catalytic materials began during the 1970s, the various catalytic applications of POMs have been summarized in the following books:

Title	Authors	Publisher and Year
Metal-oxygen Clusters: The surface and Catalytic properties of Heteropolyoxometalates	J. B. Moffat, M. V. Twing, M. S. Spencer	Kluwer Academic plenum, New York, (2001)
Catalysts for fine chemical synthesis, Vol. 2: Catalysis by polyoxometalates	I. V. Kozhevnikov	Wiley, (2002)
Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis	M. T. Pope, (Eds) S. Ted Oyama	Elesvier, (2008)
Liquid Phase Oxidation Via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications	M. G. Clerici, O. A. Kholdeeva	John Wiley & Sons, Inc., Hoboken, New Jersey, (2013)
Environmentally benign catalysts for clean organic reactions	A. Patel	Springer, Dordrecht, (2013)
Keggin Structure Polyoxometalates. In Inorganic Syntheses: Volume 36 (eds G.S. Girolami and A.P. Sattelberger)	J. A Dias, S. C. L. Dias, E. Caliman, J Bartis, L. Francesconi,	Wiley (2014)

Polyoxomolybdates as Green Catalysts for Aerobic Oxidation	A. Patel, S. Pathan,	Springer Briefs in Molecular Science-Green Chemistry for Sustainability, Springer, Dordrecht, (2015)
Polyoxometalates in Catalysis, Biology, Energy and Materials Science	S. Roy, D.C. Crans, T.N. Parac-Vogt	Frontiers in Chemistry, (2019)
Recent Progress in Selective Oxidations with Hydrogen Peroxide Catalyzed by Polyoxometalates. In: Bryliakov, K. (eds) Frontiers of Green Catalytic Selective Oxidations. Green Chemistry and Sustainable Technology.	O. A. Kholdeeva	Springer, Singapore, (2019)
Heteropolyacids as highly efficient and green catalysts applied in organic transformations	M.M. Heravi, F.F. Bamoharram	Elsevier, (2022)

Furthermore, many groups have reviewed the major achievements of POMs in the field of catalysis as follows:

Reviews		
Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions	A. Corma	Chem. Rev., 95, 559, (1995)

Catalytic Chemistry of Heteropoly Compounds	T. Okuhara, N. Mizuno, M. Misono	Adv. Catal., 41, 113, (1996)
Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions	I. V. Kozhevnikov	Chem. Rev., 98, 171, (1998)
Heterogeneous Catalysis	N. Mizuno, M. Misono,	Chem. Rev., 199, (1998)
Heteropoly acids immobilized into a silica matrix: characterization and catalytic applications	A. Molnar, C. Keresszegi, B. Torok,	Appl. Catal. A: Gen., 189, 217, (1999)
Surface Modification of Mesoporous, Macroporous, and Amorphous Silica with Catalytically Active Polyoxometalate Clusters	B. J. S. Johnson, A. Stein,	Inorg. Chem., 40, 801, (2001)
Oxidation of Alcohols with Molecular Oxygen on Solid catalysts	T. Mallat, A. Baiker	Chem Rev. 104, 3037, (2004)
Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates	N. Mizuno, K. Yamaguchia, K. Kamata	Coord. Chem. Rev., 249, 1944, (2005)
Hybrid Organic-Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications	A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane	Chem. Rev., 110, 6009, (2010)
Progress of the Application of Mesoporous Silica-Supported Heteropolyacids in Heterogeneous Catalysis and Preparation of nanostructured metal oxides	Y. Ren, B. Yue, M. Gu, H. He	Materials, 3, 764, (2010)

MIL-101 Supported Polyoxometalates: Synthesis, Characterization, and Catalytic Applications in Selective Liquid-Phase Oxidation	N. V. Maksimchuk, O. A. Kholdeeva, K. A. Kovalenko, V. P. Fedin,	Isr. J. Chem., 51, 281, (2011)
Recent advances on polyoxometalate-based molecular and composite materials	Y-F Song, R. Tsunashima	Chem. Soc. Rev., 41, 7384, (2012)
Catalytic Oxidation of Light Alkanes (C_1−C_4) by Heteropoly Compounds	M. Sun, J. Zhang, P. Putaj, V. Caps, F. Lefebvre, J. Pelletier J. M. Basset	Chem. Rev. 114, 981, (2014)
Polyoxometalate Multi-Electron-Transfer Catalytic Systems for Water Splitting	J. M. Sumliner, H. Lv, J. Fielden, Y. V. Geletii1 and C. L. Hill	Eur. J. Inorg. Chem., 4, 635, (2014)
Recent Advances in Polyoxometalate-Catalyzed Reactions	S. –S. Wang, G.-Y. Yang	Chem. Rev., 115, 4893, (2015)
Recent progress on supported polyoxometalates for biodiesel synthesis via esterification and transesterification	N. Narkhede, S. Singh, A. Patel	Green Chem., 17, 89, (2015)
Heterogeneous Catalysis of Polyoxometalate Based Organic–Inorganic Hybrids	Y. Ren, M. Wang, X. Chen, B. Yue, H. He	Materials, 8, 1545, (2015)

Keggin-type lacunary and transition metal substituted polyoxometalates as heterogeneous catalysts: A recent progress	A. Patel, N. Narkhede, S. Singh, S. Pathan	Catalysis Reviews, 58, 337, (2016)
Recent advances in transition-metal-catalyzed selective oxidation of substituted phenols and methoxyarenes with environmentally benign oxidants	O. A. Kholdeeva, O. V. Zalomaeva	Coord. Chem. Rev., 306, 302, 2016
Base Catalysis by Mono- and Polyoxometalates	K. Kamata, K. Sugahara	Catalysts, 7, 345, (2017)
Polyoxometalates as heterogeneous catalysts for organic reactions	E. Fiee, S. Eavani,	Current Organic Chemistry, 21, 752-778, (2017)
Polyoxometalates and Their Composites as Photocatalysts for Organic Pollutants Degradation in Aqueous Media	R. Dehghani, S. Aber, F. Mahdizadeh	Clen – Soil, Air, Water, 46, 1800413, (2018)
Polyoxometalates in photocatalysis	C. Streb, K. Kastner, J. Tucher	Phys. Sci. Rev., 4, 20170177, (2019)
Applications of inorganic-organic hybrid architectures based on polyoxometalates in catalyzed and photocatalyzed chemical transformations	N. Lotfian, M. M. Heravi, M. Mirzaei, B. Heidari	Appl. Organomet. Chem., 33, e4808, (2019)
Polyoxometalates: Tailoring metal oxides in molecular dimension toward energy applications	L. Zhang, Z. Chen	Int. J. Energy Res., 44, 3316, (2020)

Review on oxidative desulfurization of fuel by supported heteropolyacid catalysts	J. Li, Z. Yang, S. Li, Q. Jin, J. Zhao	J. Ind. Eng. Chem., 8, 1, (2020)
Recent Progress on Heteropolyacids for Green Fuels Synthesis	Q. Zhang, X. Liu, T. Deng, Y. Zhang, P. Ma	Curr. Green Chem., 7, 267, (2020)
Strategies for Incorporating Catalytically Active Polyoxometalates in Metal–Organic Frameworks for Organic Transformations	C. T. Buru, O. K. Farha	ACS Appl. Mater. Inte rfaces, 12, 5345, (2020)
POM@MOF Hybrids: Synthesis and Applications	J. Sun,S. Abednatanzi, P. Voort, Y.-Y. Liu, K. Leus	Catalysts, 10, (2020)
Modified Mn Substituted POMs: Synthetic strategies, structural diversity to applications	A. Patel, R. Sadasivan	Prog. Mater. Sci., 118, 100759, (2021)
Supported polyoxometalates as emerging nanohybrid materials for photochemical and photoelectrochemical water splitting	I. Ullah, A. Munir, A.; Haider, N. Ullah, I. Hussain	Nanophotonics, 10, 1595, (2021)
Photocatalytic degradation of organic pollutants in wastewater by heteropolyacids: a review	Z. Chengli, M. Ronghua, W. Qi, Y. Mingrui, C. Rui, Z. Xiaonan	J. Coord. Chem., 74, 1751, (2021)
Recent Applications of Heteropolyacids and Related Compounds in Heterocycle	A. M. Escobar, G. Blustein, R. Luque, G. P. Romanelli	Catalysts, 11, 291, (2021)

Synthesis. Contributions between 2010 and 2020		
Advances in novel activation methods to perform green organic synthesis using recyclable heteropolyacid catalysis	D. M. Ruiz, G. A. Pasquale, J. J. Martínez, G. P. Romanelli	Green Process. Synth., 11, 766, (2022)
Production of renewable biodiesel using metal organic frameworks based materials as efficient heterogeneous catalysts	S. F.Basumatary, K. Patir, B. Das, P. Saikia, S. Brahma, B. Basumatary, B.; Nath, B.; Basumatary, S. Basumatary, S.	J. Clean. Prod., 358, 131955, (2022)
Catalytic Applications of Heteropoly acid-Supported Nanomaterials in Synthetic Transformations and Environmental Remediation	M. Afshari, R. S. Varma, S. J. Saghanezhad	Comments Inorg. Chem., 1, (2022)

A number of patents are also available for the same:

1. Method of preparing heteropolyacid catalysts by Lyons et al, US Patent No. 4916101, (1990).
2. Use of supported heteropolyacids for one step production of alkylphenol from olefins under adiabatic conditions by J. F. Knifton, US Patent No. 5300703, (1994).
3. Alkylation of isoparaffin with olefins to produce alkylate using heteropolyacids supported onto MCM-41 by Kresge et al., US Patent No. 5324881, (1994).
4. Zirconium hydroxide supported metal and heteropolyacid catalysts by Soled et al., US Patent No. 5391532, (1995).

5. Heteropolyacid supported onto sulfated zirconia as heterogeneous catalyst for alkylation of isoparaffins by Angstadt et al., US Patent No. 5493067, (1996).
6. Alkylation of aromatic amines using heteropolyacid catalyst by Rhubright et al., US Patent No. 5817831, (1998).
7. Polyoxometallate catalysts and catalytic processes by Davis et al., US Patent No 6914029 B2, (2005).
8. Oxidation of methanol and/or dimethyl ether using supported molybdenum containing heteropolyacid catalysts by Liu et al., US Patent No 6956134 B2, (2005).
9. Supported polyoxometalates, process for their preparation and use in oxidation of alkanes by Richards et al., WO2007142727 A1, (2007).
10. Silica support, heteropolyacid catalyst produced there from and ester synthesis using the silica supported heteropolyacid catalyst by Bailey et al., US Patent No. 2008/004466 A1, (2008).
11. Process for alkylation of phenol by A. Patel et al., US Patent No. 7692047 B2, (2009).
12. Process for production of alkenes from oxygenases by using supported heteropolyacid catalysts by Gracey et al., US Application No. 2010/0292520A1, (2010).
13. Materials for degrading contaminants by Hill et al., US 7655594 B2, (2010).
14. Method for the breakdown of lignin by Voitl et al., US 7906687, (2011).
15. Method for producing phenolphthalein suing heteropolyacid catalyst by Bolta et al., US 7868190 B2, (2011).
16. Process for oxidizing alkylaromatic compounds by Jaensch et al., US 7906686 B2, (2011).
17. Process for water oxidation comprising the use of a polyoxometalate compound as water oxidation catalyst by Galan et al., WO2013057079 A1, (2013).

18. Methods and compositions comprising polyoxometalates by Ying et. al., EP 2321078 A4, (2013).
19. Heteropoly acid promoted catalyst for SCR of NOx with ammonia by Putluru et al., US 8685354, (2014).
20. Polyoxometalate water oxidation catalysts and methods of use thereof by Hill et al., US 8822367, (2014).
21. Hydrogenation catalysts prepared from polyoxometalate precursors and process for using same to produce ethanol while minimizing diethyl ether formation by Heiko et al., US 8658843, (2014).
22. Synthesis of polyoxometalate-loaded epoxy composites by Anderson, US 8853350 B1, (2014).
23. Preparation of aldehydes and ketones from alkenes using polyoxometalate catalysts and nitrogen oxides by Neumann et al., WO2015132780 A1, (2015).
24. High-performance polyoxometalate catalyst and preparation method thereof by Lg Chem, Ltd., WO2016006883 A1, (2016).
25. Liquid phase non solvent oxidation of styrene with molecular oxygen, P. Shringarpure by A. Patel, Indian Patent No. 275517, (2016).
26. Supported undecaphosphotungstate catalyst for aerobic epoxidation of alkenes, by Patel et al., Indian Patent No. 271230, (2016).
27. Method for catalyzing and oxidizing olefin with sandwiching-type polyoxometalates by Xue et al., CN105777515A, (2016).
28. Process for Hydrodesulphuration of gasoil cuts using a catalyst based on hetropolyanion trapped in a mesostructured silica support by Marchan et al., US930733B2, (2016).
29. Catalyst synthesized from titanium-silicon nanometer composite oxides and polyoxometalates in situ as well as preparation method and application of catalyst by Liu et al., CN107552077A, (2017).
30. Polyoxometalate-based metal-organic frameworks crystal material with polyoxometalates as template by Pang et al., CN108997594A, (2018).

31. Polyoxometalates comprising noble metals and post-transition metals and metal clusters thereof by Tian et al., WO2018162144A1, (2018).
32. MOFs composite material containing heteropoly acid and transition metal complex and preparation method and application thereof by Chang et al., CN110606959A, (2019).
33. High-performance polyoxometalate catalyst and preparation method thereof by Choi et al., EP3020478B1, (2019).
34. Polymers of polyoxometalates and hydroxy-terminated monomer units and uses in degrading noxious agents by Hill et al., WO2017146801A2, (2019)
35. Process for producing alkenes from oxygenates by using supported partially neutralised heteropolyacid catalysts by S.R. Partington, EP3233767B1, (2019).
36. Preparation method and application of rare earth modified Keggin type heteropoly acid supported catalyst by Zhang et al., CN109876836B, (2021).
37. Method for preparing olefin by catalyzing biomass polyol and polybasic alcohol acid to deoxidize and dehydrate by using heteropoly acid containing molybdenum by Lu et al., CN111253256A, (2021).
38. Porous carbon supported monomolecular heteropoly acid catalyst and preparation method and application thereof by Mao et al., CN111167516A, (2021).
39. Method for preparing rare-earth modified Keggin-type heteropolyacid-supported catalyst and use thereof by Shu et al., JP2020151703A, (2021).
40. Electrocatalytic reduction of CO under heteropolyacid ionic liquid-indium double-catalytic system2Method for preparing ethanolic acid by Li et al., CN112144073A, (2021)
41. Polymer-polymetalate composite ink, and preparation method and application thereof by Wang et al., US11345824B2, (2022)
42. Hydrogen peroxide sensing device based on heteropolyacid salt and preparation method thereof by Xi et al., CN110907508B, (2022)

43. Polyoxometallic acid salt complex and its application in cancer treatment by Song et al., CN110049866A, (2022)

Thus, the literature survey shows that plenty of studies have been carried out on POMs based catalysts (including LPOMs, TMSPOMs, MSPOMs and TME-POMs/S) by number of groups and it would be difficult to mention all references. Hence, it may be possible that few references might be missing. We would like to excuse us for the same. Please note down that in the present thesis, we have restricted ourselves for following four points:

i. *Selected Keggin structure - phosphomolybdic acid*
ii. *Selected transition metals, iron (Fe), nickel (Ni) and palladium (Pd)*
iii. *The catalysts based on phosphomolybdic acid and transition metals are designed by two ways (a) transition metals substituted phosphomolybdate and (b) transition metal exchanged supported phosphomolybdic acid*
iv. *The synthesized transitions metal substituted phosphomolybdate catalysts are used as it is*

Catalysis by transition metal (Fe, Ni and Pd) substituted phosphomolybdates:

TMSPOMs based materials have played an important role as catalysts in the field of catalysis, especially oxidation reaction, where the substituted transition metal acts as active catalytic center and POMs function as a ligand with a strong capacity for multielectron redox transformations under. Hence, majority of the applications of mono-TMSPOMs are in the field of catalysis. The substituting metal center is penta-coordinated by the parent POMs, while the octahedral coordination sphere is completed by an additional sixth labile ligand, L (usually L= H_2O). The labiality of the sixth ligand allows the interaction of the substituting transition metal atom reacting with substrate and/or oxidant. In analogy with organometallic chemistry the "pentadentate" POMs acts as an inorganic ligand. This analogy led to TMPOMss being termed "inorganic metalloporphyrins" and have distinct advantages over organometallic species, as they are rigid, hydrolytically stable and thermally robust. Further, the active sites of their transition metals and counter cations can undergo extensive synthetic modifications.

In 2001, Mizuno et al. first-time reported synthesis of $Cs_3H_1PMo_{11}FeO_{39}$, $Cs_{1.5}Fe_{0.5}PMo_{12}O_{40}$, and $Cs_2(NH_4)_2PMo_{11.5}Fe_{0.5}O_{39}$. The synthesized complex was characterized by various techniques and evaluated for selective oxidation of isobutane [88]. In 2004, the same group synthesized $Cs_{2.8}H_{1.2}PMo_{11}Fe(H_2O)O_{39}.6H_2O$ using the same method which was reported earlier [89]. The catalytic activity of the catalyst was evaluated for oxidative dehydrogenation of 2-propanol. Five years later, in 2009, Rabia group reported oxidation of propene over Ammonium salts of transition metal substituted phosphomolybdate, $(NH_4)_6HPMo_{11}MO_{40}$ (M = Ni, Co, Fe), which were synthesized using individual salts and characterized by various analytical methods [90].

In 2013, Patel et al. reported the one-pot synthesis of Mono-transition-metal-substituted phosphomolybdates, $PMo_{11}M$ (M = Co, Mn, Ni) and characterized by various physicochemical techniques [91]. The efficiency of catalysts was evaluated for liquid-phase nonsolvent oxidation of styrene. Simultaneously, in the same year, same group reported solvent free alcohols oxidation using same catalyst [92]. Further in 2014, Mono-Nickel-substituted phosphomolybdates ($PMo_{11}Ni$) was synthesized by Patel et al. for the Suzuki–Miyaura cross-coupling [93].

Later, in 2015, Wang et al. reported the synthesis of $Na_6PMo_{11}FeO_{40}$ and was studied for its inhibitory effect on mushroom tyrosine, as a preventive measure against the peroxidation of fresh-cut fruits and vegetables [94]. In the same year, Mingjun group reported epoxidation of cyclohexene over immobilized transition metal mono-substituted phosphomolybdate ($PMo_{11}M$, M = Fe, Co or Cu) or un-substituted phosphomolybdic acid (PMo_{12}) on amino-functionalized SBA-15 using molecular oxygen as oxidant and isobutyraldehydes as co-reagent [95]. Later in 2017, Rahimi et al. demonstrated the synthesis of

$Cs_4H_2PMo_{11}FeO_{40}.6H_2O$ using the same method reported by Mizuno group [89] and its catalytic efficiency was evaluated for selective adsorption of methylene blue dye form a mixture of organic dyes (methylene blue, methyl orange, and rhodamine-B) [96].

Also in 2017, Gangling group described the synthesis of cesium salts of the transition metal mono-substituted phosphomolybdates $[PMo_{11}M(H_2O)O_{39}]^{5-}$ (M = Co^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+}) using the same method as reported by Patel et al. and used as heterogeneous catalyst for catalytic oxidation desulfurization (ODS) of model oil containing refractory sulfur compounds, dibenzothiophene (DBT), benzothiophene (BT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) [97]. The same group in the following year reported the synthesis of hybrids based on transition metal mono-substituted Keggin-type phosphomolybdates, $[Bmim]_5[PMo_{11}M(H_2O)O_{39}]$ (Bmim = 1-butyl 3-methyl imidazolium; M = Co^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+}) and used as catalysts for the oxidation desulfurization of the previously mention model oil [98]. In 2019, Wang group studied the inhibition effect of α-glucosidase inhibitors using transition metals (Fe, V and Co) substituted phosphomolybdate [99]. Mingjun group demonstrated solvothermal synthesis of transition metal (Fe, Co, Ni and Cu) substituted phosphomolybdate encapsulated over the Zr-based metal-organic framework (UiO-66) and its catalytic activity evaluated for the aerobic epoxidation of styrene in 2021 [100].

Recently, in 2022, Shuang et al. reported the synthesis of iron substituted phosphomolybdate immobilized on NH_2 functionalized SBA-15 [101]. The synthesized catalyst was well characterized by various analytical methods and its catalytic efficiency was evaluated towards cyclooctene epoxidation using H_2O_2 as oxidant. Simultaneously, Wang group investigated the electrocatalytic performance of five Keggin-type POMs ($H_3PMo_{12}O_{40}$, $Na_7PMo_{11}ZnO_{40}$, $Na_7PMo_{11}CoO_{40}$, $Na_7PMo_{11}MnO_{40}$, and $Na_7PMo_{11}NiO_{40}$) on tyrosinase diphenolase activity [102].

From literature it can be seen that, there is no single article available on palladium substituted phosphomolybdate till date. Further it is also observed that all the reported Fe and Ni substituted phosphomolybdate based catalysts are studied for oxidation, oxidative dehydrogenation, dye adsorption, desulfurization and inhibitory effect on mushroom tyrosine but no single report is available on hydrogenation reaction.

Catalysis by transition metal (Fe, Ni and Pd) exchange supported phosphomolybdic acid:

In supported POMs, POMs consist of exchangeable proton as counter cation. This available exchangeable proton of POMs is exchanged with transition metal cation, to design a new class of catalyst which consist the advantage of both transition metal as well as POMs.

In 2012, Xing group reported the preparation of uniform Pd nanoparticles by using phosphomolybdic acid (PMo_{12})-assisted method for synthesis of Pd-PMo_{12}/C catalyst and characterized by various techniques [103]. The catalyst was used for electro-catalytic oxidation of formic acid. In 2013, Dai et al. reported a novel method for synthesis of phosphomolybdic acid-modified Pd/C catalysts which first involves immobilizing of phosphomolybdic acid (HPMo) on polyaniline (PAN-) functionalized carbon supports (HPMo-PAN-C) followed by the usage of HPMo-PAN-C as a support to prepare Pd/HPMo-PAN-C catalyst [104]. The physical structure of the obtained catalyst was confirmed by various characterization methods and its catalytic activity and stability were evaluated for electro-chemical oxygen reduction reaction. Two years later in 2015, Lin group demonstrate green synthesis of PdCu supported on graphene/polyoxometalate LBL films (PdCu@PDDA-GN/PMo_{12}) in two steps. The first step in the synthesis involves preparation of PDDA-GN/PMo_{12} composite films [105]. In the second step involves deposition of PdCu particles on the surface of the PDDA-GN/PMo_{12} composite films. The prepared PdCu@PDDA-GN/PMo_{12} catalyst was utilized for eletrocatalytic activity of formic acid oxidation. After that, in 2016, Yuan et al. demonstrated the synthesis of Pd nanoflowers supported on HPMo-modified graphene (Pd NF/HPMo-G) catalyst which was prepared by first supporting phosphomloybdic acid on graphene oxide followed by in-situ growth of Pd nanoflowers [106]. The synthesized catalyst was used formic acid electro-oxidation reaction. Later in 2019, Lou group reported synthesis of Fe-doped $H_3PMo_{12}O_{40}$ immobilized on covalent organic frameworks (Fe/PMA@COFs) for cyclooctene epoxidation using H_2O_2 [107].

Thus, the literature survey shows that the above all reported catalysts were evaluated for electro- catalytic oxidation of formic acid and oxygen reduction reactions.

In summary, literature survey shows that:

- Until now no attempt has been made for the synthesis of palladium substituted phosphomolybdates
- The designing of nickel exchanged phosphomolybdic acid supported on metal oxides are not available in the art
- The use of such designed catalysts for hydrogenation reaction is not reported till date
- The use of water as green solvent for hydrogenation is untouched

The hydrous zirconia (ZrO_2, an acidic support) selected as the support in the present study for the following reasons:

- Physical properties can easily be modified by surface treatment
- Mechanical properties similar to those of stainless steel
- Thermodynamically stable modification up to a temperature of 2370°C [108, 109]
- Direct anchoring surface which facilitates the easy approach of substrates to active sites via available surface hydroxyl groups for the interaction

Based on above observations, the scope and objectives of the thesis have been proposed.

Scope of thesis

In present work, phosphomolybdic acid is designed at molecular level by synthesizing mono- Fe, Ni and Pd substituted phosphomolybdic acid as well as Fe, Ni and Pd exchange with available protons of phosphomolybdic acid supported on hydrous zirconia by one-pot and ion-exchange method respectively.

To evaluate the catalytic activity of designed catalysts, hydrogenation of styrene, cyclohexene and levulinic acid were performed considering as model substrates. The heterolytic cleavage of C=C of alkene gave industrially important platform molecule, alkane. Styrene hydrogenated product ethyl benzene is one of most valuable compounds with widespread application in gasoline, paints, inks, insecticides, carpet glues. Similarly, cyclohexane is hydrogenated product of cyclohexene, a raw material for synthesis of cyclohexanol, cyclohexanone, which are further used in manufacturing of adipic acid and caprolactam, and moreover it is used as nonpolar solvent.

Hydrogenation of carbonyl C=O group in levulinic acid produces alcohol group (C-OH) which further upon hydrolysis with carboxylic acid (-COOH) gives γ-valerolactone. It is widely used in food additives, gasoline blenders, solvents, polymer precursors, and other valuable chemicals.

Tandem Suzuki–Miyaura cross coupling/ nitro hydrogenation reaction was evaluated for Pd exchanged phosphomolybdic acid supported on zirconia. As we know that Pd catalyst is widely used for industrially important Suzuki–Miyaura cross coupling and hydrogenation reaction, so keeping in mind, we carried out one-pot reaction to overcome use of catalyst amount, solvent, tedious isolation of product and time.

Objectives of the Thesis

- To tune the structural and redox properties of lacunary phosphomolybdic acid by insertion of transition metal ions into the lacuna to form transition metal (Ni, Fe and Pd) substituted phosphomolybdic acid ($PMO_{11}Fe$, $PMo_{11}Ni$ and $PMo_{11}Pd$).
- To synthesize transition metal (Ni, Fe and Pd) exchanged phosphomolybdic acid supported on ZrO_2 as a support (Fe-PMo_{12}/ZrO_2, Ni-PMo_{12}/ZrO_2 and Pd-PMo_{12}/ZrO_2).
- To characterize synthesized materials by various techniques such as Elemental analysis, TG-DTA, FT-IR spectroscopy, Raman Spectroscopy, UV-Vis spectroscopy, ^{31}P NMR, ESR, XPS, Powder XRD, BET Surface area, SEM, TEM and HRTEM.
- To use the synthesized materials as catalyst for liquid phase hydrogenation of alkenes (styrene and cyclohexene) and levulinic acid, one-pot hydrogenation via C-C coupling.
- To study all the respective reaction parameters such as ratio of substrate to catalyst, temperature, pressure, time and solvent for maximum conversion as well as product selectivity.
- To study reaction mechanism.
- To propose best catalyst for each organic transformation.

Organization of the Thesis

The work has been divided into three parts (based on transition metals), each consisting of two chapters:

Part A: Designing of catalysts based on Iron & phosphomolybdic acid

Chapter 1: Cesium salt of iron substituted phosphomolybdate ($PMo_{11}Fe$): Synthesis, characterization and application for hydrogenation of styrene

Chapter 2: Iron exchanged phosphomolybdic acid supported on zirconia (Fe-PMA/ZrO_2): Synthesis, characterization and application for hydrogenation of cyclohexene

Part B: Designing of catalysts based on Nickel & phosphomolybdic acid

Chapter 1: Cesium salt of nickel substituted phosphomolybdate ($PMo_{11}Ni$): Synthesis, characterization and application for hydrogenation of levulinic acid

Chapter 2: Nickel exchanged phosphomolybdic acid supported on zirconia (Ni-PMA/ZrO_2): Synthesis, characterization and application for hydrogenation of levulinic acid

Part C: Designing of catalysts based on Palladium & phosphomolybdic acid

Chapter 1: Cesium salt of palladium substituted phosphomolybdate ($PMo_{11}Pd$): Synthesis, characterization and application for hydrogenation of levulinic acid

Chapter 2: Palladium exchanged phosphomolybdic acid supported on zirconia (Pd-PMA/ZrO_2): Synthesis, characterization and application for Suzuki–Miyaura cross coupling and Tandem Suzuki–Miyaura cross coupling/ nitro hydrogenation

Annexure: Nickel salt of phosphomolybdic acid (NiHPMA): Synthesis, characterization and application for oxidative esterification

Brief discussion of each chapter

Part A: Designing of catalysts based on Iron & Phosphomolybdic acid

Chapter 1 describes One-pot synthesis of cesium salt of iron substituted phosphomolybdate ($PMo_{11}Fe$). The synthesized catalyst is characterized by instrumental techniques such as elemental analysis (EDX), TGA, FT-IR, FT-Raman, ^{31}P MAS NMR, ESR, XPS, and powder XRD. The activity of the catalyst is studied for hydrogenation of styrene in aqueous medium as well as neat water by varying different reaction parameters. The control experiments are carried out under optimized reaction conditions to investigate the role of each component. Hot filtration tests are performed to evaluate heterogeneity and leaching of active species of the catalyst. The used catalyst is recovered and regenerated to study its catalytic activity up to three cycles. Regenerated catalyst is characterized by EDX, FT-IR, ESR and XPS in order to check its sustainability. Scope of the substrates is also studied for different functionalities. Activity of the catalyst is also compared with the reported systems. Further, detailed mechanistic investigation is also carried out by D_2O labeling experiment and ESR study along with proposal of a probable reaction mechanism.

Chapter 2 deals with the synthesis and characterization of Fe exchanged phosphomolybdic acid supported on zirconia (Fe-PMo_{12}/ZrO_2). The catalytic activity of synthesized catalyst is evaluated for cyclohexene hydrogenation in water as a solvent by varying different reaction parameters. Control experiments, hot filtration tests were performed. The spent catalyst was recovered and regenerated to investigate its activity up to three catalytic runs. Regenerated catalyst was characterized in order to check its stability. Viability of the catalysts towards different substrates as well as activity of the catalyst with reported systems were studied. A probable reaction mechanism was also proposed.

The comparison of catalytic activity of both the catalysts were investigated and discussion on the stability of the catalyst.

Part B: Designing of catalysts based on Nickel & Phosphomolybdic acid

Chapter 1 describes the one-pot synthesis of cesium salt of nickel substituted phosphomolybdate ($PMo_{11}Ni$). The synthesized catalyst is characterized by some basic instrumental techniques such as EDX, TGA and FT-IR. The synthesized catalyst was evaluated for styrene hydrogenation reaction.

Chapter 2 deals with synthesis of nickel exchanged phosphomolybdic acid supported on zirconia (Ni-PMo_{12}/ZrO_2). The synthesized catalyst was systematically characterized by various instrumental techniques such as EDX, TGA, FT-IR, ^{31}P MAS NMR, XPS, BET and powder XRD. The catalytic activity of the synthesized catalyst was studied for solvent free aqueous phase hydrogenation of lignocellulosic biomass-derived levulinic acid (LA) using formic acid (FA) as internal hydrogen source by varying various reaction parameters. To investigate the role of each component, control experiments were carried out under optimized reaction conditions. Hot filtration tests were performed for sustainability evaluation of the catalyst. Recycling study was performed up to three cycles and regenerated catalyst was characterized in order to check its stability. Activity of the catalyst was also compared with the reported systems. Further, detailed mechanistic investigation was also carried out by control experiment.

Part C: Designing of catalysts based on Palladium & Phosphomolybdic acid

Chapter 1 describes the synthesis of cesium salt of palladium substituted phosphomolybdate ($PMo_{11}Pd$). The synthesized catalyst was thoroughly characterized by various physico-chemical techniques i.e., EDX, TGA, FT-IR, ^{31}P MAS NMR, XPS, powder XRD, TEM, HRTEM and HAADF-STEM. The catalytic efficiency of synthesised catalyst was evaluated for aqueous phase hydrogenation of biomass-derived levulinic acid (LA) using formic acid (FA) as internal hydrogen source by varying different reaction parameters. Control experiment and hot filtration test were carried out to evaluate the role of each component and leaching as well as heterogeneity of catalyst respectively. The spent catalyst was recovered and recycled to prove its catalytic activity up to three catalytic cycles. The regenerated catalyst was well characterized in order to check its sustainability.

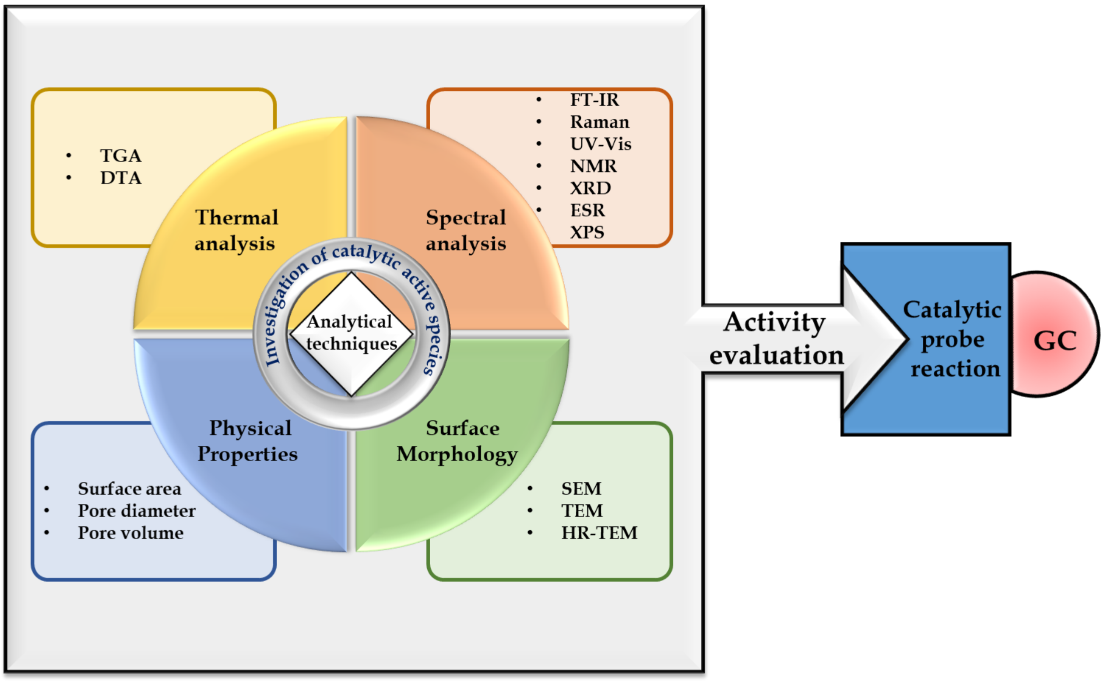
Chapter 2 deals with synthesis of palladium exchanged phosphomolybdic acid supported on zirconia (Pd-PMo_{12}/ZrO_2). The synthesized catalyst was well characterized and its catalytic activity was studied for Suzuki–Miyaura cross coupling and Tandem Suzuki–Miyaura cross coupling-nitro hydrogenation reaction in aqueous medium by varying different reaction parameters. Control experiments were carried out under optimized conditions, to study the role of each component in the synthesized catalyst. Hot filtration test was performed to investigate the sustainability of the synthesized catalyst. After completion of reaction, the catalyst was regenerated and reused up to three cycles and the regenerated catalyst was characterized by various instrumental techniques such as EDX, FT-IR, XRD, and XPS in order to check its stability. A probable reaction mechanism was also proposed.

The comparison of catalytic activity of both catalysts is investigated and stability of the catalyst was discussed.

Annexure: deals with the synthesis and characterization of nickel salt of phosphomolybdic acid ($NiHPMo_{12}$). The catalytic activity of the synthesized catalyst was evaluated for tandem oxidative esterification of benzaldehyde to ester using methanol and H_2O_2 oxidant by varying various reaction parameters. Control experiments, leaching and heterogeneity tests were carried out. Regeneration study of the catalyst as well as characterization of regenerated catalyst were performed. Tolerance limit of the catalyst was investigated for variety of the substrates. Activity of the catalyst with reported systems as well as the effect of addenda atom on the reactions were also evaluated. Also, detailed mechanistic study was carried out by UV-Visible and Raman spectroscopy.

Analytical techniques utilized in the present work

Characterization is an important aspect of catalyst development [110-112]. In particular, especially in case of supported catalysts, assessing the link between the catalytic properties of the material and its catalytic performance requires elucidating the chemical properties, structures, and composition of the synthesized materials, and also the interactions among active species and the supports [112]. It is indeed critical to understand the basis of the materials structure-catalytic properties in order to synthesize new catalysts. A summary of the various characterization tools for heterogeneous catalyst is shown in scheme 6.



Scheme 6. Various techniques for catalyst characterization

It is essential to evaluate whether the active ingredient is on the support's surface or diffused within it in the case of supported catalysts. As a matter of fact, from a scientific standpoint, investigating the surface composition and local structure of the catalyst at the atomic level, as well as the connecting these data with catalyst performance, is critical in the catalytic reaction. The fundamental knowledge of the structure-catalytic property relationship for catalyst systems will be useful in the development of novel and efficient catalysts. A variety of tools, including physicochemical and spectroscopic techniques, can be used to characterize Heterogeneous catalysts. An overview of the numerous different catalyst characterization techniques used in the latest study is provided below:

Energy-dispersive X-ray spectroscopy (EDS or EDX) [113]

EDS or EDX is a chemical characterization or elemental analysis technique. It investigates a sample via interactions between electromagnetic radiation and matter, analyzing X-rays emitted by matter in reaction to being hit with charged particles. Its characterization capabilities are largely due to the fundamental principle that each element has a unique atomic structure, which allows X-rays that are characteristic of an element's atomic structure to be distinguished from one another.

The elemental analysis was performed using the JSM 5610 LV in conjunction with the INCA instrument for EDX-SEM analyzer for the quantitative characterization.

Thermo Gravimetric Analysis (TGA) [114]

It is a method that records the weight of a substance as a function of time or temperature in an environment that is heated or cooled at a controlled rate.

A supported catalyst's temperature-weight loss profile can offer useful quantitative information about the types of water present in the sample. It is normally possible to tell the difference between loosely held "physisorbed" water and strongly bonded "chemisorbed" water, which aids in deciding the best conditions for removing the excess.

Perhaps more importantly, the degradation of less stable catalysts can be studied, which aids in measuring the optimum activation temperatures and the temperatures where the supported reagents is used safely.

TGA measurements were performed on the Mettler Toledo Star SW 7.01 at temperatures ranging from 40 ^{o}C to 600 ^{o}C. All measurements were conducted in a nitrogen atmosphere at a flow rate of 2 mL/min and a heating rate of 10 ^{o}C/min.

Fourier Transform Infrared Spectroscopy (FT-IR) [113]

The most useful and widely used technique for studying supported reagents is probably FT-IR spectroscopy. It includes the following details.

i. Surface species identification
ii. Reagent dispersion on the support surface
iii. Surface activity investigation using probe molecules

The three most common methods for studying an insoluble solid are as follows: 1) as a mull, 2) as a disc, and 3) directly as a powder. The level of difficulty (in obtaining useful spectra), ease of sample preparation, and reliability of the information obtained differ among these methods. The mull and disc methods are both transmission techniques. Transmission spectroscopy may not be suitable for FT-IR opaque or highly scattering materials.

FT-IR absorption spectra of prepared catalyst were measured at room temperature on a Shimadzu (IR Affinity 1S) instrument using KBr pellets in the range of 4000 cm-1 to 400 cm-1. To make the pellets, the powdered samples were ground with KBr in a 1:10 ratio and pressed (5 ton/cm^2). At an average of 40 scans, the data was obtained.

FT- Raman spectroscopy (LRS) [115]

Raman spectroscopy (named after Sir C. V. Raman) is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range.

Most Raman spectrometers for material characterization use a microscope to focus the laser beam to a small spot (< 1-100 mm diameter). Light from the sample passes back through the microscope optics into the spectrometer. Raman shifted radiation is detected with a charge-coupled device (CCD) detector, and a computer is used for data acquisition and curve fitting. These factors have helped Raman spectroscopy to become a very sensitive and accurate technique.

The Raman spectra were recorded on a FT-Raman Spectrophotometer Model Bruker FRA 106.

Solid state MAS Nuclear Magnetic Resonance (NMR) Spectroscopy [116]

Magic Angle Spinning (MAS) is a technique in nuclear magnetic resonance that is frequently used to conduct experiments in solid-state NMR spectroscopy.

The normally broad lines become narrower by spinning the sample (usually at a frequency of 1 to 70 kHz) at the magic angle m (ca. 54.74°, where cos2 m= 1/3) with respect to the direction of the magnetic field on intensifying the resolution for improved analysis and identification.

To analyze the environment around a specific nucleus of a synthesized material, NMR is a beneficial tool. It is also useful to know whether the synthesized material is pure or contains isomers.

The solid state JOEL ECX 400 MHz High Resolution Multinuclear FT-NMR spectrometer for solids was used for ^{31}P MAS NMR.

Powder X-Ray Diffraction (XRD) [113]

XRD can detect poorly dispersed or macrocrystalline reagents. In general theory, XRD could be used to rapidly examine the effectiveness of dispersion of any supported reagent in which the reagent normally exists in the crystalline state. XRD could also be used to identify species formed during the preparation of a supported reagent for successive chemistry. This really is particularly useful for corrosive reagents, unstable reagents, and supported reagents that have undergone high-temperature thermal treatment. The nature of surface species has also been usually characterized using XRD.

Using the Philips Diffractometer, the powder X Ray Diffraction pattern of the support and catalysts was obtained (Model PW - 1830). Cu K radiation (1.5417) was used, with a scanning angle ranging from 10° to 80°.

BET Measurement [114]

Since the surface area of the catalyst is directly proportional to the catalytic activity of heterogeneous catalysts, surface area measurement is perhaps the most important finding for the same. Further data can be retrieved from the surface area, such as pore volume and pore size, that will aid in understanding the pathway of the reaction.

The surface area and pore size distribution of various catalysts were measured using a Micromeritics Surface area Analyzer (Model: ASAP 2020) at -196 °C using the Brunauer-Emmett-Teller (BET) method, which involved nitrogen adsorption-desorption. The specific surface area was calculated using the BET method from the adsorption desorption isotherms. Prior to assessment, the samples were degassed under vacuum (5 – 10.3 mmHg) at 60 – 90 °C for 4 hours to remove the physisorbed moisture. The pore size distributions were also determined by calculating for the desorption branches of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

X-ray photoelectron spectroscopy (XPS) [117]

XPS is a surface-sensitive quantitative spectroscopic technique used to determine the elemental composition and electronic state of elements in a material. XPS spectra were recorded by irradiating a material with an X-ray beam while concurrently trying to measure the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analysed under high vacuum (P 10-8 millibar) or ultra-high vacuum (UHV; P 10-9 millibar) conditions.

Auger Electron Spectroscopy (AES) Module PHI 5000 Versa Prob II was used to perform XPS measurements.

Transmission Electron Microscopy (TEM) [114], High-Resolution Transmission Electron Microscopy (HRTEM) [118] and Scanning Transmittance Electron Microscopy (STEM) [119]

TEM and HRTEM (a specialized TEM imaging mode) are techniques that have an electron beam to image a nanoparticle sample, offering even better resolution than light-based imaging techniques. Images can be resolved using either a fluorescent screen or photographic film. Moreover, the analysis of the X-ray caused by the interaction of the accelerated electrons with the sample allows for high spatial resolution determination of the elemental composition of the sample. The primary approach for accurately measuring nanoparticle size, grain size, size distribution, and morphology is transmission electron microscopy (TEM).

STEM images are TEM images that are created by focusing an electron beam to a fine spot (typically 0.05 – 0.2 nm in size) and getting passed it through an adequately thin specimen, which would then be scanned over the sample in a raster illumination system designed to illuminate the sample at each point with the beam parallel to the optical axis. STEM imaging is being used to describe the nanoscale and atomic scale structure of specimens, revealing vital information about material properties and behavior.

TEM micrographs were captured using a PHILIPS CM 200 (Model: CM 200, Operating voltages: 20-200 kV, Resolution: 2.4). HRTEM analysis was performed on a Field Emission Gun-Transmission Electron Microscope (Resolution: 0.19 nm, Line: 0.1 nm, Magnification: 50 x - 1.5 M x accelerating voltage of 200 kV; Make: JEOL; Model: JEM 2100F) with EDS and STEM attachment systems. The specimens were indeed dispersed in ethanol for 5–10 minutes before being ultrasonicated. Before viewing, a small drop of the sample was placed on a carbon coated copper grid and dried.

Catalytic activity

The designed catalysts were evaluated for hydrogenation of styrene, cyclohexene, levulinic acid and tandem Suzuki–Miyaura cross coupling-nitro hydrogenation. For this, we have used two different types of reaction equipment, (i) high-pressure autoclave and (ii) teflon lined stainless-steel autoclave.

Hydrogenation of styrene, cyclohexene, and tandem Suzuki–Miyaura cross coupling-nitro hydrogenation was carried out in high pressure autoclave individually. It consists of three major components: the 100 mL capacity batch type reactor made of SS-316, H_2 reservoir with electronic temperature and pressure controller. The reaction vessel was charged with reactant, solvent and catalyst. The presence of air in the unfilled space of the reactor vessel was removed by purging with H_2 gas several times. Finally for the reaction, required H_2 pressure was applied and set at reaction temperature for appropriate times with a stirring rate of 500 rpm. The progress of the reaction was demonstrated by a continuous decrease in pressure inside the reactor.

The levulinic acid hydrogenation was carried out in teflon lined stainless-steel autoclave. Its inner steel wall is equipped with a Teflon container (made in-house) having 25 mL volume capacity. In typical experiment, LA, FA (hydrogen source) and catalyst was charged into the Teflon container. Finally, the autoclave was sealed and put in to oven at appropriate temperature and time.

For all the reactions, the reactant and products were analyzed using gas chromatography, Shimadzu 2014 GC. The obtained products were confirmed by comparing it with their respective standard samples.

Gas Chromatography (GC) [120]

GC is a chromatographic technique being used to distinguish and analyze material that vaporize without decomposition. Its principal implementation includes compound purity testing and separation of mixture components. In this study, GC experiments were performed on a Shimadzu GC-2014 instrument with a Rtx-5 capillary column.

The conversion and selectivity for all the reaction were calculated by the following equations:

$$\% \, Conversion = \frac{(initial\ mol\%) - (final\ mol\%)}{(initial\ mol)} \times 100$$

$$\% \, Seletivity = \frac{moles\ of\ products\ formed}{moles\ \ of\ substrate\ consumed} \times 100$$

The Turnover number (TON) was calculated by using the equation:

$$TON = \frac{moles\ of\ products\ formed}{moles\ \ of\ catalyst}$$

$$TOF = \frac{TON}{reaction\ time}$$

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