GENERAL INTRODUCTION

A comprehensive approach relevant to all aspects of chemistry is the designing of materials and methodologies that reduce or eradicate the use as well as generation of hazardous substances, also termed as Green Chemistry. During the past two decades, green synthetic and processing techniques, non-toxic chemicals and solvents have become a major part of research intending to make human life and environment more benign. In this regard, the designing and application of novel catalysts and catalytic systems have been one of the key technologies of Green Chemistry [1]. As Ron Breslow, from Chemistry Today and Tomorrow: The Central, Useful, and Creative Science, puts it,

> "No subject so pervades modern chemistry as that of catalysis"

The main role of a catalyst is to lower the raw material and energy requirements, decrease/nullify formation of unwanted side-products and reduce the hazardous effects of chemical reactions. Scientists and researchers are in pursuit of development and implementation of ecofriendly as well as environmentally benign innovative catalysts as well as catalytic processes with high efficiency, simple operations, and simple work-up procedures.

Herein comes the humungous family of inorganic porphyrin-like molecules called Polyoxometalates (POMs), whose properties and diversity in applications have not been matched by any single family of compounds. They are widely used as model systems for fundamental research providing unique opportunities for mechanistic studies on the molecular level so much so, that POM-based materials as catalysts have become a very important field of research, academically as well as industrially [2-7].

Polyoxometalates – an overview

POMs are a discrete class of anionic transition metal-oxygen clusters with unique properties of topology, size, electronic versatility as well as structural diversity ranging from nano- to micrometer scale [8]. Due to these essential properties, POMs have enjoyed a wide range of applications [9] including magnetic [10, 11], electronic and electrochemical [12-15], catalysis [16-18], optics [17, 19] and also in other fields like biology [19], nano-materials [20] and surface sciences [21].

POMs have the general formula $[X_xM_mO_y]^{q-}$, in which X is the hetero atom, usually a main group element (e.g., P, Si, Ge, As), and M is the addenda atom, being a d-block element in high oxidation state, usually $V^{IV/V}$, Mo^{VI} or W^{VI}. 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

POMs have a history aging back to early nineteenth century, when Berzilius described the formation of a canary yellow coloured precipitate of ammonium 12-phosphomolybdate on excess addition of ammonium molybdate to phosphoric acid [22]. Significant progress in POM chemistry was seen after the discovery of the first POM [23].

1. About 20 years later, Svanberg and Struve showed that the insoluble ammonium salt of this complex could be used for the gravimetric analysis of phosphate [24].
2. Research on POM chemistry received an impetus when Marignac, in 1862, discovered the tungstosilicic acids and their salts. He successfully synthesized and analysed the two isomers 12-tungstosilicic acid and 12-silicotungstic acid, today known as the α and β-isomers [25].
3. Thereafter, the field developed rapidly, so that over 60 different types of heteropoly acids (giving rise to several hundred salts) had been described by the end of first decade of this century.
4. According to the structural hypothesis of A. Miolati in 1908, the central heteroatom was assumed to have an octahedral coordination with MO_4^{2-} or $M_2O_7^{2-}$ ligands. This was further given a laboratory perspective by A. Rosenheim in the 1930s.

5. For the first time, in 1929, Linus Pauling tried to elucidate the structure of a polyoxometalate. He proposed a 12:1 complex structure based on arrangement of 12 octahedra around a central XO_4 tetrahedron. According to his structural hypothesis, twelve WO_6 octahedra surround one PO_4 or SiO_4 tetrahedron to form 12-tungstoanions in which all polyhedron linkages would involve vertices sharing rather than edge sharing in order to minimize electrostatic repulsion. Thus, the proposed structure would have 58 oxygen atoms and the moecular formula would be $[(PO_4)W_{12}O_{18}(OH)_{36}]^{3-}$ [26].
6. Soon after, in 1933, Keggin successfully solved the structure of $H_3[PW_{12}O_{40}].5H_2O$ and found that the structure was indeed based on WO_6 octahedra which were linked by egdes as well as corners [27, 28]. The application of X-ray crystallography for the determination of polyoxometalate structures further accelerated the development of polyoxometalate chemistry.
7. During the next year, Signer and Gross confirmed that $H_4SiW_{12}O_{40}$, $H_5BW_{12}O_{40}$ and $H_6[H_2W_{12}O_{40}]$ were structurally isomorphous with Keggin's structure [29].
8. Bradley and Illingworth further confirmed Keggin's elucidation of $H_3[PW_{12}O_{40}].5H_2O$ by studying the crystal structure [30] and these results were further supported by single crystal experiments of Brown and co-workers [31] after the advent of single crystal X-Ray diffraction techniques.

With the development of POM chemistry, various types of structures were discovered, as listed in table 1 [32].

Table 1. Different families of POMs

Structure	**General Formula**	**Year of discovery**
Keggin	$[XM_{12}O_{40}]^{n-}$ ($X = P^{5+}, As^{5+}, Si^{4+}, Ge^{4+}$)	1933
Evans-Anderson	$[XM_6O_{24}]^{n-}$ ($X = Te^{6+}, I^{7+}$)	1937
Dawson	$[X_2M_{18}O_{62}]^{n-}$ ($X = P^{5+}, As^{5+}$)	1953
Lindqvist	$[M_6O_{19}]^{n-}$ ($M = Nb^{5+}, W^{6+}, Mo^{6+}$)	1953
Dexter-Silverton	$[XM_{12}O_{42}]^{n-}$ ($X = Ce^{4+}, Th^{4+}$)	1968
Keplerate	$[M_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{n-}$ ($M = Mo^{6+}$)	1998
Kortz polyoxopalladate	$[Pd_{13}As_8O_{40}H_6]^{n-}$	2008

Of all the different types of POMs, the Keggin POMs are the most extensively studied because of its ease in synthesis, high thermal stability [6] as well as acidity, and the present thesis deals with Keggin type POMs only.

The Keggin POMs

The Keggin POM has the general formula is $[XM_{12}O_{40}]^{n-}$, where X is the central hetero atom, 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.

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

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

Structure

The ideal Keggin structure, $[XM_{12}O_{40}]^{3-}$ of α-type (Figure 1) 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 [27, 28], which have a common oxygen vertex connected to the central heteroatom. The oxygen atoms in this structure fall into four classes of symmetry-equivalent oxygens: X-O_a-$(M)_3$, M-O_b-M, connecting two M_3O_{13} units by corner sharing; M-O_c-M, connecting two M_3O_{13} units by edge sharing; and terminal O_d-M, where M is the addenda atom and X the heteroatom.

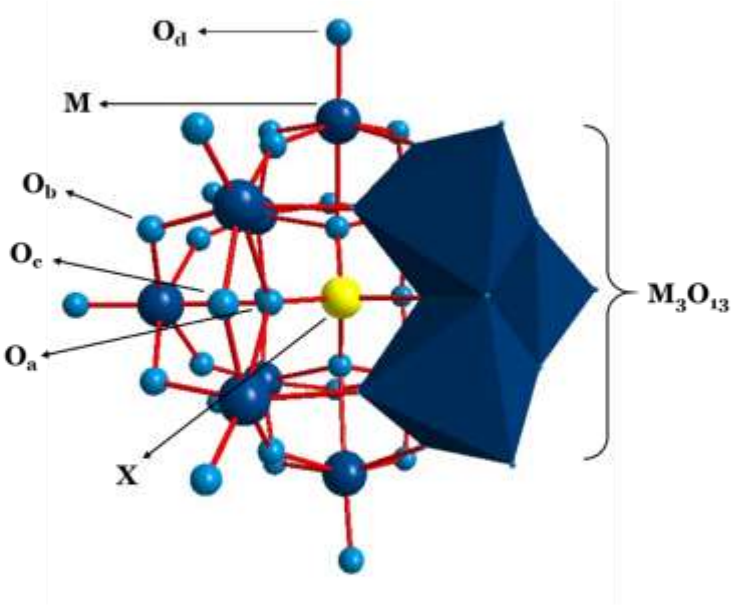


Figure 1. Structure of Keggion ion

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 and shape of the Keggin anion and the crystal structure, there is no open pore through which nitrogen molecule can penetrate. A gist of their properties in presented in table 2.

Table 2. Properties of POMs

Thermal Stability	➢ While most of the POMs in acidic forms are thermally stable, the stability varies depending upon the heteroatom, polyatom and polyanion structure. ➢ The stability trend followed by Keggin POMs is : $PW_{12}O_{40}^{3-}$ > $PMo_{12}O_{40}^{3-}$ > $SiMo_{12}O_{40}^{4-}$ [33]
Acidic properties	➢ HPAs in solid state are pure Bronsted acids and show much higher acidic strength compared to conventional SiO_2-Al_2O_3, H_3PO_4/SiO_2, HX and HY zeolites [34, 35], oxoacids of constituent elements as well as mineral acids ➢ The strong acidic nature is attributed to: • Dispersion of negative charge over a large number of atoms of the polyanion • Polarization of negative charge over the outer surface of polyanion due to the double bond character of $M=O_t$ ➢ The acid strength is found to follow the order $H_3PW_{12}O_{40}$ > $H_4SiW_{12}O_{40}$ > $H_3AsW_{12}O_{40}$ > $H_4GeW_{12}O_{40}$ [33]

Redox properties	➢ Due to the existence of the addenda atoms in their highest oxidation states (d^0), they generally tend to be strong oxidation catalysts [22]. ➢ Many polyanions tend to reduce easily to give rise to a blue species commonly called as "heteropoly blues" or more specifically "molybdenum blues" ➢ Oxidative ability decreases in the order $V^- > Mo^- > W^-$ containing heteropolyanion`
Molecular level designing	➢ Acidic and redox properties – choice of appropriate polyanion, heteroatom, etc., controls these properties ➢ Multifunctionality – Acid-Redox, Acid-Base, Multi-electron, etc. ➢ Tertiary structure and bulk behavior – controlled by choice of appropriate counter-cation [33]

Over years, an extensive survey of the synthesis, structures and properties of POMs has been gathered and summarized in various 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 Chemistry for Nano-Composite Design	T. Yamase, M. T. Pope	Springer Science & Business Media, 2002
Polyoxometalate Molecular Science	M. T. Pope, A. Muller	Kluwer Academic publishers , 2003

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 Into Supramolecular Hydrogels: From Crystalline Fibrillar to Amorphous Micellar Networks	Aoli Wu, Xinpei Gao, Panpan Sun, Fei Lu, Liqiang Zheng	Wiley-VCH Verlag GmbH, 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

Issue on Polyoxometalates	C. L. Hill	Chem. Rev., 98, (1998) 1
Tungsten-183 nuclear magnetic resonance spectroscopy in the study of Polyoxometalates	Y. G. Chen, , J. Gong, L. Y. Qu	Coord. Chem. Rev., 248, (2004) 245
Polyoxometalate clusters, Nanostructures and Materials: From self-assembly to designer materials and devices	D. L. Long, E. Burkholder, L. Cronin	Chem. Soc. Rev., 36, (2007) 105
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 (2009) 2872

Hybrid Organic-Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications	A. Dolbecq, E. Dumas , C. R. Mayer, P. Mialane	Chem. Rev., 110 (10) (2010) 6009
Polyoxometalates containing late transition and noble metal atoms	P. Putaj, F. Lefebvre,	Coord. Chem. Rev., 255 (2011) 1642
Theme issue: Polyoxometalate cluster science	L. Cronin, A. Muller	Chem. Soc. Rev., 41 (2012) 7325
The chemistry of organoimido derivatives of polyoxometalates	J. Zhang, F. Xiao, J. Hao, Y. Wei	Dalton Trans., 41 (2012) 3599
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 (2014) 141
Polyoxometalate based Open-Frameworks (POM-OFs)	H. N. Miras, L. Vila-Nadal, L. Cronin,	Chem. Soc. Rev., 43 (2014) 5679
Environmentally Benign Polyoxometalate Materials	S. Omwomaa, C. T. Gorea, Y. Ji, C. Hub, Y. -F. Song	Coord. Chem. Rev. 286 (2015) 17
A brief review of the crucial progress on heterometallic polyoxotungstates in the past decade	J. Liu, Q. Han, L. Chen, J. Zhao	CrystEngComm., 18 (2016) 842
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 (2019) 1

As it is known that amongst all, phosphotungstates are the most stable, we have selected phosphotungstates for the present study.

Modifications in POMs

The ability of tuning the acidic and redox properties of POMs at molecular level has resulted in development of new class of materials with novel structural as well as electronic properties. One of the most significant properties of modified precursors is their ability to accept and release specific numbers of electrons reversibly, under marginal structural rearrangement [36-38]. The modification of parent POMs at molecular level can be carried out in three different ways.

I. Lacunary POMs (LPOMs)

Controlled treatment of heteropoly/polyoxo species with base can produce "lacunary" heteropoly/polyoxo species wherein one or more addenda atoms have been eliminated from the structure along with the oxygens [5]. When solutions of parent $[PW_{12}O_{40}]^{3-}$ are treated with base, a series of hydrolysis reactions leads to the formation of mono-, di- and tri-lacunary phosphotungstates, with general formulae $[PW_{11}O_{39}]^{7-}$, $[PW_{10}O_{36}]^{8-}$ and $[PW_9O_{34}]^{9-}$ respectively (Figure 2).

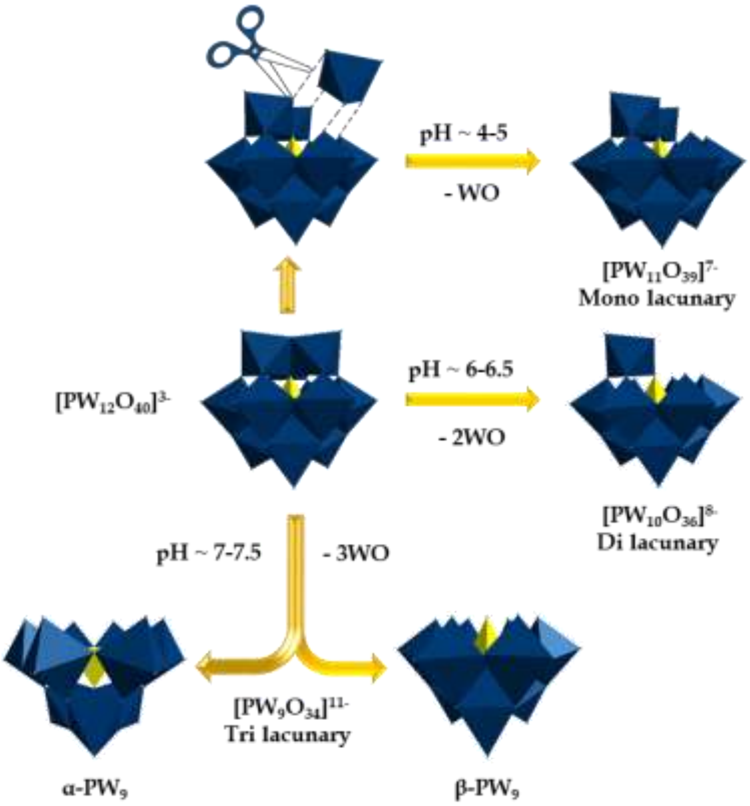


Figure 2. Formation of LPOMs

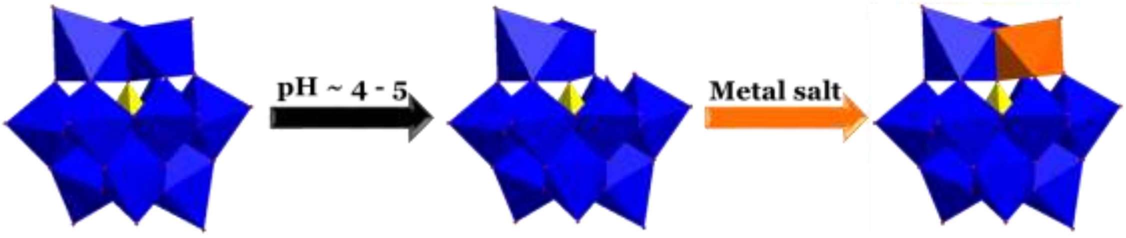
II. Transition metal substituted POMs (TMSPOMs)

TMSPOMs have attracted a continuous growing attention in the realm of POM chemistry due to the fact that their size, shape, charge density, acidity/redox, stability and solubility can be rationally modified at molecular level resulting in their outstanding unique electrochemical, magnetic, medicinal and catalytic properties [39-41], resulting in a range of applications [42-45]. It affords convenient platforms for the stabilization of unusually high oxidation state metal-oxo species. In addition, TMSPOMs have number of advantages over organometallic complexes such as (i) replacing one counter-cation with another hepls to tune their solubility (ii) replacing one heteroatom with another and one transition metal with another helps tune their redox properties (iii) unlike most organic catalysts, they are robust under oxidation conditions [46]. The enormous variety in their structures along with interesting properties gives rise to scope for many applications in magnetism, medicine and most importantly, catalysis [34, 40].

In the present work, we have focused mainly on mono- and di-transition metal substituted phosphotungstates only.

a. Mono transition metal substituted phosphotungstates

Though considered as inorganic analogs of metalloporphyrin complexes, the rigidity, hydrolytic stability and thermal robustness of Keggin type mono-TMSPOMs give them a distinct advantage over metallophorphyrins and other organometallic complexes [47, 48]. The non-oxidizable M-oxo framework of polyanions acts as an inert, multi-dentate ligand which can accommodate a multitude of transition metal centers [47-50].



Scheme 1. General synthetic route for mono-transition metal substituted phosphotungstates

The environment around the introduced transition metal tends to be near octahedral, and such complexes show many analogies to metalloporphyrins [37, 47, 51]. Due to the vastness of available literature, herein we will focus on mono-transition metal substituted phosphotungstates only.

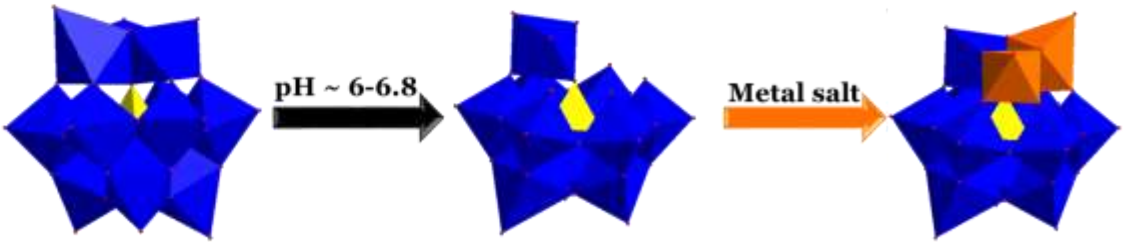
The first Keggin type mono-TMSPOMs was reported by Baker et al in 1956, i.e., $[Co^{2+}Co^{3+}W_{12}O_{42}]^{7-}$ synthesized from $NaWO_4.2H_2O$ and cobaltous acetate tetrahydrate at neutral pH and characterized for elemental analysis, oxidation state, electrochemical properties, powder XRD as well as for Single crystal analysis [52]. Later, in 1966, it was confirmed by single crystal analysis that Co ions were present in the outer sphere and not as the central heteroatom [53].

Weakley and Malik in 1967, prepared a series of mono cobalt and mono-nickel substituted polyoxotungstates, where the heteroatoms were Si, Ge and P [54]. In 1970, Tourne, Weakley and Malik jointly reported the synthesis of triheteropolyanions consisting of $XZW_{11}O_{40}H_2$"- [X = B, Zn, P, Si, Ge; Z = Cu(II) , Mn(II), Mn(III)] [55]. The synthesized complexes were characterized by elemental, magnetic susceptibility, potentiometric titrations, spectroscopic techniques and powder X-ray diffraction patterns. In 1971, Ripen et al. reported Ni-subsituted derivative for silico- and phosphotungstates as well as their pyridine derivatives [56]. In subsequent years, Weakley reported the synthesis of various cobalt substituted polyoxotungstates with varied central heteroatoms in order to understand their electronic properties [57].

Then in 1991, Klevtsova et al synthesized cesium salt of $[PW_{11}Co^{II}(H_2O)O_{39}]^{5-}$ via two-step process; synthesis of mono-lacunary phosphotungstate followed by incorporation of cobalt by addition of cobalt salt [58] and the structure confirmed by single crystal XRD. Galan-Mascaros et al for the first time, reported the X-Ray analysis of tetraethylene salt of $[PW_{11}Mn^{II}O_{39}]^{5-}$, indicating the formation of chain like structure [59]. Soon, the crystal structure of tetra ethyl ammonium salt of $[PW_{11}O_{39}Co^{II}(H_2O)]^{5-}$ was also reported by Weakley et al which also showed formation of straight chains through W–O–Co linkage [60]. In 1998, group of Coronado synthesized a series of radical salts made with bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) and mono-TMSPOMs, $[XZ(H_2O)M_{11}O_{39}]^{5-}$ (where XZM_{11} = $Si^{IV}Fe^{III}Mo_{11}$, $Si^{IV}Cr^{III}W_{11}$, $PVCo^{II}W_{11}$, $PVNi^{II}W_{11}$, $PVCu^{II}W_{11}$ $PVZn^{II}W_{11}$, $PVMn^{II}W_{11}$, and $PVMn^{II}Mo_{11}$), and studied their physical properties [61]. Cavaleiro and co-workers reported the use of extended X-ray absorption fine structure (EXAFS) as a structural characterization tool for $[PW_{11}O_{39}M(H_2O)]^{n-}$, (M= Co, Mn, Fe) [62]. The synthesis and structural as well as spectroscopic characterization of $[PW_{11}O_{39}M(H_2O)]$, (where M= Ca and Sr) involving alkaline earth metals was reported by J. Wang and group [63]. Sokolov et al. have successfully incorporated Ir into $PW_{11}O_{39}$ framework and studied the substitutional labiality at the Ir(III) site using ESI-MS and multinuclear NMR [64].

b. Di-transition metal substituted phosphotungstates

Di-vacant POMs can co-ordinate with transition metals under different conditions to give rise to a series of complexes like saturated di-TMSPOMs [65, 66], di-substituted dimers [67], and many more complexes that can crystallize in low symmetric disorder-free space groups [68-72].



Scheme 2. General synthetic route for di-transition metal substituted phosphotungstates

Di-TMSPOMs, are acquiring significance as there are two transition metals that are substituted, which can alter catalytic activity drastically. The reaction of di-lacunary POM anions with transition metal ions in aqueous medium gives di-transition metal substituted POMs**.** Significant contributions in the field of di-substituted POMs, by Kortz and co-workers, as they have mainly silicotungstate and germanotungstate of monomer, dimer, trimer and tetramer form of di-substituted POMs [72]. Apart from him, number of groups like Pope [73, 74], Lunk [75], Mizuno [66, 76, 77], Hill [78] and Proust [79] have also contributed towards di-substituted POMs. But, as mentioned earlier, our main focus is on phosphotungstates, and hence only the relevant references have been included.

Domaille et al, in 1983, synthesized di-titanium substituted phosphotungstate, $K_7[PW_{10}Ti_2O_{40}]$, from individual salts at pH 8.2 and confirmed the structure using FT-IR and ^{183}W NMR [80]. Later, in 1986, the same group reported synthesis of γ-$Cs_5[PV_2W_{10}O_{40}]$, consisting of slow addition of solid $Cs_7[P_2W_{10}O_{36}]$ to a preformed solution of VO^{2+} at pH 0.8 and confirmed the presence of edge shared VO polyhedra joining the adjacent W_3O_{13} units by multi-nuclear NMR and single crystal studies [81]. Using the synthetic route by Domaille et al [80], Ozeki and Yamase crystallized $[PW_{10}Ti_2O_{40}]^{7-}$ and found that it preserved its C_2 symmetry with distinguishable substituted sites [82]. Nomiya et al. reported preparation of $K_7[PW_{10}Ti_2O_{40}]$, by pH dependent interconversion of its dimeric compound $K_{10}[\alpha,\alpha'\text{-}P_2W_{20}Ti_4O_{78}].12H_2O$ at pH 7.8 [83]. They also reported that during evaporation of the aqueous solution, $K_7[PW_{10}Ti_2O_{40}]$ readily converted to the dimer and thus isolation of analytically pure $K_7[PW_{10}Ti_2O_{40}]$ was found to be difficult. In 2014, Patel et al. established the one-pot synthesis of monomeric $Cs_7[PW_{10}Mn_2(H_2O)_2O_{38}].7H_2O$ by addition of $MnCl_2.4H_2O$ to commercially available $H_3PW_{12}O_{40}.29H_2O$ at pH 6.4, followed by reflux and addition of CsCl [84].

III. Functionalized POMs

The tailoring and synthesis of Functionalized (organic–inorganic hybrid) materials constructed from distinctive building blocks represents an outstanding research area in inorganic chemistry, coordination chemistry, crystal engineering and materials science, as they provide additional and/or enhanced functions and properties because of synergistic interactions between the inorganic and organic components. They are of great interest owing to their extensive theoretical and practical applications in molecular recognition, non-linear materials, absorption, magnetic and photosensitive materials [38, 40, 41, 85-90].

In its widest sense, functionalization of POMs consists of replacing one or more metal-oxo groups by other functional groups [91]. POMs can act as an excellent inorganic multidentate O-donor ligands to assemble various inorganic–organic hybrid compounds with a vast range of structural properties. Incorporation of organic substructures into inorganic oxide framework provides a powerful method for structural modification and synthesis of novel organic-inorganic hybrid materials. This combines the unique features of both the organic and inorganic components [92, 93]. POMs, especially TMSPOMs, have unique structural diversity along with the ability to co-ordinate with organic group via replacement of aqua ligand and hence, are excellent candidates for functionalization. The obtained materials have potential applications in the fields of medicine, magnetism, optics, biology catalysis, electro/photo/ thermochromic systems, electrode cathodes, batteries and super-capacitors, and solar energy conversion [17, 39, 94-98].

Functionalization of POMs with organic moiety remains a synthetic challenge, as the two parts (the POMs and the organic moiety) present very different chemical and structural properties. The structure and properties obtained from such materials depend on the nature of both the components and can be mainly of two classes depending upon nature of the interaction between the organic and inorganic components.

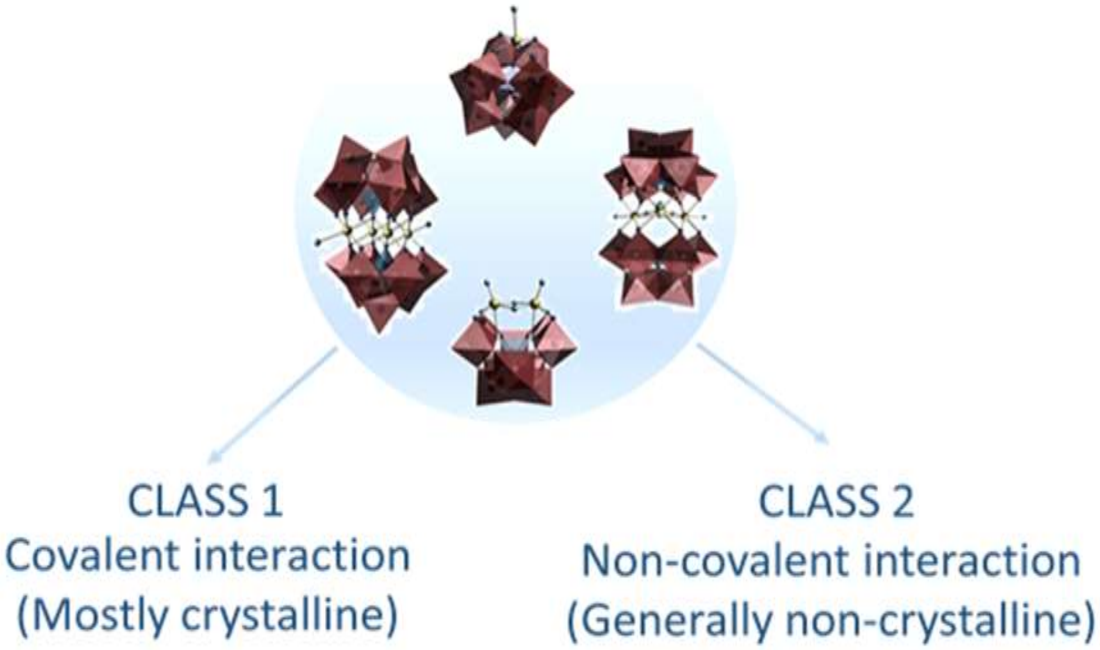


Figure 3. Types of functionalization based on interaction

Class I gathers those complexes where the organic and inorganic moieties are linked via strong covalent or iono-covalent interactions. On the other hand, class II consists of complexes where purely weak the interactions exist between inorganic and organic moieties, like electrostatic, hydrogen bonds, or van der Waals interactions.

Four basic strategies have been explored for the synthesis of functionalized material based on POMs [99, 100].

I. **Co-ordination competition:** This approach consists of lacunary POMs (LPOMs) as ligands. These LPOMs react with organic metal complexes through coordination competition (Figure 44) to form new POMs coordinated metal complexes [101, 102]

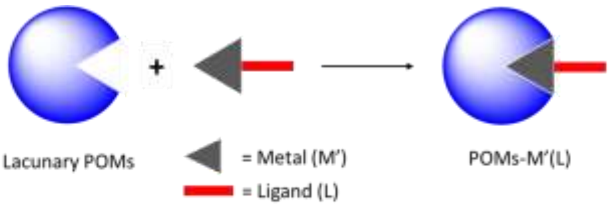


Figure 4. Co-ordination competition

II. **Terminal modification:** This route involves modification of the POMs surface by substituting terminal O atoms of POMs with organic species. Generally, such kind of synthesis was carried out in organic solvents [103].

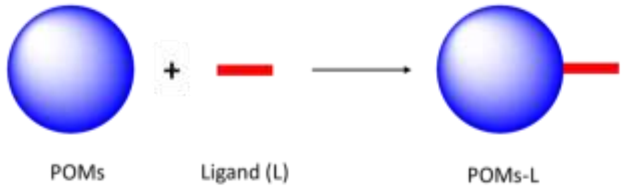


Figure 5. Terminal modification

III. **In-situ synthesis:** This strategy consists of self-condensation of the simple inorganic and organic units (sometimes pre-synthesized POMs/TMSPOMs) (Figure 44). Most of the successful syntheses using this route were carried out under hydrothermal conditions [104].

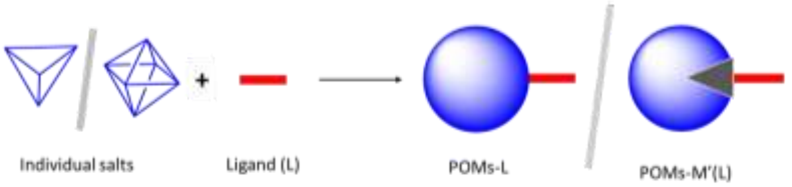


Figure 6. In-situ synthesis

IV. **Ligand substitution:** This method consists of TMSPOMs as starting materials, in which, five oxygen atoms of the POM coordinate with the transition metal from five sides, while an aqua ligand occupies the sixth coordination site. Thus aqua ligand is labile and can be replaced by any organic group or even by organometallic groups [105].

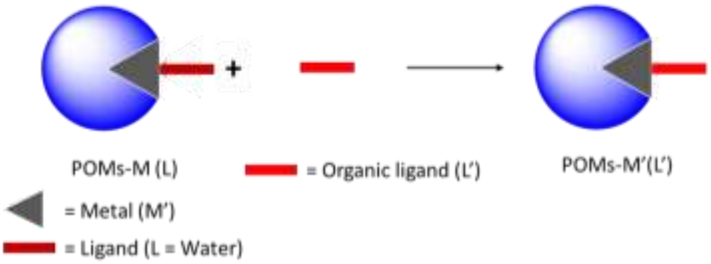


Figure 7. Ligand substitution

Functionalized mono-transition metal substituted phosphotungstates

Functionalization of POMs presents a huge scope as POMs have been functionalized using various organic groups like alkoxy, organosilyl, organogermanyl, organotin, and other organometallic groups, organo-imido, carboxy, and imidaloze and its derivatives. But due to the vastness of the available literature, we have focused on functionalized mono-transition metal substituted phosphotungstates only.

Weakley et al, in 1973, replaced the aqua ligands of cobalt and nickel substituted phosphotungstates, $[PW_{11}M(H_2O)O_{39}]^{n-}$, where M = Co(II), Co(III) and Ni(II), and studied the relevance of the same using diffuse reflectance spectroscopy [57]. Klemperer et al reacted $Ti^{IV}(C_5H_5)$ with lacunary phosphotungstate to produce an organometallic derivative of mono-titanium substituted phosphotungstate, $[PW_{11}Ti^{IV}(C_5H_5)O_{39}]^{4-}$, and characterized the same using ^{17}O NMR and IR spectroscopies [106]. In 1986, Ti(IV)-substituted POMs were functionalized using cyclopentadienyl group by Keana et al and characterized using various spectroscopic techniques [107, 108]. In 1992 Pope group studied substitution of water molecules in ruthenium substituted phosphotungstate ($[PW_{11}Ru(H_2O)O_{39}]^{4-}$) using pyridine, sulfoxides, dialkyl sulfides, and various active alkenes (maleic, fumaric, crotonic acids, 1-4-dihydroxybut-2-ene) and characterized by electronic absorption spectroscopy and multinuclear NMR spectroscopy [109]. A few years later, in 1998, Wei and Pope successfully isolated mono-ruthenium substituted phosphotungstate functionalized with various organic ligands, $[PW_{11}O_{39}RhL]^{n-}$, where L = CH_3COO^-, pyridine, or S-bonded dimethyl sulfoxide, by photochemical, electrochemical, and ligand substitution routes respectively [110]. A couple of years later, Bonchio and group reported synthesis of $[PW_{11}Ru^{II}(DMSO)O_{39}]^{5-}$ by a fast and selective replacement route from mono-lacunary $[PW_{11}O_{39}]^{7-}$ with cis-$[Ru(DMSO)_4Cl_2]$ in water, under microwave irradiation [111].

Proust and co-workers reported the synthesis of nitride functionalized POMs $[PW_{11}O_{39}(MN)]^{n-}$ (M= Os, Re) [112] and organiimido functionalized POMs $[PW_{11}O_{39}(Re^{V}NPh)]^{4-}$ in presence of triethylene amine [113]. Further, the same author reported reactivity of $[PW_{11}O_{39}]^{7-}$ towards $[Ru^{II}(arene)Cl_2]_2$ (arene = benzene, toluene, p-cymene, hexamethylbenzene) leading to the formation of monomeric or dimeric compounds, where cationic $\{(arene)Ru(H_2O)\}^{2+}$ groups are covalently bound to the nucleophilic oxygen atoms of lacunary phosphotungstate. Similar functionalized compounds were also synthesized for Os derivatives of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ with organic ligands like DMSO, η^6-p-cymene and η^6-C_6H_6 [114, 115].

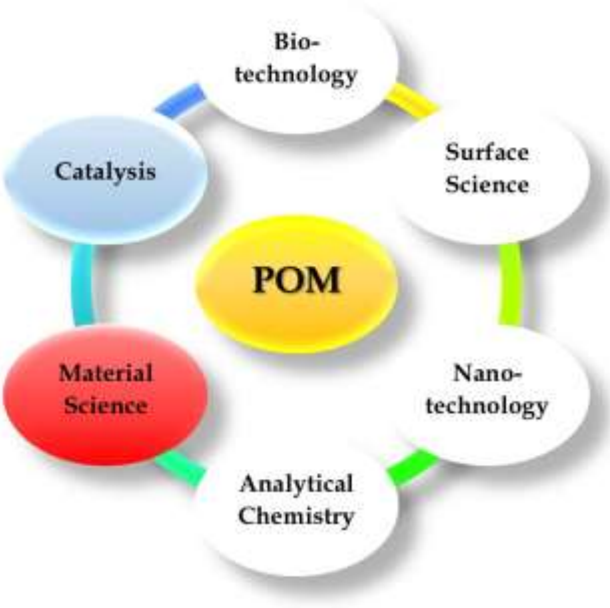
Peng et al in 2005, synthesized a novel organic capped POM structure comprising a pendant tricyclic, aromatic entity and mono-cobalt substituted phosphotungstate, $(Hpbpy)_5[PW_{11}O_{39}Co(pbpy)].2H_2O$, [pbpy = 5-phenyl-2-(4-pyridinyl)pyridine)] [116]. Proust and co-workers have worked extensively on nitride-functionalized $PW_{11}Ru$. They synthesized $[PW_{11}O_{39}(Ru^{VI}N)]^{4-}$ from mono-lacunary $[PW_{11}O_{39}]^{7-}$ and the complex $[Ru^{VI}NCl_5]^{2-}$ or $[Ru^{VI}NCl_4]^-$ and characterized using multinuclear NMR (^{31}P and ^{183}W), EXAFS, XANES analysis [117]. They further synthesized two more species, $[(Ru^{III}N(OH)PPh_3)PW_{11}O_{39}]^{4-}$

and $[(Ru^{III}OPPh_3)PW_{11}O_{39}]^{4-}$, which were closely related to the first nitride species [118].

Later, Pope et al successfully synthesized a series of $[PW_{11}Ru(L)O_{39}]^{5-}$ complexes where L = H_2O, pyridine or DMSO, and recorded their EPR spectra. With the results obtained, they suggested that the coordination between Ru and DMSO molecules may be of the S-type [119]. Extending further into POM-nitrido derivatives, Proust and co-workers synthesized a stable manganese-nitrido complex, $[PW_{11}O_{39}Mn^{III}N_3]^{5-}$, by photochemical activation of Mn-azido group [120]. Further, they also synthesized a chromium-nitrido derivative, $[PW_{11}O_{39}Cr^{V}N]^{5-}$, and described its potentiality towards trifluoroacetic anhydride by synthesizing the acylimido derivative, $[PW_{11}O_{39}(Cr^{V}NCOCF_3)]^{4-}$ [121]. In 2011, they synthesized the functionalized mono-ruthenium containing phosphotungstate complex, $[PW_{11}O_{39}Ru^{III}(NC(N(Mes)CH_2)_2)]^{5-}$, by the N-atom transfer from the N-heterocyclic carbene, $(CH_2(Mes)N)_2C$ [122]. A year later, A. Patel and K. Patel synthesized a series of mono-manganese substituted phosphotungstates functionalized by various organic moieties like R-(-)-1-cyclohexylethylamine [123] and S-(+)-sec-butylamine [124] and systematically characterized by various physico-chemical techniques.

Applications of POM family

The diverse applications of POMs in various fields of science and engineering have resulted in rapid and continuous growth of POM chemistry despite being over two centuries old. Wide range of applications are seen in the fields off carbon electrodes modification, capacitors, colorant for pigmenting paints, dye for polyester, dopants, clinical analysis, food chemistry, solar cell and catalysis [29, 36, 125-133].



Scheme 3. Applications of POMs

POMs show high Bronsted acidity as well as the tendency to exhibit fast reversible multi-electron redox transformations under rather mild conditions and their inherent stability towards strong oxidants. Furthermore, they display inherent stability towards strong oxidants as well as an ability to remain stable at high temperature. Due to these reasons, POMs are extensively used as acid as well as oxidation catalysts.

POMs as catalysts [134]

POMs have multiple practical advantages as catalysts, as they have several unique properties.

(1) Designing at molecular level

(a) Acidic and redox properties - These properties of catalyst can be controlled by choosing appropriate elements (type of polyanion, heteroatom counter-cation etc.)

(b) Multifuntionality - Acid-Redox, Acid-Base, multielectron transfer etc.

(c) Tertiary structure, bulk type behavior etc for solid state are well controlled by counter cations

(2) Molecular metal-oxide clusters

(a) Molecular designing of catalyst

(b) Cluster models of mixed oxide catalyst and relationships between solution and solid catalyst

(c) Description of catalytic processes at atomic/molecular level, spectroscopic study and stoichiometry are realistic

(3) Unique reaction fields – In solution, POMs dissociate completely, and hence are stronger than the usual mineral acids like HCl, HNO_3 and H_2SO_4. On the other hand, under heterogeneous conditions, POM catalysts can behave in three ways: (a) Surface type catalysts, (b) Bulk type (I) catalysts and (c) Bulk type (II) catalysts [134].

(a) Surface type catalysis is the most ordinary type of catalysis, where the reaction takes place on the surface of the solid catalyst. Here, the rate of reaction is proportional to the surface area.

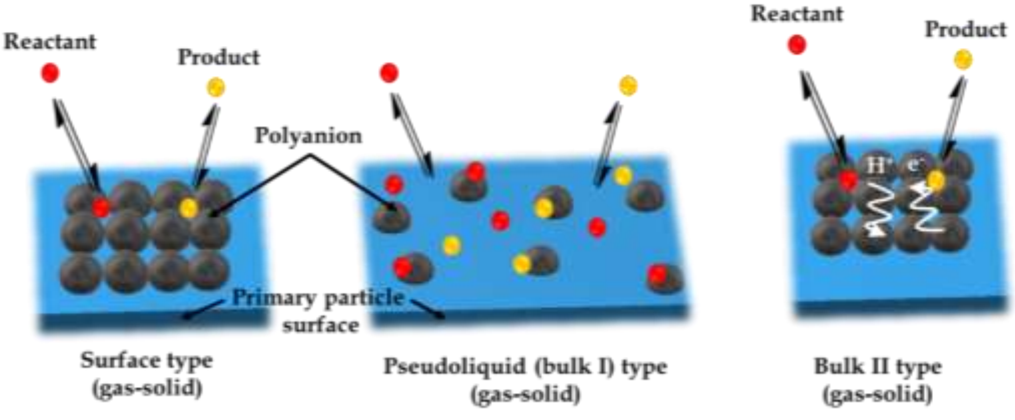


Figure 8. Modes of heterogeneous catalysis using POMs

(b) Bulk type I catalysis in which the reactant molecules are adsorbed in the interpolyanion spaces of the ionic crystal and the reaction occurs there. Then the products desorb from there. The classic example of this type is the acid catalysed reaction of polar molecules over group A salts at relatively low temperature. In a sence, the solid behaves like a solution and the reaction surface becomes three-dimensional, and hence termed “pseudeliquid” catalysis. Here, the reaction rate depends on the volume of the catalyst, for instance, an acid catalysed reaction would depend on the bulk acidity of the catalyst.

(c) Bulk type II catalysis in which although the reaction occurs on the surface, there is a rapid migration of redox carriers like electrons and protons, because of which in principle, the bulk catalyst participates in the reaction. Dehydrogenation and oxidation of hydrogen at high temperatures are classic examples of this type, and the rate of reaction is proportional to the bulk volume of the catalyst.

In case of POMs, they behave as “pseudoliquids” and hence follow bulk type II catalysis, which provide unique three dimensional environment, and make spectroscopic and stoichiometric studies feasible and realistic.

(4) Soft basicity of polyoxoanions play an important role in their high catalytic activities as they help in selective co-ordination as well as stabilization of reactive intermediates in solution, pseudoliquid and in solid phases.

A thorough investigation of POMs as catalytic materials began during the 1970s and 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 Publications, 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	(Ed) A. Patel	Springer, Dordrecht, 2013
Polyoxomolybdates as Green Catalysts for Aerobic Oxidation	A. Patel, S. Pathan,	Springer Briefs in Molecular Science-Green Chemistry for Sustainability, Springer, Dordrecht, 2015

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 (3), (1995) 559
Catalytic Chemistry of Heteropoly Compounds	T. Okuhara, N. Mizuno, M. Misono	Adv. Catal., 41 (1996) 113
Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions	I. V. Kozhevnikov	Chem. Rev., 98, (1998) 171
Heterogeneous Catalysis	N. Mizuno, M. Misono,	Chem. Rev., 199, (1998)
Oxidation of Alcohols with Molecular Oxygen on Solid catalysts	T. Mallat, A. Baiker	Chem Rev. 104 (2004) 3037
Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates	N. Mizuno, K. Yamaguchia, K. Kamata	Coord. Chem. Rev., 249, (2005) 1944
Hybrid Organic-Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications	A. Dolbecq, E. Dumas , C. R. Mayer, P. Mialane	Chem. Rev., 110 (10) (2010) 6009
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 (2014) 981

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 (2014) 635
Recent Advances in Polyoxometalate-Catalyzed Reactions	S. –S. Wang, G.-Y. Yang	Chem. Rev., 115 (2015) 4893
Recent progress on supported polyoxometalates for biodiesel synthesis via esterification and transesterification	N. Narkhede, S. Singh, A. Patel	Green Chem., 17 (2015) 89
Heterogeneous Catalysis of Polyoxometalate Based Organic–Inorganic Hybrids	Y. Ren, M. Wang, X. Chen, B. Yue, H. He	Materials, 8 (2015) 1545
Base Catalysis by Mono- and Polyoxometalates	K. Kamata, K. Sugahara	Catalysts, 7 (2017) 345

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. 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).
10. Process for alkylation of phenol by A. Patel et al., US Patent No. 7692047 B2, (2009).
11. Process for production of alkenes from oxygenases by using supported heteropolyacid catalysts by Gracey et al., US Application No. 2010/0292520A1, (2010).
12. Materials for degrading contaminants by Hill et al., US 7655594 B2 (2010).
13. Method for the breakdown of lignin by Voitl et al., US 7906687 (2011).
14. Method for producing phenolphthalein suing heteropolyacid catalyst by Bolta et al., US Patent No 7868190 B2, (2011).
15. Process for oxidizing alkylaromatic compounds by Jaensch et al., US 7906686 B2 (2011).
16. Methods and compositions comprising polyoxometalates by Ying et. al., EP 2321078 A4 (2013).
17. Polyoxometalate water oxidation catalysts and methods of use thereof by Hill et al., US 8822367 (2014).
18. Hydrogenation catalysts prepared from polyoxometalate precursors and process for using same to produce ethanol while minimizing diethyl ether formation by Heiko and Zhenhua, US 8,658,843 (2014).
19. Synthesis of polyoxometalate-loaded epoxy composites by Anderson, US 8853350 B1 (2014).
20. Preparation of aldehydes and ketones from alkenes using polyoxometalate catalysts and nitrogen oxides by R. Neumann et al., WO2015132780 A1, (2015).

21. High-performance polyoxometalate catalyst and preparation method thereof by Lg Chem, Ltd., WO2016006883 A1, (2016).
22. Liquid phase non solvent oxidation of styrene with molecular oxygen, P. Shringarpure, A. Patel, Indian Patent No. 275517 (2016).
23. Supported undecaphosphotungstate catalyst for aerobic epoxidation of alkenes, P. Shringarpure, A. Patel, Indian Patent No. 271230 (2016).
24. Method for catalyzing and oxidizing olefin with sandwiching-type polyoxometalates, H. Liu, D. He, C. Ci, H. Xue, Z. Qi, L. Su, L. Zhao, CN105777515A (2016).
25. Catalyst synthesized from titanium-silicon nanometer composite oxides and polyoxometalates in situ as well as preparation method and application of catalyst, D. Liu, L. Chen, H. Yan, Y. Jia, L. Yuan, Z. Zhang, L. Far, W. Zhang, K. Ma, CN107552077A (2017).
26. Polyoxometalate-based metal-organic frameworks crystal material with polyoxometalates as template, H. Pang, B. Li, H. Ma, Q. Shen, C. Zhang, X. Wang, CN108997594A (2018).
27. Polyoxometalates comprising noble metals and post-transition metals and metal clusters thereof, M. A. Tian, U. Kortz, Y. Peng, L. Zhengguo, W. Ayass, WO2018162144A1 (2018).

Catalysis by transition metal substituted phosphotungstates

The catalytically active site in a mono-TMSPOM is the substituted transition metal, as a result of which the POM functions as a ligand with a strong capacity for accepting electrons. 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). This lability 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 TMSPOMs 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 this regard, Hill and co-workers have contributed the most in the field of oxidation catalysis. They reported the oxidation of olefins using oxidants like Iodosylbenzene (PhIO) and Pentafluoroiodosylbenzene (PFIB) catalysed by tetra-n-butylammonium salts of $PW_{11}O_{39}M$, where M = Mn^{II} and Co^{II} [42]. Further, they reported the oxo-transfer oxidation of alkanes by a mono-transition metal substituted phosphotungstates with a range of transition metals like Co^{II}, Mn^{II}, Fe^{II} and Cu^{II} using tert-butyl hydroperoxide oxidant [135]. In 1989, Kuznetsova et al reported the oxidation of hydrogen sulfide by molecular oxygen, using $[PW_{11}M(H_2O)O_{39}]^{5-}$, where M = Fe, Co and Ni [136]. Lyons et al have reported several TMSPOMs for the aerobic oxidation of several alkanes [137, 138]. Pope and Rong, in 1992, demonstrated the oxidation of alkenes over $[PW_{11}O_{39}Ru^{III}(H_2O)]$ in acetonitrile solvent with PhIO oxidant [109]. In 1994, Hill et al have further reported a series of polyoxotungstates, $[XMW_{11}O_{39}]$, where, M = Fe, Co, Ni, Zn, Mn, Cu and X= P, Si, for the oxidation of hydrogen sulfide to produce sulfur [139]. In 1993, Mizuno et al synthesized a range of mono-transition metal substituted phosphotungstates, $[PW_{11}O_{39}M]$, where M=Co, Mn, Fe, Cu and Ni, and used them as cataysts for aerobic oxidation of cyclohexene to epoxide [140].

In 1996, Kholdeeva reported a series of tetra-n-butylammonium salts of $[PW_{11}O_{39}M]$, where M = Co^{II}, Mn^{II}, Cu^{II}, Pd^{II}, Ti^{IV}, Ru^{IV}, and V^{V}, for epoxidation of alkenes using dioxygen in presence of isobutyraldehyde and acetonitrile solvent [141]. In 1999, Cavaleiro et al synthesized a range of first row transition metal substituted Keggin type phosphotungstates and evaluated the catlytic activity for oxidation of cyclohexane using hyderogen peroxide oxidant [142]. Nam et al, in 2002, reported the use of $[PW_{11}CoO_{39}]^{5-}$ catalyst for the epoxidation of alkenes using buffered persulfate solution as oxidant [143]. In the same year, Kozhevnikov et al reported the homogeneous oxidation of methyl isobutyrate with oxygen using $PW_{11}MO_{39}$ where M=Ni(II), Co(II), Cu(II), Fe(III), and Ru(III) as catalysts and compared them with the respective metalloporphyrins [144]. In 2005, Liu et al reported oxidation of benzene to phenol by molecular oxygen over first row transition metal substituted phosphotungstates with ascorbic acid as a reducing agent in an acetone/sulfolane/water mixed solvent [145]. Around the same time, Kholdeeva et al synthesized monomeric as well as dimeric titanium substituted phosphotungstates, $H_5PW_{11}TiO_{40}$ and $[Bu_4N]_8[(PTiW_{11}O_{39})_2O]$, and evaluated their activity for oxidation of 2,3,6-trimethylphenol with H_2O_2 in MeCN to give 2,3,5-trimethyl-p-benzoquinone and 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol [105]. In 2009, Bamoharram et al reported lactonization of various diols (1,4-butane diol, 1,6-hexane diol and 1,2-benzene dimethanol) over potassium salts of the monosubstituted Keggin polyoxometalates, $[PW_{11}MO_{40}]^{7-}$ where M= Co(II), Ni (II), Cu(II), Zn(II) using H_2O_2 oxidant [146]. Jiang et al, in 2010, carried out the oxidation of benzothiophene using metal-substituted catalysts $PW_{11}M$ (M = Ti, Mn, Fe, Co, Ni and Cu) [147].

Our group has pubished a number of reports on Keggin type phosphotungstates, $PW_{11}O_{39}M$, where M = Ru, Co, Mn and Ni, and their catalytic activity for oxidation of alkenes, alcohols and oxidative esterification reactions [148-153].

Coming to di- transition metal substituted phosphotungstates, in 2014, Patel et al reported the one pot synthesis of in-pocket Cs salt of di-manganese(II) substituted phosphotungstate, $Cs_7[PW_{10}Mn_2(H_2O)_2O_{38}].7H_2O$, from the commercially available $H_3PW_{12}O_{40}$ and $MnCl_2.4H_2O$. The synthesized compound was evaluated for it catalytic activity for the solvent-free liquid phase oxidation of styrene using environmentally benign H_2O_2 and molecular O_2 as oxidants [84]. This remains the only instance in which, a di- transition metal substituted phosphotungstates is evaluated for its catalytic properties.

Catalysis by functionalized transition metal substituted phosphotungstates

Similarly, despite wonderful contributions by groups of Proust, Pope and Kortz towards synthesis and characterization of organic functionalized transition metal substituted phosphotungstates, only two reports are available in art on the application of organic-functionalized transition metal substituted phosphotungstates compounds as catalysts for organic transformations. In 2005, Kholdeeva et al synthesized methoxy and aryloxy functionalized mono-titanium substituted phosphotungstate, $[Bu_4N]_4[PTi(OMe)W_{11}O_{39}]$ and $[Bu_4N]_4[PTi(OAr)W_{11}O_{39}]$, and used the same in the catalytic oxidation of 2,3,6-trimethylphenol using H_2O_2 as oxidant to yield 2,3,5-trimethyl-p-benzoquinone and 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol as the main reaction products [105]. More than 14 years later, Patel et al reported the functionalization of mono-ruthenium substituted phosphotungstate functionalized with R-(-)-1-cyclohexyl ethylamine and its catalytic activity for the aerobic asymmetric oxidation of styrene [154].

Supported TMSPOMs

Another technique of modification of POMs is via supporting them on to appropriate supports. Here too, we have only restricted our literature survey to TMSPOMs only, as this is the main focus of this work.

As mentioned earlier, most of the TMSPOMs suffer from traditional disadvantages like high solubility, low surface area, recovery and reusability. Supporting of TMSPOMs on to suitable supports to develop heterogeneous catalysts is a means to overcome the mentioned issues. Supports provide large surface area for dispersion of catalyst molecules and thus, the catalyst molecules remain available for combination with reactant just like in case of homogenous catalyst. In spite of operating as a separate immobile phase, the heterogeneous catalyst can function mechanically as if it were in solution. Thus the advantages of homogenous catalysts are retained, while at the same time, advantages of heterogeneous catalyst are obtained.

As far as organic transformations are concerned, the advantages of heterogeneous catalytic systems are:

- Kinetically and thermodynamically difficult reactions can be carried out at a wide range of temperatures even in gas phase.
- 'Tailoring' of catalysts for specific feedstock or for selective product synthesis is made possible.

Advantages of supported POMs include:

- Increase in thermal stability
- Increase in surface area
- Higher catalytic activity and selectivity
- Ease of separation
- Easy to recycle and reuse

Different methods of supporting POMs [155]

Supporting or anchoring forms an important step in designing of heterogeneous catalyst. The support is either prepared separately or both, the support as well as the catalyst material can be synthesized together in a one-pot technique. Different methods of supporting/anchoring are as follows:

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

As impregnation is one of the most accepted method for preparation of supported catalysts, we will hereby on this method only.

Impregnation

It is the technique in which a solution of the precursor of the active species is brought in contact with the support. It can be carried out in two methodologies. Dry impregnation or pore volume impregnation involves the application of a fixed volume of the solution containing the active ingredients, equivalent to the pore volume, on to the support, uniformly and slowly by spraying. Dispersion of active species is controlled by concentration of solution, while the maximum loading capacity is determined by solubility of active species as well as the pore volume.

Wet impregnation involves the immersion of support into excess quantity of solution containing the active species, followed by drying and calcination (if required). In this case, the nature and concentration of solution containing the precursor and equilibrium time determine the dispersion of active species on to the support.

Choice of support

The choice of support is a crucial step in heterogeneous catalysis.

- The most important is stability. The support must be stable up to high temperature, under reaction condition and regeneration conditions. It should also not interact with solvent, reactants or reaction products.
- A support must be easily available, either commercially or should be easily synthesized.
- Dispersing POMs on supports with high surface area is important for catalytic application. In general, POMs strongly interact with supports at low loading levels, while the bulk properties of POMs prevail at high loading levels.
- Nature of the support also plays a crucial role in determining the activity of catalyst. Acidic or neutral substances are suitable supports and enhanced catalytic activity of POMs was found when they were supported on to

strongly acidic support. The higher activity was explained by the synergism due to the interaction of the POMs and protons of the support. In addition, basic support cannot be used for anchoring POMs, since they get decomposed in the basic environment.

A literature survey also shows that there are number of articles available on catalytic aspects of POMs anchored on to different supports, such as silica [156-158], silica modified zirconia [159], titania [156, 159, 160], alumina [156, 161], carbon [162-164], acidic ion exchange resins [165], clays [166-169], montmorillonite k10 [170, 171], Mesoporous pillared clay/Kaolin [172, 173], Metal organic frameworks (MIL) [174-178] and Polymer [179]. Due to the vastness of literature, we will, here, focus only on supported phosphotungstates.

In 2004, the synthesis and catalytic applications of TiO_2-APS-$PW_{11}M$ (M = Ni/Co) was reported by Yang et al [180]. In 2009, various transition metal substituted polyoxotungstates, $K_{10-n}X^{n+}MW_{11}O_{39}$ (X = P/Si,M = Co/Ni/Cu/Mn) were supported on Schiff base modified SBA-15 by Guo et al. These were further used for selective oxidation of styrene to benzaldehyde [181]. In 2012, $[PW_{11}O_{39}M1]^{5-}$ (M1 = Ni^{2+}, Co^{2+} or Cu^{2+}) anchored to MCM-41 was synthesized by Li et al and its catalytic evaluation for esterification reaction of n-butanol with acetic acid was carried out [182]. In 2014, Balula et al successfully incorporated zinc-substituted phosphotungstate over silica nano-sized particles comprising amino-organosilicane surrounded by silica shell, and used the same as catalyst for oxidation of various olefins and also oxidative desulfurization processes [183]. In a different set up in the following year, Romanelli et al synthesized a number of transition metal substituted POMs using Co, Ni, Cu and Zn, supported them on activated carbon and used the same for the sulfoxidation of 2-(methylthio)-benzothiazole [184]. In 2016, Patel et al supported Cs salt of mono-nickel substituted phosphotungstate over zirconia by wet impregnation, and evaluated its catalytic activity for one-pot oxidative esterification of benzaldehyde using H_2O_2 as oxidant [185].

A literature survey shows that:

(i) Despite distinct advantages of copper such as its redox properties, economical availability and non-toxic nature, reports on synthesis as well as catalytic activity of mono-copper substituted phosphotungstates is scanty.
(ii) The extent to which work has been carried out on synthesis as well as catalytic evaluation of monomeric di-copper substituted phosphotungstate is negligible.
(iii) Further modifications of mono-copper substituted phosphotungstate by supporting it on to appropriate supports are also sparse and scattered.
(iv) Finally, mono-copper substituted phosphotungstate functionalized by organic ligands and their applications in catalysis also remains unexplored

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

Scope and Objectives of the Thesis

In the present work, the parent 12-tungstophosphoric acid has been modified at the molecular level to synthesize mono- as well as di-copper substituted phosphotungstates. Along with the traditional one-pot synthesis, a novel microwave technique has been developed.

To evaluate the catalytic activity of synthesized materials, oxidation of alkenes have been selected and styrene and cis-cyclooctene have been chosen as model substrates. The oxidative cleavage of C–C double bonds to give aldehydes, epoxides, ketones and diols, due to their important industrial applications. Of all the aldehydes, benzaldehyde is one of the most valuable compounds with widespread applications in perfumery, dye and agro chemical industries [186]. It is second only to vanillin amongst aromatic compounds used in cosmetics and flavour industry. Similarly, epoxides like styrene oxide are widely used as raw materials in synthesis of resins, paints, surfactants and intermediates for various organic reactions.

Oxidation products of cis-cyclooctene include cyclooctene-oxide and cyclooctanone amongst others. Cyclooctene-oxide can be converted to 1,2-diols which can further be used to synthesize C_8 carboxylic acids. Cyclooctanone is an essential intermediate for various industrially important compounds. It is also used in the total synthesis of the natural product, (-)-vulgarolide, which is a flavouring agent.

As already mentioned, supports do not merely play a mechanical role but have the potential to modify the overall properties of the catalyst. Based on the nature of the support, the activity in terms of conversion and selectivity of products can be affected. Hence, in the present work, it was thought of interest to understand the effect of the nature of support on catalytic activity of copper substituted phosphotungstates for which, an acidic support, hydrous zirconia, and a neutral support, alumina have been selected.

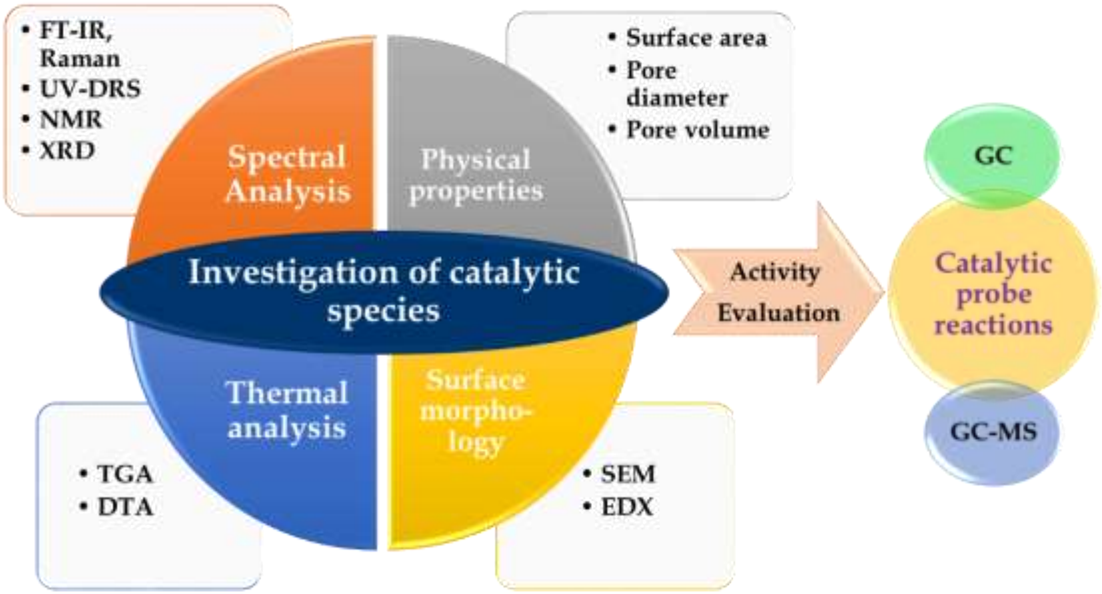
Finally, functionalization of mono-copper substituted phosphotungstate has been carried out using three organic moieties. First, imidazole, a well-known co-catalyst, has been chosen in order to see its effect on the activity of mono-copper substituted phosphotungstate, when the two are chemically bonded. Finally, in an attempt to induce chirality in the phosphotungstate moiety, (*S*)-1-phenyl ethylamine were selected to functionalize the POM.

Accordingly, the following objectives were planned:

- To tune the properties of phosphotungstates (PW_{12}) at the molecular level by synthesizing mono- as well as di-copper substituted phosphotungstates.
- To characterize the synthesized materials using EDX, TGA-DTA, FT-IR, ^{31}P NMR, UV-Vis, ESR, Powder XRD and CV.
- To use the synthesized materials as catalysts for the liquid phase oxidation of styrene and cis-cyclooctene under mild conditions.
- To support the synthesized material on different supports (ZrO_2 and Al_2O_3), characterize and evaluate the catalytic activities of the same for oxidation of styrene and cis-cyclooctene, and to identify the better support.
- Further, to synthesize and characterize hybrid inorganic-organic materials using normal as well as chiral organic moieties [Imidazole, (*S*)-1-phenyl ethylamine], and use the same as catalysts for oxidation of alkenes.
- To study the recyclability and reusability of the different catalysts.
- To study the chemical kinetics and mechanism for each catalytic system.
- Finally, to generate a comparative study between all catalysts, and thereby choose the best catalyst from each series.

Analytical techniques used in the study

A prime aspect in a catalyst development is the characterization of the catalyst [187-189]. In general, and especially in supported catalysts, the elucidation of the structures, composition as well as chemical properties of the synthesized materials and the interactions between active species as well as the supports is essential to understand the relationship between the catalytic properties of the material and its catalytic performance [189]. It is also crucial to know the basis of the structure-catalytic properties of the materials to further synthesize new catalysts. A summary of the various characterization tools for heterogeneous catalysts is shown in scheme 4.



Scheme 4. Various techniques used for catalyst characterization

In the present study, the following characterization techniques have been used.

Thermal Analysis (Thermo Gravimetric-Differential Thermal Analysis) is a technique in which weight of a substance is recorded as a function of temperature in a controlled environment under heating or cooling conditions. The subsequent curve obtained provides for the stability of the material at higher temperatures as well as the temperatures at which the material starts to decompose and is completely decomposed. In the present case, it helps stipulate the types of water present; for instance, the loosely held 'physisorbed' water and the strongly bonded 'chemisorbed' water. TG-DTA has been carried out on the Mettler Toledo Star SW 7.01 up to 600 ^{0}C.

Elemental Analysis (Energy-dispersive X-ray spectroscopy and Inductive Coupled plasma atomic emission spectroscopy) is essential for the determination of elemental composition of the synthesized complex. Various techniques like volumetric titration and gravimetric analysis, EDX and ICP-AES have been used for elemental analysis. Elemental analysis was carried out using a Perkin Elmer Optima-3300 RL ICP Spectrometer and JSM 5610 LV EDX-SEM analyzer.

Fourier Transform Infrared Spectroscopy (FT–IR) is probably one of the most basic and widely used spectral analysis techniques. It provides important information like identification of functional groups and surface activity studies with the help of probe molecules. FT-IR spectra of the sample were obtained by using the KBr pellet on the Perkin Elmer instrument.

Nuclear Magnetic Resonance (NMR) Spectroscopy is an important tool to understand the environment around a particular nucleus of the synthesized material. Further, it also help to know whether the synthesized material is pure or shows presence of isomers. Solution state NMR was carried out in D_2O solvent on a Bruker AVANCE 161.97-MHz instrument while solid state MAS NMR was recorded in JOEL ECX 400 MHz High Resolution Multinuclear FT-NMR spectrometer for solids.

Electron Spin Resonance (ESR) Spectroscopy is an excellent technique to understand the symmetry around the transition metal ion. It also gives information about the location and the environmental symmetry of the transition metal species in the synthesized material. It can tell us whether the metal ion is present in the lacuna or exists as a counter ion. ESR spectra were recorded on a Varian E-line Century series X-band ESR spectrometer at Liquid nitrogen temperature and scanned from 2000 to 3000 Gauss.

Powder X-Ray Diffraction (P-XRD) is a non-destructive tool for multi-component materials and provides in-depth details about their phase identification, lattice parameters, crystallinity and crystal structure determination and refinement. In stark contrast to single crystal XRD, powder XRD does not require a single, well-ordered crystal for analysis. The powder XRD patterns for the present work were obtained by using PHILIPS PW-1830 instrument. The conditions were: Cu Ka radiation (1.54 Å), scanning angle from 0^0 to 60^0.

UV-Visible Spectroscopy is an important technique that provides information about charge transfer from oxygen to the metal in a heteropoly compound, and also the d-d charge transfer in the lower oxidation state transition metals. The UV–Vis spectrum was recorded at room temperature on Perkin Elmer 35 LAMDA instrument using the 1 cm quartz cell in range of 200–1100 nm.

Surface Area Measurement (Brunauer-Emmett-Teller method) is a necessary technique to understand the surface adsorption phenomena, which is general tendency of heterogeneous catalysts. Further, the catalytic activity of a material is directly proportional to the surface area, which makes it even more essential. Adsorption–desorption analysis for specific surface area calculations was carried out in the Micrometrics ASAP 2010 instrument at -196 ^{0}C.

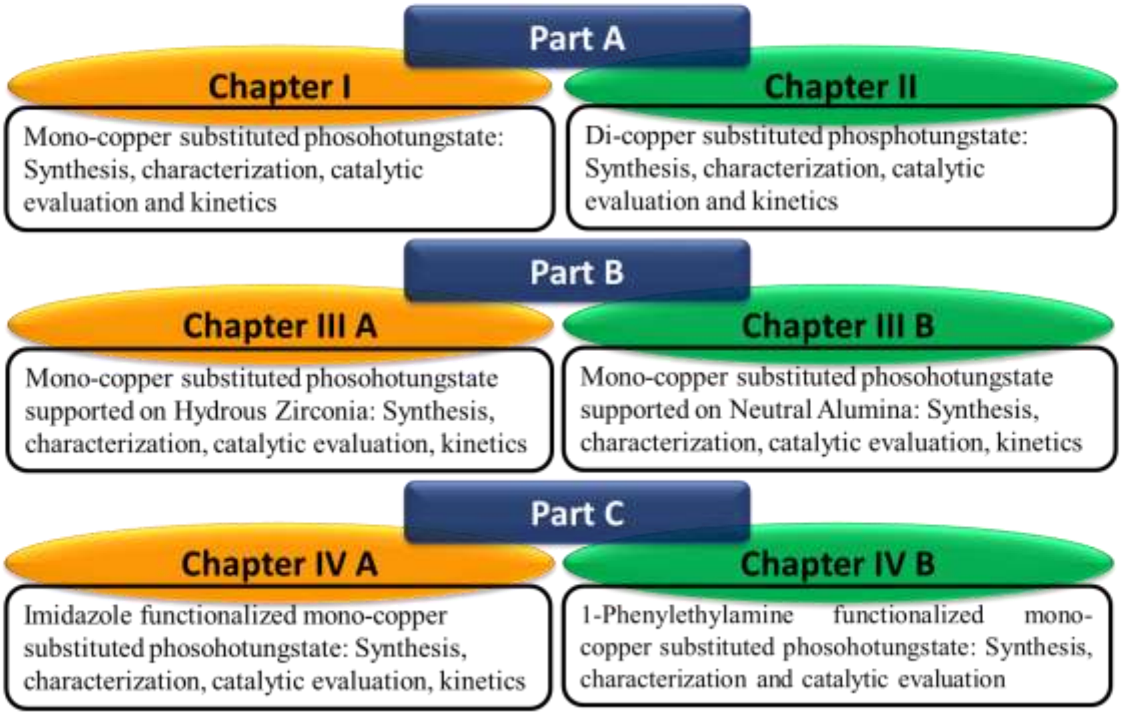
Temperature Programmed Reduction (TPR) is often used in heterogeneous catalysis to determine the most efficient reduction conditions. This too, helps determine the stability of the active species, before and after anchoring on to the support. For the present systems, TPR studies were investigated in a self-made reactor set-up with a quartz reactor vessel. 50 mg of sample was taken and heated up to 800 ^{0}C and the linear ramping rate was 10 ^{0}C min^{-1} with 5% (35 mL min^{-1}) H_2/Ar flow for 60 min. the consumption of H_2 gas was monitored using GC instrument equipped with TCD (m/s, CIC Instruments, India).

Cyclic Voltammetry (CV) is a technique used to understand the electrochemical and redox properties of the synthesized materials. Cyclic voltammetry was performed on CHI660E Electrochemical Workstation, Model 600E Series. A glassy carbon working electrode, an Ag/AgCl reference electrode and Pt-wire counter electrode were used.

Gas Chromatography (GC) is a type of chromatography used to separate and analyze that can be vaporized without decomposition. Its main applications include testing purity of a compound and separation of components of a mixture. In the present work, GC experiments were carried out on Shimatzu GC-2014 instrument using RTx-5 capillary column

Organization of the thesis

The work has been divided into three parts consisting of two chapters each:



Part A

Chapter I

Mono-copper substituted phosohotungstate: Synthesis, characterization, catalytic evaluation and kinetics

Chapter II

Di-copper substituted phosphotungstate: Synthesis, characterization, catalytic evaluation and kinetics

Part B

Chapter III A

Mono-copper substituted phosohotungstate supported on Hydrous Zirconia: Synthesis, characterization, catalytic evaluation, kinetics

Chapter III B

Mono-copper substituted phosohotungstate supported on Neutral Alumina: Synthesis, characterization, catalytic evaluation, kinetics

Part C

Chapter IV A

Imidazole functionalized mono-copper substituted phosohotungstate: Synthesis, characterization, catalytic evaluation, kinetics

Chapter IV B

1-Phenylethylamine functionalized mono-copper substituted phosohotungstate: Synthesis, characterization and catalytic evaluation

Chapter I describes the synthesis and characterization of mono-copper substituted phosphotungstate. This is followed by a detailed study to explore the catalytic activity of the synthesized complexes for the oxidation of styrene and cis-cyclooctene using 3°-butyl hydroperoxide (TBHP) as the oxidant. The conditions for maximum conversion and selectivity of the desired products have been optimized by varying different reaction parameters. In order to get an insight on the role of each component in the reaction, a comprehensive kinetic study has been carried out and the order of reaction and activation energy have been determined. Further, the mechanism of the reaction has been studied in detail using ESR and CV studies as probes.

Chapter II describes the synthesis and characterization of di-copper substituted phosphotungstate. A detailed study to explore the use of synthesized complex for the oxidation of styrene and cis-cyclooctene with TBHP as the oxidant has been carried out under mild reaction conditions, by varying different parameters. Further, a detailed kinetics and mechanistic study has also been carried out.

Chapter III is divided into two sections describing the supporting of mono-copper substituted phosphotungstate to hydrous zirconia and neutral alumina, respectively, by wet impregnation technique and their characterization by various physico-chemical techniques. Further, the catalytic activity of both the supported materials for the oxidation of styrene and cis-cyclooctene using TBHP as the oxidant has been evaluated and the role of different supports have been discussed. Finally, the kinetics of the reaction using both catalysts has also been studied in detail. Based on the results obtained, the better support amongst the two was proposed.

Chapter IV describes the study on hybrid material comprising of mono-copper substituted phosphotungstate and imidazole and (*S*)-1-phenyl ethylamine via ligand substitution method in two sections, and their characterization by various physico-chemical and spectral techniques. The catalytic activity of the synthesized material has evaluated for the oxidation of styrene and cis-cyclooctene using TBHP as the oxidant. A detailed kinetic study has been carried out to get an insight on the role of each component in the reaction, and the order of reaction and activation energy have been determined.

In the end, the thesis contains comparison of activity of all the synthesized catalysts and discussion of effect of active species, supports (ZrO_2 and Al_2O_3) as well as effect of functionalization by different organic ligands (Imidazole and (*S*)-1-phenyl ethylamine).

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