PART
B

Transition Metal Substituted Polyoxometalates

Chapter
4

Introduction

Transition Metal Substituted Polyoxometalates

As mentioned in General Introduction, the modification of the precursors of parent POMs can lead to development of a new class of compounds with unique structural as well as acidic/redox properties. This modification of properties can be done basically in two ways. Of them the first way, **LPOMs** was already discussed in detail in **PART-A**.

The second way of modification of POMs is via incorporation of transition metal ions into the defect structures, forming a new class of compounds more commonly known as Transition Metal Substituted Polyoxometalates **(TMSPOMs)**. TMSPOMs, $[XM_{11}AO_{39}]^{(n-m)-}$ (X= P, Si, B; M=W, Mo; A= transition metal), have received increasing attention because substitution of a transition metal into the POM has been explored as a route to increase the range of application of these compounds [1-4]. This mostly due to the fact that TMSPOMs can be rationally modified on the molecular level including size, shape, charge density, acidity, redox states, stability and solubility resulting in their outstanding chemical properties. 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) their solubility is tunable by changing counter cations (ii) their redox properties are adjustable by changing the central (hetero) atom and the incorporated transition metal (iii) they are robust under oxidation conditions, under which most organic ligands decompose [5].

This unique class of metal oxygen clusters, are outstanding inorganic building blocks due to their undisputed structural beauty and controllable sizes, shapes and high negative charges [6-13]. They exhibit an enormous variety of structures, which leads to interesting and unexpected properties that give rise to many applications in magnetism, medicine and catalysis [14,15].

Most of the known TMSPOMs are mono-, di-, or trisubstituted derivatives of the Keggin type POM, e.g. $[M'(H_2O)XM_{11}O_{39}]^{n-}$, $[M'_2(H_2O)_2XM_{10}O_{38}]^{m-}$ and $[M'_3(H_2O)_3XM_9O_{37}]^{p-}$. Among these, Mono-substituted Keggin derivatives are explored extensively. Mono TMSPOMs recognized as inorganic analogs of metalloporphyrin complexes [16]. They have distinct advantages over the metalloporphyrin and organometallic complexes that they are rigid, hydrolytically stable and thermally robust. The non-oxidizable M-oxo framework of polyanions acts as an inert, multi-dentate ligand which can accommodate a multitude of transition metal centers [16-19].

The reaction of the mono lacunary $\{XM_{11}O_{39}\}^{m-}$ (where X = P, B, Si or Ge; M = W^{VI}, Mo^{VI}, $V^{V,VI}$, etc.) anion with transition-metal cations M' **in aqueous solution** leads to the formation of mono transition-metal-substituted POMs **(TM'SPOMs)** $\{XM_{11}O_{39}M'(L)\}$, (where M' = d- electron transition metal and L = monodentate ligand, generally H_2O) (Figure 1).

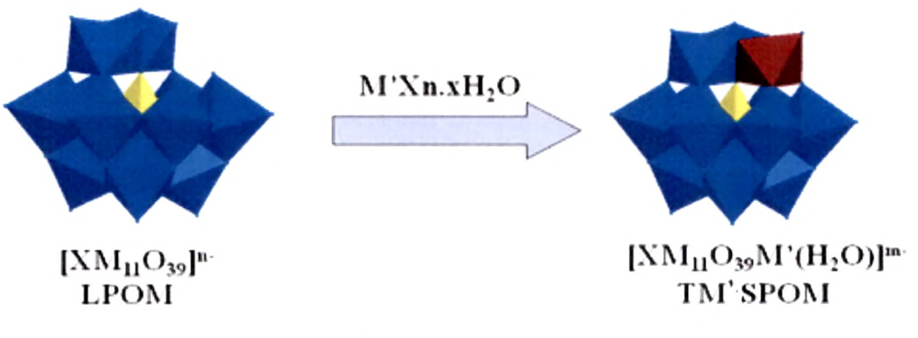

Figure 1. Formation of TMSPOMs from LPOMs

The environment around the substituent M' in the metal substituted polyanions $[XM_{11}O_{39}M'(H_2O)]^{n-}$ is considered to be near octahedral. In particular, the complexes of the type $[XM_{11}O_{39}M'(H_2O)]^{n-}$ show many analogies to metalloporphyrins [16,20,21].

A literature survey shows that most of the work have been carried out on synthesis and characterization of mono transition metal substituted polyoxotungstates **(TM′SPW)** $[XW_{11}O_{39}M(H_2O)]$ (X= P, Si; M= Co^{II}, Mn^{II}, Ni^{II}, Ru^{II}, Fe^{III}, Cr^{III}, Ru^{III}, Mn^{IV}, Re^{V}) and are well documented in art by several research groups mainly M. T. Pope, A. Muller, U. Kortz, L Cronin, P Mialane, J Reedijk. Among huge numbers, some important reviews and books are as below:

1. Polyoxometalate Molecular Science", M. T. Pope, A. Muller, Kluwer Academic Publishers, (2003)
2. 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).
3. Hybrid Organic–Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications, A. Dolbecq, E. Dumas , C. R. Mayer, P. Mialane, Chem. Rev., 110 (10), 6009, (2010)
4. Polyoxometalates containing late transition and noble metal atoms, P. Putaj, F. Lefebvre, Coord. Chem. Rev., 255, 1642, (2011)
5. Theme issue: Polyoxometalate cluster science, Edited by L. Cronin, A. Muller, Chem. Soc. Rev., 41, 7325, (2012)
6. Theme issue: Polyoxometalate, Edited by D-L. Long, L. Cronin, Dalton Trans., 9799, (2012)
7. Special Issue: Polyoxometalates (Cluster Issue), edited by: U. Kortz, T. Liu, Eur. J. Inorg. Chem., 2013, 1556, (2013)
8. Polyoxometalate Chemistry: Some Recent Trends, edited by: Francis Secheresse, World Scientific Publishing Company (2013).
9. Polyoxo Anions: Synthesis and Structure, M. T. Pope, in Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Edited by: Jan Reedijk. Elsevier (2013).

At the same time report on mono transition metal substituted polyoxomolybdates, $[XMo_{11}O_{39}M(H_2O)]$ (X= P, Si; M= transition metal except vanadium) are very less. In the present work **we have restricted ourselves to** mono transition metal substituted phosphomolybdates, **(TM'SPMo),** mainly because of two reasons (i) all available number of references on TM'SPW would result in increasing the bulk of the thesis (ii) TMSPMo have generated substantial interest as oxidation catalysts.

Among TM'SPMo, most of the results are available on vanadium substituted phosphomolybdate. Synthesis of vanadium substituted phosphomolybdate was reported by Tsigdinos and Hallada [22]. In this report, $H_3[PMo_{11}VO_{40}].H_2O$ has been synthesized by mixing the aqueous solutions of $Na_2HPO_4.12H_2O$, $NaVO_3$ and $Na_2MoO_4.2H_2O$ in appropriate molar ratio in acidic medium. The formed product was extracted with diethyl ether and recovered by evaporation of the ether layer. They also reported NH_4^+ salt of vanadium substituted phosphomolybdate. Other method for synthesis of $H_3[PMo_{11}VO_{40}].H_2O$ involves dissolving MoO_3 and V_2O_5 with stoichiometric amount of phosphoric acid in water [14]. Synthesis of sodium salt [23], tetrabutyl ammonium salts [24], Cs salt [25], cupric salts [26] and lanthanide salt [27] of $[PMo_{11}VO_{40}]^{3-}$ has also been reported which involves the mixing of the aqueous solutions of $H_3[PMo_{11}VO_{40}]$ and cation salt in appropriate molar concentrations.

Apart from various salts of $[PMo_{11}VO_{40}]^{3-}$, reports are also available on synthesis of other TM'SPMo. Massart et al. reported synthesis of ammonium salt of $[PMo_{11}ZnO_{40}].25H_2O$ by mixing of equiv-molar orthophosphoric acid, monochloracetic acid, ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ and zinc chloride solution [28].

Hill et al. reported two steps synthesis of $TBA_4H[PMo_{11}TM(L)O_{39}]$ (TM= Co, Mn, Cu and Zn; TBA= tetra butyl ammonium) [29]. Using same method, Neumann et al. reported synthesis of TBA salt of $[PMo_{11}Ru(L)O_{39}]$ [30]. The synthesized complex was well characterized with IR and ^{31}P NMR. Mizuno et al reported one pot synthesis of caesium and ammonium salt of $PMo_{11}FeO_{39}$ from $H_3[PMo_{12}O_{40}]$ and $Fe(NO_3)_3$ [31].

C. Rabia et al. reported synthesis of NH_4- salt of $[PMo_{11}MO_{40}]$ (M = Co, Ni, Fe) from individual transition metal salts (Ammonium heptamolybdate, Cobalt sulphate) [32]. Burns et al reported synthesized and characterized a series of $Na_2[(C_4H_9)_4N]_4[PZ(II)(Br)Mo_{11}O_{39}]$, where Z = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)) [33]. Vazquez and group reported hydrothermal synthesis of $H_6PMo_{11}BO_{40}$, $H_6PMo_{11}BiO_{40}$, $H_6PMo_{11}LaO_{40}$, and $H6PMo_{11}YO_{40}$ [34,35]. Vishnikin et al reported guanidinium salt of $PBiMo_{11}O_{40}$ and $PMo_{11}(TiO)O_{40}$ from their indivisual metal salts [36,37].

Few reports are also available describing structural determination of TM'SPMo with Single crystal X-Ray diffraction analysis. The synthesis, crystal structures and physical properties of the series of radical salts made with bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) and $[PMn(H_2O)Mo_{11}O_{39}]^{5-}$ have been reported by Coronado et al. [38]. Lin et al reported chain like crystal structure of $[(CH_3)_3NH]_{5n}[PMo_{11}MO_{39}]$ xH_2O (M = Mn^{2+}, x = n; Co^{2+}, x = 2n) [39]. This method involves the synthesis from the individual transition metal salts (i.e. $Na_2MoO_4.2H_2O$ and $Co(CH_3COO)_2$). They investigated electrochemical and magnetic properties of these compounds. Recently, Neumann et al. reported synthesis of TBA salt of $[PSb^{III}(H_2O)Mo_{11}O_{39}]$ from their individual component (Sb_2O_5, Na_2HPO_4, $Na_2MoO_4 \cdot 2H_2O$) [40]. Synthesized complex has been characterized with Single crystal XRD, UV/Visible spectroscopy, ESR and magnetic susceptibility.

Catalysis by TMSPOMs

TMSPOMs based materials have played an important role as catalysts in the field of oxidation catalysis due to their tendency to exhibit fast reversible multi-electron redox transformations under rather mild conditions and their inherent stability towards strong oxidants. Hence they are widely used as a model system for fundamental research providing unique opportunities for mechanistic studies on the molecular level. At the same time they become increasingly important for applied catalysis.

Majority of applied work was carried out in field of catalysis, especially oxidation of various organic substrates. Because the catalytically active site is at the substituted transition metal centre and POMs functions as a ligand with a strong capacity for accepting electrons. The substituting metal center is thus pentacoordinated by the "parent" POMs. 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 transition metal-substituted polyoxometalates being termed "inorganic metalloporphyrins" and has distinct advantages over organometallic species, *e.g.* they are rigid, hydrolytically stable and thermally robust. Further, the "active sites" of their transition metals and countercations can undergo extensive synthetic modifications.

In 1986, Hill and Brown [1] reported the following mechanism for oxidation process.

$$\underset{\text{oxometal}}{\mathbf{M{=}O}} + \underset{\text{alkene or alkane}}{\mathbf{Sub}} \xrightarrow{k_{ox}} \mathbf{M} + \underset{\text{epoxide}}{\mathbf{SubO}} \qquad \text{-- (1)}$$

This proposed mechanism is related to the work through earlier investigations of analogous metalloporphyrin systems by the Hill group (catalytic profiles, characterization of intermediates, product distributions, kinetics and other studies in many papers) [41-50].

In 2001, Pope and coworkers showed that the POMs catalyzed oxidations may be categorized by the principle mode of the catalytic reaction. There are two major reaction mechanisms [51]. In the first case, the catalytic cycle can be best described by the division of the reaction into two stages (Eq 2). Initially, the substrate is oxidized by the POM to yield the product and the reduced POM catalyst. The reduced POM catalyst is then reoxidized, often by oxygen to form water, hence completing the catalytic cycle.

$$\begin{aligned} &\mathbf{Substrate + POM_{ox}} \longrightarrow \mathbf{Product + POM_{red} + 2H^+} \\ &\mathbf{POM_{red} + O_2 + 2H^+} \longrightarrow \mathbf{POM_{ox} + H_2O} \end{aligned} \qquad \text{-- (2)}$$

In the liquid phase, the oxidation of the substrate is often a dehydrogenation (electron and proton transfer from the substrate to the catalyst) and regeneration of the catalyst implies electron donation of oxygen to the catalyst with co-formation of water or insertion.

The second reaction type views the oxidation catalyzed by the POM as an interaction with a primary oxidant (Eq 3). This interaction yields an activated catalyst intermediate e.g. peroxo, hydroperoxo or high valent oxo species which can be used to oxidize the organic substrate

$$\textbf{Oxidant + POM} \longrightarrow [\textbf{POM-Ox}]_{\textbf{activated}}$$

-- (3)

$$[\textbf{POM-Ox}]_{\textbf{activated}} + \textbf{Substrate} \longrightarrow \textbf{POM + Product}$$

In this second type of oxidation reactions, the actual reaction mechanism certainly varies as a function of the transition metal and oxidant, but can be considered as taking place via a general intermediate "transition metal - oxidant" species.

Numbers of groups have given a significant contribution in this field of oxidation catalysis. They have established unique and efficient catalytic systems based on $[XW_{11}O_{39}M(H_2O)]$ (X= P, Si; M= transition metal) as catalysts with various oxidants such as O_2, H_2O_2, PhOI, TBHP, $NaIO_4$. The major contribution has been given from research groups such as O. Kholdeeva, C. L. Hill, R. Neumann, N. Mizuno, T. Oyama, U. Kortz, M. Bonchio, J. C. Vedrine and J. M. Poblet. Among huge numbers, some important references are as below:

1. Polyoxometalates: Reactivity, by C. L. Hill, in Comprehensive Coordination Chemistry II, Edited by: J. A. McCleverty, T. J. Meyer, Elsevier, 4, 679, (2003)
2. Activation of Hydrogen Peroxide by Polyoxometalates, by N. Mizuno, K. Yamaguchi, K. Kamata, Y. Nakagawa, in Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis, Edited by: S. T.Oyama, Elsevier, 155, (2008).
3. Heteropolyoxometallate Catalysts for Partial Oxidation, by J. C. Védrine, J-M M. Millet, in Metal Oxide Catalysis, Edited by: S. D. Jackson, J S. J. Hargreaves, Wiley-VCH (2009).

4. "Modern heterogeneous oxidation catalysis, Edited by N. Mizuno, Ch 6 Liquid-Phase Oxidations with Hydrogen Peroxide and Molecular Oxygen Catalyzed by Polyoxometalate-Based Compounds". N. Mizuno, Wiley (2009)
5. Polyoxometalates as Homogeneous Oxidation Catalysts, M. Carraro, A. Sartorel, M. Ibrahim, N. Nsouli, C. Jahier, S. Nlate, U. Kortz, M. Bonchio, in Innovative Catalysis in Organic Synthesis: Oxidation, Hydrogenation, and C-X Bond Forming Reactions, Edited by P. G. Andersson, Wiley-VCH 1, (2012)
6. Liquid Phase Oxidation Via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications, Edited by M. G. Clerici, O. A. Kholdeeva, John Wiley & Sons (2013)
7. Structure and Reactivity of Polyoxometalates, From Elements to Applications, by J.J. Carbó, C. Bo, J.M. Poblet, in Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Comprehensive Inorganic Chemistry II (Second Edition), Edited by: Jan Reedijk and Kenneth Poeppelmeier, Elsevier, 9, 887 (2013)

However, similar reports on analogous TM'SPMo are scanty. Among TM'SPMo, use of vanadium substituted phosphomolybdate, $[PV(H_2O)Mo_{11}O_{39}]^{4-}$ as catalysts for oxidation reactions with different oxidant have been investigated extensively. Numbers of reports are available on $[PV(H_2O)Mo_{11}O_{39}]^{4-}$ based catalysts for oxidation/hydroxylation of benzene with H_2O_2 by Gopinath et al. [52], Hu et al [53], Nomiya et al. [54], Mizuno et al. [55], You et al. [56], Wang et al. [57] and Zhang et al. [58].

Similarly, oxidative dehydrogenation of isobutyric acid over $[PV(H_2O)Mo_{11}O_{39}]^{4-}$ based catalysts has also been reported by Herve et al. [59,60], Guelton et al. [26], Kaiji et al. [61], Akimoto et al. [62] and Misono et al. [63]. Oxidative dehydrogenation of propane catalyzed by Cs salt of [$PVMo_{11}O_{40}$] has also been reported by Vedrine and co-worker [64,65] and Wan et al. [66]. Mizuno et al. reported aerobic oxidation of adamantane over [$PV(H_2O)Mo_{11}O_{39}$] based catalyst at 356 K [67]. Vapour phase oxidation of n-Pentane over H_4[$PVMo_{11}O_{40}$] has been reported by Centi. Et al. [68]. H_4[$PVMo_{11}O_{40}$] catalyzed oxygenation of Methane with H_2O_2 in $(CF_3CO)_2O$ solvent at 353 K has been reported by Mizuno and group [69,70]. Oxidation of isobutane on $(NH_3)_3H$[$PVMo_{11}O_{40}$] [71], $Cs_{2.5}Ni_{0.08}H_{1.34}$[$PVMo_{11}O40$] [72,73], H_4[$PVMo_{11}O_{40}$] [74], $(NH_4)_3HPMo_{11}VO_{40}$ [75] has also been reported.

Kholdeeva and co-worker reported oxidation of 2,3,6- trimethylphenol catalyzed by [$PVMo_{11}O_{40}$]$^{4-}$ based catalyst in presence of organic:H_2O solvent system [76]. Oxidation of phenol with air using [$(C_nH_{2n+1})N(CH_3)_3$]$_{3+x}$[$PVxMo_{12-x}O_{40}$] (n=8-18; x=1,2,3) at room temperature has been reported by Huo et al. [77]. Ecofriendly liquid phase oxidation of 2,6-dimethylphenol catalyzed by $H_4PMo_{11}VO_{40}$ with H_2O_2 as an oxidant in acetone has been reported by Villabrille [34].

Series of cesium salt of [$PVMo_{11}O_{40}$] have been used as catalysts for gas phase oxidation of propylene by Dimitratos et al. [78]. Lee at al. [79], Hibst et al. [80] and Zhang et al. [81] explored use of Cs salt of [$PVMo_{11}O_{40}$] for Methacrolein oxidation. Zhizhina et al. reported aerobic oxidation of propene and butane-1 using Pd+H_4[$PVMo_{11}O_{40}$] as a catalysts at 333 K in homogeneous medium [82]. Reports on the oxidation of norbornene with aqueous H_2O_2 as an oxidant in different solvents, [83] and epoxidation of different alkenes with TBHP/ H_2O_2 in CH_3CN and CH_2Cl_2 [84] over [$PVMo_{11}O_{40}$]$^{4-}$ are also available. Vapour-phase oxidation of propene over $H_{3+x}PMo_{12-x}V_xO_{40}$ based catalysts has also been reported [85].

Lee et al. established use of $Cs_nH_{4-n}[PVMo_{11}O_{40}]$ as active and selective catalysts for vapour phase oxidation of ethanol [86]. Peng et al. studied the oxidation of liquid phase benzyl alcohol over a series of Cs salts of $[PVMo_{11}O_{40}]^{4-}$ using H_2O_2 as oxidant [87].

In India, extensive studies have been carried on transition metal substituted phosphomolybdates by Sai Prasad and group. Especially, number of reports on oxidation reactions using $[PVMo_{11}O_{40}]$ as catalysts have been reported by them [88-93].

Apart from $[PVMo_{11}O_{40}]$ based catalysts, use of other TM'SPMo as catalysts have also been established by several groups. Neumann et al reported use of $[PXMo_{11}O_{39}]^{n-}$ (X=Co, Mn, Ru) as bifunctional catalysts for the aerobic oxidation of cumene to hydroperoxo/peroxo intermediate followed by oxygen transfer to an alkene to yield epoxide in acetonitrile [30]. Later on, use of TBA-salt of $[PRu(H_2O)Mo_{11}O_{39}]^{4-}$ as catalysts for the epoxidation of alkenes with molecular oxygen in acetonitrile under mild condition has been reported by them[94]. Oxidative dehydrogenation of alcohols has been investigated under aerobic as well as anaerobic conditions over $[PSb^V(O)Mo_{11}O_{39}]^{4-}$ and $[PSb^V(Br)Mo_{11}O_{39}]^{3-}$ in benzonitrile at 135 °C by the same group [40].

Knapp et al reported vapour phase selective oxidation of isobutene over $Cs_3H_1PMo_{11}FeO_{39}$ [95]. Oxidative dehydrogenation of 2-propanol over $Cs_{2.5}H_{1.2}PMo_{11}Fe(H_2O)O_{39}.6H_2O$ has been reported by Mizuno et al. [31]. Tundo et al. reported multiphase oxidation of alcohols and sulfides with hydrogen peroxide catalyzed by $H_6PMo_{11}AlO_{40}$ at 70 °C [96]. Use of $H_6PMo_{11}BO_{40}$, $H_6PMo_{11}BiO_{40}$, $H_6PMo_{11}LaO_{40}$, and $H_6PMo_{11}YO_{40}$ as catalysts in the green and selective oxidation of diphenyl sulphide with H_2O_2 has been established by Vazquez and co-workers [35].

Burns et al. reported homogeneous oxidation of isobutyraldehyde catalyzed by $[PZ(II)(Br)Mo_{11}O_{39}]^{6-}$, (Z= Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)) using H_2O_2 as an oxidant in acetonitrile at 50 °C [33]. Rabia et al. investigated use of ammonium salt of $PMo_{11}MO_{40}$ (M= Co, Fe, Ni) for oxidation of propane with molecular oxygen at temperature 380 °- 420 °C [32]. Use of TBA salt of $PMo_{11}MO_{40}$ (M= Co, Mn) as catalysts for oxidation of phenol in acetonitrile has been explored by karcz et al [97]. Recently, Cavaleiro et al reported homogeneous catalytic oxidation of olefins with hydrogen peroxide catalyzed by $TBA_4H[PMo_{11}Mn(H_2O)O_{39}].2H_2O$ in acetonitrile [98].

From literature survey it can be seen than, almost all reported articles describe syntheses of the TM'SPMo either in two steps or from the individual transition metal salts. Also, except three reports, no report on X-ray crystal structure is available. At the same time, in most of applied protocols catalyzed by TM'SPMo, oxidation requires harsh conditions of temperature, use of relatively expensive metals (V, Ru, Bi, La, Y) as well as use of organic solvent.

Considering these aspects, it was thought of interest to design a new easy synthetic pathway for synthesis of TM'SPMo, and to use them as sustainable catalysts for oxidation reaction. As Co, Mn and Ni are most important from the view point of their redox properties, they were selected for the present work.

The main objectives are as follows

1. To modify the present two step synthesis of mono substituted transition metal phosphomolybdates and to establish easy synthetic pathway i.e. one pot synthesis of Co, Mn and Ni substituted phosphomolybdates.
2. To characterize synthesized complexes by elemental analysis (EDX), Single-crystal X-ray diffraction, (TG-DTA), powder X-ray diffraction (XRD), Fourier

Transform Infrared Spectroscopy (FT-IR), Diffused Reflectance Spectra (DRS), electron spin resonance (ESR), and ^{31}P Magic-Angle Spinning Nuclear Magnetic Resonance (^{31}P MAS- NMR).

3. To establish the use of synthesized complexes as sustainable catalysts for solvent free liquid phase oxidation of alcohols and alkenes with economically and environmentally benign oxidants, O_2 (Heterogeneous) and H_2O_2 (Homogenous).
4. To study the effect of substitution on the catalytic activity of different substrates and to propose the best catalyst among them.
5. To study reaction mechanism for aerobic oxidation alkenes and alcohols
6. To study kinetic of oxidation of styrene with H_2O_2.

Chapter 5 consists of one pot synthesis of cesium salt transition metal (Co, Mn, Ni)- substituted phosphomolybdate; **$PMo_{11}M$** (M= Co, Mn, Ni). The synthesized complexes were systematically characterized by elemental analysis, Single crystal XRD, TG-DTA, powder XRD, FT-IR, DRS, ESR, and ^{31}P NMR.

Chapter 6 describes the catalytic activity of $PMo_{11}M$ (M= Co, Mn, Ni) for solvent free liquid phase oxidation of alcohols and alkenes using environmentally benign oxidants viz. O_2 and 30% aqueous H_2O_2.
Comparison of catalytic activity of $PMo_{11}M$ (M= Co, Mn, Ni) was studied. Reaction mechanism for aerobic oxidation of alcohols and alkenes was also proposed.
Comparative and Kinetic study for oxidation of styrene with H_2O_2 was studied.

Chapter 7 Use of $PMo_{11}Ni$ was explored as a sustainable catalyst for Suzuki coupling.

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