Chapter 1:

Introduction

1.1 Overview

Polyoxometalates belong to a large class of nanosized metal-oxygen cluster anions [1, 2]. These form by a self-assembly process, typically in an acidic aqueous solution as illustrated by equation 1.1 and 1.2 and can be isolated as solids with an appropriate counter cation, for example H^+, alkali metal cation, NH_4^+etc.

$$8\ H^+ + 7\ WO_4^{2-} \rightarrow [W_7O_{24}]^{6-} + 4\ H_2O \qquad (1.1)$$

$$23\ H^+ + HPO_4^{2-} + 12\ MoO_4^{2-} \rightarrow [PMo_{12}O_{40}]^{3-} + 12\ H_2O \qquad (1.2)$$

Generally, two types of polyoxometalates are distinguished, based on their chemical compositions - isopoly anions and heteropoly anions. These anions may be represented by the general formulae:

$[M_mO_y]^{p-}$ Isopoly anions

$[X_xM_mO_y]^{q-}$ ($x \leq m$) Heteropoly anions

where M is the addenda atom and X is the heteroatom also called the central atom when located in the centre of the polyanion. The distinction between the two groups is frequently artificial, especially in the case of mixed-addenda polyoxometalates [2]. Heteropoly compounds are by far most important for catalysis as well as for other applications; hence this work is mainly focused on them. Heteropoly acids - strong acids composed of heteropoly anions and protons as the counter cations - constitute a special case of heteropoly compounds that is particularly important for catalytic applications.

The most common addenda atoms are molybdenum or tungsten, less frequently vanadium and niobium or mixtures of these elements in their highest oxidation states (d^0, d^1). Much broader range of elements act as heteroatoms; as such, almost all elements of the Periodic Table can be incorporated in heteropoly anions, most typical ones being P^{5+}, As^{5+}, Si^{4+}, Ge^{4+}, B^{3+} etc. Molybdenum (VI) and tungsten (VI) are the best polyoxometalate forming elements, as the result of a favorable combination of ionic radius and charge and of accessibility of empty *d*-orbitals for metal-oxygen π bonding [2].

1.2 Structures of Polyoxometalates

Dozens of structural types and stoichiometries of polyoxometalates are known to date. The minimum degree of condensation of addenda atoms is arbitrarily set to be in the range of 2 to 6 [2, 3]. The maximum can go to as high as a few hundred. For example, the giant heteropoly tungstate $[La_{16}As_{12}W_{148}O_{524}]^{76-}$ includes 28 heteroatoms (La, As) and 148 addenda atoms (W) [4].

Two general principles apply to polyoxometalate structure: [2-5]

1. Addenda atoms occupy a metal-oxygen polyhedron MO_x that is most commonly an octahedron. In this polyhedron, the metal atom is displaced from the inversion centre towards the peripheral vertices because of metal-oxygen π bonding.
2. Structures with MO_6 octahedra that contain more than two free vertices are generally not found among the typical polyoxometalates. This is known as the Lipscomb restriction, which may be explained as a result of the strong *trans* influence of the terminal M=O bonds that facilitates dissociation of MO_3 from the polyanion [6].

According to Pope and Muller, it is convenient to discuss the variety of polyoxometalate structure starting from a few highly symmetrical 'parent' polyanions; then many other polyoxometalate structures maybe considered as their 'derivatives' [2, 5]. There are three such parent structures, with a tetrahedron, an octahedron and an icosahedron as their central polyhedron XO_n (n = 4, 6 or 12) that determines the symmetry of the whole polyanion. These structures, that have already been mentioned, are: the Keggin structure (T_d symmetry); the structure of a hypothetical anion $[XM_{12}O_{38}]$ (O_h), that has not yet been observed itself but its derivatives, for example the Anderson-Evans anion $[XM_6O_{24}]$, are well known and the Dexter-Silverton structure (I_h). These structures will be briefly discussed below.

1.2.1 The Keggin structure

This is the first characterized and the best known structure that is adopted by many polyoxometalates [7]. Among a wide variety of heteropoly compounds, the Keggin are the most stable and more easily available. These, together with some of their derivatives, are the most important for catalysis.

The Keggin heteropoly anions are typically represented by the formula $[XM_{12}O_{40}]^{x-8}$, where X is the heteroatom, x is its oxidation state and M is the addenda atom (usually Mo^{6+} or W^{6+}). The M^{6+} ion can be substituted by many other metal ions e.g, V^{5+}, Co^{2+}, Zn^{2+}etc. The Keggin anion has a diameter of *ca.* 1.2 nm and is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6 (Figure 1). The octahedra are arranged in four M_3O_{13} groups. Each group is formed by three octahedra sharing edges and having a common oxygen atom which is also shared with the central tetrahedron XO_4. The total assemblage contains 40 close-packed oxygen atoms. The oxygen atoms are of four types: twelve terminal M=O, twelve edge-bridging angular M-O-M shared by the octahedra within a M_3O_{13} group, twelve corner-bridging quasi-linear M-O-M connecting two different M_3O_{13} groups and four internal X-O-M. These oxygen atoms can be discriminated by ^{17}O NMR [2]. The corresponding bonds exhibit characteristic infrared bands in the range of 600-1100 cm^{-1} [2].

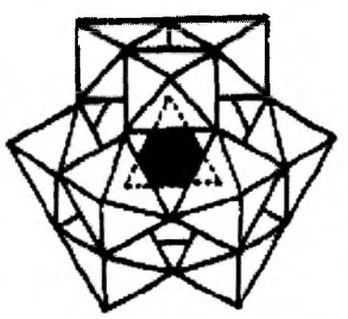


Figure 1: The Keggin structure of the $[X^xM_{12}O_{40}]^{x-8}$ anion (α-isomer) [2]

Each of the M_3O_{13} groups can be rotated by 60° about its 3-fold axis which leads to geometrical isomers. The structure shown in Figure 1 is the most common α isomer of the Keggin structure. Rotation of one of its M_3O_{13} group produces the β isomer. In some cases, these isomers can be separated, e.g, by fractional crystallization. Rotation of two, three or all four M_3O_{13} produces the γ, δ and ε isomers, respectively [2].

Lacunary derivatives of the Keggin anion result from the removal of one or more M atoms. Examples of the lacunary derivatives (one monovacant and two trivacant) of the α-Keggin anions are shown in Figure 2. The two trivacant species correspond to loss of a corner-shared group of MO_6 octahedra (A-type $[XM_9]$) or an

edge-shared group (B-type $[XM_9]$) [2]. Such species can assemble into larger polyoxometalate structures, either directly or without incorporation of metal ion linkers.

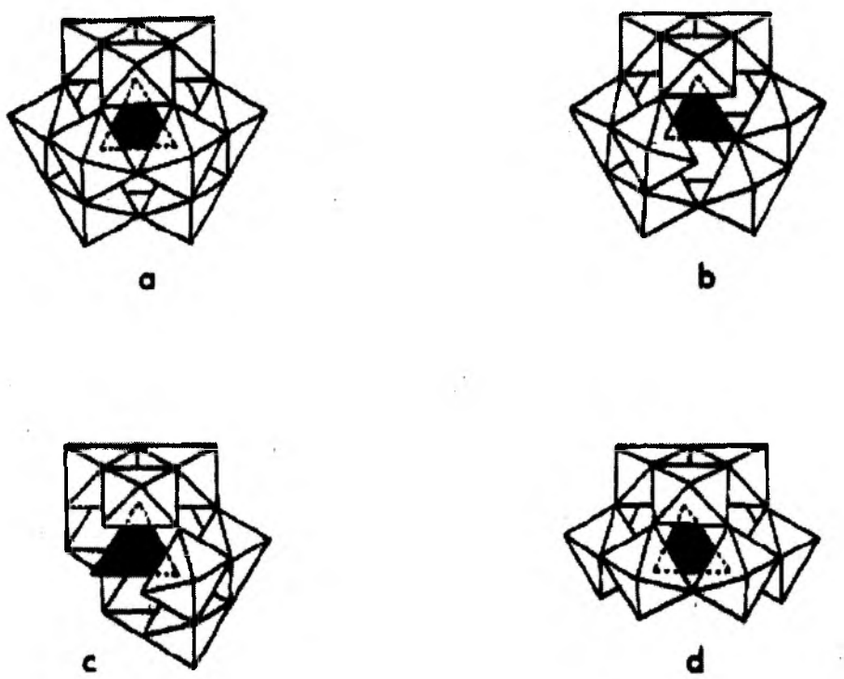


Figure 2: The structures of the α-Keggin anion $[XM_{12}O_{40}]^{x-8}$ (a) and its lacunary derivatives: (b) monovacant, (c) trivacant B-$[XW_9]$ and (d) trivacant A-$[XW_9]$ [2]

1.2.2 The Well-Dawson structure

One of these derivatives is the Well-Dawson dimeric (2:18) heteropoly anion $[X_2M_{18}O_{62}]^{2x-16}$ (M = Mo^{6+} or W^{6+}, X = P^{5+} or As^{5+}, x = charge on the 'X' atom). Its structure (α-isomer) is shown in Figure 3. The anion consists of two trivacant lacunary Keggin species A-$\{XM_9\}$ linked directly across the lacunae. The Well-Dawson structure contains two M_3O_{13} groups. A 60° rotation of one of these groups about its 3-fold axis gives the β-isomer. The molybdenum anion is chiral because of a displacement of the molybdenum atoms within their MoO_6 octahedra. The tungsten complex shows no such chirality probably because of the greater rigidity of the tungsten framework [2, 8].

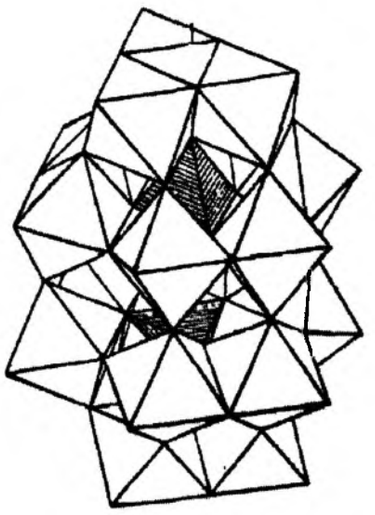


Figure 3: The Well-Dawson structure of the $[X_2M_{18}O_{62}]^{2x-16}$ anion (α-isomer) [8]

1.2.3 The Anderson-Evans structure

This example represents a different structural type with an octahedron as a central polyhedron. The Anderson-Evans structure is adopted by 6-heteropoly anions (e.g. $[TeMo_6O_{24}]^{6-}$) [2, 9]. It consists of six coplanar MO_6 octahedra arranged in a closed ring sharing edges. The heteroatom occupies the octahedral pocket in the centre of the ring (Figure 4).

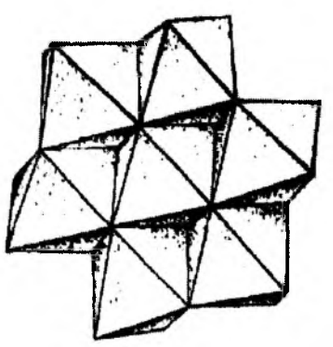


Figure 4: The Anderson-Evans structure of the $[X_6M_6O_{24}]^{2x-16}$ anion [9]

1.2.4 The Dexter-Silverton structure

A less common type of 12-heteropoly anions $[XM_{12}O_{42}]^{x-12}$, where M is molybdenum (VI) and X is cerium (IV), uranium (IV) or thorium (IV), adopt this structure (Figure 5). In this anion, the central atom is surrounded by twelve oxygen

atoms that form an icosahedron as a central polyhedron. The MO_6 octahedra are arranged in face-sharing pairs [2, 10].

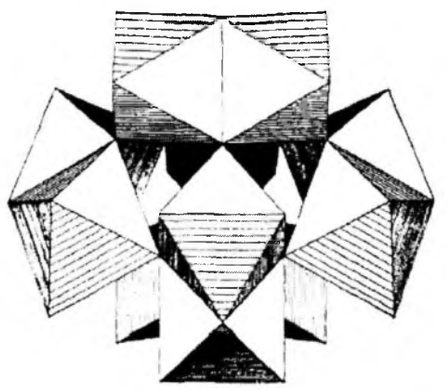


Figure 5: The Dexter-Silverton structure of the $[XM_{12}O_{42}]^{x-12}$ anion [10]

1.2.5 Transition metal substituted Sandwich type Polyoxometalates

In 1973 Tourne *et al* reported a 'sandwich-type' polyoxometalate for the first time, which dawned new area in the polyoxometalate world [11]. The reported polyoxometalate was formulated as $[P_2Co_4(H_2O)_2W_{18}O_{68}]^{10-}$ and it was observed that the four cobalt atoms were actually sandwiched between two lacunary trivacant Keggin units composed of $(PW_9O_{34})^{9-}$, as can be seen in Figure 6, hence the name sandwich type polyoxometalates.

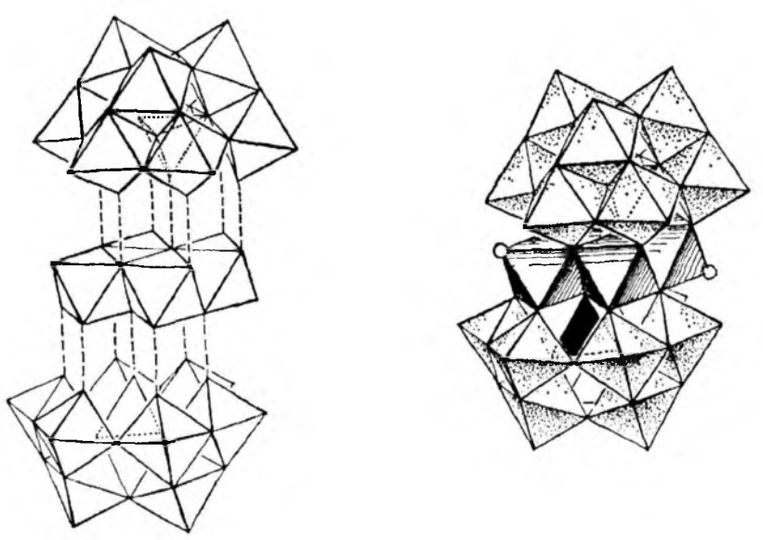


Figure 6: The $[P_2Co_4(H_2O)_2W_{18}O_{68}]^{10-}$ anion, where the four Co atoms occupy the central octahedra and the circles denote water molecules [11]

Soon after this polyoxometalate was reported; a variety of other sandwich type polyoxometalates with similar structure, but with different central atoms and transition metal ions followed the suite. Some prominent amongst them were, $[M_4(H_2O)_2(XW_9O_{34})_2]^{n-}$ (n = 12, X = Ge^{IV}, Si^{IV}, M = Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; n = 10, X = P^V, As^V, M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; n = 6, X = P^V, As^V, M = Fe^{3+}; n = 14, X = Ga^{III}, M = Cu^{2+}, Zn^{2+}) [12-32]. The central atom in all these sandwich type polyoxometalates assumes a tetrahedral geometry.

Similar to these sandwich type polyoxometalates, some other structurally different sandwich type polyoxometalates were also reported, as shall be seen further. The fundamental difference in these polyoxometalates and the above sandwich type polyoxometalates was that, here the geometry of the central atom was pyramidal. Additionally, in these polyoxometalates either three or four transition metal ions could be sandwiched between the two lacunary trivacant Keggin units, depending on the central atoms and the transition metal atoms. The structures of these two kinds of polyoxometalates are shown in Figure 7. Some examples of three transition metal ions sandwiched between two lacunary trivacant Keggin units are, $[M_3(H_2O)_3(XW_9O_{33})_2]^{n-}$ (n = 12, X = As^{III}, Sb^{III}, M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; n = 10, X = Se^{IV}, Te^{IV}, M = Cu^{2+}) and $[(VO)_3(XW_9O_{33})_2]^{n-}$; n = 12, X = As^{III}, Sb^{III}, Bi^{III}; n = 11, X = As^{III} [33-40]. Further, few examples of four transition metal ions sandwiched between two lacunary trivacant Keggin units are $([M_2(H_2O)_6(WO_2)_2(SbW_9O_{33})_2]^{(14-2n)-}$ (M^{n+} = Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}), $([M_2(H_2O)_6(WO_2)_2(BiW_9O_{33})_2]^{(14-2n)-}$ (M^{n+} = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), $[(VO(H_2O)_2)_2(WO_2)_2(BiW_9O_{33})_2]^{10-}$, $[Sn_{1.5}(WO_2(OH))_{0.5}(WO_2)_2(XW_9O_{33})_2]^{10.5-}$ (X = Sb^{III}, Bi^{III}), $[M_3(H_2O)_8(WO_2)(TeW_9O_{33})_2]^{8-}$ (M = Ni^{2+}, Co^{2+}), $[(Zn(H_2O)_3)_2(WO_2)_{1.5}(Zn(H_2O)_2)_{0.5}(TeW_9O_{33})_2]^{8-}$, $[(VO(H_2O)_2)_{1.5}(WO(H_2O)_2)_{0.5}(WO_2)_{0.5}(VO(H_2O))_{1.5}(TeW_9O_{33})_2]^{7-}$ and $[M_4(H_2O)_{10}(XW_9O_{33})_2]^{n-}$ (n = 6, X = As^{III} and Sb^{III} , M = Fe^{3+} and Cr^{3+}; n = 4, X = Se^{IV}, Te^{IV}, M = Fe^{3+} and Cr^{3+}; n = 8, X = Se^{IV}, Te^{IV}, M = Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, $Cd^{2+}$and Hg^{2+}) [40-45].

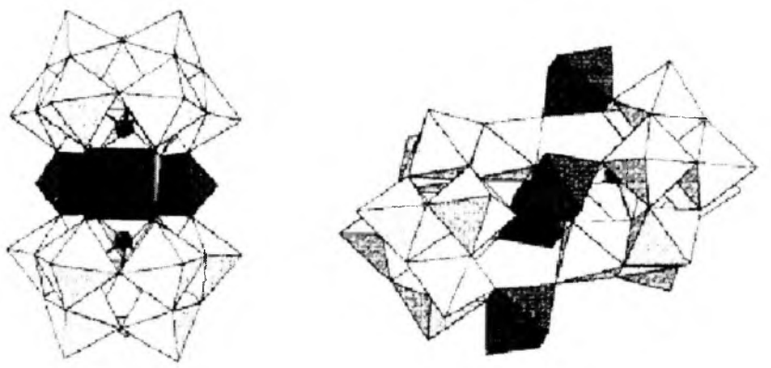


Figure 7: Structure of sandwich type polyoxometalates with three (left) and four (right) transition metal atoms sandwiched by two lacunary trivacant Keggin units, with pyramidal central atoms (seen as black circles, in the lacunary trivacant Keggin unit). The black polyhedrons represent the transition metal polyhedrons, which are square pyramidal in the case of 'left', while octahedral in the case of 'right' [34]

1.2.6 Zinc and Cobalt based Sandwich type Polyoxometalates

In 1991 Tourne *et al* reported zinc and cobalt central atoms based sandwich type polyoxotungstates, using common chemicals and simpler reaction conditions, with the general formula $[WM_3(H_2O)_2(MW_9O_{34})_2]^{12-}$, where M = Zn^{2+}, Co^{2+} [46]. The structure of these two sandwich type polyoxoanions was similar to the structure, seen in Figure 6. However, here in the central belt of transition metal atoms, one of the inner side transition metal atoms is replaced by a tungsten atom. The other three atoms, as well as the two central atoms above and below are zinc or cobalt atoms. Thus total three kinds of zinc/cobalt atoms are present in these polyoxoanions, first is the central atoms, second is the inner side atom of the central belt and thirdly the outer side atoms of the central belt, surrounded by a labile water molecule on one side each (please see Figure 6).

Although the structure appears to be very complicated, the synthesis is relatively very simple. The experimental procedure follows as, dropwise addition of zinc or cobalt nitrate solution to a hot solution of sodium tungstate (temperature maintained at 90-95 °C). Prior to the addition of the nitrate solution, appropriate amount of concentrated nitric acid is added to the sodium tungstate solution under stirring, to adjust the pH. Once the addition of nitrate solution is over, the mixture is transferred to a dish and left covered for crystallization of the desired polyoxometalate

to take place. It can be noted that he syntheses of all the other sandwich type polyoxometalates normally follow a two step procedure, the first is synthesis of the lacunary trivacant Keggin unit and the next step is synthesis of the desired polyoxoanion, by treating this lacunary trivacant Keggin unit with the appropriate transition metal salt solution.

Interestingly, in the case of these zinc and cobalt containing sandwich type polyoxotungstates, the outer side zinc or cobalt atoms in the central belt, that are attached to labile water molecules can be relatively easily and selectively knocked out, without affecting the original structure polyoxoanion. Thus a variety of transition metal ions can be introduced in the polyoxoanion frame work depending on the choice or requirement. The substituting transition metal atoms reported in the case of zinc polyoxoanion are Co^{2+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, VO^{2+}, Pd^{2+} and Pt^{2+}, while in the case of cobalt polyoxoanion are Zn^{2+}, Mn^{2+}, Cu^{2+} and Ni^{2+}. In the case of former, even Ru^{3+} and Rh^{3+} have been reported to substitute the zinc atoms by other groups in later reports [47, 48]. In the case of zinc polyoxoanion, even the third zinc atom in the central belt can be substituted by increase of the reaction times and/or the concentration of the transition metal salt solutions. Thus, trisubstituted derivatives of the zinc polyoxoanions with Co^{2+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Cu^{2+} and Fe^{3+} were also reported by the original authors.

1.3 Historical Background

The history of polyoxometalates dates back to 1826 when Berzelius discovered the first heteropoly salt, ammonium 12-molybdophosphate [49]. Later on in 1848, Svanberg and Struve introduced this compound in analytical chemistry as the basis for the determination of phosphorus that has been widely used since [50]. By 1908, approximately 750 heteropoly compounds had been reported. However, the structure of polyoxometalates had remained a mystery for more than a century since their discovery. Werner, Miolati, Rosenheim and Pauling proposed structures based on sharing metal-oxygen polyhedra [51-54]. It was Keggin who in 1933 solved the structure of the most important 12:1 type of heteropoly anion by a powder diffraction study of $H_3[PW_{12}O_{40}]$ [7]. This structure, now named after its discoverer, contained 12 WO_6 octahedra linked by edge and corner sharing, with the heteroatom occupying a tetrahedral hole in the centre. In 1948, Evans determined the structure of another widespread type - the Anderson's 6:1 heteropoly anion - by single-crystal X-ray

analysis of $[TeMo_6O_{24}]^{6-}$ salts; this structure is now referred as the Anderson-Evan's structure [9]. In 1953, Dawson reported the next new structure (now frequently referred as the Well-Dawson's) of an 18:2 (or 9:1) heteropoly anion $[P_2W_{18}O_{62}]^{6-}$ [8]. This structure was shown to be closely related to the Keggin structure. Next, in 1968, Dexter and Silverton reported the X-ray structure of $[CeMo_{12}O_{42}]^{8-}$ and showed the large Ce heteroatom to be in a CeO_{12} central icosahedron [10]. By early 1970s, the chemistry of polyoxometalates had been greatly expanded. This period is associated with extensive work of many groups all over the world and in the 1980-90s; the number of groups involved in the field further increased with expanding applications of polyoxometalates in various areas.

By 1995, the X-ray structure of approximately 180 polyoxometalates had been reported [3]. Among them, salts of giant heteropoly anions such as $[La_{16}As_{12}W_{148}O_{524}]^{76-}$ (ion mass *ca.* 40000, diameter 40 Å) and others were prepared and characterized by Muller *et al* [4]. The application of modern characterization techniques had led to much better understanding of the structural principles of polyoxometalates and their properties. However, there is still plenty of scope for further work in this field, as many fundamental questions regarding the structural principles, mechanisms of synthesis and reactivity of polyoxometalates remain unanswered.

1.4 Nomenclature in Heteropolyoxometalates

A systematic nomenclature of polyoxometalates has been developed [2, 55]. It uses a labeling system for the metal atoms and, in some cases, for the oxygen atoms to avoid ambiguity. The resulting names, however, are too long and complicated; these are practically never used for routine purposes.

In catalytic applications, only a relatively small number of well-known types of polyoxometalates have been involved so far, largely limited to the Keggin compounds and their derivatives. Usually, simplified conventional nomenclature, sometimes even trivial names, are sufficient for reporting and retrieving information in the field. Here we adopt the current nomenclature that treats polyoxometalates (also referred to as heteropoly anions, heteropoly compounds, polyoxoanions or polyanions) as quasi coordination complexes [2]. The heteroatom, if present is considered as the central atom of the complex and the addenda as the ligands. In the formulae of heteropoly anions, the heteroatoms are placed before the heteroatoms; the

heteropoly anion is placed in square brackets and thus separated from the counter cations as illustrated by the following examples:

$[SiW_{12}O_{40}]^{4-}$	12-tungstosilicate or dodecatungstosilicate
$H_3[PMo_{12}O_{40}]$	12-molybdophosphoric acid
$Na_5[PMo_{10}V_2O_{40}]$	Sodium decamolybdodivanabdophosphate

For simplicity, the counter cations and the charge of polyanion and even the oxygen atoms may be omitted; for example, $Na_6[P_2Mo_{18}O_{62}]$ may be abbreviated to $\{P_2Mo_{18}O_{62}\}$ or P_2Mo_{18}.

1.5 Crystal Structure of Keggin type Polyoxometalates

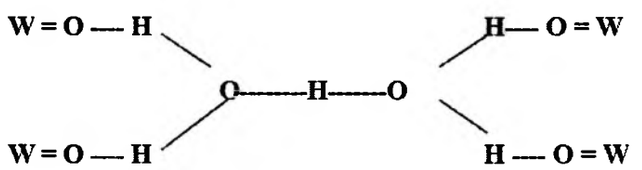
1.5.1 Primary structure

The heteropoly acids in the solid state are ionic crystals (sometimes amorphous) which consist of large polyanions that are linked together. This polyanionic Keggin structure specially the α-type has T_d symmetry and consists of a centrally located XO_4 tetrahedron (X = central atom or central atom) surrounded by twelve edge and corner sharing MO_6 octahedra (M = addenda atom). The octahedra are arranged in four M_3O_{13} groups. Each group is formed by three octahedra sharing edges and having a common oxygen atom which is also shared with the central tetrahedron XO_4.The oxygen atoms in the Keggin structure are classified into four classes of symmetry equivalent oxygen atoms: $X\text{-}O_a\text{-}M$, $M\text{-}O_b\text{-}M$ ('inter' bridges between corner sharing octahedra), $M\text{-}O_c\text{-}M$ ('intra' bridges between edge sharing, i.e., within a M_3O_{13} set) and $M\text{-}O_d$ (the terminal oxygen atoms) where M is the addenda atom and X is the central atom. The anion contains twelve quasi-linear M-O-M linkages between the octahedra forming part of different M_3O_{13} triads twelve angular M-O-M bonds between the octahedra within a single triad, four X-O-M bonds where the triads are joined to the central atom and twelve terminal M=O bonds.

1.5.2 Secondary structure

The three dimensional arrangement consisting of the large polyanions, cations, water of crystallization and other molecules constitute the secondary structure of heteropoly compounds. Acid forms of heteropoly compounds in solid state, contain

counter cations or the protons which play an important role in the structure of the crystal, by linking the neighboring heteropoly anions. For e.g., protons of crystalline $H_3PW_{12}O_{40}.6H_2O$ are presented in hydrated species, $H_5O_2^+$, each of which links four neighboring heteropoly anions by hydrogen bonding to the terminal W-O_d oxygen atoms and the polyanions are packed in a bcc structure. This is shown in the following Figure.



Secondary structures may also contain organic molecules for e.g., $H_4SiW_{12}O_{40}.9DMSO$ which contains nine molecules of DMSO in a unit cell where there are weak hydrogen bonds between methyl groups and oxygen atom of the heteropoly anions. Another interesting example is $PW_{12}O_{40}$. $[(C_5H_5N)_2H]_3$ is obtained by the reaction of anhydrous $H_3PW_{12}O_{40}$ with pyridine.

1.5.3 Tertiary structure

Structure of the solid heteropoly acid as assembled constitutes the tertiary component of the complex. The size of the particles, pore structure and distribution of protons in particles are the elements of the tertiary structure. The primary, secondary and tertiary structures are represented in Figure 8 [56].

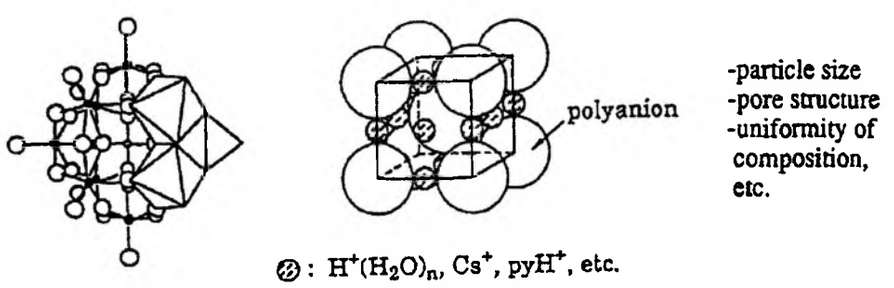


Figure 8: Primary, secondary and tertiary structure of $H_3[PW_{12}O_{40}]$ [56]

1.6 General Properties of Heteropoly Compounds

1.6.1 Solubility of heteropoly compounds

Free acids and most salts of heteropoly anions are extraordinarily soluble in water and are often very soluble in a wide range of organic solvents.

In water: Most free acids are generally extremely soluble (up to 85 % by weight of solution). In general, the heteropoly salts of small cations, including those of many heavy metals, are also very soluble. Heteropoly acids with large size counter cations are less soluble. Thus Cs^+, Ag^+, Tl^+, Hg^{2+}, Pb^{2+} and the larger alkaline earth metal salts are often insoluble. The NH_4^+, K^+ and Rb^+ salts of some of the important series of heteropoly anions are insoluble. Salts of heteropolymolybdate and heteropoly tungstate anions with cationic coordination complexes, alkaloids or organic amines are usually insoluble. Solubility of the heteropoly compounds in water must be attributed to very low lattice energies and solvation of cations. Solubility is governed by packing considerations in the crystals. The counter cations are fitted in between the large negative anions. When large cations like Rb^+, Cs^+ are present they allow stable packing in the large interstices, causing sufficient lowering of lattice energy to produce insolubility.

In organic solvents: Many of the free acids and a few of the salts are very soluble in organic solvents, especially if the latter contain oxygen. Ethers, alcohols and ketones (in that order) are generally the best solvents. Free acids are insoluble in non-oxygen solvents such as benzene, chloroform and carbon disulphide. The dehydrated salts sometimes dissolve readily in organic solvents; the hydrated salts are insoluble.

Many studies show that the typical Keggin heteropoly acids retain the structure of polyanion in aqueous solution, at least at a relatively high concentration [2]. This has been demonstrated by XRD, IR and Raman spectroscopy as well as by ^{17}O NMR [57]. However, in dilute ($<10^{-2}$ mol^{-1}) solutions, degradation of polyanion may occur.

Generally, the stability of 12-heteropoly anions towards hydrolysis in aqueous solution decreases in the order of addenda atoms [1, 58].

$$W\ (VI) > Mo\ (VI) > V\ (V)$$

12-Heteropolymolybdates with different central atoms differ markedly in their stability to degradation in water solution in the following decreasing order [1, 58].

Si > Zr, Ti > Ge > P > As

The crystalline free acids and salts of heteropolymolybdate and heteropoly tungstate anions are almost always highly hydrated. A given acid or salt will often form several solid hydrates. Most of the heteropolymolybdate series form isomorphous 30-hydrates.They melt in their own water of hydration between 40 and 100°C. In dry air they begin to lose water and they give up all thirty water molecules in vacuum over sulfuric acid.

1.6.2 Redox properties of heteropoly compounds

Some heteropoly compounds especially heteropolymolybdates are strong oxidizing agents and can be very readily changed to fairly stable, reduced heteropolymolybdates. These reduced species are called 'heteropoly blues'. Redox chemistry of polyoxometalates is extremely diverse [1, 2]. It has been subject of many studies and found many applications in chemical analysis as well as in selective oxidation reactions [58].

According to Pope, polyoxometalates, regarding their redox abilities, can be divided into two groups- 'mono-oxo' (type I) and 'cis-dioxo' (type II) [1, 5]. This classification is based on the number of terminal oxygen atoms attached to each addenda atom. Examples of type I polyanions are the Keggins, the Well-Dawsons and their derivatives that have one terminal M=O per each addenda atom. Type II polyanions can be represented by the Dexter-Silverton anion which has two terminal oxygen atoms in cis positions on each addenda atoms. In type I octahedra MO_6, the LUMO is a nonbonding metal-centered orbital, whereas for type II MO_6 octahedra, the LUMO is antibonding with respect to the terminal M=O bonds. Consequently, type I polyoxometalates are reduced easily and frequently reversibly to form mixed-valence species (heteropoly blues), which retain the structure of the parent oxidized anions. In contrast, type II polyoxometalates are reduced with more difficulty and irreversibly to complexes with yet unknown structures [1, 5]. For this reason, only

type I heteropoly compounds, by and large the Keggins, are of interest for oxidation catalysis.

The total number of accepted electrons on reduction of type I polyoxometalates can be quite high. As the anion structure retains upon this process, the additional negative charge is compensated for by protonation of the anion from solvent. Thus the reduction is frequently pH dependent, which is represented by the following equation

$$[XM_{12}{}^{6+}O_{40}]^{x-8} + p\,e^- + q\,H^+ \leftrightarrow H_q[XM_{12-p}{}^{6+}M_p{}^{5+}O_{40}]^{x+q-p-8}$$

where $q \leq p$ [1, 2]. On reduction in acidic solution pH = 1, the Keggin tungsten anions, e.g., $[SiW_{12}O_{40}]^{4-}$, can add two electrons without protonation, i.e. the anion charge becoming -6. In a more neutral solution, the pH independent reduction can proceed up to the anion charge of -9. The reduced Well-Dawsons anions $\{X_2W_{18}O_{62}\}$ can bear up to -12 without protonation [2].

1.6.3 Acidic properties of heteropoly compounds

Heteropolytungstates and molybdates are strong acids. The acidity is generally determined by dissociation constants and the Hammet acidity function [59]. The free acids generally have several replaceable hydrogen ions. Protons are dissociated completely from the structure in aqueous solution. Since in heteropoly acids the negative charge of similar value is spread over much larger anions than those from mineral acid and the electrostatic interactions between proton and the anion is much less for heteropoly acids than for mineral acids. An additional important factor is possibly the dynamic delocalization ability of the charge or electron. The change in the electronic charge caused by de-protonation may be spread over the entire polyanion unit.

The strength and the number of acid centers as well as related properties of heteropoly acids can be controlled by the structure and composition of heteropoly anions, the extent of hydration, the type of support, the thermal treatment etc. Solid heteropoly acids such as $H_3PW_{12}O_{40}.xH_2O$ and $H_3PMo_{12}O_{40}.xH_2O$ are pure Brønsted acids and are stronger than conventional solid acids such as SiO_2-Al_2O_3 or H-X and H-Y zeolites [56, 60, 61]. Thermal desorption of basic molecules also reveals the

acidic properties. Pyridine adsorbed on SiO_2-Al_2O_3 is completely desorbed at 573 K. On the other hand, sorbed pyridine in $H_3PW_{12}O_{40}$ mostly remains at 573 K, indicating that $H_3PW_{12}O_{40}$ is a very strong acid. The acid strength can also be demonstrated by temperature programmed desorption (TPD) with NH_3. The general trend for acid strength among the common heteropoly acids is as follows [62].

$$H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} \geq H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$$

1.6.4 Thermal properties of heteropoly compounds

Thermal stability of the free acids of the heteropolymolybdates and heteropolytungstates is quite high and is of great importance for their use in heterogeneous catalysis [56, 63]. The stability is dependent on the nature of the central atom and addenda atom. Complexes containing phosphorous as the central atom are generally more stable than the compounds containing silicon as the central atom. Heteropoly compounds containing tungsten as the addenda atom are more stable than those with molybdenum atoms. The decomposition at high temperatures causes loss of acidity. The phosphomolybdic acid gets decomposed to the corresponding MoO_3 and P_2O_5 [63]. The Keggin structure is reconstructed when the complex is exposed to an atmosphere containing water vapour whereas in the case of less labile polyoxotungstates this kind of reconstruction is less likely.

Heteropoly acids are used as solid acid catalysts for vapour phase reactions at high temperatures. The substitution of transition metals in the anionic framework generally reduces the thermal stability in these complexes. The substitution of molybdenum in phosphomolybdic acid by addenda atoms such as vanadium reduces the thermal stability of the resulting phosphomolybdovanadates. The thermal stability reduces with the vanadium atoms in the polyanion framework. At higher temperature there is eviction of vanadium from the primary structural framework and the subsequent degradation into simple oxides i.e., MoO_3 and V_2O_5. The formation of such species is detected by X-ray diffraction analysis which clearly distinguishes between the heteropoly and the metal oxide phases. The structure of such complexes can be reconstructed on exposure to atmosphere of water vapour.

1.7 Catalytic Applications of Polyoxometalates

1.7.1 Polyoxometalates as catalysts in Industrial processes

Catalysis by heteropoly acids (HPA) and related compounds is a field of growing importance, attracting attention worldwide in which many novel and exciting developments are taking place, both in the areas of research and technology. Among numerous applications of heteropoly compounds, catalysis is by far the most important. Presently, over 80 % of the patent applications concerning with polyoxometalates is related to catalysis [64]. First attempts to use polyoxometalates as catalysts can be traced back to the beginning of the twentieth century.

Heteropoly compounds have several advantages as catalysts, the most important being their multifunctionality and structural mobility. On one hand they have a very strong Brønsted acidity; on the other hand, they are efficient oxidants, exhibiting fast reversible multi-electron redox transformations under mild conditions. Their acid-base and redox properties can be varied over a wide range by changing the chemical composition. Solid heteropoly compounds possess a discrete ionic structure, comprising fairly mobile structural units - heteropoly anion and counter cations - unlike the network structure of zeolites or metal oxides. The structure is frequently preserved upon substitution or oxidation/reduction and manifests itself to exhibit extremely high proton mobility. On the top of that many heteropoly compounds have a very high solubility in polar solvents and fairly high thermal stability in the solid state.

Because of their unique properties heteropoly compounds are promising acid, redox and bifunctional (acid and redox) catalysts. The catalytic reactions can be performed in homogeneous as well as heterogeneous (gas-solid, liquid-solid or biphasic liquid-liquid) systems. Heteropoly compounds are frequently used as model systems for fundamental research providing unique opportunities for mechanistic studies on the molecular level. At the same time, they become increasingly important for applied catalysis.

In the late 1970-80s several new industrial chemical processes utilizing polyoxometalate catalysts were developed and commercialized in Japan [65, 66]. The first commercial process was the liquid phase hydration of propene to 2-propanol launched in 1972. It was followed by the vapour-phase oxidation of methacrolein to methacrylic aid in 1982, the liquid-phase hydration of isobutene for its separation from the butane-butene fraction in 1984, the biphasic polymerization of

tetrahydrofuran to polymeric diol in 1985, the hydration of n-butenes to 2-butanol in 1989 and other processes. More recently, in 1997, the direct oxidation of ethylene to acetic acid was industrialized by Showa Denko and, in 2001; the production of ethyl acetate using a heteropoly acid catalyst was launched by BP AMOCO.

1.7.2 Catalytic Applications of the Keggin type Polyoxometalates in Oxidation reactions

As soon as one (or more) molybdenum atom(s) of phosphomolybdic acid are replaced by vanadium atom(s), a redox center gets generated in the Keggin unit, thereby making it an excellent redox catalyst. Over the years several reports have been published displaying the excellent catalytic activity of molybdovanadophosphoric acids with both aqueous hydrogen peroxide as well as molecular oxygen as the oxidants [67-76]. Thus it can be seen that these vanadium incorporated Keggin units are active for the oxidation of several types of substrates viz. alkene epoxidation, aromatic hydroxylation, cyclohexane oxidation to KA oil, adamantane hydroxylation, ketonization of active methylene groups, oxidation of cyclic ketones etc.

Not only in academia, but also vanadium substituted phosphomolybdic acid is the first and perhaps the only heteropoly anion based redox catalyst till date that has been used for any of the oxidation processes by chemical industries. It is used as a catalyst in the making of methacrylic acid from methacrolein with molecular oxygen as the oxidant. At a methacrolein conversion of 70-90 %, the selectivity of methacrylic acid is between 80-85 %, in the temperature range of 270-350 °C [77].

Similar to vanadium substituted phosphomolybdic acid, even the transition metal substituted polyoxotungstates (TMSP) are reported to be efficient catalysts with a variety of oxidants *viz.* molecular oxygen, hydrogen peroxide, ozone, TBHP, PhIO, NaIO4, NaOCl etc. In these TMSP compounds, one or more of the tungsten atoms of the Keggin unit are replaced by transition metal ions from the first series like Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} etc, thus generating a redox center thereby, which catalyzes the oxidation reactions similar to the salen or porphyrin complexes of these transition metals [78-83].

1.7.3 Catalytic Applications of the Sandwich type Polyoxometalates in Oxidation reactions

The structure and the synthesis of the zinc polyoxoanion along with its di- and tri-substituted derivatives were reported in 1991 by Tourne *et al* [46]. Within three years since then, Ronny Neumann and coworkers reported the catalytic applications of all these polyoxoanions for the epoxidation of alkenes and ketonization of alcohols [84, 85], especially with $[WZnMn_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ as the catalyst. Very high turnover numbers with excellent selectivities for the desired product were reported in the presence of a phase transfer catalyst in a liquid-liquid biphasic solvent system, with aqueous hydrogen peroxide as the oxidant. Additionally, it was also claimed that these sandwich type polyoxometalates are not only oxidatively and thermally but also solvolytically more stable than the simple Keggin type polyoxoanions.

The detailed procedure followed the dissolution of the corresponding polyoxoanion in water in the first step. Subsequently, a phase transfer catalyst like Aliquat 336 (i.e. methyltrioctylammonium chloride) was dissolved in 1,2 dichloroethane. The two solutions were mixed in a separating funnel, where upon the polyoxoanion was transferred to dichloroethane layer under the virtue of Aliquat 336. The dichloroethane layer was collected and dried and to it was added known amount of alkene/alcohol and calculated amount of the oxidant. The reaction was carried out in the temperature range of 2-70 °C for a desired time interval or till the completion of the reaction. A variety of other reports by the same group in the years to follow showed the versatility of the system and the increasing scope of polyoxometalates as catalysts in oxidation reactions with hydrogen peroxide and molecular oxygen, as well as other oxidants [47, 48, 86-98].

Amongst other Sandwich type polyoxometalates, Hill's group has reported $[Co_4P_2W_{18}O_{68}]^{10-}$ as well as $[Fe_3P_2W_{18}O_{68}]^{9-}$ as redox catalysts with molecular oxygen as the oxidant for the epoxidation of alkenes and autoxidation of aldehydes respectively [99, 100].

1.7.4 Catalytic applications of the Anderson type Polyoxometalates in Oxidation reactions

There is only one report in the literature till date, where an Anderson type polyoxometalate $[IMo_6O_{24}]^{5-}$ has been used a catalyst for the oxidation of vicinal diols with molecular oxygen as the oxidant [101]. Thus, the major application of this type of polyoxometalates seems to be; as catalyst precursors for making different varieties of mixed metal oxides, as shall be seen in Chapter 5 of this thesis.

1.8 Heterogenization of Polyoxometalates

The diversity of research fields connected to the chemistry of polyoxometalates is significant and includes their application in many areas, including structural chemistry, analytical chemistry, surface chemistry, medicine, electrochemistry and photochemistry [102]. However, one of the most extensively studied applications of polyoxometalates has been in the area of catalysis, where their use as both Brønsted acid catalysts and oxidation catalysts has been going on since the late 1970's. A basic premise behind the use of polyoxometalates in oxidation chemistry is the fact that polyoxometalates are oxidatively stable. This leads to the conclusion that for practical purposes polyoxometalates would have distinct advantages over widely investigated organometallic compounds that are vulnerable to decomposition due to oxidation of the ligand bound to the metal center.

Along with the development of concepts, synthetic techniques and mechanistic understanding of the use of polyoxometalates as efficient oxidation catalysts, future practical application of polyoxometalate oxidation catalysis will also require methods for catalyst 'engineering' to aid in catalyst recovery and recycle. The basic approach is to immobilize a catalyst with proven catalytic properties onto a solid support leading to a catalytic system that may be filtered and reused. Such approaches include concepts such as simple use of catalysts as insoluble bulk material, impregnation of a catalyst onto a solid and usually inert matrix and attachment through covalent or ionic bonds of a catalyst to a support. These approaches or strategies are described in details in further paragraphs.

The strategy followed by Yamaguchi and Mizuno was usage of a solvent that won't dissolve the polyoxometalate under reaction conditions. Thus they used $[(n\text{-}C_4H_9)_4N]_4H[SiW_{11}Ru^{III}(H_2O)O_{39}].2H_2O$ as the catalyst and used isobutyl acetate, trifluorotoluene, 1,2dichloroethane and tert-butyl acetate as solvents for the oxidation

of a variety of organic substrates with molecular oxygen, *viz.* adamantane, cyclohexane and cyclooctane to name a few [103]. Earlier in 2001, Zuwei *et al* reported an interesting method of taking advantage of both homogeneous and heterogeneous nature of catalysts. Thus, the catalyst $[C_5H_5NC_{16}H_{33}]_3[PO_4(WO_3)_4]$ was used for the epoxidation of propylene with *aq.* H_2O_2 as the oxidant and 2-ethylanthraquinone as the co-reductant, with aqueous/oil biphasic solvent system. The catalyst was observed to be heterogeneous in oil phase before the addition of H_2O_2 and was homogeneous in the same after the addition of H_2O_2 due to its transformation into a new species, *viz.* $[C_5H_5NC_{16}H_{33}]_3[PO_4[W(O)_2(O_2)]_4]$. Once all the H_2O_2 was consumed, the new species reverted back to the original one and again became heterogeneous in the oil layer. It could be noted that the reactant, product and co-reactant were always present in the oil layer, so the catalyst could be easily separated after the reaction and reused again [104]. In another example, Okun *et al* reported $[(Fe^{III}(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ supported on cationic silica nanoparticles as a new material for selective aerobic oxidation reactions. This material was used for oxygenation of sulfides and autoxidation of aldehydes. The principle behind the binding of the polyoxoanions to the cationic silica nanoparticles was electrostatic force between the positively charged cationic silica nanoparticles on one side and negatively charged polyoxoanions on the other side [99].

In the preceding years, Ronny Neumann reported the modification of support of MCM-41 by amine functionalization and anchoring of $H_5PV_2Mo_{10}O_{40}$ and using this catalytic system for the aerobic oxidation of hydrocarbons, with isobutyraldehyde as sacrificial oxidant. Maintaining appropriate conditions, it was observed that there was not any leaching of catalyst and the catalyst could be easily separated and reused without much loss of activity [105]. In another report, the same author replaced the protonic/ sodium or potassium counter cations with tripodal polyammonium cations that made it insoluble in solvents, otherwise which dissolve these $[WZn_3(ZnW_9O_{34})_2]^{12-}$ based polyoxometalates. The polyoxometalates thus formed were reported for hydrogen peroxide mediated oxidation reactions of allylic alcohols [106]. In the following report, Neumann reported the use of silica tethered poly-ethylene-poly-propylene oxide as support for the polyoxoanions, in order to use the catalytic system in a heterogeneous fashion. Thus silicates containing combinations of hydrophilic poly ethylene oxide PEO, hydrophobic poly propylene oxide PPO and

cationic quaternary ammonium 'Q' groups were prepared. These silicates coupled with $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ based polyoxometalates led to active catalytic assemblies. Thus, heterogeneous catalysts with hydrogen peroxide as the oxidant, for the oxidative dehydrogenation of dihydroanthracene with improved activity and selectivity, as compared to the unsupported polyoxoanions, were obtained [107, 108].

1.9 Scope and Organization of the Thesis

1.9.1 Scope and Objective of the present work

As mentioned above, polyoxometalates constitutes an important class of materials and their catalytic applications, both as acid catalysts on one side and as redox catalysts on the other side are truly very versatile. Of these two major classes of reactions we will be chiefly concentrating on redox reactions. This is because; selective oxidation reactions are one of the most encountered ones in academia and industry. All the oxidation products of all such reactions find lot of applications in various areas. Millions of tons of these products are produced annually and find applications in all areas of chemical industries ranging from pharmaceutical to large scale commodities.

Currently most of the oxidation processes involve the common use of stoichiometric oxidants resulting in tedious work up procedures at the end of reaction processes. Alternatively, they also lead to the formation of large amount of chromium, manganese and other toxic salts as by-products. Thus developing a process that will use environment friendly oxidants like molecular oxygen or hydrogen peroxide is highly desirable. However, it is known that both these eco friendly oxidants generally do not show any direct activity towards the organic substrates. Thus the important challenge involved here is make use of catalysts that will make these oxidants react with the organic substrates at ambient conditions.

Currently there are various transition metal ions based catalyst systems that are known to activate molecular oxygen or hydrogen peroxide. However, most of them are of metal-organic ligand origin like metal-salen complexes or metal-porphyrin complexes. The problem with these systems is that the organic part of the catalyst is vulnerable to oxidation itself, thus the further activity is lost. In order to overcome this problem, various strategies have been adopted *viz.* polyfluorination of the porphyrin ligand etc. An alternative to the process is use of robust molecules like polyoxometalates, substituted by transition metals or otherwise. The advantages of

polyoxometalates are that they are easy to synthesize as compared to zeolites or molecular sieves and they are compatible with dioxygen and hydrogen peroxide.

Although the polyoxometalates are gaining popularity as catalysts for oxidation reactions, in most of the cases they are used as catalysts in a homogeneous fashion. Since the separation of catalyst from the product mixture involves costly and time staking procedures, it is always preferred to make the use of any catalyst in heterogeneous manner. Similarly, not much work has been done on mechanism elucidation and investigation of the active intermediates responsible for the oxidation process. Albeit there are some reports on the mechanistic aspects, there is some ambiguity in the literature when it comes to the exact nature of the active intermediates and overall reaction mechanism. Thus a detailed study in which all the shortcomings seen above could be overcome is certainly desired.

1.9.2 Organization of the Thesis

The thesis is divided into six chapters which includes a general introduction (Chapter 1).

Chapter 2

Chapter 2 describes the synthesis and characterization of manganese and zinc containing sandwich type polyoxotungstates with antimony, bismuth and tellurium as the heteroatoms and the applications of the same towards the epoxidation of a variety of olefins is described further. The in-depth studies were carried out to investigate the exact role of manganese ions and tungsten octahedrons with hydrogen peroxide as the oxidant. Attempts have also been made to study the active intermediate and possible mechanism of the reactions by UV-visible and FT-IR and also towards the recycling of the catalyst. Further, the catalyst system is extrapolated for the ketonization a variety of secondary alcohols as well as allylic alcohols.

Chapter 3

Chapter 3 describes the synthesis and characterization of neat as well as anchored vanadium substituted phosphomolybdic acids. The anchoring of heteropoly acids was carried on amine functionalization of SBA-15. The details of synthesizing SBA-15 and its amine functionalization, followed by characterization of the same by ICP, UV-visible, N_2 sorption, SEM, XRD, FT-IR and ^{31}P-NMR is mentioned. After

anchoring, sufficient discussion is provided to show the presence of the heteropoly acids inside the pores of SBA-15. A detailed comparison has been done between the activities shown by neat as well as the anchored vanadium substituted phosphomolybdic acids with both, hydrogen peroxide and TBHP as the oxidants. For the anchored heteropoly acids, leaching test and recycling studies are also described as a part of the study.

Chapter 4

Chapter 4 describes the activity of simple and vanadium substituted phosphomolybdic acids supported on titania or zirconia towards the epoxidation of a variety of olefins. Details for the preparation of titania and zirconia and the wet impregnation of heteropoly acids on the same are briefly discussed. The supported heteropoly acids are characterized by powder XRD, solid state UV-visible and FTIR studies. Further, the use of organic solvent extracted TBHP as the oxidant and hydrophobic volatile liquids as the solvents in the epoxidation studies is justified. Synergistic effect observed between titania and vanadium substituted phosphomolybdic acids is also discussed.

Chapter 5

Chapter 5 describes the selective oxidation of ethane to ethylene and acetic acid over molybdenum-vanadium mixed metal oxides as catalyst. Initially the background and the scope of this work are discussed. This is followed by introduction to fixed bed vapor phase reactors. The experimental details, including hydrothermal synthesis of mixed metal oxides at various pH's, pretreatment of catalysts, precautions followed, step by step reaction procedure and characterization of the catalysts and the reaction system by ICP, EDAX, XRD, UV-visible, Raman, EPR and SEM is thoroughly discussed. The best catalyst for the selective oxidation of ethane to ethylene and acetic acid is also subjected to some further studies. These studies are to observe the effect of change in temperature, pressure and flow rate of reactants on the same reaction. The possible reaction mechanism is also described further.

Chapter 6

Chapter 6 summarizes the overall conclusion from the work presented in this thesis.

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