General Introduction

With the advent of new millennium, the importance of green chemistry has found widespread recognition. In order to achieve the goal of sustainability, "Green Chemistry" is clearly evolving as an essential part of the foundation from which efficient and sensible solutions to the challenges at hand are derived. "Green Chemistry" is characterized by a move away from the "command and control" approach to environmental protection to a more scientifically based and economical approach [1].

Green Chemistry deals with the reduction of environmental impact of chemicals and chemical processes. It involves design, manufacture and development of environmentally benign, safer and economically viable processes [2]. Following are the principals of green chemistry (Figure 1) which necessitates a paradigm shift from traditional concepts of process efficiency which focuses exclusively on chemical yield, to one that assigns economic value to eliminating waste and avoiding the use of toxic and/or hazardous substances.

Figure 1. Principals of Green chemistry.

In the recent times to satisfy the increasing demands for the green and sustainable production of fine chemicals and chemical intermediates, catalytic processes with high atom efficiency, simple operations, and simple work-up procedures are desirable [1-2]. Synthesizing heterogeneous catalysts will be an attractive synthetic tool, particularly because it often satisfies some of the principles of green chemistry:

1) It allows selectively to conduct different transformations by tuning some simple reaction parameters
2) The reaction conditions are easily accessible
3) High thermal stability
4) Increased surface area
5) High catalytic activity and selectivity
6) The catalyst system can be conveniently recovered and recycled
7) The product can be easily separated.

Hence on combining principles of Green chemistry and Heterogeneous catalysis, ***"Sustainability"*** can be achieved.

In this context, the use of ***Polyoxometalates*** as catalysts have become a very important field of research, industrially as well as academically [3-8]. They are widely 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. They provide good basis for the molecular design of mixed oxide catalyst and have high capability in practical uses.

A Brief overview of Polyoxometalates

Polyoxometalates (POMs) are discrete anionic metal oxygen clusters which can be regarded as soluble oxide fragments [3]. They are a distinctive class with unique properties of topology, size, electronic versatility as well as structural diversity. Due to the combination of their added value properties such as redox properties, large sizes, high negative charge, nucleophilicity they play a great

role in various fields such as medicine, material science, photochromism, electrochemistry, magnetism as well as catalysis.

History of POMs

POMs have been known since the work of Berzelius [9] on the ammonium 12-molybdophosphate in 1826. After the discovery of this first POM, the field of POM chemistry progressed significantly [10].

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 [11].
2. However, the study of polyoxoanion chemistry did not accelerate until the discovery of the tungstosilicic acids and their salts in 1862 by Marignac [12]. He prepared and analyzed two isomers of 12-tungstosilicic acid viz. tungstosilicic acid and silicotungstic acid now known as α and β isomers.
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. In 1908, A. Miolati suggested a structural hypothesis for heteropoly compounds based on coordination theory. According to his hypothesis, the heteroatom was considered to have octahedral coordination with MO_4^{2-} or $M_2O_7^{2-}$ ligands.
5. In the mid 1930's, A. Rosenheim had given a laboratory perspective for the synthetic and descriptive research of Miolati.
6. The first steps towards understanding the structure of polyoxometalate anions was taken by L. C. Pauling in 1929. Pauling [13] proposed a structure for 12:1 complexes based on an arrangement of twelve MO_6 octahedra surrounding a central XO_4 tetrahedron. He proposed the structure of 12-tungstoanions based on the central PO_4 or SiO_4 tetrahedrons surrounded by WO_6 octahedrons. In order to minimize electrostatic repulsions, he proposed that all the polyhedral linkages involved sharing of vertices rather

than edges. As a result the resulting formula required 58 oxygen atoms i.e. $[(PO_4)W_{12}O_{18}(OH)_{36}]^{3-}$.

7. After Pauling's proposal, in 1933 Keggin [14, 15] solved the structure of $[H_3PW_{12}O_{40}].5H_2O$ by powder X-ray diffraction and showed that the anion was indeed based on WO_6 octahedral units. As suggested by Pauling, these octahedra being linked by shared edges as well as corners. The application of X-ray crystallography to the determination of polyoxometalate structures accelerated the development of polyoxometalate chemistry.
8. An year later in 1934, Signer and Gross demonstrated 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 [16].
9. Bradley and Illingworth confirmed Keggin's work in 1936, by studying the crystal structure of $H_3PW_{12}O_{40}.29H_2O$.
10. These results of (Bradley's and Illingworth's) were largely supported by the single crystal experiments of Brown and co-workers, which were reported in 1977.

With the development of POMs chemistry various types of structures were discovered. General information about different types of POMs are listed in Table 1.

Table 1. Different types of POM families [3].

Structure	**[a] General Formula**	**Charge**	**X^{n+}**
Keggin	$XM_{12}O_{40}$	8-n	P^{5+}, As^{5+}, Si^{4+}, Ge^{4+}
Silverton	$XM_{12}O_{42}$	8^-	Ce^{4+}, Th^{4+}
Dawson	$X_2M_{18}O_{62}$	6^-	P^{5+}, As^{5+}
Waugh	XM_9O_{32}	6^-	Mn^{4+}, Ni^{4+}
Anderson (Type A)	XM_6O_{24}	12-n	Te^{6+}, I^{7+}

[a]where M = Mo^{VI}, W^{VI}, $V^{IV, V}$ etc.

Among different POMs, Keggin type POMs are investigated extensively because of their easy synthesis as well as high stability [8].

The general formula for Keggin type POM is $[XM_{12}O_{40}]^{n-}$, 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} and formed by different mononuclear oxoanions as shown in the following equation.

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

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

Structure of Keggin type POMs

The ideal Keggin structure, $[XM_{12}O_{40}]^{3-}$ of α-type has T*d* symmetry and consists of a central XO_4 tetrahedron (X = heteroatom or central atom) surrounded by twelve MO_6 octahedra (M = addenda atom). The twelve MO_6 octahedra comprise four groups of three edge-shared octahedra, the M_3O_{13} triplet [14-15], 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 comer sharing; M-O_c-M, connecting two M_3O_{13} units by edge sharing; and O_d-M, where M is the addenda atom and X the heteroatom. The schematic representation of Keggin type is shown in Figure 2. **Our main focus would be to study the Keggin type POMs.**

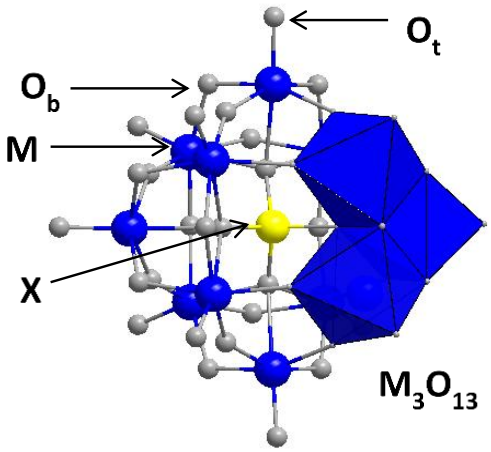


Figure 2. Keggin type $[XM_{12}O_{40}]$.

Properties of POMs

POMs have usually low surface area (1-10 m^2/g) reflecting their high solubility in water. The pores of POMs are inter-particle, not intra-crystalline. Considering the size and shape of the Keggin anion and the crystal structure, there is no open pore through which nitrogen molecule can penetrate. Figure 3 shows schematic of some of the significant properties of POMs.

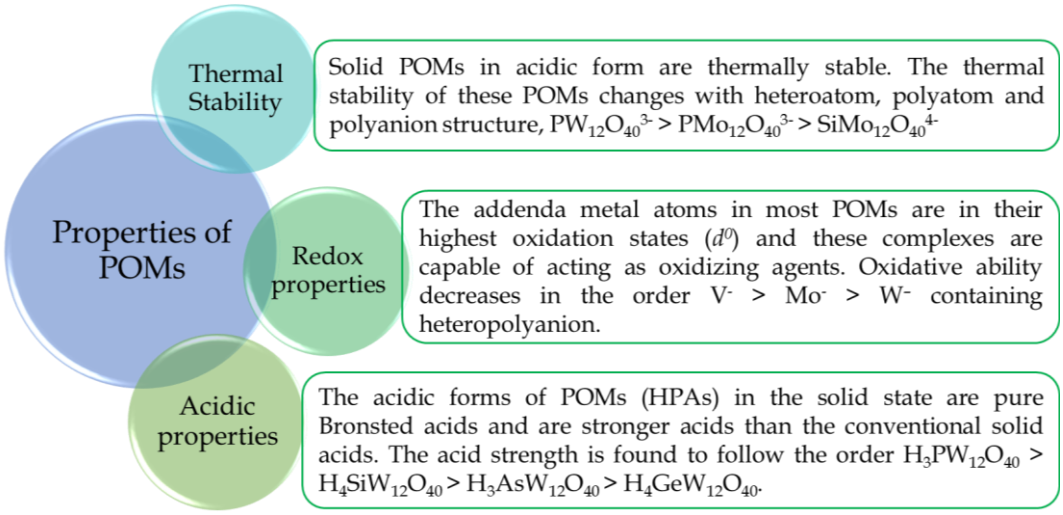


Figure 3. Various properties of POMs.

An extensive literature on their synthesis, structure and properties has been accumulated and summarized in various books namely:

Authors	Year & Publishing	Title of Book
M. T. Pope, (Eds.) C. K. Jorgensen	(1983) Springer-Verlag, Berlin	Heteropoly and Isopoly Oxometalates
J. B. Moffat, M. V. Twing, M. S. Spencer	(2001) Kluwer Academic plenum, New York, (2001)	Metal-oxygen Clusters: The surface and Catalytic properties of Heteropolyoxometalates
I. V. Kozhevnikov	Vol. 2 (2002) Wiley	Catalysts for fine chemical synthesis: Catalysis by polyoxometalates
M. T. Pope, A. Muller	(2003) Kluwer Academic publishers	Polyoxometalate Molecular Science
M. T. Pope, (Eds) S. Ted Oyama,	(2008), Elesvier Publications	Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis

M. G. Clerici, O. A. Kholdeeva	(2013), JohnWiley & Sons, Inc., Hoboken, New Jersey	Liquid Phase Oxidation Via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications
F. Secheresse	(2013) World Scientific Publishing Company	Polyoxometalate Chemistry: Some Recent Trends
(Ed) A. Patel	(2013) Springer, Dordrecht	Environmentally benign catalysts for clean organic reactions
A. Patel, S. Pathan,	(2015) Springer Briefs in Molecular Science-Green Chemistry for Sustainability, Springer, Dordrecht	Polyoxomolybdates as Green Catalysts for Aerobic Oxidation
S. Herrmann	(2015) Springer Spektrum	New Synthetic Routes to Polyoxometalate Containing Ionic Liquids An Investigation of their Properties

Applications of POMs

Since the discovery of POMs, they found significant importance in various fields of science and technology. The field of POM chemistry is about more than two centuries old but still they are a large and rapidly growing class of compounds, especially because of their large domains of applications (such as in modification of carbon electrodes, capacitors, colorant for pigmenting paints, dye for polyester, dopants, clinical analysis, food chemistry, solar cell and catalysis) [16-26].

In last two decades POMs have attracted significant interest in variety of fields. *Apart from these applications, POMs have played an important role in the field of acid as well as oxidation catalysis due to their high Bronsted acidity as well as their tendency to exhibit fast reversible multi-electron redox transformations under rather mild conditions and their inherent stability towards strong oxidants.*

The advantage of POMs as catalysts [27]

Practical advantages of POMs as catalysts are mentioned in Figure 4.

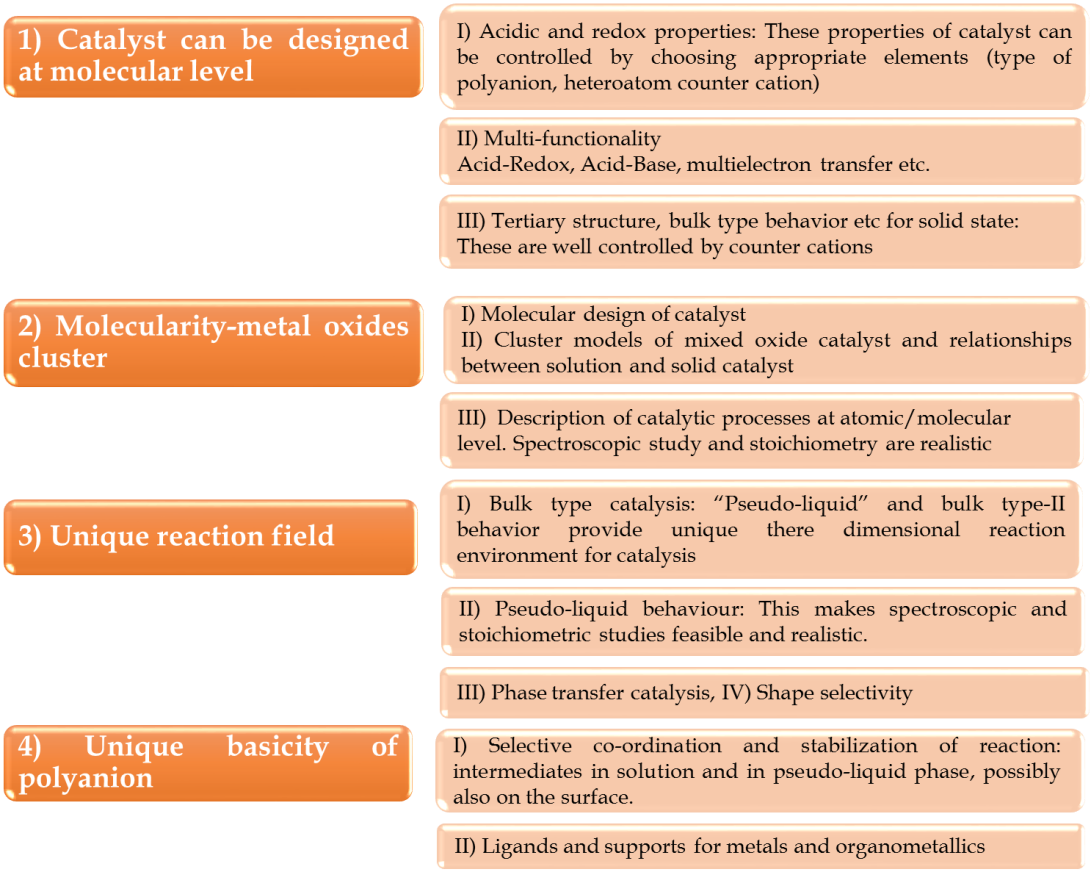


Figure 4. Advantages of Keggin type POMs as catalysts.

Systematic investigation of catalysis by POMs began in the early 1970's. Some of the major achievements of POM based compounds in the field of catalysis have been reviewed by number of groups.

Reviews		
A. Corma	Chem. Rev., 95 (3), (1995) 559	Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions
T. Okuhara, N. Mizuno, M. Misono	Adv. Catal., 41 (1996) 113	Catalytic Chemistry of Heteropoly Compounds
C. L. Hill	Chem. Rev., 98, (1998) 1	Issue on Polyoxometalates
I. V. Kozhevnikov	Chem. Rev., 98, (1998) 171	Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions

N. Mizuno and M. Misono,	Chem. Rev., 199, (1998)	Heterogeneous Catalysis
T. Mallat, A. Baiker	Chem Rev. 104 (2004) 3037	Oxidation of Alcohols with Molecular Oxygen on Solid catalysts
Y. G. Chen, , J. Gong, L. Y. Qu	Coord. Chem. Rev., 248, (2004) 245	Tungsten-183 nuclear magnetic resonance spectroscopy in the study of Polyoxometalates
N. Mizuno, K. Yamaguchia, K. Kamata	Coord. Chem. Rev., 249, (2005) 1944	Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates
D. L. Long, E. Burkholder, L. Cronin	Chem. Soc. Rev., 36, (2007) 105	Polyoxometalate clusters, Nanostructures and Materials: From self assembly to designer materials and devices
R. Yu, X. E. Kuang, W. Y. Wu, C. Z. Lu, J. P. Donahue	Coord. Chem Rev. 253 (2009) 2872	Stabilization and Immobilization of Polyoxometalates in Porous coordination polymers through host-guest interactions
A. Dolbecq, E. Dumas , C. R. Mayer, P. Mialane,	Chem. Rev., 110 (10) (2010) 6009	Hybrid Organic-Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications
P. Putaj, F. Lefebvre,	Coord. Chem. Rev., 255 (2011) 1642	Polyoxometalates containing late transition and noble metal atoms,
L. Cronin, A. Muller	Chem. Soc. Rev., 41 (2012) 7325	Theme issue: Polyoxometalate cluster science
J. M. Sumliner, H. Lv, J. Fielden, Y. V. Geletii1 and C. L. Hill	Eur. J. Inorg. Chem., 4 (2014) 635	Polyoxometalate Multi-Electron-Transfer Catalytic Systems for Water Splitting
H. N. Miras, L. Vila-Nadal, L. Cronin,	Chem. Soc. Rev., 43 (2014) 5679	Polyoxometalate based Open-Frameworks (POM-OFs)
S. Omwomaa, C. T. Gorea, Y. Ji, C. Hub, Y. -F. Song	Coord. Chem. Rev. 286 (2015) 17	Environmentally Benign Polyoxometalate Materials
S. -Sa Wang and Guo-Yu Yang	Chem. Rev., 115 (2015) 4893	Recent Advances in Polyoxometalate-Catalyzed Reactions

Apart from these, a number of patents describing use of POMs based compounds in catalysis are also available:

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).

The acidic as well as redox properties of POMs can be tuned at molecular level which can lead to development of a new class of materials with unique 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 [28-30]. As a result, they are expected to play an important role in catalysis. Thus, the modification of parent POMs are likely to help in development of new generation catalysts with enhanced properties of acidity, redox potential and stability.

The modification of properties can be basically done by tuning the structural properties at the atomic or molecular level in two ways (i) By creating defect (lacuna) in parent POM structures (i.e. Lacunary Polyoxometalates, LPOMs) and (ii) Incorporation of transition metal ions into the defect structures (i.e. Transition Metal Substituted Polyoxometalates, TMS POMs).

What are Lacunary Polyoxometalates?

Lacunary polyoxometalates (LPOMs) are a sub class of POMs with a set of unique properties such as multidenticity, rigidity, thermal and oxidative stability [3, 5-6]. 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 [7].

Removal of one or two -MO units from the fully occupied POMs, $[XM^{VI}_{12}O_{40}]^{n-}$, gives rise to mono- or di- lacunary POMs, $[XM^{VI}_{11}O_{39}]^{(n+4)-}$ and $[XM^{VI}_{10}O_{36}]^{(n+5)-}$. When the solution of $[XM_{12}O_{40}]^{n-}$ are treated with base (pH 4~5), a series of hydrolysis reactions occurs leading to the formation of mono and di lacunary polyoxometalates (Figure 5).

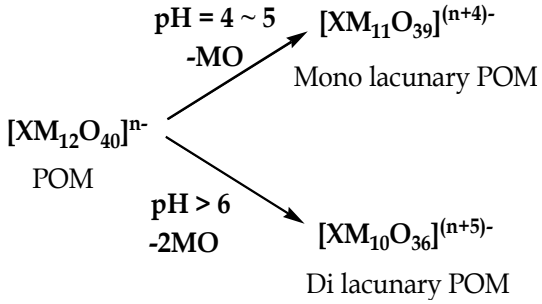


Figure 5. Formation of lacunary polyoxometalate.

These lacunary POMs have exclusive advantages such as:

- ***Best amongst POMs in terms of stability.***
- ***Efficient oxidants***
- ***Environmentally benign***
- ***Act as bulky poly-dentate ligand***

- ***Depending upon co-ordination requirement the geometry of reaction product can be predicted***
- ***Can be functionalized***
- ***Activation of surface oxygen atoms***
- ***Efficient Bi-Functional catalysts***

Classification and Properties of LPOMs

The formation of mono, di or tri lacunary species is mainly pH dependent, each possessing its own reactivity and stability trend. Hence, synthetically, special attention is paid to fine changes in reaction conditions such as: pH, temperature, buffer capacity, ionic strength, and cation size. All having the potential to exert a considerable effect on the polyanion equilibria and formation of products [31-32].

In the case of phosphotungstate system, the reaction patterns are similar to those of the silicotungstates, but a series of remarkable differences exists, which can be visualized from the Figure 6.

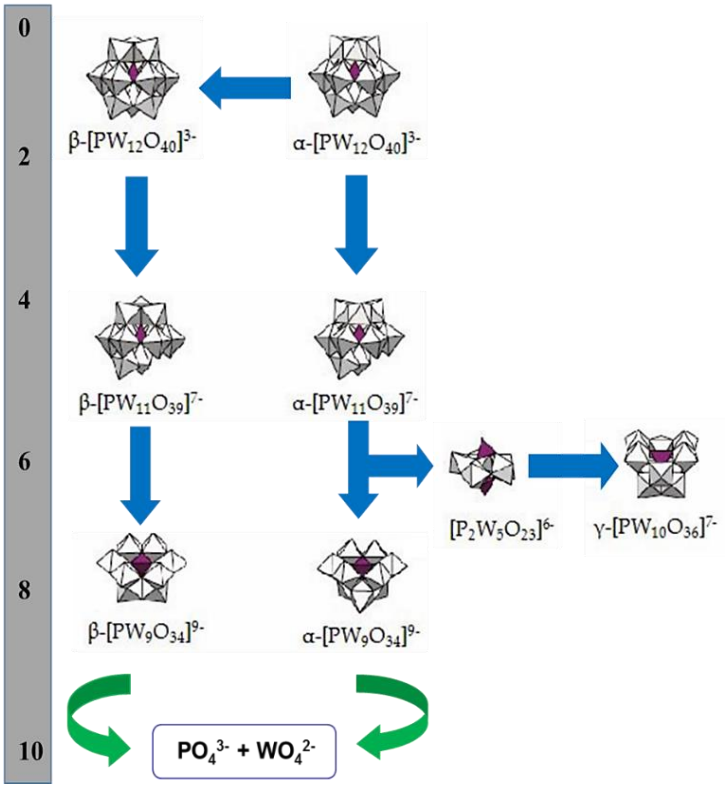


Figure 6. pH dependent formation of lacunary phosphotungstates.

Among the mono, di and tri lacunary POMs, mono lacunary POMs form the most versatile class of LPOMs (Figure 7). The removal of one WO at suitable pH from parent $[PW_{12}O_{40}]^{3-}$ leads to the formation of mono lacunary $[PW_{11}O_{39}]^{7-}$.

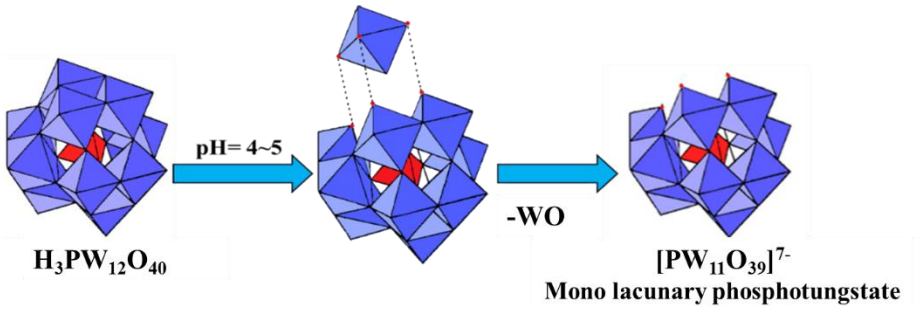


Figure 7. Formation of mono lacunary POMs.

After the invention of the first ever lacunary polyoxometalate species by Pope in 1966 [33], there was no significant contribution in the field of LPOMs. After about one and half decade, in 1981, Knoth and Harlow reported the structure of dilacunary phosphotungstate derivative, $[PW_{10}O_{36}]^{7-}$. They investigated the effect of pH and counter cation on the stability of this dilacunary species [34] and till date, this is the only report. In 1983, Brevard et al. came up with the synthesis as well as characterization of the sodium salt of mono lacunary phosphotungstate [35].

The first crystal structure of mono lacunary phosphotungstates $[PW_{11}O_{39}]^{7-}$, was reported by Ozeki and co-workers [36]. According to a recent report by H. Gerard and co-workers, α isomer of mono lacunary phosphotungstate, dominates in stability over the β isomer. They have also shown that isolation of the $[PW_{11}O_{39}]^{7-}$, as a sodium salt leads to stabilization of α isomer relative to the β isomer by more than 0.2 kcal mol^{-1} [37].

A literature study shows that number of reports on homogeneous catalysis using mono lacunary phosphotungstates are available. The first report on the catalytic evaluation of monolacunary phosphotungstates was made in 1988, by M. Schwegler et al., for oxidation of cyclohexene [38]. Then in 1995, Hill and

coworkers studied the role of lacunary phosphotungstates for oxidation of various organic substrates such as alkenes, alkanes and sulfides [4]. The same group reported the use of mono lacunary silicotungstate as well as phosphotungstate for aerobic oxidation of H_2S to obtain elemental sulphur [39]. They have also evaluated the catalytic activity for alkene epoxidation over the quarternary ammonium salt of mono lacunary phosphotugstate [40]. The protonated $[PW_{11}O_{39}]^{7-}$ species was also used for alkene epoxidation by Kuznetsova et al. [41]. Z. Weng et al. reported the use of $[PW_{11}O_{39}]_{7-}$ for oxidation of benzyl alcohol using H_2O_2 as an oxidant [42]. Recently, studies on the mechanisms of radical reactions for generation of mono lacunary phosphotungstate species and it's reactivity with methyl radicals for production of propene and 2-methylpropene was demonstrated by Dan Meyerstein's group [43].

Later in 2011, epoxidation of olefins with H_2O_2 catalyzed by a reusable lacunary-type phosphotungstate catalyst has been reported [44]. In the same year, epoxidation of 1,3-butadiene with aqueous H_2O_2 has been studied with tetrabutylammonium or 1-ethyl-3-methylimidazolium salts of phosphotungstate anions by Kuznetsova and group [45]. Oxidation of pyridine and alcohol using the Keggin-type lacunary polytungstophosphate as a temperature-controlled phase transfer catalyst was carried out by Ding and Zhao [46]. Counterion effects on the ^{183}W NMR spectra of the lacunary Keggin polyoxotungstate $[PW_{11}O_{39}]^{7-}$ by DFT calculations was carried out by Bagno in 2012 [47].

Very recently, Li et al. [48] prepared a mono-lacunary phosphotungstic ammonium salt $(NH_4)_7PW_{11}O_{39}$ and its Zr^{2+}-substituted $(NH_4)_5ZrPW_{11}O_{39}$. The mono-lacunary compounds (PW_{11}) showed preferable activity in the ammoximation of cyclohexanone. Like parent POMs, the LPOMs are also expected to suffer from the traditional disadvantages such as high solubility, low surface area, recovery and recycling.

The mentioned problems can be overcome by development of heterogeneous catalysts. This can either be done by supporting them onto suitable supports or by converting them into insoluble salts. The supporting of LPOMs onto the suitable supports is better way to make heterogeneous catalysts.

Supports provide large surface area for dispersion. The catalyst molecule gets dispersed on the surface of the support and thus available for the combination with reactant as in homogenous catalyst. The resulting heterogeneous catalyst can function mechanically as if it was in solution but it would operate as a separate immobile phase. Thus the advantages of both homogenous catalysts and heterogeneous catalyst are retained.

Most important advantages of heterogeneous catalysts from the point of view of chemical reaction system are:

• Kinetically and thermodynamically difficult reactions can proceed with wide range of temperatures even in gas phase

• Catalysts can often be 'tailored' for specific feedstock or for selective product synthesis

The anchored POMs can be advantageous for:

1. Thermal stability is increased

2. Surface area is increased

3. They have high catalytic activity and selectivity

4. Separation from a reactions mixture is easy

5. Repeated use is possible

Different methods of supporting/anchoring [49]

One of the important steps in designing a catalyst is supporting of POMs species onto the support. Either the support can be in a preformed state or both can be formed together from the solution simultaneously.

Commonly used methods for supporting/anchoring are as follow.

1. Co-precipitation.
2. Deposition precipitation.

3. Dry impregnation/incipient wetness.
4. Equilibrium adsorption/ion exchange/wet impregnation.

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

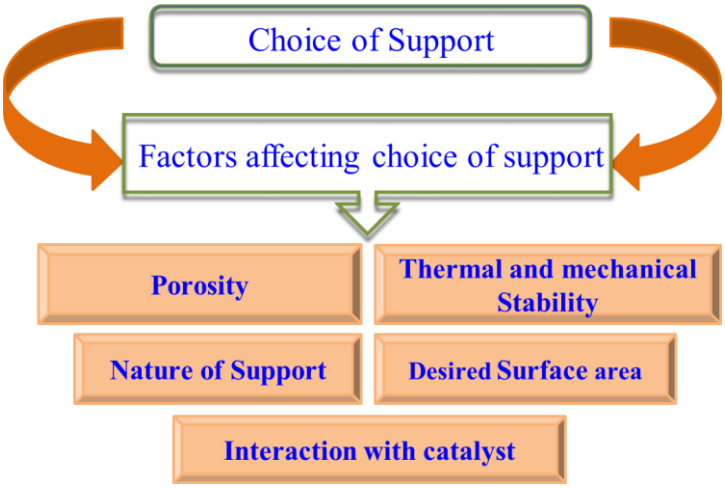
Impregnation

Impregnation is a preparation technique in which a solution of the precursor of the active phase is brought in contact with the support. Two methodologies exist. In dry impregnation, also referred to as "pore volume impregnation", just enough liquid (solution of the precursors) is used to fill the pore volume of the support. In wet impregnation, the support is dipped into an excess quantity of solution containing the precursor(s) of the active phase. In dry impregnation, the solubility of the catalyst precursors and the pore volume of the support determine the maximum loading available each time of impregnation. If a high loading is needed, successive impregnations (and heat treatments) may be necessary.

Choice of the 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.

Critical properties of a support include surface area and the ability to give rise to catalyst-support interactions. The most important factors affecting the choice of support are summarized in block diagram as shown in Scheme 1.



Scheme 1. Factors affecting choice of supports.

Dispersing POMs on supports with high surface areas 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. 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 it gets decomposed in the basic environment. As mentioned when acidic supports are used, strong interaction is expected between available non-bonding oxygens of POMs and available protons from –OH groups of the supports.

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 [50-56], silica modified zirconia [57], titania [51, 53, 57-58], alumina [53, 59-60], carbon [51, 61-67], acidic ion exchange resins [68-69], clays [70-73]. montmorillonite k10 [74-76], Mesoporous pillared clay/Kaolin [77-78], Metal organic frameworks (MIL) [79-83] and Polymer [84].

Physical and chemical properties of supports also affect the catalytic activity. The most important parameters are specific surface area and porosity from the

view point of activity and selectivity. In general, the mesoporous materials have following advantages:

Why Mesoporous materials?

- Ordered porosity at mesoscale with tunable pore volumes (>0.6 cm^3 g^{-1}) and pore size (20 to 100 Å).
- High specific surface area (>1000 m^2/g) and High adsorption capacity.
- High concentration of surface Si-OH groups.
- High mass transfer efficiency.
- Shape- selectivity (in reactions involving large organic molecules).
- Higher Hydrothermal stability.

Keeping in mind these aspects, in the present thesis, mesoporous silica materials (MCM-41 and MCM-48) of M41S family were selected as supports (Figure 8) because,

- ***MCM-48 has an interpenetrating network of three dimensional pores whereas MCM-41 has a hexagonal array of one dimensional pore system.***
- ***They possess favorable mass transfer kinetics, which allows proper diffusion of reactants and products.***
- ***The reliable and facile synthesis of high quality mesoporous materials, particularly the cubic phase has been a challenge.***

The reliable and facile synthesis of high quality mesoporous materials, particularly the cubic phase has been a challenge. It is also known that thermal stability as well as surface acidity of these materials (MCM-41/ MCM-48) can be enhanced by introducing strong acid sites. MCM-41/MCM-48 can prove to be excellent supports for preparing bifunctional catalysts and for expanding the catalytic capability of traditional acidic materials for specific applications.

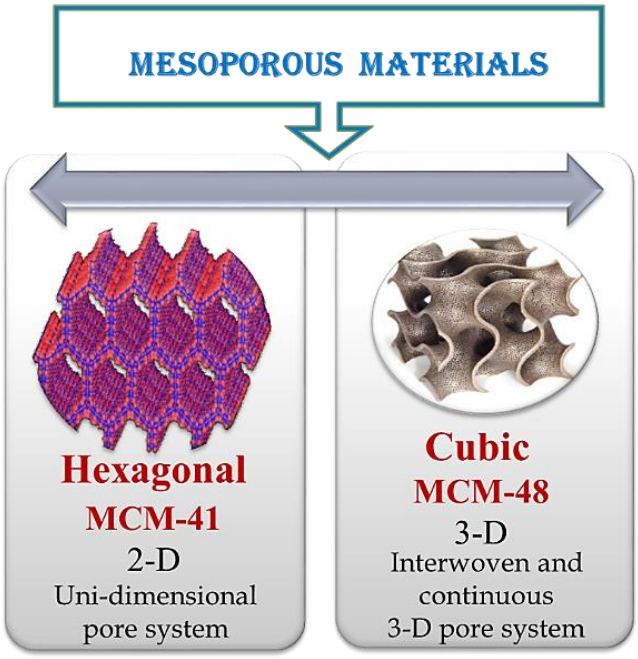


Figure 8. Pore network and geometry of MCM-41 and MCM-48.

Synthesis of these materials are also dependent on the synthesis conditions and non-hydrothermal synthesis over hydrothermal synthesis possess significant advantage

- ***The traditional hydrothermal procedures have some disadvantages, such as the obligatory crystallization time and high ageing temperature.***
- ***Developing a non-hydrothermal synthesis procedure for these material will be interesting due to the mild conditions and easily fascinating approach.***

The world of catalysis by POMs has largely expanded and we would also like to excuse us if some of the references are missing as it is quite difficult to summarize such a huge number of available references for the same. Hence, in the present thesis, we would like to restrict ourselves, especially for Phosphotungstate anchored to MCM-41 (lot of work has been carried out) or MCM-48 and new developing field of anchored lacunary phosphotungstate, for acid, oxidation and bifunctional catalysis. In addition, in contrast to the reported hydrothermal synthesis method, in the present thesis an attempt was made to synthesise the mesoporous materials by non-hydrothermal method.

Literature study for phosphotungstate anchored to mesoporous silica

I. V Kozhevnikov et al. in the year 1994 for the first time, reported a new acid catalyst comprising $H_3PW_{12}O_{40}$ on a mesoporous molecular sieve MCM-41, characterized by different techniques and catalytic activity was carried out for liquid-phase alkylation of 4-t-butylphenol (TBP) by isobutene and styrene [85-86].

A. Corma and group [87] demonstrated a comparative study by supporting $H_3PW_{12}O_{40}$ on three different carriers: a commercial silica, a high surface area amorphous aluminosilicate (MSA), and an all-silica mesoporous MCM-41 and their catalytic properties have been determined for the alkylation of 2-butene with isobutane at 33°C and 2.5 MPa. Pore blockage could be decreased, and the catalytic activity of catalyst increased, by using a MCM-41 sample with larger pore diameter.

Y. Sugi et al. reported various catalysts comprising $H_3PW_{12}O_{40}$, anchored to mesoporous silica such as MCM-41, FSM-16 and SBA-15. These supported solid catalysts were used in the benzylation of benzene and substituted aromatics with benzyl alcohol [88].

C. H. F. Peden et al. studied the catalytic behaviour of $H_3PW_{12}O_{40}$ anchored on modified mesoporous silica materials for the dehydration of 2-butanol and methanol was studied [89].

J. Wang et al. [90] have reported the $H_3PW_{12}O_{40}$ anchored on amino-functionalized MCM-41 via condensation as reusable catalysts for esterification of n-butanol with acetic acid. Keggin and Preyssler-structured POMs were anchored on the surface of amino-functionalized MCM-41 by chemically bonding to amino groups. $H_3PW_{12}O_{40}$ directly anchored to MCM-41 by impregnation were also prepared for comparison.

Z. Zhu and co-workers reported two step impregnation synthesis of $K_{2.5}H_{0.5}PW_{12}O_{40}$/MCM-41, $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$/MCM-41 and $Ce_{0.83}H_{0.5}PW_{12}O_{40}$/MCM-41 and shape-selective catalysis in alkylation reaction of benzene and 1-dodecene to monoalkyl-benzene with high reactivity [91]. Recently, El-Shall et al. reported acid catalyzed organic transformations such as Pechmann, esterification and Friedel–Craft acylation reactions over $H_3PW_{12}O_{40}$ supported on MCM-41 [92].

A. Pandurangan et al. reported the synthesis of mesoporous Si-MCM-41 and Al-MCM-41 molecular sieves in four Si/Al ratios: 25, 50, 75 and 100, under hydrothermal, for anchoring $H_3PW_{12}O_{40}$. The catalytic activity of these materials were tested for the acetalization of carbonyl compounds with 2,2-bis(hydroxymethyl)propane-1,3-diol [93]. The same group [94] reported, hydrothermal synthesis of Si-MCM-41 and various loading of wt.% (20 and 30 wt.%) of $H_3PW_{12}O_{40}$ by wet impregnation method. They found the catalyst to be very efficient and environmentally benign heterogeneous catalyst for the liquid-phase synthesis of diamino triphenyl methane (DATPM) derivatives. The catalytic activity of the catalysts showed the following order: $H_3PW_{12}O_{40}$ ·n H_2O> $H_3PMo_{12}O_{40}$ ·n H_2O> $H_4SiW_{12}O_{40}$ ·n H_2O> 20 wt.% $H_3PW_{12}O_{40}$/MCM-41 > 30 wt.% $H_3PW_{12}O_{40}$/MCM-41 >HM(12) >Hβ (8) >HY (4) > HZSM-5 (15) > Al-MCM-41 (25). The same group has also reported the synthesis of a series of xanthenedione derivatives by condensation of various aromatic aldehydes using MCM-41-supported $H_3PW_{12}O_{40}$ [95]. In order to generate surface acidity of Si-Sn-MCM-41, $H_3PW_{12}O_{40}$ was impregnated on it [96]. The acidity of $H_3PW_{12}O_{40}$ loading on Sn-MCM-41 was investigated by temperature programmed desorption of NH_3. The catalytic activity was examined in desulfurization of dibenzothiophene in vapour phase system.

Murugesan et al. [97-98] prepared a series of anchored $H_3PW_{12}O_{40}$ by impregnation of $H_3PW_{12}O_{40}$ on mesoporous aluminophosphate (AlPO), Al-MCM-41, and SBA-15. Their catalytic activity was evaluated for *t*-butylation of

phenol with *tert*-butanol. Later, the same group [99] reported hydrothermal synthesis of Mesoporous Al-MCM-41 (Si/Al = 20) molecular sieve and 10-40 wt% $H_3PW_{12}O_{40}$ were supported on Al-MCM-41. Their catalytic activities were evaluated in the unsymmetrical alcoholysis of succinic anhydride with ethanol in the temperature between 60 and 120 ^oC. Monoethyl succinate (MES) and diethyl succinate (DES) were obtained as products.

S. B. Halligudi and group have carried out extensive study on the anchored $H_3PW_{12}O_{40}$ catalysts for the various reactions. They have carried out veratrole acetylation over $H_3PW_{12}O_{40}$ supported onto zirconia in mesoporous channels of MCM-41 [100].

Wang et al. reported epoxidation of styrene with 30% H_2O_2 as an oxidizing agent over $H_3PW_{12}O_{40}$/Ti-MCM-41 catalysts for selective synthesis of styrene oxide [101]. Although, Ti-MCM-41 structure is distorted slightly after loaded with $H_3PW_{12}O_{40,}$ the conversion of epoxidation for styrene was higher than that of parent $H_3PW_{12}O_{40}$, indicating that coordinated effect took place between support and active species. Later, Xu et al. [102] reported liquid phase alkylation of toluene with 1-octene catalyzed by bulk and MCM-41 supported Keggin type $H_3PW_{12}O_{40}$.

K.M. Parida's group have reported acylation of anisole over cesium salts of $PW_{12}O_{40}$ immobilized on MCM-41 [103]. In another report they carried out synthesis of bisphenol using acetonitrile as solvent using Cs salt of $H_3PW_{12}O_{40}$ promoted zirconium titanium phosphate solid acid catalyst [104].

Alibeik et al. studied [105] one pot three-component imino Diels-Alder reactions of various types of aldehydes, aniline and dihydropyrane in the presence of nano sized MCM-41 supported $H_3PW_{12}O_{40}$ as solid acid catalyst. $H_3PW_{12}O_{40}$ on the nano-sized MCM-41 proved to be an efficient, reusable and stereoselective catalyst for imino Diels-Alder reaction of imines and dihydropyranes.

Dias et al. [106] reported that impregnation of 20% $H_3PW_{12}O_{40}$ on the surface of MCM-41 decreased the characteristic crystallographic reflections of support, suggesting that $H_3PW_{12}O_{40}$ modifies the long-range order. This catalyst showed 96% conversion and 65% selectivity for stereoisomer (-)-isopulegol, under 1 h reaction by intramolecular cyclisation of (+)-citronellal. In the same year, Rode and group [107] demonstrated a novel application of $H_3PW_{12}O_{40}$ supported on MCM-41 as a solid acid catalyst. The utility of 20% $H_3PW_{12}O_{40}$/MCM-41 catalyst was established by its efficient activity for hydroxyalkylation of phenol and p-cresol with formaldehyde to the corresponding dihydroxydiarylmethane products.

Mendez et al. reported $H_3PW_{12}O_{40}$ anchored to MCM-41 and compared with their unsupported analogues [108]. The solids were tested in thiophene hydrodesulfurization reaction at 400 °C, atmospheric pressure. Furthermore, a correlation between surface acidity and calcination temperature with the activity and stability of these catalysts in the hydro-desulfurization reaction was proved.

Patel et al. reported $H_3PW_{12}O_{40}$ supported onto MCM-41 and its application for di-esterification of bioplatform molecule- succinic acid esterification of lauric acid with butanol-1, and biodiesel production by oleic acid esterification with methanol under mild conditions [109-112]. The excellent catalytic performance is attributed to the large surface area and pore diameter of the mesoporous support, MCM-41 as well as the Bronsted acid strength of $H_3PW_{12}O_{40}$, as active sites. The catalyst shows the potential of being used as a recyclable catalytic material after simple regeneration without significant loss in activity.

Chen and co-workers, [113] studied catalytic activity of $H_3PW_{12}O_{40}$ supported to MCM-41 for catalytic oxidation of benzaldehyde to benzoic acid using 30% H_2O_2 in the absence of any organic solvent and co-catalysts. Liu and group [114] reported a new method for the synthesis of 5-ethoxymethylfurfural from

5-hydroxymethylfurfural and fructose in ethanol using MCM-41- $H_3PW_{12}O_{40}$ as the catalyst through one-pot reaction with a moderate yield of 42.9%.

In addition, currently the use of anchored POMs for production of biodiesel through esterification/transesterification reactions and valorisation of glycerol are growing field of research. Many groups have reported the use of $H_3PW_{12}O_{40}$ supported onto various supports including mesoporous materials for biodiesel production and literature cited has been included in *Chapter 2*.

Even though MCM-48 is much superior, very few reports are available for the same. A probable reason for this might be the difficulty in synthesis conditions and extended time requirement in hydrothermal conditions. There are few reports on synthesis and catalytic activity of MCM-48 as support for anchoring $H_3PW_{12}O_{40}$ and other counterparts.

Mukhopadhyay et al. [115], reported POMs ($H_3PMo_{12}O_{40}\cdot 24H_2O$, $H_3PW_{12}O_{40}\cdot 24H_2O$) as a promoter in the rapid and convenient synthesis of MCM-41 and MCM-48. The crucial role for the rapid nucleation of MCM-41 and MCM-48 was played by the oxoanions generated from the POMs dissociation in the syntheses media (pH ≈ 11). They also observed a 3 to 4 fold decrease in the syntheses times of the mesoporous materials by catalytic addition of POMs, compared to the conventional approaches.

In the 2007, Halligudi and group [116], emphasized on synthesis of inorganic-organic hybrid materials by immobilization of POMs with general formula $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 0-3)$\cdot n H_2O$, onto MCM-48 through an organic linker for selective oxidation of anthracene with 70% aqueous *tert*-butylhydroperoxide (TBHP) oxidant in benzene.

Bhagiyalakshmi et al. [117] monitored CO_2 adsorption capacity with Copper-encapsulated $H_3PW_{12}O_{40}$-impregnated mesoporous MCM-48. The synthesized material was found to be reusable, selective, thermally stable and a promising nominee for CO_2 capture.

A recent comparative study on hydrothermal (HTS) and room temperature synthesis (RTS) of $H_3PW_{12}O_{40}$-MCM-48 was carried out by Gucbilmez et al. in 2012 [118]. They concluded that the simpler and more economical RTS method was more successful than the HTS method for $H_3PW_{12}O_{40}$ incorporation into MCM-48. In the same year, Wang and Navarrete [119] described surface grafting and acidity of $H_3PW_{12}O40$ impregnated Zr-MCM-48. The material was characterised thoroughly and non-destruction of pores as well as structures was evidenced by FT-IR, TEM and ^{31}P MAS-NMR.

Further, a literature survey shows that only few reports are available on catalytic applications using $H_3PW_{12}O_{40}$ incorporated in MCM-48. Yijun and Shuijin in 2008, [120] synthesised $H_3PW_{12}O_{40}$/MCM-48 by impregnation method and carried out esterification of methacrylic acid with n-butyl alcohol. The Keggin structure of $H_3PW_{12}O_{40}$ kept unchanged after being impregnated on surface of the molecular sieve support. In the same year Sakthivel et al., carried out esterification of long chain fatty acid (Lauric acid, Myristic acid, Palmitic acid, Stearic acid, Oleic acid) with long chain alcohol (Cetyl alcohol, 1-octanol, 2-decanol etc.) in supercritical CO_2 over MCM-48-supported $H_3PW_{12}O_{40}$ catalysts [121]. The yields of esters were enhanced with the increase in the chain length of acids and alcohols in the esterification in sc-CO_2 medium. In both the cases, MCM-48 was synthesized by hydrothermal process and the catalyst preparation needed extensive procedure.

In a separate investigation [122], $H_3PW_{12}O_{40}$ supported on MCM-41 and MCM-48 showed potential for alkylation of benzene with propylene in order to produce cumene. The results showed that the MCM-48 with (30 wt. % $H_3PW_{12}O_{40}$) catalyst had the best behaviour in catalytic activity, showing the higher conversion and selectivity toward cumene as the main product.

Wu et al. recently [123] synthesised $H_3PW_{12}O_{40}$ supported onto MCM-48 by wet impregnation. The characterization results indicated that the mesoporous phase of MCM-48 remained almost unchanged upon the $H_3PW_{12}O_{40}$ loading,

while the long-range order decreased noticeably. They studied the catalytic oxidation of benzyl alcohol and benzaldehyde with 30% H_2O_2 over $H_3PW_{12}O_{40}$/MCM-48 for an efficient green synthesis of benzoic acid.

Literature study for anchored mono Lacunary phosphotungstate

Few reports are available on synthesis and characterization of supported phosphotungstates, hence irrespective of the support used we have included all the references related to phosphotungstates only. The equilibrium adsorption on TiO_2, SiO_2 and Al_2O_3 of $[PW_{11}O_{39}]^{7-}$ anion from solution in water was studied by Pizzio et al. [124]. PW_{11} clusters were incorporated into the wall structures of hybrid silica materials (three-dimensionally ordered macroporous- 3DOM), resulting in hybrid PW_{11}-SiO_2 composites, which was further investigated for photochemical properties [125]. Photocatalytic degradation of aqueous formic acid over the silica composite films based on PW_{11} was also carried out [126]. Preparation, characterization and photocatalytic property of the $PW_{11}O_{39}^{7-}$/TiO_2 composite film towards azo-dye degradation was carried out [127]. Highly ordered macroporous XW_{11}-SiO_2 and XW_{11}-TiO_2 composite films (X: P, Si, and Ge) were prepared, characterized and their photo-oxidative properties investigated [128]. Similar studies were carried out for POM-grafted mesoporous hybrid silicas, XW_{11}/MHS (X = P, Si) and TBA-$PW_{11}Si_2$/MHS, prepared by co-condensation and post-synthesis routes [129]. Study was carried out on optimum conditions for intercalation of lacunary tungstophosphate(V) anions into layered Ni(II)-Zn(II) hydroxyacetate [130].

Effect on selective adsorption of ethane and ethylene by PW_{11}/SiW_{11} impregnated to metal-organic framework MIL-101 was studied [131]. It was found that the impregnation of POMs by post-synthetic method resulted in alteration in selective adsorption behaviour of MOFs, since it introduces adsorption sites that are able to develop specific interactions.

Few reports are available on the catalytic applications of anchored PW_{11}. In 2009, Li et al. [132] reported direct synthesis of mesoporous silica support in acidic media in the presence of cetyltrimethylammonium bromide and monovacant lacunary PW_{11} associated with quaternary ammonium salt. The mechanism of formation of CTA-POM/SiO_2 material was also proposed. They carried out extensive study for oxidative desulfurization (ODS) of bulky organosulfur compound, dibenzothiophene (DBT) using H_2O_2 as an oxidizing agent.

Ordered mesoporous MCM-41 materials incorporated with PW_{11} were prepared via an original direct synthesis method by Li and group [133]. The catalytic performance of the materials was tested using the esterification of n-butanol with acetic acid.

Abdulla and Li, in 2012 [134] demonstrated the synthesis of tertabutylammonium salt encapsulated $(TBA)_4H_3(PW_{11}O_{39})$ supported to MCM-41 in acidic condition. The catalyst showed high efficiency for ODS of both DBT and thiophene and lowered their sulfur contents. Similar work has been carried out by Li et al. recently [135], where synthesis of lacunary PW_{11} encapsulated into mesoporous silica pillared in clay interlayer galleries has been discussed for ODS of DBT as model oil as a probe reaction.

A direct method for incorporating the PW_{11} into hexagonal mesoporous silica (HMS) to prepare PW_{11}-HMS hybrid catalyst was also reported by Li and group [136]. Catalytic activity esterification of n-butanol esterification with acetic acid was carried over the hybrid catalyst.

The immobilization of PW_{11} in (3-aminopropyl) triethoxy silane functionalized SBA-15 as well as porous metal organic frameworks (MOFs)-PW_{11}@MIL(Cr) were reported by Balula and group [137-138]. They reported synthesis of hybrid composite material, PW_{11}@MIL-101 and SiW_{11}@MIL-101, by the inclusion of the potassium salt of mono-lacunary

phosphotungstate/silicotungstate into the MOF, MIL-101(Cr) by post synthesis grafting method [139]. The composites were tested for the oxidation of cis-cyclooctene, geraniol and R-(+)-limonene, using H_2O_2 as oxidant was reported by Balula and group [138]. It was observed that the structure of MIL(Cr) has related influence in the stability of PW_{11} in presence of H_2O_2, which was further reflected in better catalytic activity by this catalyst. PW_{11}@MIL-101 proved to be more efficient catalyst as compared to the homogeneous PW_{11} for the epoxidation of cis-cyclooctene into 1, 2-epoxycyclooctane (in 10 min). A complete conversion of geraniol into 2, 3-epoxygeraniol was achieved after 1 h of reaction in the presence of SiW_{11}@MIL-101, however, for R-(+)-limonene oxidation, complete conversion was enhanced after 3 h in the presence of PW_{11}@MIL-101.

Hua et al. [140] synthesized and characterized ionic liquid consisting of PEG-functionalized ammonium cation and PW_{11} anion. The immobilized ionic liquid was used as a catalyst for olefin epoxidation with aqueous H_2O_2 in ethyl acetate. It was found that immobilized ionic liquid catalysts showed better catalytic activities and stability than the homogeneous analogue in consecutive runs. Difference in interactions between active species and polymer support influences the catalytic performance.

Scope of the Thesis

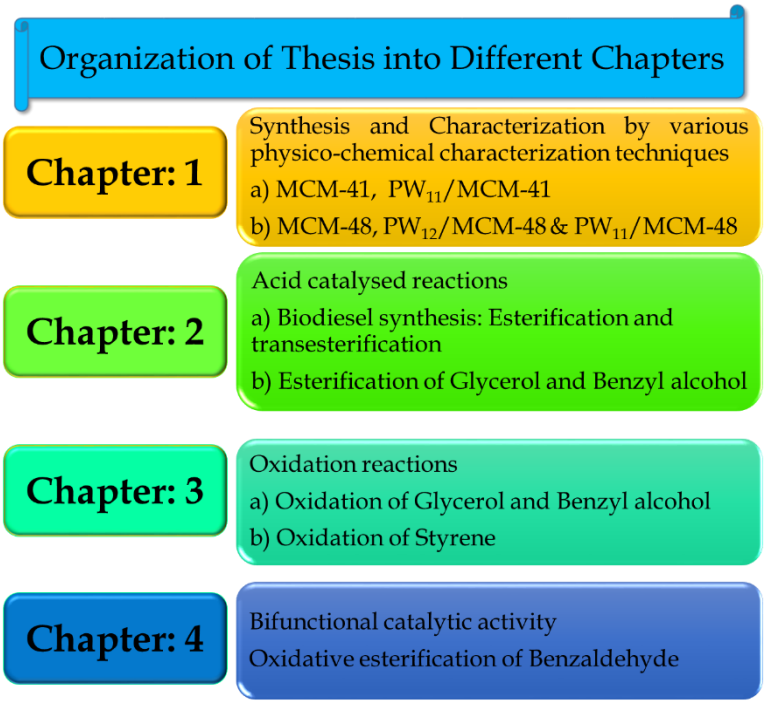
In present thesis, catalysts comprising parent phosphotungstate (PW_{12}) as well as monolacunary phosphotungstate (PW_{11}) and mesoporous supports (MCM-41 and MCM-48) were synthesized and successfully characterized by various physicochemical and spectral techniques. An efficient way for synthesis of biodiesel as well as cost minimization of biodiesel production by transformation of by-product glycerol to value added chemicals was demonstrated. In addition, bifunctional activity of the synthesized catalysts towards oxidative esterification was also demonstrated. Considering the all these aspects following objectives were planned.

Objectives of the work:

1) To tune the acidic and redox properties of Phosphotungstates (PW_{12}) by designing them at molecular level (i.e. formation of mono lacunary phosphotungstate- PW_{11}).
2) To synthesize and develop environmentally benign bifunctional heterogeneous catalysts by anchoring phosphotungstate and mono lacunary phosphotungstate to different mesoporous supports (MCM-41 & MCM-48).
3) To characterize the supports as well as the catalysts by different physicochemical and spectroscopic techniques.
4) To establish the use of synthesized catalysts for acid catalyzed as well as oxidation reactions.
5) To establish the use of synthesized catalysts as bi-functional catalysts by carrying out oxidative esterification transformations of aldehydes.
6) To study the regeneration and recycling of the catalysts as well as characterization of regenerated catalysts by FT-IR, XRD and surface area analysis.
7) To study the effect of supports (MCM-41 and MCM-48) on the catalytic activity.
8) To study the effect of active species (parent and lacunary POMs) on the catalytic activity.
9) To screen the best catalyst based on the performance for the mentioned reactions under similar reaction conditions.

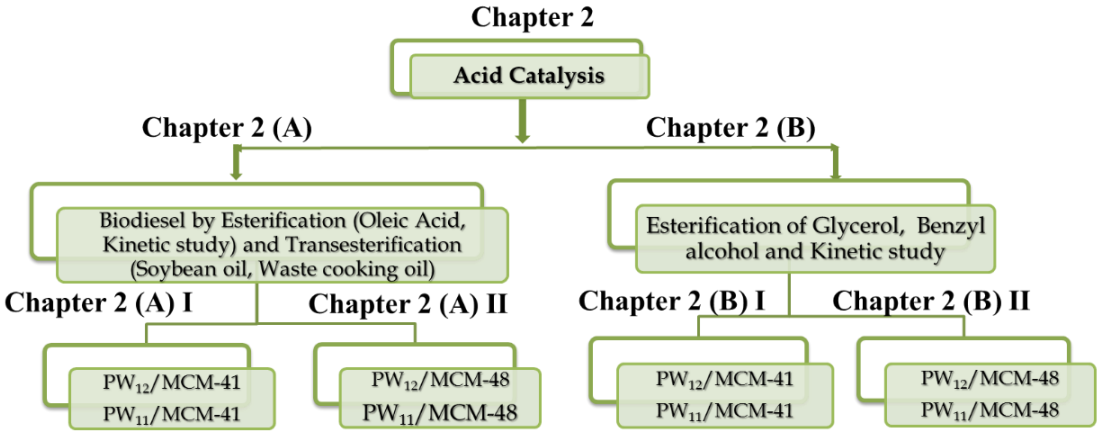
Organization of the thesis

The work was divided in following four chapters, aiming at above set objectives:

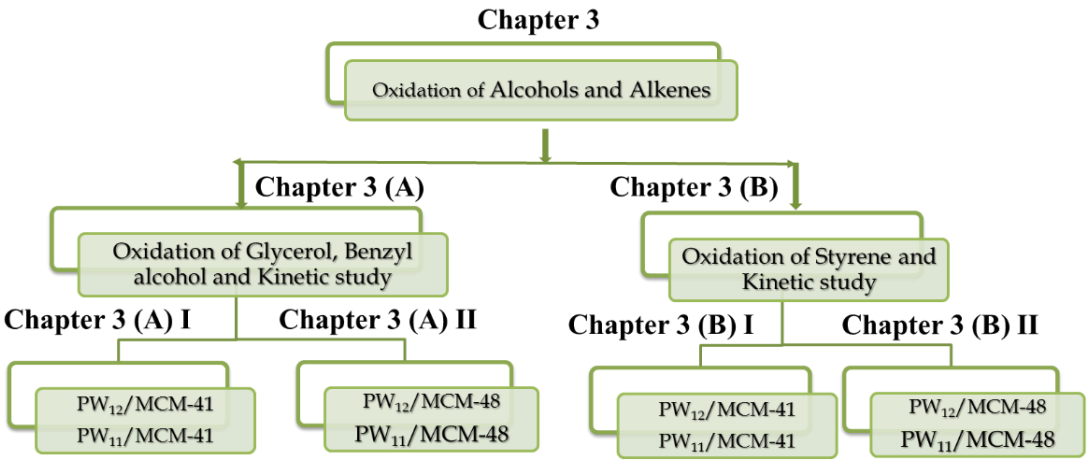


Chapter 1 describes synthesis, characterization of lacunary phosphotungstate (PW_{11}) from parent 12-tungstophosphoric acid (PW_{12}), supports and anchored catalysts.

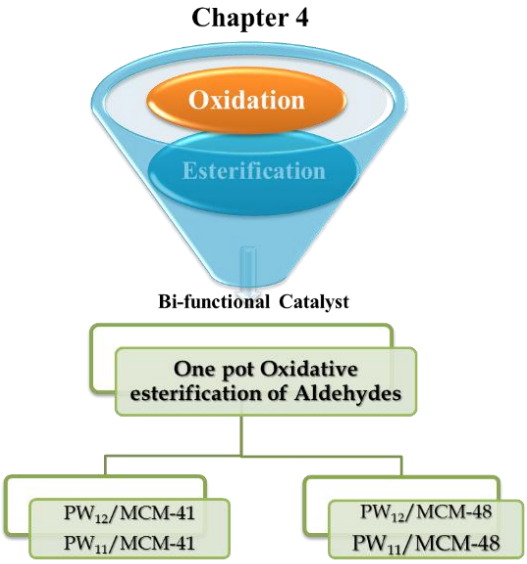
Chapter 2 *describes catalytic activity for acid catalyzed reactions.*



Chapter 3 *describes catalytic activity for oxidation reactions.*



Chapter 4*. Bifunctional catalytic activity by oxidative esterification of benzaldehyde.*



In the end, the thesis contains comparison of activity of all the synthesized catalysts and discussion of effect of active species (PW_{12}/PW_{11}) as well as supports (MCM-41, MCM-48). Based on these comparisons the best catalyst was also proposed.

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