Chapter 1

Introduction……

The 21st century demands technology ensuring cleaner and more sustainable production methods. **'Catalysis'** is the only concept or principle which combines economical and ecological values very closely for sustainability and sustainable developments. A sustainable society is one that "meets the needs of future generation without scarifying the ability to meet the needs of future generation."

In the past century, catalysis became the basis of large-scale processes in bulk chemistry and petrochemistry. Changes in our energy economy have driven a growing demand for gas and coal, presenting new challenges for catalytic technology. There are also tremendous new developments in the application of catalysis for fine chemicals and pharmaceuticals. This brings new challenges to the field and increases the possibilities for greater efficiency and sustainability of such systems. Therefore our new research community should head towards the challenges of the 21st century, in which we are faced with the depletion of natural resources and the limits of environmental stamina.

New scientific discoveries have been rewarded by recent Nobel Prizes. New catalysts that are found, are metal-organic complex molecules, that are highly selective, in a way that compares to the properties of enzymes. Yves Chauvin, Robert Grubbs, and Richard Schrock got the Nobel Prize for the development of the metathesis method in organic synthesis. In 2001 William Knowles, Ryoji Noyori, and Barry Sharpless received the same honour for their chirally catalyzed hydrogenation and oxidation reactions. Recently the 2010 Nobel Prize in Chemistry was awarded to Richard Heck, Ei-Ichi Negishi and Akira Suzuki for palladium-catalyzed cross coupling reactions. This shows the enormous progress, that has been achieved in the field of catalysis.

Catalysis by ***'Heteropolyacids'*** is the most successful areas in contemporary catalysis as well as in fundamental catalysis. Heteropolyacids possess unique physicochemical properties, such as very strong Brönsted acidity, structural mobility and multifunctionality, the most important for catalysis [1, 2]. These polynuclear molecules present a wide range of structures with the ideal frameworks of the polyhedra, which exhibit useful magnetic, electroionic, catalytic, bioactive and photochemical properties. Hence, a new trend towards the application of these remarkable species in materials science and in *Catalysis* is beginning to develop.

What are Heteropolyacids?

Heteropolyacids are complex proton acids that incorporate anions (**heteropolyanions**) having metal-oxygen octahedral as basic structure units. They are a distinctive class with unique properties of topology, size, electronic versatility as well as structural diversity [3].

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

Heteropolyanions are polymeric oxoanions formed by different mononuclear oxoanions. These oxoanions tend to polymerize, by dehydration at low pH forming polyanion and water as shown in the following equation.

$$12MO_4^{m-} + XO_4^{p-} + 23H^+ \longrightarrow [XM_{12}O_{40}]^{n-} + H_2O$$

The free acids or acidic forms of heteropolyanions are known as heteropolyacids (HPAs).

History of Heteropolyacids

The heteropolyacids have been known since the work of Berzelius [4] on the ammonium 12-molybdophosphate in 1826.

After the discovery of this first heteropolyanion, the field of HPA chemistry progressed significantly [2].

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 [4].

2. However, the study of heteropolyanion chemistry did not accelerate until the discovery of the tungstosilicicacids and their salts in 1862 by Marignac[5]. He prepared and analyzed two isomers of 12-tungstosilicic acid viz. tungstosilicic acid and silicotungsticacid now known as α and β isomers.

3. Thereafter, the field developed rapidly, so that over 60 different types of heteropoly anions (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 step towards understanding the structure of heteropoly anions was taken by L. C. Pauling in 1929. Pauling [6] 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 [7, 8] 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 heteropoly structures accelerated the development of heteropolyacid 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 [9].

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 heteropolyacid chemistry various types of structures were discovered. General information and polyhedral representation of various types of heteropolyacids are listed in Table 1.

Table 1. Different types of Heteropolyanions [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}, $V^{V,VI}$ etc.

The structure of $[PW_{12}O_{40}]^{3-}$ (dodecaphosphotungstate) was first reported by Keggin in 1933. The ideal Keggin structure of the 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 [7, 8], 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 heteropolyanion is shown in Figure 1.

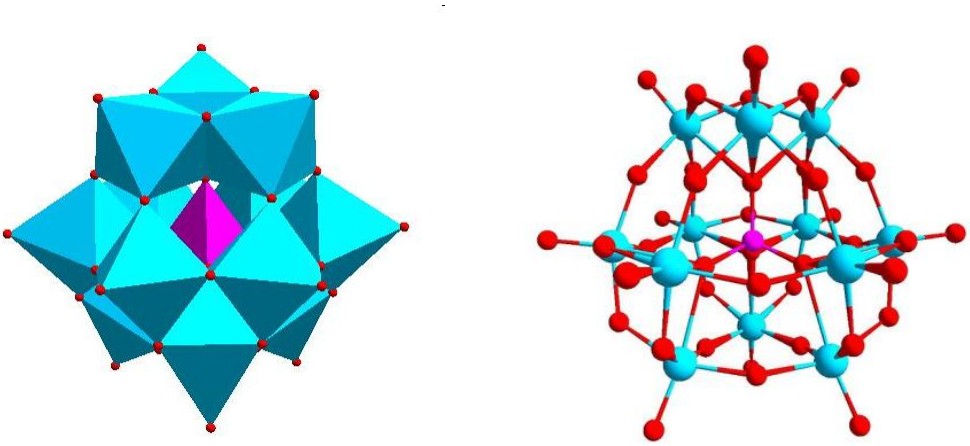


Figure 1. Keggin type $[PW_{12}O_{40}]^{3-}$

The basic structure of heteropolyanion molecule itself is called a "primary structure" and is formed from the condensation of oxoanions.

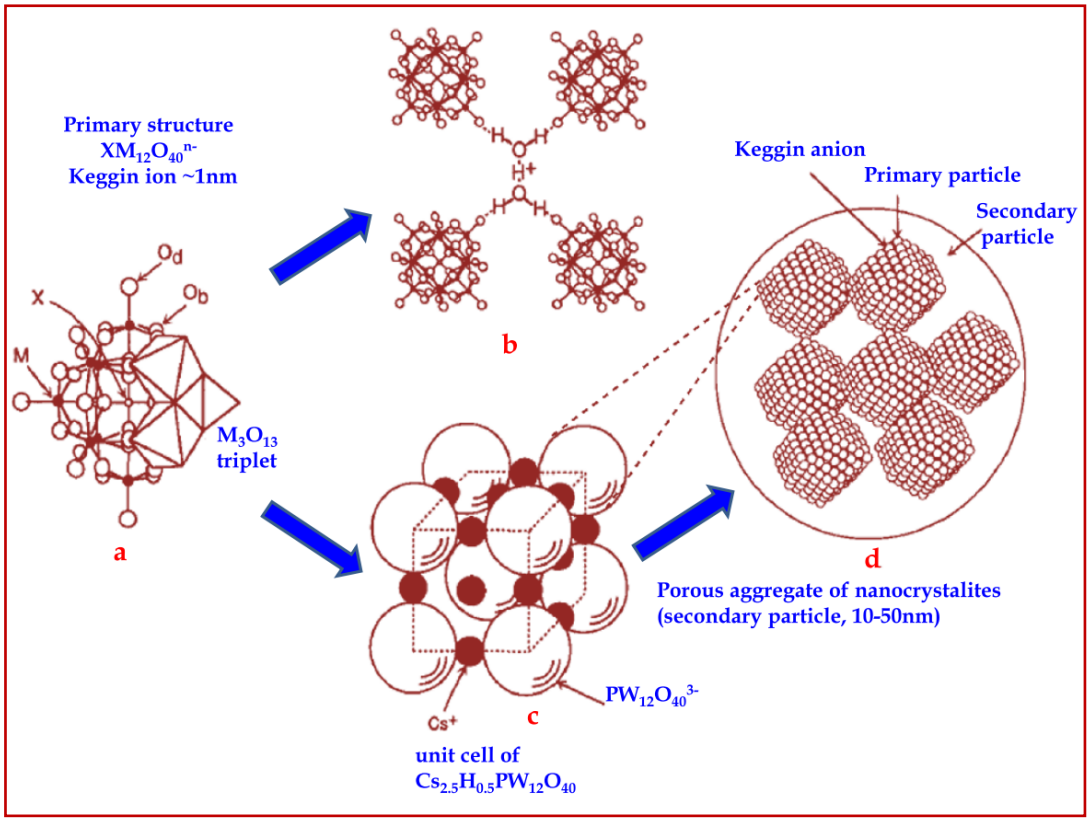


Figure 2. Primary, secondary, and tertiary structures of Keggin type heteropolyacid; (a) Primary structure (Keggin structure, $XM_{12}O_{40}$); (b) secondary structure ($H_3PW_{12}O_{40}.6H_2O$); (c) secondary structure for unit cell of ($Cs_3PW_{12}O_{40}$); (d) tertiary structure with porous aggregates [$Cs_{2.5}H_{0.5}PW_{12}O_{40}$]; {Taken from "Advances in Catalysis", by M. Misono and N. Mizuno, 41, 113, (1996)}

The secondary structure of the solid HPAs is formed from the coordination of the heteropolyanion with acidic protons, other cations and/or water molecules of hydration. A stable form contains six water molecules of hydration per Keggin unit, forming a body centered cubic (bcc) structure with Keggin units at the lattice points and $H_5O_2^+$ bridges along the faces. Each terminal oxygen atom is bound to a hydrogen atom of an $H_5O_2^+$ bridge. In this

structure, the acidic protons are located in the $H_5O_2^+$ bridges between lattice points. If less than six water molecules are present, acidic protons may be located in remaining $H_5O_2^+$ bridges, in H_3O^+ or may be directly coordinated to oxygen atoms of the Keggin unit. The tertiary structure is the structure of solid HPAs as assembled. The size of the particles, pore structure, distributions of protons in the particle etc. is the elements of the tertiary structure (Figure 3c).

Where is the proton?

HPAs are strong Bronsted acids [10-14]. Structural characterization of the HPA proton sites is an important step toward understanding the catalytic activity [11-13, 15]. Keggin anions have three types of outer oxygen atoms as potential protonation centers: terminal oxygens M=O and two types of bridging oxygens M-O-M, edge sharing and corner sharing (Figure 1). Bond length-bond strength correlations [16] as well as ^{17}O nuclear magnetic resonance (NMR) data [17, 18] indicate that in the free polyanions (e.g., $V_{10}O_{28}^{6-}$) in solution, the bridging oxygen atoms, having a higher electron density than the terminal oxygen atoms, are protonated. Hypothetically, in the free Keggin anion in the gas phase, edge- bridging M-O-M oxygens may be assumed to be the predominant protonation sites. In solid HPAs, the protons take part in the formation of the HPA crystal structure, linking the neighboring heteropolyanions. In this case the more accessible terminal oxygens can be protonated. Thus, from single-crystal X-ray and neutron diffraction data [19], the crystal structure of 12-tungstophosphoric acid (TPA) hexahydrate is formed by packing heteropolyanions into a body-centered cubic structure. The bulk proton sites in 12-tungstophosphoric acid (TPA) hexahydrate are represented as di-aquahydrogen ions, $H_5O_2^+$, each of which links four neighboring heteropolyanions by forming hydrogen bonds with the terminal W=O oxygens (Figure 3).

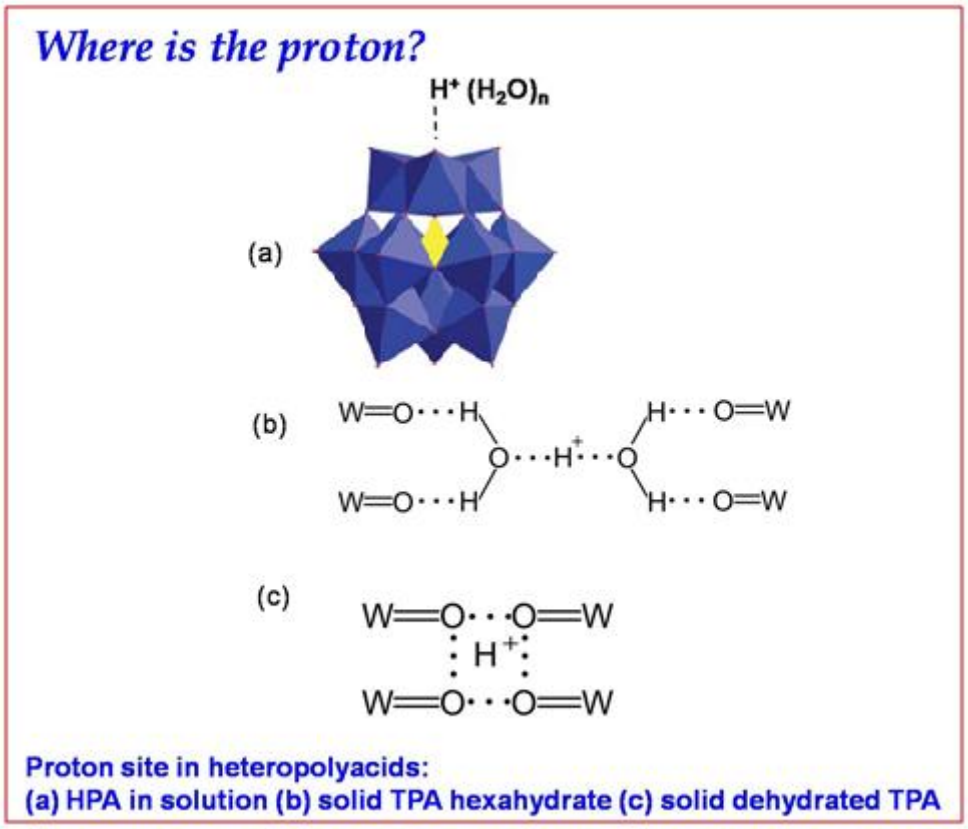


Figure 3. Proton sites in heteropolyacids.

Note, however, that the protons cannot be found directly from X-ray data; their positions are localized on the basis of a sensible hydrogen-bonding scheme and the known geometry of the water molecule.

Direct evidence of the predominant protonation of the terminal oxygens in solid 12-tungstophosphoric acid and 12-tungstosilicic acid has been obtained by ^{17}O NMR by comparison of solution and solid-state spectra for these HPAs [20-23]. The resonance for the terminal oxygen in solid TPA exhibits a large 60 ppm upfield shift compared to the aqueous solution spectrum, whereas the bridging oxygen resonances have practically the same positions in both spectra [19-21]. Since in aqueous solution TPA is completely deprotonated, this unambiguously identifies the terminal oxygens as the predominant protonation sites in solid HPA. The structure of proton sites in the dehydrated TPA is shown in Figure 3. This structure is assumed to be

directly formed from the proton structure of the TPA hydrate upon dehydration. Stoichiometrically, each proton is shared by four equivalent terminal oxygens, belonging to four different heteropolyanions, like in TPA hexahydrate. Interestingly, the same structure was suggested [19] for the structurally similar HPA salts, e.g., $Cs_3PW_{12}O_{40}$, in which the Cs^+ ions each have four equivalent terminal oxygens as the closest neighbors.

Properties of Heteropolyacids

Heteropolyacids have usually low surface area (1-10 m^2/g) reflecting their high solubility in water. The pores of HPAs 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.

Thermal Stability

There are various kinds of stabilities, for example, thermal stability and hydrolytic stability in solution, and those stabilities change very much depending on the kind of HPAs [12, 13, 24]. Some solid HPAs are thermally stable and applicable to vapor phase reactions conducted at high temperatures. The thermal stability of these heteropolyacids changes with heteroatom, polyatom and polyanion structure as follows:

$$PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-} > SiMo_{12}O_{40}^{4-}$$

But the thermal stability of mixed addenda heteropolyanions is generally low. The thermal stability of Keggin type heteropoly compounds is studied extensively by TGA, DTA, XRD, etc.

The Differential Thermal Analysis (DTA) results of different HPAs shows an endotherm at lower temperature and an exotherm at higher temperature. (Table 2) The low temperature endotherm is due to removal of water. The high temperature exotherm is ascribed to the decomposition of cage like structure of heteropolyanion compound to yield a more compact crystalline product consisting largely of oxides of Mo (VI) and W(VI).

Table 2. DTA results of different HPAs.

Heteropolyacid	Endotherm (K)	Exotherm (K)
$H_3PW_{12}O_{40}$	448-569	853-868
$H_4SiW_{12}O_{40}$	413-551	743-773
$H_3PMo_{12}O_{40}$	336-432	663-681
$H_4SiMo_{12}O_{40}$	337-453	609-628

From TGA and DTA two types of water are observed in heteropoly compounds i. e., water of crystallization and constitutional water molecules. The former usually lost at temperature below 473 K. The constitutional water molecules (acidic protons bound to oxygen of the polyanion) of $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ are lost at 623 K and 543 K respectively.

In situ XRD, ^{31}P NMR and thermoanalysis, it was concluded that thermolysis of $H_3PMo_{12}O_{40}$ proceeds in two steps, as shown below:

$$H_3PMo_{12}O_{40}.nH_2O \underset{nH_2O}{\overset{473-623\,K}{\rightleftharpoons}} H_3PMo_{12}O_{40} \underset{-1.5H_2O}{\overset{658\,K}{\rightleftharpoons}} H_xPMo_{12}O_{38.5+\frac{x}{2}(x=0.01)}$$

The MoO_3 phase appears at temperature higher than 573 K.

Hodnett and Moffat assumed that the same decomposition proceeded via $H_3PW_{12}O_{40}$. Thermal gravimetric analysis of $H_3PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed that entire water molecules of crystallization are lost at temperature as low as 573 K and acidic groups are removed as water is formed from protons and lattice oxygens at temperatures exceeding 623 K. The number of protons lost, x, in $Cs_{2.5}H_{0.5-x}PW_{12}O_{40-x}$ were 0.24, 0.31 and 0.32 after treatment at 623 K, 673 K and 773 K respectively. Similar removal of protons of $K_{2.5}H_{0.5}PMo_{12}O_{40}$ begins by 500 K. The thermal stability of $H_3PMo_{12}O_{40}$ and its salts changes with counter cations. Bi and tetravalent metal salts are not stable. The hydrogen form and ammonium salts decomposed at 693 and 743 K respectively. Cs and K salts are stable up to their melting point.

Adsorption and Absorption properties

HPAs have remarkable characteristics that some solid HPAs absorb easily a large quantity of polar or basic molecules such as alcohols and nitrogen bases in the solid bulk [25-27]. The absorption depends on basicity and the size of the molecule to be absorbed and the rigidness of the secondary structure. As for the desorption, alcohols absorbed can readily leave the bulk, but the desorption of pyridine and ammonia needs a high temperature.

HPAs are typical strong Bronsted acids and catalyze a wide variety of reactions in homogeneous phase offering strong option for efficient and cleaner processing. Heteropolyacids have high potential as catalyst.

HPAs have a very strong approaching the super acid region, Bronsted acidity. Further they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under mild conditions. HPAs are widely used as a model system for fundamental research providing unique opportunities for mechanistic studies on the molecular level. At the same time they become increasingly important for applied catalysis. They provide good basis for the molecular design of mixed oxide catalyst and they have high capability in practical uses.

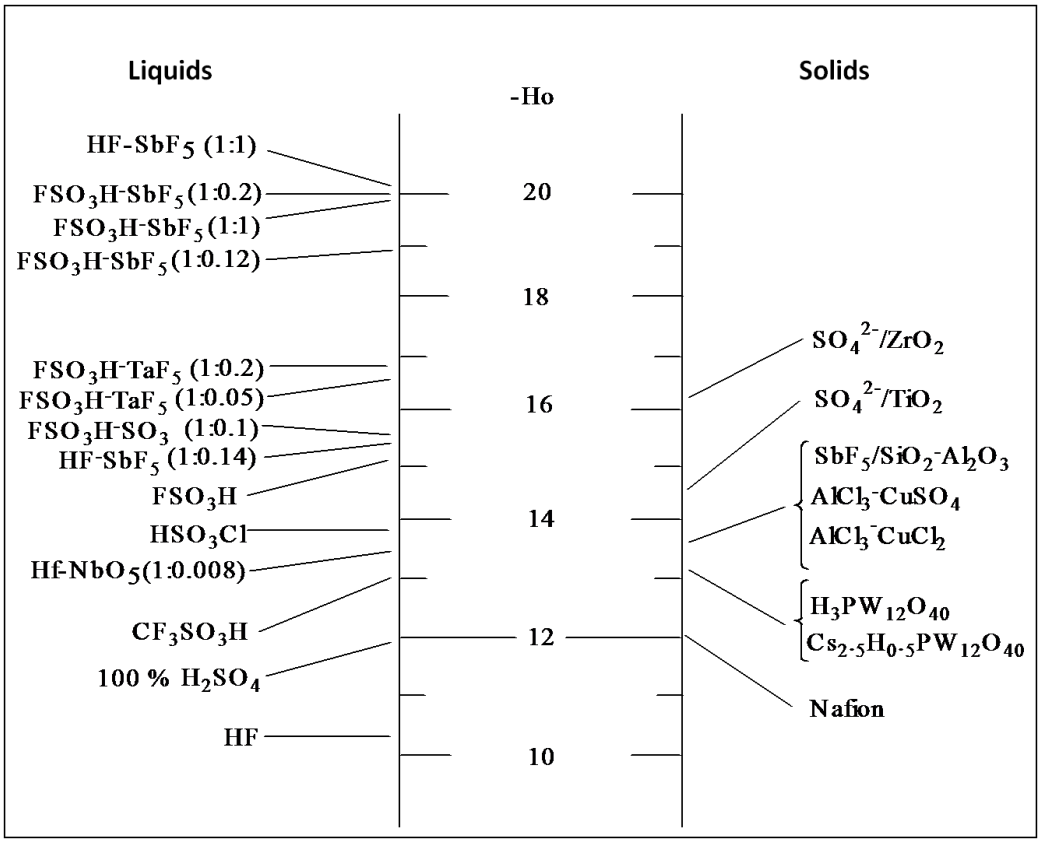


Figure 4. Superacids and Hammet acidity scale [28]

Heteropoly compounds are highly acidic and the acidity of these compounds are higher than that of well known solid acid catalysts such as silica-alumina and the free acid of the heteroatom [29-30]. The central atom is the important factor in determining the acid strength and the acidity is related to the total charge on the anion than to the type of metal atom in the shell HPA. The H_0 values (figure 4) are found to be between +6 and -13. The acid strength of heteropoly acids is found to follow the order :

$$H_3PW > H_4SiW > H_3AsW > H_4GeW$$

Acidic properties [31]

It was proved that HPAs such as $H_3PW_{12}O_{40}$ and H_3PMoO_{40} in the solid state are pure Bronsted acids and are stronger acids than the conventional solid acids (figure 5) such as SiO_2-Al_2O_3, H_3PO_4/SiO_2, HX and HY zeolites [29-30]. Heteropolyacids are much stronger than the oxoacids of constitute elements and ordinary mineral acids (table 3). The strong acidity is caused by:

I. Dispersion of the negative charge over many atoms of the polyanion
II. The fact that the negative charge is less distributed over the outer surface of the polyanion owing to the double-bond character of the M=O bond, which polarizes the negative charge of O_t to M.

Table 3. Dissociation Constants of various HPAs. [31]

Dissociation Constants of HPAs in Acetone at 25 ^{0}C			
Acid	Pk_1	pK_2	pK_3
$H_3PW_{12}O_{40}$	1.6	3.0	4.0
$H_4PW_{11}VO_{40}$	1.8	3.2	4.4
$H_4SPW_{12}O_{40}$	2.0	3.6	5.3
$H_3PMo_{12}O_{40}$	2.0	3.6	5.3
$H_4SiMo_{12}O_{40}$	2.1	3.9	5.9
H_2SO_4	6.6	-	-
HCl	4.3	-	-
HNO_3	9.4	-	-

In aqueous solution, heteropolyacid such as 12-tungstophosphoricacid, 12-tungstosilicicacid and 12-tungstomolybdicacid are strong, fully dissociated acids [11]. $SiW_{12}O_{40}^{4-}$, $PW_{12}O_{40}^{3-}$, anions remain deprotonated even after accepting two and three extra electrons respectively. HPAs in solution are stronger than the usual mineral acids such as H_2SO_4, HCl, HNO_3 (figure 4).The strength of the Keggin HPAs depends weakly on their composition. Yet the tungsten acids are markedly stronger than molybdenum ones. The strongest acid in the Keggin series is $H_3PW_{12}O_{40}$.

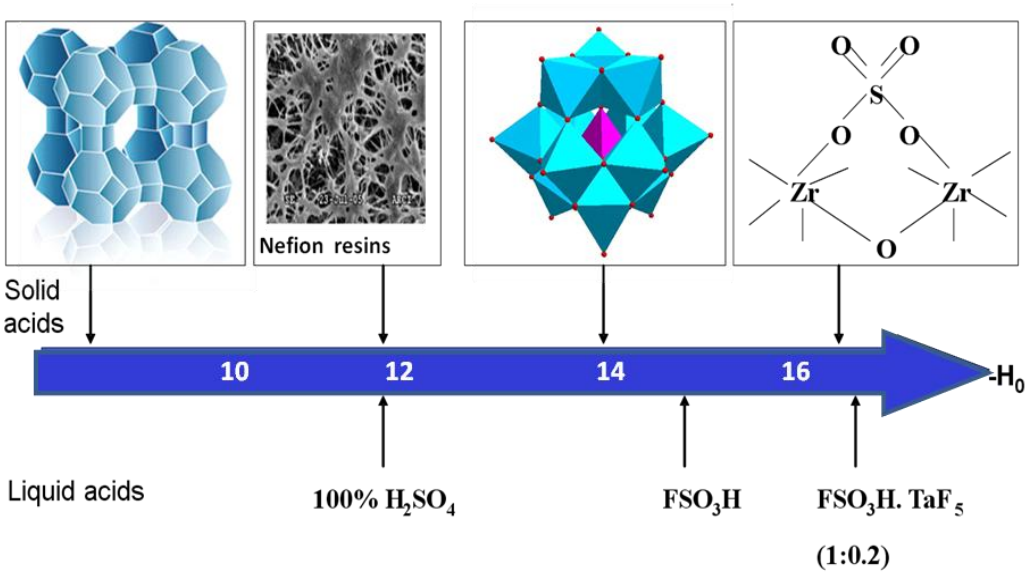


Figure 5. HPAs as stronger solid acids than the conventional solid acids.

After that, an extensive literature on their synthesis, structure and properties has been accumulated and summarized in the form of books and reviews namely:

1. Use of heteropolyacid compounds in acid catalyzed hydrocarbon reactions had studied by A. Corma, *Chem. Rev.*, 95, 559 (1995)
2. The catalytic properties of heteropoly compounds have been studied and reviewed by T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.*, 41, 113 (1996)
3. "Metal-oxygen clusters: The surface and catalytic properties of heteropolyoxometalates", by J. B. Moffat, (Eds.) M. V. Twing, M. S. Spencer, Kluwer Academic plenum, New York, (2001)
4. "Catalysts for fine chemical synthesis: Catalysis by polyoxometalates", I. V. Kozhevnikov, Vol. 2, Wiley (2002)
5. "Mechanisms in homogeneous and heterogeneous epoxidation catalysis", (Eds) S. Ted Oyama, Ch 4 "Activation of hydrogen peroxide by polyoxometalates" , N. Mizuno, Elesvier Publications, (2008)
6. "Modern heterogeneous oxidation catalysis, Edited by N. Mizuno, Ch 6 Liquid-Phase Oxidations with Hydrogen Peroxide and Molecular Oxygen Catalyzed by Polyoxometalate-Based Compounds". N. Mizuno, Wiley (2009)
7. "Green chemistry and catalysis", by R. A. Sheldon, Ch 2 Solid acids and bases as catalysts, Wiley (2007)

Applications of Heteropolyacids

Since the discovery of HPAs, they found significant importance in various fields of science and technology. The field of HPA 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 [32]. The applications of HPAs are summarized in block diagram (figure 6).

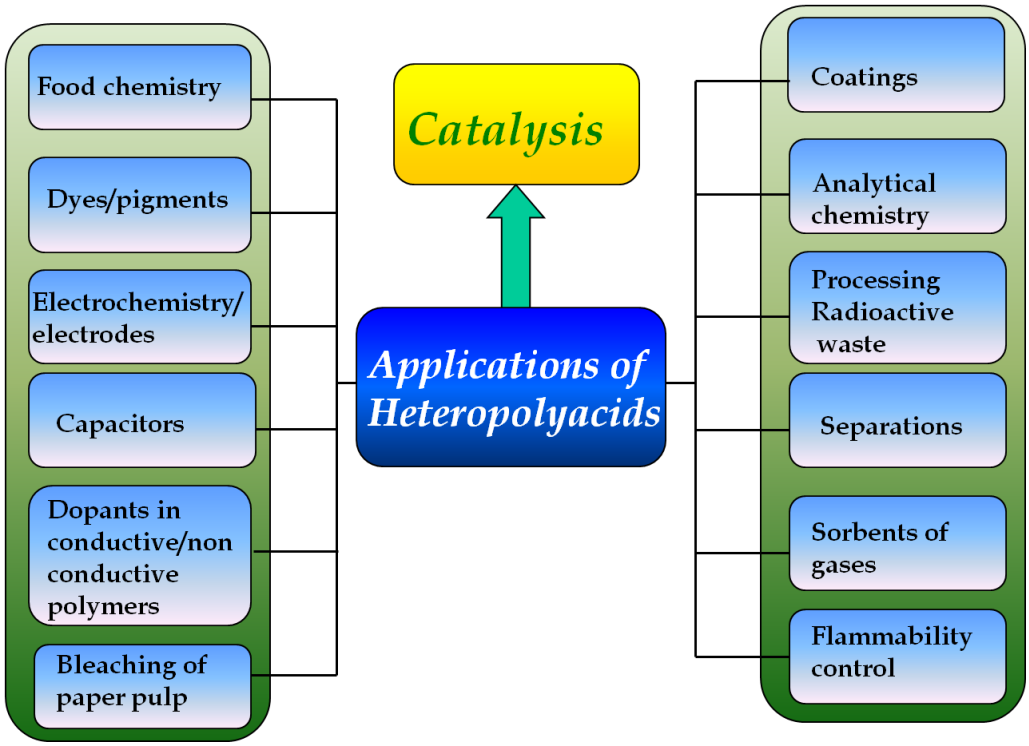


Figure 6.Block diagram showing applications of Heteropolyacids

About 80-85% of patent and applied literature claims about applications of HPAs in the field of catalysis [32]. The first attempt to use heteropolyacids as catalysts were tracked way back in the 19th century. Systematic investigation of catalysis by heteropolyacids began in the early 1970's.

Among all, most deal with HPA salts, and supported HPAs which are summarized here in the following references.

1. "Heteropoly and Isopoly Oxometalates" (Eds.) M. T. Pope, C. K. Jorgensen, Springer-Verlag, Berlin (1983)
2. Issue on Polyoxometalates, Eds. C. L. Hill, *Chem. Rev.*, 98, 1(1998)
3. "Polyoxometalate chemistry: From topology via self-assembly to applications" (Eds.) M. T. Pope and A. Mucler, Kluwer Academic. (2001)
4. "Polyoxometalate Molecular Science", M. T. Pope, A. Muller, Kluwer Academic Publishers (2003)
5. Use of heteropolyacid compounds in acid catalyzed hydrocarbon reactions had studied by A. Corma, *Chem. Rev.*, 95, 559 (1995)
6. The catalytic properties of heteropoly compounds have been studied and reviewed by T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.*, 41, 113, (1996)
7. Different reactions such as hydration, esterification, condensation, miscellaneous reactions, polymerization, alkylation, oxidation of various organic compounds has been studied and reviewed by I. V. Kozhevnikov, *Chem. Rev.98*, 171(1998)
8. Structural and catalytic properties of heteropolyacids have also been studied and reviewed by N. Mizuno and M. Misono, *Chem. Rev.*, 199, (1998)
9. A review on application of heteropolyacid in many areas rather than the traditional area of catalysis, such as coating, membranes, films, electrochemical devices, pigments, analytical reagents by D. E. Katsoulis, *Chem Rev* 98, 359 (1998)
10. Polyoxoanion Chemistry Moves toward the Future: From Solids and Solutions to Surfaces by Walter G. Klemperer *Chem. Rev.* 98,297 (1998)

11. Use of different heteropolyacids for oxidation of alcohols using molecular oxygen has been demonstrated by T. Mallat, *Chem. Rev.*, 104, 3037 (2004)
12. Chemical immobilization of heteropolyacid catalyst on inorganic mesoporous material for use as an oxidation catalyst by In Kyu Song *Catal Surv Asia*., 11,114 (2007)
13. Recent applications of heteropolyacids and related compounds in heterocycles synthesis by Romanelli, Gustavo P.; Autino, Juan C. *Mini-Reviews in Org Chem*., 6, 359 (2009)
14. Catalytic evaluation of different organic substrates over supported polyoxometalates has been studied by Y. Ren, B. Yue, M. Gu and H He, *Materials*, 3, 764, (2010)
15. Progress of the application of mesoporous silica-supported heteropolyacids in heterogeneous catalysis and preparation of nanostructured metal oxides by Y. Ren, B. Yue. *Materials* 3, 764(2010)
16. Recent developments in dehydration of glycerol toward acrolein over heteropolyacids by Ingvild J. Haug. *Eur. J. Lipid Sci. Technol*. 114, 10 (2012)

Apart from these number of patents are also available; describing HPAs based compounds in the field of catalysis.

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. Oxidation of methanol and /or dimethyl ether using supported molybdenum containing heteropolyacid catalysts by Liu et al., US Patent No 6956134 B2, (2005)
8. 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)
9. Process for alkylation of phenol by N. Bhatt et al., US Patent No. 7692047 B2, (2009)
10. Process for production of alkenes from oxygenases by using supported heteropolyacid catalysts by Gracey et al., US Application No. 2010/0292520A1, (2010)
11. Method for producing phenolphthalein suing heteropolyacid catalyst by Bolta et al., US Patent No 7868190 B2, (2011)

A literature survey also shows that there are number of articles available on catalytic aspects of heteropolyacids supported on to different supports, such as silica [23, 24, 33-41], titania [34,37,41], alumina [34, 42,43], carbon [37, 44-51], mesoporous silica [52-56], acidic ion exchange resins [57-58] and clays [59-61].

Supported HPAs have been used in variety of organic transformations such as acylation, akylation esterification, isomerization, oxidation and hydrogenation. Enormous studies have been carried out on supported HPAs by different groups. **As the present thesis focuses on acid catalysis, we would like to restrict ourselves for the same only.**

A. Corma and coworkers reported acylation reactions using α, β- unsaturated organic acids as acylating agents [62], continuous alkylation of isobutane with 2-butene [63], acylation of anisole [64] over supported $H_3PW_{12}O_{40}$.

Ivan Kozhevnikov and his group have reported esterification of 2, 6-pyridinedicarboxylic acid with n-butanol catalyzed by $H_3PW_{12}O_{40}$ or its Ce(III) salt [65], hydration and acetoxylation of dihydromyrcene [66], ter-butylation of phenols [67] over silica supported $H_3PW_{12}O_{40}$. They have also reported esterification of camphene [68], Isomerization of styrene oxide to phenylacetaldehyde [69], valorization of the essential oils over silica supported $H_3PW_{12}O_{40}$ [70]. Recently they have reported acidic and catalytic properties of heteropolyacids supported on SiO_2, TiO_2, Nb_2O_5, ZrO_2[71], isomerization of α-pinene and longifolene [72,73] and liquid-phase esterification and transesterification over heteropolyacids supported on SiO_2, TiO_2, Nb_2O_5, ZrO_2 [74] also dehydration of glycerol to acrolein over caesium heteropoly salt [75].

The majority of Misono's work reports use of HPAs as homogeneous catalysts. As in the present discussion we have restricted ourselves to supported catalysts, the reports on supported HPAs has been only included. Misono and co-workers have reported the acid catalyzed reaction using heteropolyacids [76, 77]. They have also reported green aspects of heteropolyacids in acid catalyzed reactions [78] and applications of supported heteropolyacids as solid acid to industrial processes [79].

In India, some groups are also working on heteropolyacids:

G. D. Yadav and his group has carried out various reactions such as selective Claisen rearrangement of allyl-2,4-di-tert-butylphenyl ether to 6-allyl-2,4-ditert butylphenol over $H_3PW_{12}O_{40}$ supported on hexagonal mesoporous silica [80], synthesis of acetoveratrone using $H_3PW_{12}O_{40}$ supported on hexagonal mesoporous silica [81], decomposition of cumene hydroperoxide into phenol and acetone by a novel cesium substituted $H_3PW_{12}O_{40}$ on clay [82], alkylation of aniline with methyl-tert-butyl ether (MTBE) and tert-butanol over solid $H_3PW_{12}O_{40}$ [83], Friedel–Crafts benzoylation of p-xylene over cesium substituted $H_3PW_{12}O_{40}$ on K-10 clay [84], selectivity engineering in isopropylation of benzene to cumene over cesium substituted $H_3PW_{12}O_{40}$ on K-10 clay [85], synthesis of methyl phenyl glyoxylate via clean oxidation of methyl mandelate over a nanocatalyst based on $H_3PW_{12}O_{40}$ supported on clay [86], synthesis of hydroquinone monomethyl ether from hydroquinone and methanol over $H_3PW_{12}O_{40}$ supported on clay [87] and selectivity engineering of 2,6-Diisopropylphenol in isopropylation of phenol over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 clay [88] alkylation of xylene over 20% $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ /K-10 clay [89], dodecatungstophosphoric acid supported on acidic clay catalyst for disproportionation of ethylbenzene [90].

S. B. Halligudi and his group have carried out extensive study on the supported heteropolyacid 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 [91], benzylation of phenol with benzyl alcohol and alkylation of p-cresol with tert-butanol over $H_3PW_{12}O_{40}$ supported on titania [92, 93]. They have used $H_3PW_{12}O_{40,}$ [94-100], $H_3PMo_{12}O_{40}$ [101,102] and $H_4SiW_{12}O_{40}$ [103, 104] supported onto zirconia for different organic transformations. They have also reported titania supported silicotungsticacid for veratrole acylation [105] as well as liquid phase

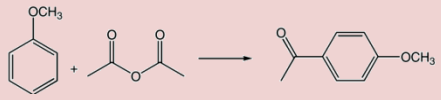
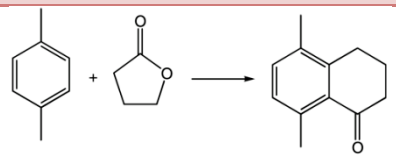
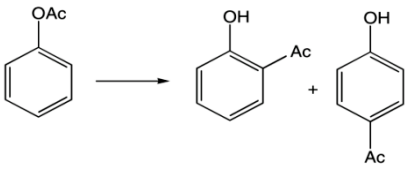
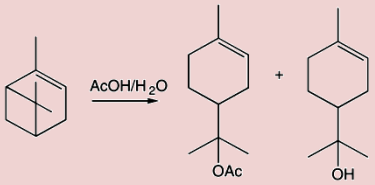
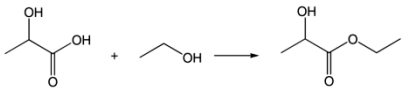
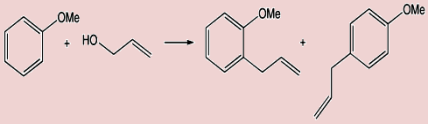
alkylation of 2-methylnaphthalene with long chain olefins over isopoly and heteropoly ions supported on zirconia and titania [106].

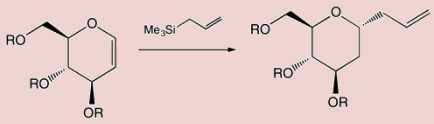
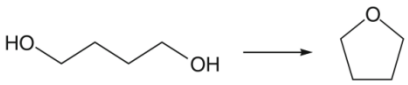
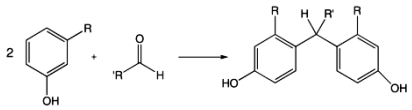
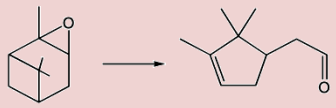
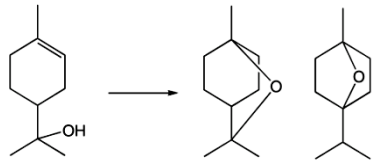
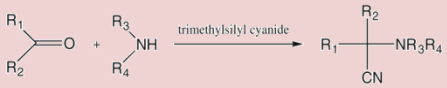
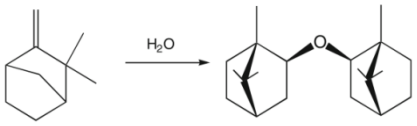
K. M. Parida and his group has carried out various reactions such as bromination of phenol using $H_3PW_{12}O_{40}$ supported on zirconia [107], over $H_3PW_{12}O_{40}$ impregnated titanium phosphate [108], $H_3PW_{12}O_{40}$ impregnated zirconium phosphate [109], $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ intercalated zinc aluminium hydrotalcite for bromination of phenol [110], $H_3PW_{12}O_{40}$ impregnated titanium phosphate for bromination of phenol[111] and various organic substrates $H_3PW_{12}O_{40}$ supported zirconia [112], selective nitration of phenol over $H_3SiW_{12}O_{40}$ supported zirconia [113], esterification of acetic acid using n-butanol over heteropoly acid intercalated Zn/Al HTlc [114]. They have also reported hydroxylation of phenol over molybdovanadophosphoric acid modified zirconia [115], acylation of anisole over 12-heteropolyacid of tungsten and molybdenum promoted zirconia [116].

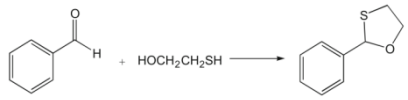
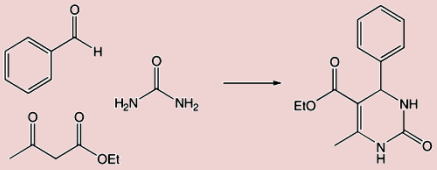
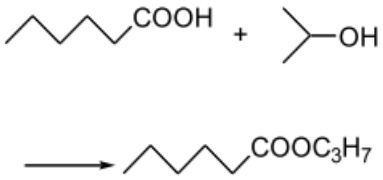
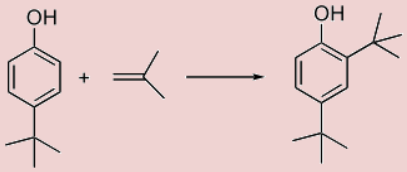
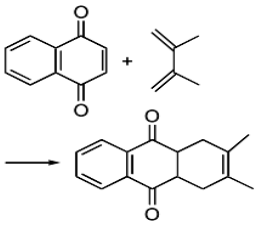
Our group has also significantly contributed in the field of supported heteropolyacids. Esterification of 1° and 2° alcohols, alkylation of phenols and cresols over $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ supported onto zirconia as well as neutral alumina have been reported by us [117-130]. Recently our group has reported new class of catalyst, supported lacunary polyoxometalates [131-133] for esterification as well as solvent free greener organic transformations.

Thus enormous studies have been carried out on supported HPAs. In addition to these, Table 4 summarizes recent studies on acid-catalyzed reactions over supported HPA catalysts [134-153].

Table 4 . Acid catalyzed reaction over Supported Heteropolyacids.

Reaction	Catalyst	Remarks	References
	$H_3PW_{12}O_{40}/SiO_2$	T = 363–383 K Y = 98% (para)	[134]
	$H_4SiW_{12}O_{40}/SiO_2$	T = 483 K S = 86%	[135]
	Pd-$H_4SiW_{12}O_{40}$ /SiO_2	T = 453 K S = 95%	[136]
	$H_3PW_{12}O_{40}/SiO_2$	T = 373–443 K S = 92–100%	[137]
	$H_3PW_{12}O_{40}/SiO_2$	T = 288–333 K S = 85%	[138]
	$H_3SiMo_{12}O_{40}$ /ion-exchange resin (Lewatit S100)	T = 343 K	[139]
	$H_3PW_{12}O_{40}/ZrO_2$	Calcined at 1023 K T = 413–473 K S [90%	[140]

Reaction	Catalyst	Remarks	References
	$H_3PMo_{12}O_{40}/SiO_2$	T = 298 K Y = 85–94%	[141]
	$H_4SiW_{12}O_{40}/TiO_2$	T = 503 K	[142]
	$H_3PMo_{12}O_{40}/SiO_2$	T = 298 K Y = 92–99%	[143]
	$H_3PW_{12}O_{40}/SiO_2$	T = 288 K S > 70%	[144]
	$H_3PW_{12}O_{40}$ /MCM-41	T = 373–383 K Y = 51–95%	[145]
	$H_3PW_{12}O_{40}$ /SiO_2	T = 333 K S = 60%	[146]
	$H_3PW_{12}O_{40}/SiO_2$	T = 298 K Y = 96%	[147]
	$H_3PW_{12}O_{40}/SiO_2$	T = 298 K S = 95%	[148]

Reaction	Catalyst	Remarks	References
	$H_3PW_{12}O_{40}/SiO_2$	T = 298 K Y > 99%	[149]
	$H_3PW_{12}O_{40}/SiO_2$	T = 353 K Y = 95%	[150]
	$H_3PW_{12}O_{40}/MCM\text{-}41$ $H_4SiW_{12}O_{40}/MCM\text{-}41$	Liquid phase reflux : 20 Wt% $H_3/MCM\text{-}41$ > β-zeolite	[151]
	$H_3PW_{12}O_{40}/MCM\text{-}41$	T= 343 K, S = 91%	[152]
	$H_3PW_{12}O_{40}/SiO_2$	T = 293 K , Y = 75 %	[153]

The world of catalysis by HPAs is largely expanded and it would be difficult to mention all references. We would also like to excuse us if some of the references are not there as it is quite difficult to summarize such a large number of available references for the same.

Thus a literature survey shows that a number of different supports have been used for supporting/anchoring the HPAs (Figure 7).

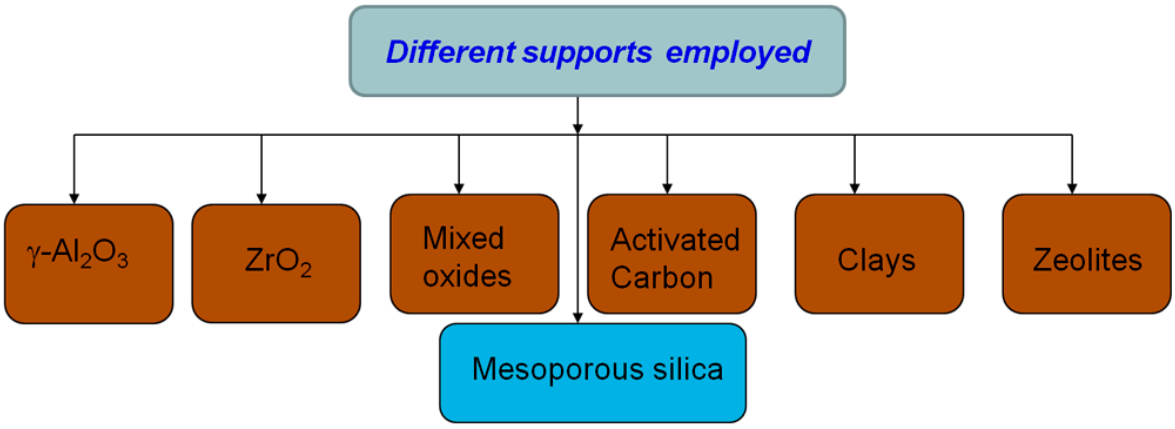
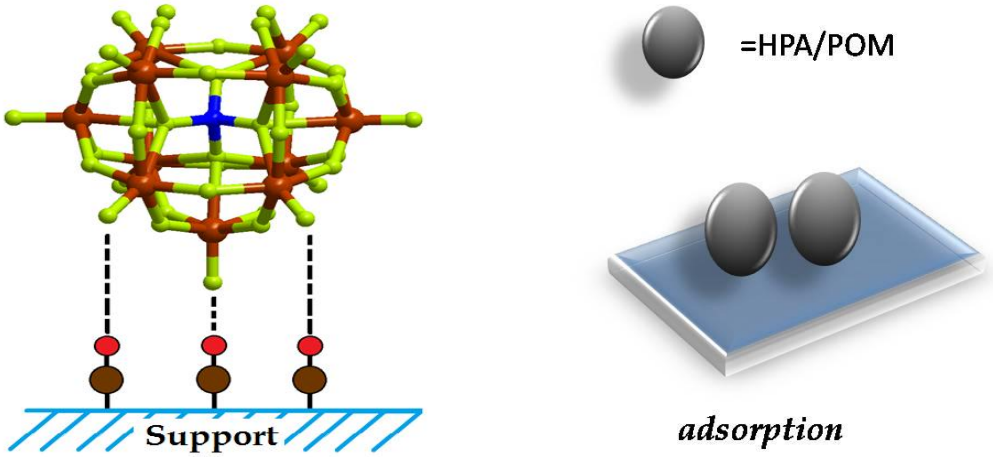


Figure 7. Use of different supports for supporting/anchoring

Depending on the nature of the support as well as method of supporting [154] the different interactions between HPAs and supports are expected as follows.

1. When the support is hydrous metal oxide/metal oxide, hydrogen bonding or adsorption type of interaction is possible (Figure 8)



(a) (b)

Figure 8. (a) Hydrogen bonding [155] (b) Adsorption type [reproduced from reference 156]

2. When the support is clay, intercalation is expected (figure 9)

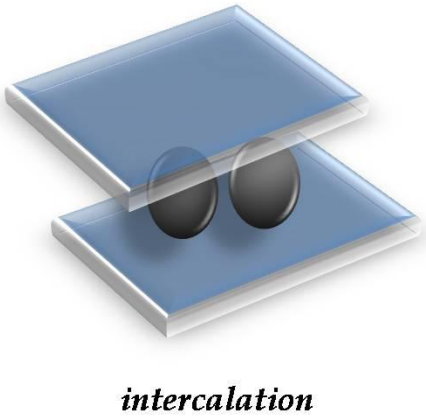


Figure 9. Intercalation of HPA in clay type of supports [reproduced from reference 156]

3. In case of mesoporous materials, encapsulation takes place. A strong hydrogen bonding type of interaction exists between the terminal oxygens of heteropolyanions and the silanol hydroxyl groups of mesoporous materials (figure 10)

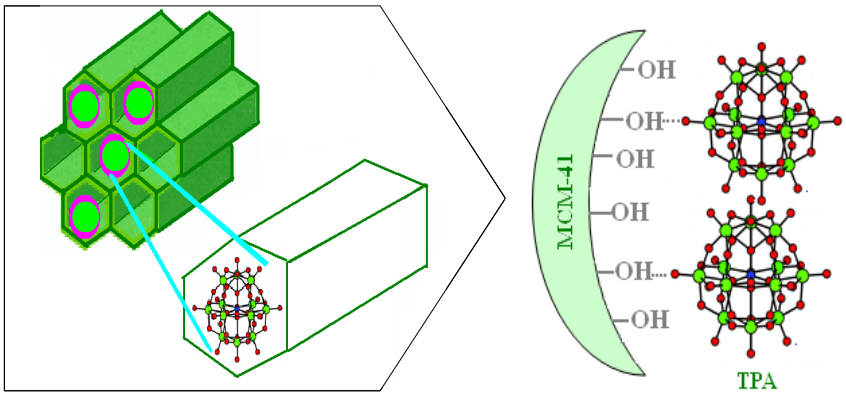


Figure 10. Probable interaction of heteropolyanions with the mesoporous support [157]

4. In addition, ion exchange and covalent bonding type of interactions are also possible (figure 11).

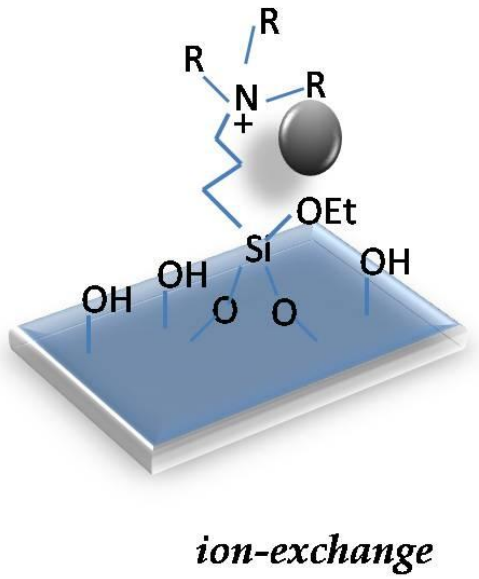


Figure 11. Ion exchange type of interaction for supported HPA catalysts [156]

S*upported Heteropolyacid can be advantageous for:*

- **Thermal stability is increased**
- **Surface area is increased**
- **They have high catalytic activity and selectivity**
- **Separation from a reactions mixture is easy**
- **Repeated use is possible**

Different methods of supporting/anchoring [154]

One of the important steps in designing of a catalyst is supporting of HPA 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. Pore filling/dry impregnation/incipient wetness.
4. Equilibrium adsorption/ion exchange/wet impregnation.

As impregnation, is 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. When several precursors are present simultaneously in the impregnating solution, the impregnation is called "co-impregnation". In the first step of impregnation, three processes occur:

— transport of solute to the pore system of the support bodies;
— diffusion of solute within the pore system; and
— uptake of solute by the pore wall.

In the case of wet impregnation, a fourth process is operative, *viz.* transport of solute to the outer particle surface. Depending on the process conditions, different profiles of the active phase over the support body will be obtained. For instance, depending on the pH, the interaction with the support can be strong or weak, and even repulsion can exist.

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 figure 12.

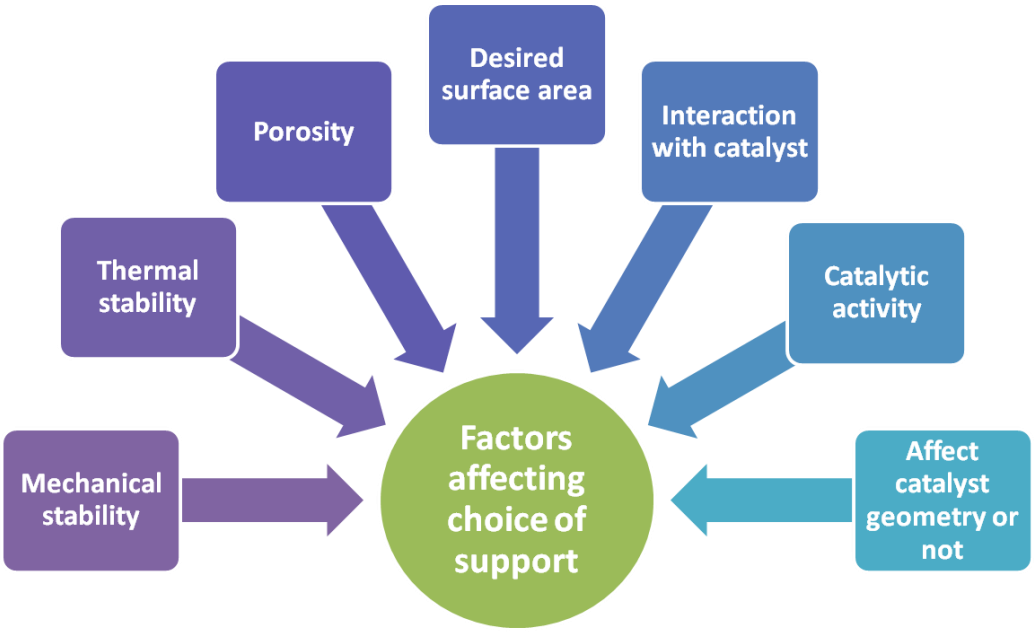


Figure 12. Block diagram showing factors affecting choice of support

Dispersing of HPAs on solid supports with high surface areas is important for catalytic application. In general, HPAs strongly interact with supports at low loading levels, while the bulk properties of HPAs prevail at high loading levels. Acidic or neutral substances such as SiO_2, active carbon, acidic ion exchange resin are suitable supports. Enhanced catalytic activity of HPAs 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 heteropolyanion and protons of the support.

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.

It is well known that basic support cannot be used for supporting HPAs, since it gets decomposed on the same. As mentioned when HPAs are supported onto acidic supports, strong interaction is expected between oxygens of HPAs and protons of the supports. **Keeping in mind these aspects, in the present thesis, mesoporous silica materials were chosen as supports.**

It is also known that support does not play always merely a mechanical role but it can also modify the catalytic properties of the HPAs. In order to see the effect of support, it was thought to use different supports with different pore pore size for anchoring heteropolyacids.

Why Mesoporous Silica materials?

- **Ordered porosity at the mesoscale.**
- **Variable pore size.**
- **High specific surface area.**
- **High adsorption capacity.**
- **High concentration of surface Si-OH groups.**
- **Their pore size and pore volume can be designed according to substrate molecules for particular applications**
- **High mass transfer efficiency**
- **Shape- selectivity (in reactions involving large organic molecules)**

⇒ IDEAL support for anchoring HPAs

In 1992, a new family of ordered mesoporous materials was reported [158, 159] and this became the starting point of a new research field. These materials are named MCM-X (Mobil Crystalline of Materials) and were synthesized by Mobile Corporation laboratories. Mesoporous silica with different pore structures were synthesized e.g. MCM-41 with hexagonally ordered cylindrical pores and MCM- 48 with a cubic pore structure (figure 13). These materials are synthesized with cationic surfactants under basic conditions.

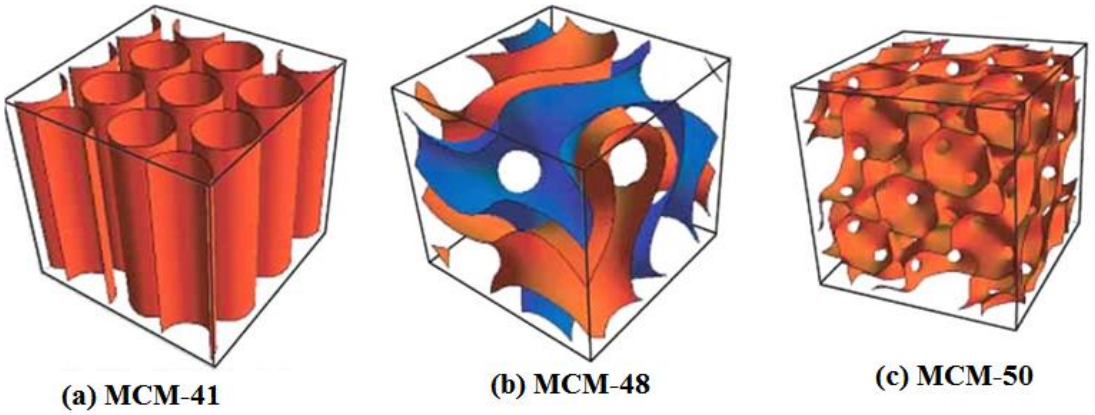


Figure 13. Structures of mesoporous M41S materials: a) MCM-41 b) MCM-48 C) MCM-50

This was though not the first attempt of synthesizing mesoporous silica. There is a patent from 1971 regarding synthesis of low-density silica where cationic surfactants were used [160]. In this patent there is no report concerning porosity, only the low bulk density was of importance. Later this material has been synthesized, characterized and compared to MCM-41 [161]. It is clear that this material is a predecessor to the mesoporous silica that is synthesized today, even though the importance of this type of material was not recognized then.

The first mesoporous silicas synthesized with non-ionic triblock polymers were reported in 1998 by Zhao et al. [162-163]. These materials are named SBA-X (Santa Barbara Amorphous) where X is a number corresponding to a specific pore structure and surfactant, e.g. SBA-15 has hexagonally ordered cylindrical pores synthesized with P123 as surfactant while SBA-16 has spherical pores arranged in a body centered cubic structure and is synthesized with F127.

Other families of mesoporous silicas are e.g. MSU [164], KIT [165], FDU [166] and AMS [167] where the materials are synthesized with variations in e.g. synthesis conditions and surfactants. The mesoporous material with various channels systems are summarized in table 5.

Table 5. Channel systems in different mesoporous materials

Material	Channel system	Mesophase	Space group
MCM-41, SBA-15, SBA-3	1D unbranched	Hexagonal	*P6mm*
MCM-48	3D branched	Cubic	*Ia3d*
SBA-1	Cagelike	Cubic	*Pm3n*
SBA-2	Cagelike	Hexagonal	*P63/mmc*
KIT-5	Cagelike	Cubic	*Fm3m*
SBA-16	Cagelike	Hexagonal	*Im3m*
MCM-50		Lamellar	*P2*

The structure and pore diameter of mesoporous materials can be altered by varying the surfactant/SiO_2 ratio [159]. It has been found that as the surfactant/silica molar ratio increased, the siliceous products obtained could be grouped into following categories [168] as shown in table 6.

Table 6. Effect of Sur/Si molar ratio

Category	Mesophase	Parameter (Sur/Si molar ratio)
MCM-41	Hexagonal	<1
MCM-48	Cubic	1-1.5
MCM-50	Lamellar	1-2.2

The pore diameter (2 to 10 nm) of MCM-41 materials can be controlled by three different methods:

(i) by varying the chain length of alkyl groups (8 to 22 C-atoms) of surfactants, [159,169]
(ii) by adding auxiliary chemicals (viz.1,3,5 trimethylbenzene) which dissolve in the hydrophobic region of the micelles, thus increasing their size.
(iii) by varying aging conditions [170] (viz. temperature and aging periods).

The pore diameter of MCM-41 also depends on other factors such as temperature, pH and crystallization time [171,172].

Synthetic and Mechanistic aspects of mesoporous silica

Ordered mesoporous silica materials are obtained by condensation of silica around organic micelles via a co-operative or true templating process [173,174]. Surfactant molecules such as alkyl ammonium cations, can form different types of micelles. At low concentrations they build spherical micelles while at higher concentrations extended micelles are formed. Lamellar, hexagonal, and cubic micellar phases are obtained depending on the temperature and surfactant concentration. The silica forms a rigid-wall structure around the surfactant micelles by condensation of silanol groups. The condensation of the silica is catalyzed either by a base or an acid. The organic micelles act as templates for the porous silica. After the formation of the silica walls, the surfactant molecules are removed to open the pore system of the silica. Most commonly, the organics are simply combusted at temperatures of about 400 to 600 °C. The resulting material has pores that are arranged in exactly the same manner as the parent micelles.

There have been a number of models proposed to explain the mechanism of formation of mesoporous materials [175, 176] and to provide rational basis for the various synthetic routes followed. All these models are proposed on the basis of surfactants or templates in solution guiding the structure which are as follows.

- **Liquid Crystal Templating Mechanism**
- **Silicate Rod Assembly**
- **Folded Sheet Mechanism**
- **Mechanism of Transformation from Lamellar to Hexagonal Phase**
- **Cooperative Formation Mechanism**

The advantage of using ordered mesoporous silica as supports in heterogeneous catalysis are the relatively large pores which facilitate mass transfer and the very high surface area which allows a high concentration of active sites per mass of material [177]. Further the amorphous pore walls give mesoporous silicas a great deal of flexibility in terms of their composition and pore channel structure and allow post-synthesis modifications which may be performed for pore size control framework stabilisation, compositional modifications or the formation of mesoporous/zeolite composite materials [178].

A literature survey shows that various mesoporous silica materials such as MCM-41 and SBA-15 have been used as supports. A literature survey also shows that they have been used for anchoring HPAs. However, in all the cases the mesoporous materials used, were synthesized by hydrothermal methods.

I . V Kozhevnikov et al. in the year 1994 reported for the first time, a new acid catalyst comprising heteropoly acid on a mesoporous molecular sieve MCM-41, and characterization by nitrogen physisorption, X-ray diffraction, FT-IR, and ^{31}P magic angle spinning NMR as well as catalytic activity for liquid-phase alkylation of 4-t-butylphenol (TBP) by isobutene and styrene [179-180]

Y. Sugi et al reported various catalysts comprising HPAs and mesoporous silica. HPAs, such as tungstophosphoricacid ($H_3PW_{12}O_{40}\cdot xH_2O$), molybdophosphoric acid ($H_3PMo_{12}O_{40}.xH_2O$) and tungstosilicic acid ($H_4SiW_{12}O_{40}.xH_2O$) were supported on 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 [181].

C.H. F. Peden et al studied the catalytic behaviour of tungstophosphoric acid supported on modified mesoporous silica materials for the dehydration of 2-butanol and methanol was studied. The supports evaluated here consisted of unmodified MCM-41 and SBA-15 mesoporous silicas, and these materials coated with sub-monolayer quantities of alumina, titania, and zirconia [**182].**

J. Wang et al have reported the heteropolyacids anchored on amino-functionalized MCM-41 via condensation as reusable catalysts for esterification. Amino-functionalized MCM-41 was synthesized via direct condensation, as well as post-grafting, using 3-aminopropyltrimethoxysilane as the functionalization agent. Keggin and Preyssler-structured heteropolyacids (HPAs) were anchored on the surface of amino-functionalized MCM-41 by chemically bonding to amino groups. HPAs directly supported on MCM-41 by impregnation were also prepared for comparison. They have also reported that MCM-41 supported HPA catalysts prepared by direct impregnating lose their catalytic activities rapidly due to the leaching of HPA active sites [183].

Z. Zhu and co-workers have 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 [184]**.** Recently M. Samy El-Shall et al reported acid catalyzed organic transformations such as Pechmann, esterification and Friedel–Craft acylation reactions over tungstophosphoric acid supported on MCM-41 [185].

J. Kim et al have reported direct synthesis, characterization and catalytic application of SBA-15 containing $H_3PW_{12}O_{40}$ for esterification reactions [186]. J. Ogonowski et al have reported liquid phase cyclization of pseudoionone into a-ionone over heteropolyacid supported on mesoporous silica SBA-15 [187]**.** J.A. Martens and co-workers have reported bifunctional conversion of n-decane over 12-tungstophosphoric acid incorporated into SBA-15 [188]. S. Qiu and co-workers have reported a series of catalysts, SiPW-X, mesoporous silica with Keggin type heteropolyacids encapsulated into their framework and their catalytic activity was evaluated in chemical reactions of both small (cumene cracking and esterification of ethanol with acetic acid) and bulky (1,3,5-triisopropylbenzene cracking and esterification of benzoic acid with tert-butanol) molecules [189].

M.V. Landau's group has reported cesium salt of 12-tungstophosphoric acid in nanotubular channels and on the external surface of SBA-15 crystals and its catalytic performance in MTBE synthesis, propionylation of anisole and alkylation of catechol with t-butanol [190]. Y. K. Shan and co-workers have reported 12-tungstophosphoric acid nanocrystals in SBA-15 and its catalytic activity in cyclodimerization of α-methylstyrene [191],

A. Popa et al have reported highly dispersed heteropolyacids supported on modified MCM-41. Solid acid catalysts consisting of heteropolyacids (HPAs) molybdophosphoric acid ($H_3PMo_{12}O_{40}{\cdot}xH_2O$) and 1-vanado-11-

molybdophosphoric ($H_4PVMo_{11}O_{40}.yH_2O$) supported on mesoporous pure-silica molecular sieve MCM-41 and modified molecular sieves Al-MCM-41 and Fe-MCM-41 have been prepared and characterized by XRD, FT-IR, ^{31}P MAS NMR, nitrogen adsorption and scanning electron microscopy [192]. Recently they have reported the influence of surface coverage on textural, structural and catalytic properties of cesium salts of 12-molybdophosphoric acid supported on SBA-15 mesoporous silica. The dehydration of ethanol was used to probe the catalytic activity of this catalyst [193].

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 supporting 12-tungstophosphoric acid. The catalysts were characterized using powder X-ray diffraction (XRD), FT-IR, BET and TEM. The catalytic activity of these materials were tested for the acetalization of carbonyl compounds with 2,2-bis(hydroxymethyl)propane-1,3-diol [194]. The same group has also reported the synthesis of a series of xanthenedione derivatives by condensation of various aromatic aldehydes using MCM-41-supported 12-tungstophosphoric acid [195].

Murugesan et al. [196-197] prepared a series of supported HPAs by impregnation of phosphotungstic acid on mesoporous aluminophosphate (AlPO), Al-MCM-41, and SBA-15. Their catalytic activities in t-butylation of phenol with tert-butanol. Halligudi et al. [198] reported the immobilization of $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 0–3) onto mesoporous silicas such as MCM-41, MCM-48, and SBA-15, through APTES (3-aminopropyltriethoxy silane) linkers. These heterogeneous catalysts were tested in the liquid-phase oxidation of anthracene with tert-butylhydroperoxide oxidant in benzene. They have also reported effect of pretreatment conditions on the catalytic activity of nano-sized tungstophosphoric acid/ZrO_2 dispersed in SBA-15 channels in acetylation reactions [200].

A. Vinu and co-worker reported 12-tungstophosphoric acid encapsulated SBA-15/TiO_2 nanocomposites and their use in various acid catalysed organic transformations such as hydroamination, Mannich reaction and Claisen rearrangement [201]. K.M. Parida's group have reported acylation of anisole over cesium salts of heteropoly acid immobilized on MCM-41 [202].They have also reported palladium based lacunary phosphotungstate supported mesoporous silica for hydrogenation of p-nitrophenol to p-aminophenol [203]. Recently supported HPAs have got tremendous interest in biodiesel production and the literature sited has been included in chapter 4.

However a literature survey shows that MCM-41 and SBA-15 were synthesized by hydrothermal procedures. Due to the known disadvantages of hydrothermal procedures, **developing a non-hydrothermal synthesis procedure for these materials as well as to use them as supports for anchoring HPAs will be interesting.**

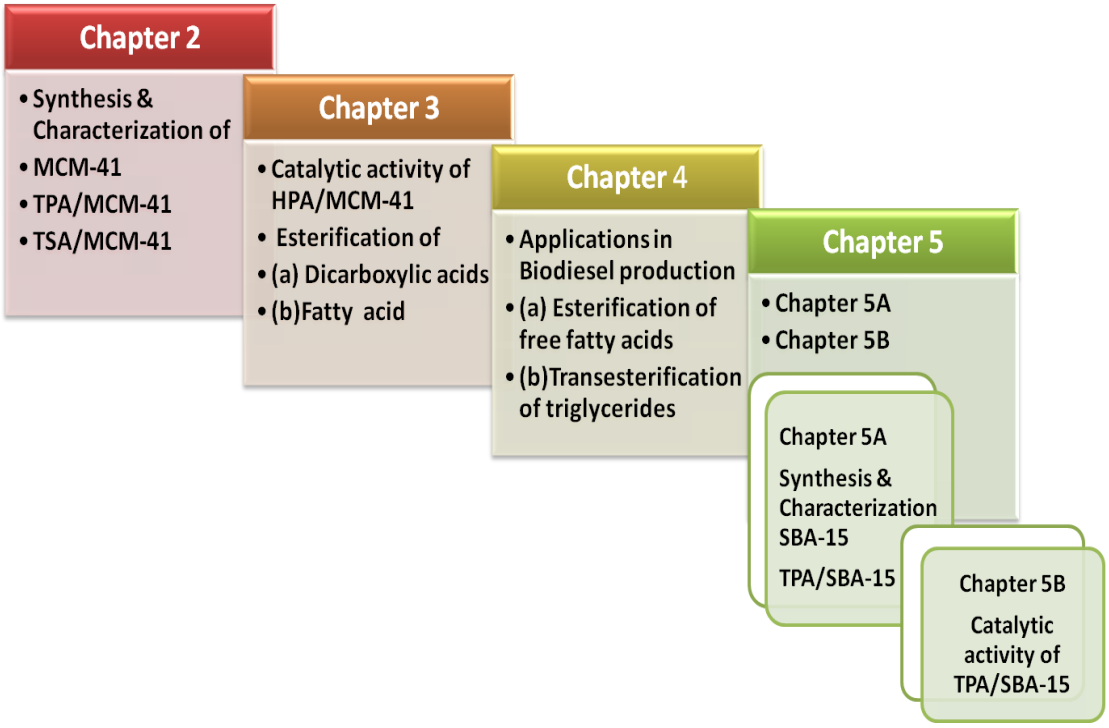
Scope of the Thesis

In present thesis, an attempt was made to use MCM-41 and SBA-15, synthesized by non-hydrothermal approach, as supports for anchoring heteropolyacids. Considering the importance of anchored heteropolyacids, as well as the need of future fuel, Biodiesel, it was thought of interest to develop an efficient heterogeneous acid catalysts comprising heteropolyacids and mesoporous silica. Thus based on the available literature as well as ensuring cleaner and more sustainable production methods using "Anchored Heteropolyacids" for sustainable society, the following work has been planned.

Objectives of the work

1) To develop a non- hydrothermal approach for synthesis of mesoporous silica materials, MCM-41 and SBA-15.
2) To develop heterogeneous catalysts with high surface area as well as high dispersion, by anchoring different heteropolyacids (12-tungstophosphoricacid and 12-tungstosilicicacid) to MCM-41 and SBA-15.
3) To characterize all synthesized supports as well as catalysts.
4) To establish the use of synthesized catalysts as environmentally benign eco-friendly catalysts for acid catalyzed reactions such as esterification and transesterification.
5) To explore the use of synthesized catalyst for Biodiesel production by esterification of free fatty acids such as palmitic acid and oleic acid with methanol.
6) To study the reaction kinetics of esterification of free fatty acid and determination of kinetic parameters such as order of reaction and activation energies.
7) To establish the use of synthesized catalysts as an environmentally benign for Biodiesel production by transesterification of triglycerides feedstock such as waste cooking oil and Jatropha oil.
8) To study the regeneration and recycling of the catalysts.
9) To study the effect different heteropolyacids on the catalytic activity.
10) To study the effect of support (MCM-41) pore diameter expansion on catalytic activity.
11) To study the effect of nature of support on the catalytic activity.
12) To screen the best catalyst for esterification of dicarboxylic acids and free fatty acids as well as their applications in biodiesel production.

The work has been carried out to complete the set objectives which are presented in the following four chapters.



Chapter 2 describes synthesis and characterization of support, MCM-41. Two series of catalyst containing different loadings of 12-tungstophosphoric acid (TPA) and 12-tungstosilisic acid (TSA) anchored to MCM-41 were synthesized by dry impregnation method. The support and the catalysts were characterized by different physico-chemical techniques. Based on the characterization studies probable interaction between TPA/TSA and MCM-41 was proposed.

Chapter 3 consists of catalytic activity of all the synthesized catalysts towards esterification of dicarboxylic acids such as succinic acid and malonic acid. Also esterification of long chain carboxylic acids, lauric acid with butanol was studied. Effect of different reaction parameters such as mole ratio, amount of the catalyst and reaction time were studies to optimize the conditions for obtaining maximum yields for esters. A study on the kinetic behavior was also carried out and the various kinetics parameters such as order of reaction, rate constant as well as activation energy was determined.

The chapter 4 is divided in to two part, (a) and (b)
Chapter 4 (a): Biodiesel production by esterification of free fatty acids
Chapter 4 (b): Biodiesel production by transesterification of triglycerides.

A study on the kinetic behavior for estreification of free fatty acids was also carried out. Further study on comparison of catalytic activity of TPA/MCM-41 and TSA/MCM-41 was carried out. Based on the catalytic study the best catalyst was also proposed. To study the effect of support pore diameter, catalytic activity of TPA anchored to MCM-41 and to pore-expanded MCM-41, was compared.

Chapter 5 was divided into two parts, A and B.
Chapter 5A consists of synthesis and characterization of support, SBA-15 as well as catalyst, TPA anchored to SBA-15.

In chapter 5B catalytic activity of TPA/SBA-15 was evaluated for esterification of dicarboxylic acids, succinic acid and malonic acid. Also esterification of lauric acid with butanol was studied. Effect of different reaction parameters were studied to optimize the conditions including the kinetic studies. As an application, catalytic activity of TPA/SBA-15 was explored for biodiesel production by esterification of free fatty acids such as palmitic acid and oleic acid and transesterification of triglycerides.

Finally, a comparison was also made between TPA/MCM-41 and TPA/SBA-15, and based on the catalytic studies the best catalyst was proposed.

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