General Introduction

Although, traditionally almost all the chemical reactions were catalyzed by homogeneous catalysts, the enforcement of stringent environmental regulations has forced the replacement of these environmentally hazardous materials by heterogeneous catalysts. Replacement of technologies based on homogeneous catalysts with heterogeneous ones is intrinsically more likely to lead to important technical improvements in terms of catalyst design as well as recycling, process simplification and milder or more sustainable reaction conditions. Thus in last two decades, heterogeneous catalysis has gained so much attention and becoming more and more popular in chemical, petrochemical, and life science industries. Among all, as the growth of industrial heterogeneous catalysts continues to accelerate, the role of researchers in the field of basic and applied catalysis is in demand.

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

- Catalysts can often be 'tailored' for specific feedstock or for selective product synthesis.
- Kinetically and thermodynamically difficult reactions can proceed with wide range of temperatures even in gas phase.

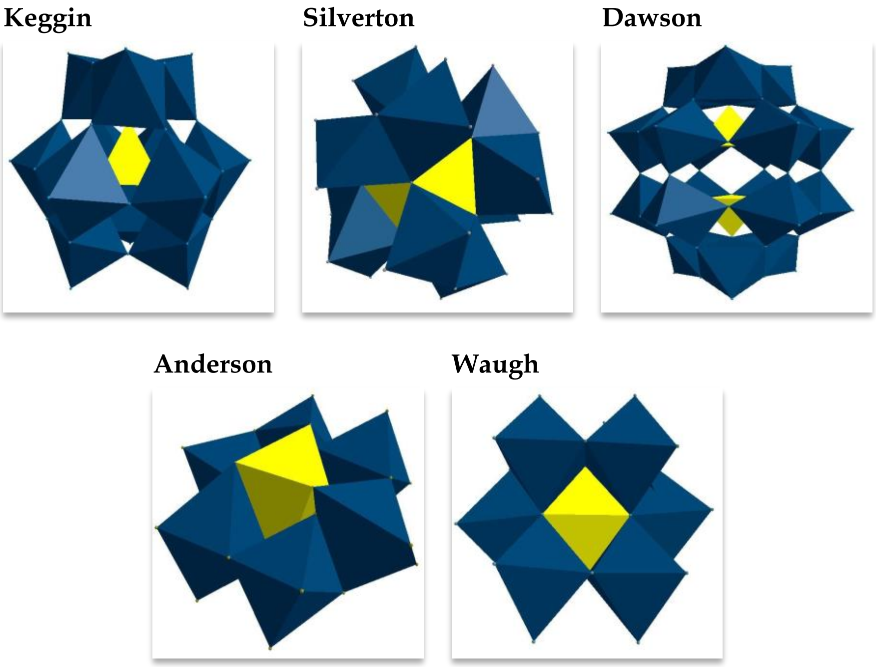
In this regard, catalysis by ***'Anchored Polyoxometalates'*** **has become a very important field of research and** most successful area in industry as well as in fundamental catalysis [1-3]. Also, the ability to tune the acidic properties of the polyoxometalates for the probe reaction makes these species the most useful in the acid catalysed transformations. Hence, a new trend towards the application of these remarkable species in materials science and in *Catalysis* is beginning to develop.

What are Polyoxometalates?

Polyoxometalates (POMs) 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 [4-7].

POMs are a rich class of inorganic metal-oxide cluster compounds with transition metals in their highest oxidation state and have general formula $[X_xM_mO_y]^{n-}$, 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^{V}, Mo^{VI} or W^{VI} [8]. These compounds are always negatively charged, although the negative charge density is widely variable depending on the elemental composition and the molecular structure.

With the development of POMs chemistry various types of structures were discovered. Polyhedral representations of various types of POMs are presented in Figure 1. Among different POMs, Keggin type POMs are investigated extensively because of their easy synthesis as well as high stability [8].



Keggin Silverton Dawson

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Figure 1. Polyhedral representation of different types of POMs.

The general formula for the 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}. These compounds are always negatively charged although the negative density is widely variable depending on the elemental composition and the molecular structure.

POMs are polymeric oxoanions 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

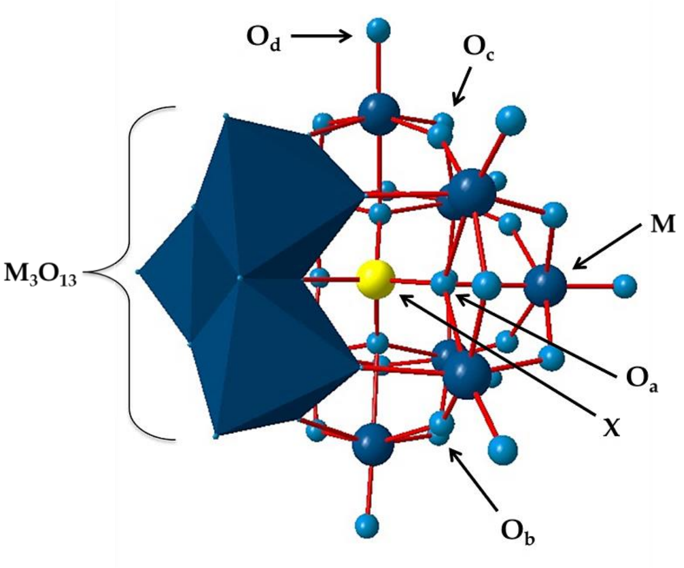


Figure 2. Structural representation of Keggin type $[XM_{12}O_{40}]$.

The ideal Keggin structure, $[XM_{12}O_{40}]^{3-}$ of α-type has *Td* 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} triplets [9-10], 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 POM is shown in Figure 2.

An extensive literature on their synthesis and structure has been accumulated and summarized in the form of reviews as well as books namely:

1. M. T. Pope, "Heteropoly and Isopoly Oxometalates" (Eds.) C. K. Jorgensen, Springer-Verlag, Berlin (1983).
2. Issue on Polyoxometalates, Edited by C. L. Hill, Chem. Rev., 98, 1, (1998).
3. J. B. Moffat, "Metal-oxygen clusters: The surface and catalytic properties of heteropolyoxometalates", (Eds.) M. V. Twing, M. S. Spencer, Kluwer Academic plenum, New York, (2001).
4. M. T. Pope and A. Muller, "Polyoxometalate chemistry: From topology via self-assembly to applications" Kluwer Academic, (2001).
5. I. V. Kozhevnikov, Catalysts for Fine Chemical Synthesis, Catalysis by Polyoxometalates (Volume 2), Wiley (2002).
6. M. T. Pope, A. Muller, "Polyoxometalate Molecular Science", Kluwer Academic Publishers, (2003).
7. R. Neumann, Book Review: Catalysis by Polyoxometalates, (Eds.) I.V. Kozhevnikov, Angew Chem, 42, 3577, (2003).
8. C.L. Hill, Polyoxometalates: Reactivity Comprehensive Coordination Chemistry II, 4, 679, (2003).
9. C. Hu, D. Li, Polyoxometalate complexes of layered double hydroxides, Interface Science and Technology, 1, 374, (2004).
10. Z. Peng, Synthesis of Main-Chain Polyoxometalate-Containing Hybrid Polymers and Their Applications in Photovoltaic Cells, Chem. Mater., 17 (2), 402, (2005).
11. P. Gouzerh, M. Che, From Scheele and Berzelius to Müller: polyoxometalates (POMs) revisited and the "missing link" between the bottom up and top down approaches, L'Actualité Chimique, 298, 9, (2006).
12. D-L Long, E. Burkholder, L. Cronin, Polyoxometalate clusters, nanostructures and materials: From self-assembly to designer materials and devices, Chem. Soc. Rev., 36, 105, (2007).

13. N. Mizuno, Activation of Hydrogen Peroxide by Polyoxometalates, in Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis, (EDs.) S. Ted Oyama, 155 (2008).
14. A. Müller, Polyoxometalate Chemistry from Topology via Self-Assembly to Applications, Springer (2010).
15. A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, Hybrid Organic-Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications, Chem. Rev., 110 (10), 6009, (2010).
16. Polyoxometalates containing late transition and noble metal atoms, P. Putaj, F. Lefebvre, Coord. Chem. Rev., 255, 1642, (2011).
17. Theme issue: Polyoxometalate cluster science, Edited by L. Cronin, A. Muller, Chem. Soc. Rev., 41, 7325, (2012).
18. Theme issue: Polyoxometalates, Edited by D-L Long and L. Cronin, Dalton Trans., 41, 9799, (2012).
19. F. Secheresse, Polyoxometalate Chemistry: Some Recent Trends, World Scientific Publishing Company (2013).
20. Special Issue: Polyoxometalates (Cluster Issue), Edited by U. Kortz, T. Liu, Eur. J. Inorg. Chem., Eds. 10-11, 1556, (2013).
21. "Environmentally benign catalysts for clean organic reactions", Edited by A. Patel, Springer, Dordrecht (2013).
22. H. N. Miras, L. Vila-Nadal, L. Cronin, Polyoxometalate based open-frameworks (POM-OFs), Chem. Soc. Rev., 43, 5679, (2014).
23. L. Ruhlmann and D. Schaming, Trends in Polyoxometalates Research, Nova Science Publishers, (2015).
24. A. Patel, S. Pathan, "Polyoxomolybdates as Green Catalysts for Aerobic Oxidation" in Springer Briefs in Molecular Science-Green Chemistry for Sustainability Springer, Dordrecht (2015).

Applications of POMs

Since the discovery of POMs, they found significant importance in various fields of science and technology, and they have large domains of applications [11-25]. 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 systematic investigation of catalysis using POMs began in 1970's.

Some of the major achievements of POM based compounds in the field of catalysis have been reviewed by number of groups.

1. Polyoxomolybdates with Palladium salts were used for oxidation of alkenes and alcohols was studied by K. I. Matveev, Kinet. Katal., 18 , 862, (1977).
2. Catalysis of heteropoly acids entrapped in activated carbon was demonstrated by Y. Izumi, K. Urabe, Chem. Lett., 663, (1981).
3. The application of POMs as catalysts of oxidation and acid-type reactions and understanding of the mechanism of their catalytic action were examined by I. V. Kozhevnikov, K. I. Matveev, Russ. Chem. Rev., 51, 1075, (1982).
4. Skeletal isomerization of n-butane catalyzed by an acidic cesium salt of 12-tungstophosphoric acid was studied by Y. Izumi, R. Hasebe, K. Urabe, J. Catal., 84, 402, (1983).
5. A homogeneous catalytic functionalization of alkanes by polyoxometalates was studied by R. F. Renneke, C. L. Hill, J. Am. Chem. Soc., 108 (12), 3528, (1986).

6. Oxidation of alkynes catalyzed by molybdenum(VI) and tungsten(VI) polyoxometalates was carried out by F. P. Ballistreri, S. Failla, E. Spina, G. A. Tomaselli, J. Org. Chem., 54 (4), 947, (1989).
7. Recent progress in catalytic technology in japan by M. Misono, N. Nojiri, Appl. Catal., 64, 1, (1990).
8. Selective Homogeneous Catalytic Epoxidation of Alkenes by Hydrogen Peroxide Catalysed by Oxidatively- and Solvolytically-resistant Polyoxometalate Complexes by A. M. Khenkin, C. L. Hill, Mendeleev Commun., 3, 140, (1993).
9. Use of heteropolyacid compounds in acid catalyzed hydrocarbon reactions by A. Corma, Chem. Rev., 559, (1995).
10. The catalytic properties of heteropoly compounds have been studied and reviewed by T. Okuhara, N. Mizuno, M. Misono, Adv. Catal., 41, 113, (1996).
11. 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., 171, (1998).
12. Structural and catalytic properties of POMs have also been studied and reviewed by N. Mizuno and M. Misono, Chem. Rev., 199, (1998).
13. Heteropoly acids immobilized into a silica matrix: Characterization and catalytic applications by A. Molnar, C. Keresszegi, B. Torok, Appl. Catal. A: Gen., 189, 217, (1999).
14. Surface modification of mesoporous macroporous and amorphous silica with catalytically active polyoxometalate clusters was done by B. J. S. Johnson, A. Stein, Inorg. Chem., 40, 801, (2001).
15. “Catalysts for fine chemical synthesis: Catalysis by polyoxometalates”, I. V. Kozhevnikov, Vol. 2, Wiley (2002).

16. Use of different POMs for oxidation of alcohols using molecular oxygen has been demonstrated by T. Mallat, Chem. Rev., 104, 3037, (2004).
17. “Green chemistry and catalysis”, by R. A. Sheldon, Ch. 2 Solid acids and bases as catalysts, Wiley (2007).
18. "Mechanisms in homogeneous and heterogeneous epoxidation catalysis", (Eds) S. T. Oyama, Ch. 4 "Activation of hydrogen peroxide by polyoxometalates" , N. Mizuno, Elsevier Publications, (2008)
19. “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).
20. Catalytic evaluation of different organic substrates over anchored polyoxometalates has been studied by Y. Ren, B. Yue, M. Gu, H He, Materials, 3, 764, (2010).
21. A Review on MIL-101 encapsulated Polyoxometalates: Synthesis, Characterization, and Catalytic Applications in Selective Liquid-Phase Oxidation by N. Maksimchuk, O. Kholdeeva, K. Kovalenko, V. Fedin, Isr. J. Chem., 51, 281, (2011).
22. Recent advances on polyoxometalate-based molecular and composite materials by Y-F Song, R. Tsunashima, Chem. Soc. Rev., 41, 7384, (2012).
23. Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications, Edited by M. G. Clerici, O. A. Kholdeeva, John Wiley & Sons (2013).
24. Environmentally benign catalysts for cleaner organic reactions, Edited by A. Patel, Springer (2013).
25. Keggin Structure Polyoxometalates, Inorganic Synthesis Volume: 36, by J. A Dias, S. C. L. Dias, E. Caliman, J Bartis, L. Francesconi, Wiley (2014).
26. Recent progress on supported polyoxometalates for biodiesel synthesis, by A. Patel, Green Chem., 17, 89 (2015).

27. "Polyoxomolybdates as green catalysts for aerobic oxidation", A. Patel and S. Pathan, Series: Springer Briefs in Molecular Science, Green Chemistry for Sustainability, Springer Inc., New York, (2015**).**

Apart from these, a number of patents describing use of POMs based compounds in catalysis are also available however, only important ones are included.

1. Method of preparing heteropolyacid catalysts by Lyons et al, US 4916101, (1990).
2. Use of anchored POMs for one step production of alkylphenol from olefins under adiabatic conditions by J. F. Knifton, US 5300703, (1994).
3. Alkylation of isoparaffins with olefins to produce alkylates using heteropolyacids supported onto MCM-41 by Kresge et al., US 5324881, (1994).
4. Zirconium hydroxide supported metal and heteropolyacid catalysts by Soled et al., US 5391532, (1995).
5. Heteropolyacid supported onto sulfated zirconia as heterogeneous catalyst for alkylation of isoparaffins by Angstadt et al., US 5493067, (1996).
6. Alkylation of aromatic amines using heteropolyacid catalyst by Rhubright et al., US 5817831, (1998).
7. Conversion of alkanes to unsaturated carboxylic acids over heteropoly acids supported on polyoxometalate salts by Lyons et al., US 5990348, (1999).
8. Polyoxometalate supported catalysis by Devlin et al., EP1078687, (2001).
9. Method for preparing heteropolyacid catalyst and method for producing methacrylic acid by Kasuga et al., US 6458740, (2002).
10. Polyoxometalate catalysts and catalytic processes by Davis et al., US 6914029 B2, (2005).

11. Oxidation of methanol and/or dimethyl ether using supported molybdenum containing heteropolyacid catalysts by Liu et al., US 6956134 B2, (2005).
12. Supported polyoxometalates, process for their preparation and use in oxidation of alkanes by Richards et al., WO2007142727 A1, (2007).
13. Silica support, heteropolyacid catalyst produced there from and ester synthesis using the silica supported heteropolyacid catalyst by Bailey et al., US 2008/004466 A1, (2008).
14. Process for alkylation of phenol by A. Patel et al., US 7692047 B2, (2009).
15. Process for production of alkenes from oxygenases by using supported heteropolyacid catalysts by Gracey et al., US 0292520A1, (2010).
16. Method for the breakdown of lignin by Voitl et al., US 7906687 (2011).
17. Process for oxidizing alkyl-aromatic compounds by Jaensch et al., US 7906686 B2 (2011).
18. Process for preparing an alkene by Partington et al., US 0302810 A1 (2012).
19. Process for water oxidation comprising the use of a polyoxometalate compound as water oxidation catalyst by Galan et al., WO2013057079 A1, (2013).
20. Heteropoly acid promoted catalyst for SCR of NOx with ammonia by Putluru et al., US 8685354 (2014).
21. Polyoxometalate water oxidation catalysts and methods of use thereof by Hill et al., US 8822367 (2014).
22. Preparation of aldehydes and ketones from alkenes using polyoxometalate catalysts and nitrogen oxides by R. Neumann et al., WO2015132780 A1, (2015).

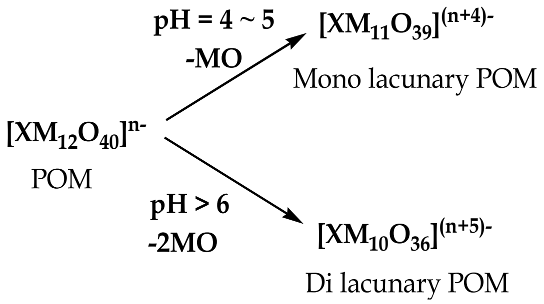
A careful investigation of the literature shows that a lot of work has been reported on catalytic aspect of phosphotungstates; however studies on silicotungstates are comparatively less. Hence silicotungstates have been chosen for the present work.

As discussed earlier, 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 [26-28]. 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. Due to the structural diversity as well as the unique electronic properties [1, 29], they are of potential importance.

The modification of properties can be basically done by tuning the structural properties at the atomic or molecular level. One of the ways to modify the structural properties is by creating defect in the parent POMs leading to the formation of lacunary 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 [1-3]. 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 [2].



Scheme 1. Formation of LPOMs.

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 4-7), a series of hydrolysis reactions occurs leading to the formation of mono and di lacunary POMs (Scheme 1).

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 [30, 7].

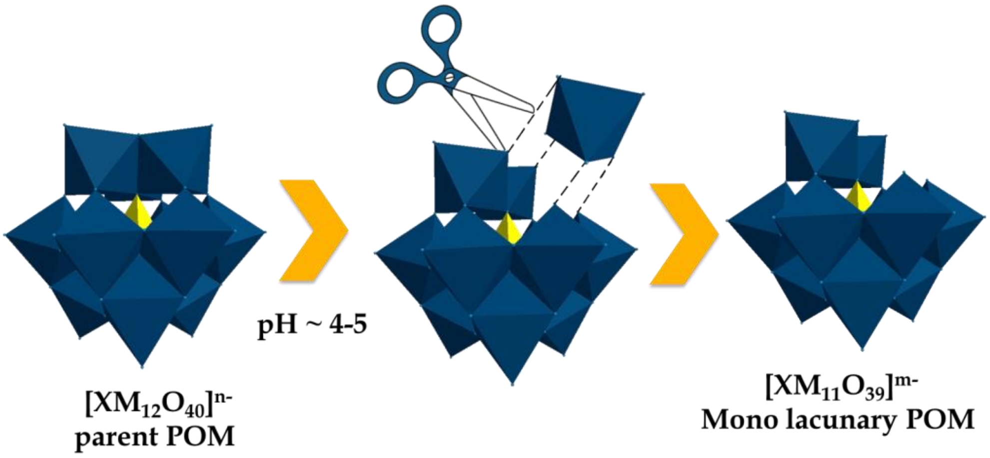


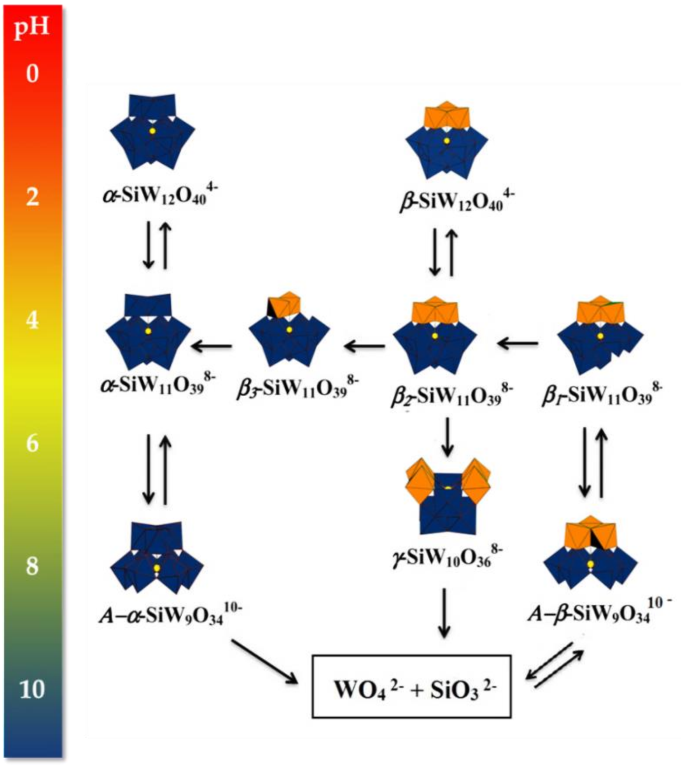
Figure 3. Formation of Mono LPOMs.

Among mono, di or tri lacunary POMs, the mono lacunary POMs forms the most versatile class of LPOMs. As mentioned earlier, the removal of one MO at suitable pH from parent POMs leads to the formation of mono LPOMs (Figure 3).

It was found from the literature survey that among LPOMs, lacunary silicotungstates are most studied, especially dilacunary silicotungstate [31-55], because of the high stability of the fragmented lacunary species [41-42,47].

Further, the reports on monolacunary silicotungstates are very scanty [56-60]. Hence, monolacunary silicotungstate (SiW_{11}) has been selected for the present work.

The pH dependent formation of lacunary silicotungstates from parent species has been shown in Scheme 2. Four monolacunary, one dilacunary and two trilacunary silicotungstates are known.



Scheme 2. pH dependent formation of lacunary silicotungstate.

The first report on synthesis of mono lacunary silicotungstates was reported by Marignac in 1864 [61]. In 1972, Souychay et al. showed the inter-conversion of α-$SiW_{11}O_{39}^{8-}$ species into α-$SiW_{12}O_{40}^{4-}$ [62]. Later in 1976, Matsumoto et al. reported the first crystal structure analysis of $K_8SiW_{11}O_{39}$ species [63]. Herve and Teze in 1977 reported synthesis and polarographic as well as spectroscopic measurements on the monolacunary β2- $SiW_{11}O_{39}^{8-}$ [64]. Later in 1986 they reported synthesis and structural characterization of the γ-$SiW_{10}O_{36}$, dilacunary silicotungstate [65]. In 1990, structural co-relation between different isomers (i.e. α, β and γ) of $[SiW_{10}O_{36}]^{8-}$ as a function of pH was also reported by the same group [66].

Large numbers of reports on homogeneous catalysis using dilacunary silicotungstates are available in the literature. The main contribution was from Mizuno's group [38-55]. The acid–base properties of a series of dilacunary γ-$SiW_{10}O_{36}$ derivatives [44] were also investigated by them in order to study the catalytic performances for acid- or/and base-catalyzed C–C bond formation reactions (Mukaiyama-Aldol condensation, Diels–Alder reaction, Knovenagel reaction, and cyanosilylation of ketones).

Ren et al. described highly efficient utilization of H_2O_2 for oxygenation of organic sulfides catalyzed by γ-$SiW_{10}O_{36}$ [67]. Bonchio and co-workers reported catalytic application of hybrid α-$SiW_{11}O_{39}$, γ- $SiW_{10}O_{36}$ and α-SiW_9O_{34} for microwave assisted epoxidation of cyclooctene with H_2O_2 [68]. One year later they have reported how asymmetric tetraprotonation of γ-$SiW_{10}O_{36}$ triggers a catalytic epoxidation of cyclooctene [69]. Kortz and his group reported the reactivity of γ-$SiW_{10}O_{36}$ with the effect of electrophiles resulting loss/gain of tungsten, isomerization, and dimerization [70]. B. Ma et al. reported a new reaction-controlled phase-transfer catalyst based on γ-$SiW_{10}O_{36}$ for oxidation of hydrocarbons with >99% selectivity to epoxides [71]. 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 non-porous supports and inside the channels for porous supports 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 are retained and at the same time the advantages of heterogeneous catalyst is also obtained.

The anchored POMs 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 [72]

One of the important steps in designing of 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 follows,

1. Co-precipitation.
2. Deposition precipitation.
3. Pore filling/dry impregnation/incipient wetness.
4. Equilibrium adsorption/ion exchange/wet impregnation.

We are focusing mainly on the impregnation method as it is the most accepted one for the preparation of studied class of catalysts.

Impregnation method

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, following processes generally occur:

- ✓ Transport of solute to the pore system of the support bodies;
- ✓ Diffusion of solute within the pore system;
- ✓ Uptake of solute by the pore wall.

In the case of wet impregnation, a next 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.

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.

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 4.

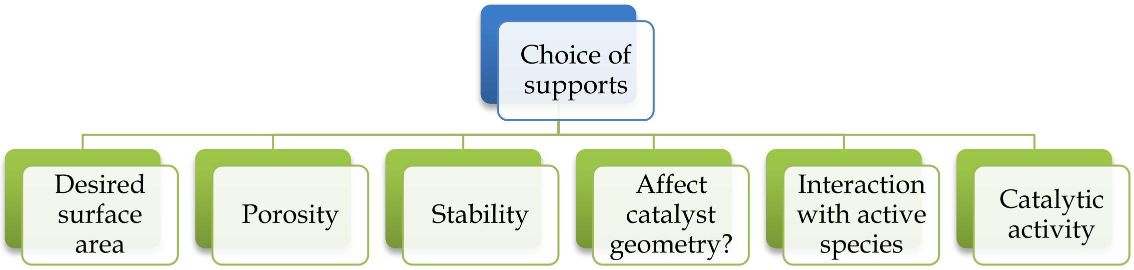


Figure 4. Block flow diagram showing factors affecting choice of supports.

The dispersion of POMs on supports with high surface area is the 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 was found when they were anchored to strongly acidic support. The higher activity was explained by the synergism due to the interaction of the POMs and protons of the support.

It is well known that basic support cannot be used for supporting, as POMs gets decomposed in the basic environment. On the other side, 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. Keeping these aspects in mind, in the present work, mesoporous silica (MCM-41) and strong acidic microporous material (Zeolite Hβ) were selected as supports.

The main reasons of selecting MCM-41 as a support are:

- MCM-41 possess a series of attractive features, such as high surface area, narrow pore size distribution and high adsorption capacities which enable it to be used as catalytic "Support".
- Having a highly ordered distribution of mesopores, MCM-41 materials offer the possibility of incorporating catalytic active species into its structures, which improves hydrothermal stability and produces active sites, thus broadening their field of applications [73].
- The available surface silanol groups of MCM-41 are able to undergo a strong interaction with anchored LPOMs.
- This basic structural chemical feature of the mesoporous materials would allow processing of large molecules and the eventual accommodation of intermediate transition states.
- Our expertise in using MCM-41 as a support [74-77].

Similarly, Zeolite Hβ is a high silica zeolite with large pores. It is highly disordered, made up of an intergrowth of two or more polymorphs comprising a three-dimensional system of 12-membered ring channels [78] having pore diameters of 0.76 × 0.64 nm and 0.55 × 0.55 nm. Owing to large pore size, surface area, and pore volume with controllable Si/Al ratios accompanied by ion-exchange capacity, zeolite beta is a good candidate for catalysis. It possesses high thermal and chemical stability, surface silanol groups and hydrophobic character which are the characteristics of ideal support [78].

There are number of articles available on catalytic aspects of different Keggin type POMs, silicotungstates as well as phosphotungstates anchored to different supports, such as silica [79-87], titania [80,83,87], alumina [80,88-89], carbon [88,90-97], mesoporous silica [98-102], acidic ion exchange resins [103-104] and clays [105-107]. Thus, the world of catalysis by POMs is largely expanded and it would be difficult to mention all the references. ***Hence, we would like to restrict ourselves to silicotungstates anchored to MCM-41 as well as different zeolites, especially for acid catalysis.*** 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.

Lee et al. [108] in 1986, for the first time used Y-zeolite as a support for encapsulation of POMs (H_3PWO_{40}, H_3SiWO_{40}, H_4SiMoO_{40} and H_3PMoO_{40}). They demonstrated alkylation of toluene with methanol in a fixed bed reactor with a continuous flow system. Catalysts impregnated with lower loadings showed higher initial activity, and the catalytic activity was enhanced by more electronegative metal ion salt of POMs impregnated on Y-zeolite.

Richter et al. [109] synthesized a medium-pore zeolite ZSM-5 modified by impregnation with an aqueous solution of $H_4SiW_{12}O_{40}$. Ethylbenzene conversion and m-xylene isomerization was used as the catalytic probe reactions. They showed that the Keggin unit cannot penetrate the ZSM-5 pore system but merely becomes deposited on the external zeolite surface. It was believed that the specific modification of external molecular-sieve surfaces by a metallic (hydrogenating) component could be extended to other elements as well, provided that there exists a polyanion with a molecular size larger than the mean pore size of the molecular sieve to be modified.

Verhoefa et al. reported application of MCM-41-anchored POMs ($H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) as catalysts in the liquid-phase esterification of 1-propanol and hexanoic acid, and in the gas-phase esterification of acetic acid and 1-butanol [110]. For both reactions MCM-41- anchored POMs proved to be active catalysts. However, X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies showed that the initially high dispersion of POMs was lost during reaction. Large clusters (~10 nm) of were formed on the outer surface of the MCM-41 support. Since this clustering also occurred when less polar substrates were applied, not only the polarity of the substrates was responsible for the cluster formation. It was expected that water, formed in esterification, plays a major role in the transport of the POMs from the MCM-41 pores to the outer surface, leading to formation of clusters on the outer surface.

Y. Sugi et al. reported various catalysts comprising POMs ($H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) anchored to mesoporous silica such as MCM-41, FSM-16 and SBA-15 by impregnation method. These catalysts were used in the benzylation of benzene and substituted aromatics with benzyl alcohol [111]. The mesoporous architecture of the supports enhances the activity of benzylation because of the high dispersion on the support with high surface area, however no steric restriction by the pores of mesoporous silica was observed. The catalysts used in the present study retained their catalytic activity for five reaction cycles. The rate of benzylation of substituted benzenes and benzylating agents was influenced by the electronic nature of the substituent. Electron-donating groups enhanced the rate of reaction; however, electron-withdrawing groups retard the benzylation.

Lefebvre and co-workers demonstrated a simple wet-impregnation method and controlled calcination process for preparing nano-sized $H_4SiW_{12}O_{40}$ impregnated zirconia embedded inside the various mesoporous silicas such as

SBA-15, MCM-41 and MCM-48 [112]. Catalysts with different % loadings were also synthesized and characterized by various physicochemical techniques. The effect of calcination temperature on the textural parameters of the catalysts and the integrity of $H_4SiW_{12}O_{40}$ on the surface of the catalyst were also examined. Moreover, the performance of these catalysts was investigated in the esterification of isoamyl alcohol with acetic acid. Catalytic activities were correlated with the acidity of the catalysts. Effects of reaction parameters such as mole ratio of reactants, reaction temperature, catalyst concentration and reusability of the catalyst were studied to get higher substrate conversions and product selectivities. The reaction was found to be heterogeneously catalyzed and no contribution from homogeneous (leached) $H_4SiW_{12}O_{40}$ into the medium under the reaction conditions was observed.

Dogu and group reported synthesis of mesoporous nanocomposite $H_4SiW_{12}O_{40}$ incorporated MCM-41 and mesoporous aluminosilicate catalysts with narrow pore size distributions, in the range of 2.5–3.5 nm, following different impregnation procedures [113]. Results showed that the catalyst preparation procedure had significant influence on its activity as well as the product distribution in ethanol dehydration. The catalyst prepared by the impregnation of $H_4SiW_{12}O_{40}$ into calcined MCM-41 containing a W/Si ratio of 0.24 showed very high activities in dehydration of ethanol. Ethylene yield showed an increasing trend with temperature, reaching to about 100% above 250 ^{o}C. In contrast to ethylene, DEE was formed at lower temperatures, reaching to a yield value of about 70% at 180 °C due to the presence of Bronsted acid sites of the catalyst.

Xu and co-workers carried out liquid phase alkylation of toluene with 1-octene catalyzed by bulk and MCM-41 anchored Keggin-type POMs, such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ was studied [114]. Among these catalysts, the anchored catalysts exhibited more activity than bulk POMs, especially, $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, anchored to MCM-41. The conversion of 1-octene was 100% and selectivity for monoalkylation products was 99.9% after 2 h of reaction at 120 °C using HSiW/MCM-41. The studies of FT-IR, thermogravimetric analyses (TGA) and X-ray diffraction (XRD) confirmed the presence and high dispersion of POMs on MCM-41 mesoporous structure. The catalysts retained their catalytic activity for five times.

Lu et al. have synthesized $H_4SiW_{12}O_{40}$/MCM-41 nano-spheres for etherification of 5-hydroxymethylfurfural (HMF) to 5-ethoxymethylfurfural (EMF) [115]. The catalyst showed 84.1% selectivity to EMF when HMF conversion reaches 92.0%, during etherification of HMF with ethanol under mild conditions. The catalyst could be reused, and its activity remained unaffected over five cycles. The strong acidity of the catalyst significantly enhanced etherification. The acetalized byproducts, 5-(diethoxymethyl)-2-furanmethanol and the HMF-dimer (5,5′(oxy-bis(methylene))bis-2-furfural), can be converted into HMF and then transformed to the main product, EMF, by using this catalyst to shift the reaction equilibrium.

Chen and co-workers synthesized $H_4SiW_{12}O_{40}$ anchored to different porous materials (MCM-41, MCM-48) and characterized by different physicochemical techniques [116]. No Keggin diffraction peaks were observed for loadings up to 33-50 wt% on various mesoporous materials. The cubic mesostructure of MCM-48 was stable while MCM-41 loses its regular hexagonal mesostructure upon loading of $H_4SiW_{12}O_{40}$. Several factors account for different behaviour of various supports, including pore size and curvature of mesopore interface. The resulting 33-50 wt% $H_4SiW_{12}O_{40}$ anchored MCM-48 solid acid catalyst have large surface area (550 m^2/g), regular pore arrangement with uniform pore size (25 Å), finely dispersed $H_4SiW_{12}O_{40}$ and good thermal stability. They exhibit significantly improved activity in acid-catalyzed cracking of long-chain hydrocarbons in comparison with bulk as well as MCM-41 anchored $H_4SiW_{12}O_{40}$.

Tayebee and co-workers synthesized inorganic–organic nanohybrid material $H_4SiW_{12}O_{40}$/pyridino-MCM-41 and performed as an efficient, eco-friendly, and highly recyclable catalyst for the one-pot multi-component synthesis of different substituted 1-amidoalkyl-2-naphthols under solvent free conditions [117]. The catalyst was prepared through electrostatic anchoring of $H_4SiW_{12}O_{40}$ on the surface of MCM-41 nanoparticles modified by *N*-[3-(triethoxysilyl)propyl]isonicotinamide (TPI). The prepared material was characterized by different spectroscopic methods. Findings confirmed that the $H_4SiW_{12}O_{40}$ is well dispersed on the surface of the solid support and its structure is preserved after immobilization on the TPI modified MCM-41 nanoparticles. The recovered catalyst was easily recycled for at least seven runs without considerable loss of catalytic activity.

A literature survey shows that, from the view point of applications, no reports are available on the applications of supported monolacunary silicotungstates in fields of acid catalysis. However, only one report is found on acid catalysis by using supported SiW_{11} and that was by our research group only [118]. In the present thesis, for the first time, we have carried out studies on SiW_{11} anchored to MCM-41 and Zeolite Hβ.

Scope of the Thesis

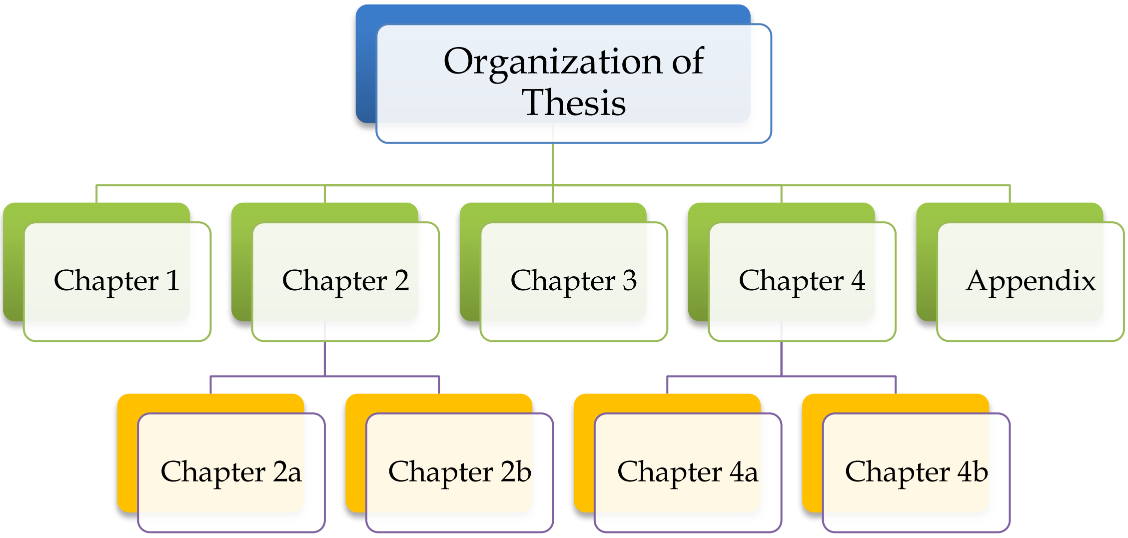
In present thesis, solid acid catalysts comprising parent silicotungstic acid (SiW_{12}) as well as monolacunary silicotungstate (SiW_{11}) and porous supports (MCM-41 and Zeoliite Hβ) were synthesized and successfully characterized by various physicochemical and spectral techniques. Further, an efficient way for synthesis of biodiesel as well as cost minimization of biodiesel production by transformation of glycerol to value added products via carboxylation and acetalization of glycerol was demonstrated. Considering the all the aspects following objectives were planned.

Objectives of the work

1. To explore the new catalytic applications of the catalyst, silicotungstic acid anchored to MCM-41 (SiW_{12}/MCM-41).
2. To synthesize, isolate and characterize monolacunary silicotungstate, SiW_{11}.
3. To synthesize heterogeneous catalyst by anchoring SiW_{11} onto MCM-41 (SiW_{11}/MCM-41).
4. To characterize MCM-41 as well as SiW_{11}/MCM-41 by various physicochemical techniques.
5. To synthesize heterogeneous catalysts, SiW_{12} anchored to zeolite Hβ (SiW_{12}/Hβ) as well as SiW_{11} anchored to zeolite Hβ (SiW_{11}/Hβ).
6. To characterize zeolite Hβ as well as both the catalysts by various physicochemical techniques.
7. To establish the use of synthesized catalysts for biodiesel production via esterification of free fatty acid, oleic acid with methanol.
8. To study the reaction kinetics of esterification of free fatty acid and determination of kinetic parameters such as order of reaction and activation energies.
9. To establish the use of synthesized catalysts for biodiesel production via transesterification of soybean oil as well as characterization of the obtained biodiesel.
10. To explore the use of catalysts for valorisation of glycerol to value added product via acetalization with benzaldehyde.
11. To explore the use of catalysts for valorisation of glycerol to value added product via carboxylation with urea.

12. To study the regeneration and recycling of the catalysts as well as characterization of regenerated catalysts by FT-IR, XRD and Surface area analysis.
13. To study the effect of the supports (MCM-41 and Hβ) on the catalytic activity.
14. To study the effect created lacuna on the catalytic activity of silicotungstates.
15. To screen the best catalyst based on the performance for the mentioned reactions under identical reaction conditions.

The work has been carried out to complete the set objectives and presented in the subsequent chapters.



Chapter 1 describes synthesis as well as characterization of monolacunary silicotungstate (SiW_{11}). Synthesis of a series of catalysts comprising SiW_{11} anchored to MCM-41 was also carried out. The support and the catalyst was characterized by different physicochemical techniques such as Elemental Analysis (EDS), Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FT-IR), Laser-Raman Spectroscopy, X-ray Diffraction

(XRD), Surface Area Measurement (BET method), Pore Size, Pore Volume and ^{29}Si MAS- NMR. Further, the surface morphology of support and catalyst was studied by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The total acidity and types of acidic sites as well as acidic strength were determined by n-butylamine potentiometric titration.

Chapter 2 is divided in to two parts, 2a and 2b.

Chapter 2a consists of catalytic activity of all the synthesized MCM-41 based catalysts towards biodiesel synthesis via esterification of oleic acid as well as transesterification of Soybean oil. 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 conversion. A study on the kinetic behavior was also carried out for esterification reaction and the various kinetics parameters such as order of reaction, rate constant as well as activation energy were determined. The catalyst recyclability was tested up to four cycles and regenerated catalysts were characterized by FT-IR, BET surface area and acidity measurements. Further, probable reaction mechanism was also discussed for esterification as well as transesterification reactions.

Chapter 2b includes catalytic activity of SiW_{12}/MCM-41 as well as SiW_{11}/MCM-41 for the efficient valorisation of glycerol via acetalization and carboxylation reactions. Influence of different reaction parameters was studied. Regeneration studies of the catalysts as well as characterization of regenerated catalysts were also performed. The mechanism for acetalisation as well as carboxylation reactions was also discussed.

Chapter 3 describes synthesis as well as characterization of SiW_{12} as well as SiW_{11} anchored to Zeolite Hβ. The support and the catalysts were characterized by different physicochemical techniques to evaluate textural properties, structural integrity as well as dispersion of the active species.

Chapter 4 is divided in to two parts 4a and 4b.

Chapter 4a consists of Biodiesel production by esterification of free fatty acid, oleic acid and transesterification of soybean oil with methanol over SiW_{12}/SiW_{11} anchored to Hβ. A study on the kinetic behavior was also carried out for esterification reaction and the various kinetics parameters such as order of reaction, rate constant as well as activation energy were determined. The catalyst recycling study was carried out up to four cycles and regenerated catalysts were characterized by FT-IR, BET surface area and acidity measurements.

Chapter 4b includes glycerol valorisation by acetalization with benzaldehyde and carboxylation with urea over SiW_{12}/SiW_{11} anchored to Hβ. Influence of different reaction parameters on the conversion of glycerol was studied. Regeneration studies of the catalysts as well as characterization of regenerated catalysts were also performed.

Appendix

This part of the thesis contains comparison of the activity of all the synthesized catalysts and discussion of effect of active species, SiW_{12}/SiW_{11} as well as supports (MCM-41, Hβ).

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