GENERAL INTRODUCTION

"We are in the midst of an energy transition that continues to evolve"

Long-ago to the discovery of reasonably priced fossil fuels, the never-ending demands of society for energy supplements were satiated by plant biomass. The discovery of crude oil from fossil fuels in the 19th century and the other cost-effective liquid fuels brought global industrialization and improved standards of living. Exploitation of these crude-derived petroleum products by mankind occurs for propelling automobiles, heating buildings, and electricity production. Nevertheless, the major contribution of petroleum in the world of petrochemical industries, as a feedstock or a raw material in global industries of end-user goods cannot be overlooked. [1,2]

Looking to this era of advancement, the world transportation sector participates in the maximum consumption of petroleum products in terms of liquid fuels. However, it is a fact that there is a limit to these petroleum-derived liquid fuels on the earth. Since the upsurge in the global population has created more demand for energy and as our civilization is dependent on fossil fuels, it is inevitable for us to know when these fuels will run out.

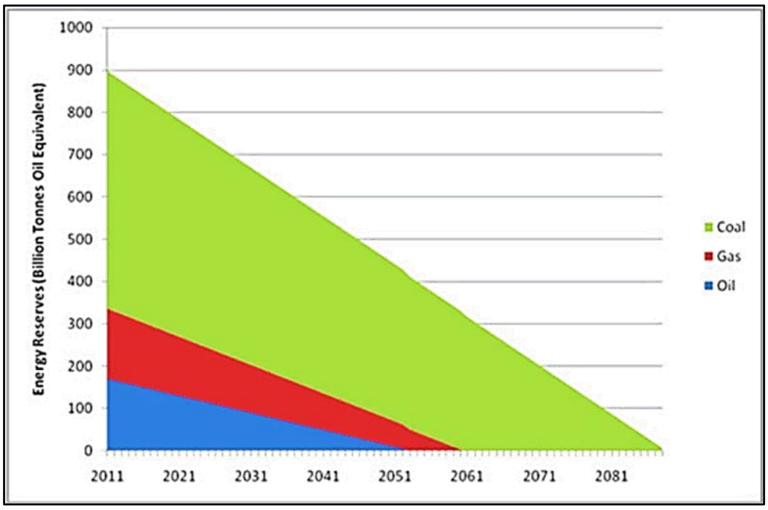

Figure 1 Future Energy Reserves

According to the report, "When Fossil Fuels Run Out, What Then? – by MABH (The Millennium Alliance for Humanity and the Biosphere), the future energy reserves in Billion tonnes oil equivalent (Btoe), as a function of year (Figure 1) show that the oil reverse will end nearly in 30 years.

Thus, the increasing shortage of fossils, upsurge in oil charges, environmental concerns regarding Green House Gases (GHG) emissions, and the anticipated growing demand for energy in the future are attracting a worldwide mass of prospective scientists towards the search for new renewable resources that can act as an efficient replacement for fossil fuels in the current energy system. In this regard, several renewable sources, for instance, solar, wind, hydroelectric and geothermal activity are substituting the roles of natural gas and coal in the production of heat and electricity. While biomass, the only sustainable source of organic carbon on the earth, possesses an ability to be a perfect equivalent to petroleum for the production of fuels, chemicals and other value added products [3,4].

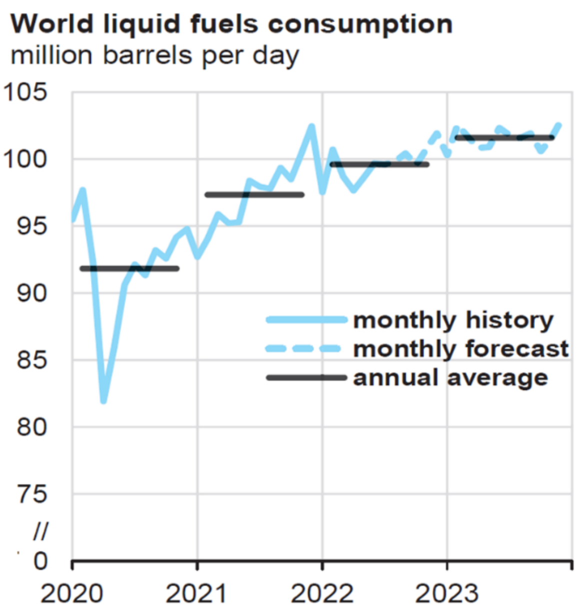

Figure 2 World Liquid fuel consumption
Source: U.S. Energy Information Administration, Short-Term Energy Outlook, July 2022

Figure 2 shows the U.S. Energy Information Administration (EIA) (July 2022) statistics on global consumption of liquid fuels. With the increasing energy demands, the global consumption of liquid fuels will grow by 2.2 million b/d in 2022 and by 2.0 million b/d in 2023. Thus, the production of transportation fuels based on crude oil must be seen in the background of diminishing petroleum resources. Collectively, looking at the statistical data on future energy reserves and the world's liquid fuel consumption, an important conclusion is highlighted, if we rely solely on fossil fuels to supply global energy demand, then the proven reserves would be predicted to be completely depleted between 2069 and 2088. As a solution, the demand restraint measures, mostly target the transportation sector, because that is generally where most oil is consumed.

Looking at the current scenario, the biorefinery concept, holding its roots in the amazing capability of biomass conversion, has started a revolution and is receiving considerable attention from researchers. However, the transformation of large biomass feedstock to simpler molecules is a challenging and developing domain. In this direction, valorizing biomass can become a commencing objective for converting biobased feedstock including bioplatform molecules to valuable chemicals, commodity materials, and biofuels [4–6].

Thus, biomass can be a perfect alternative to liquid fuels, which can be directly converted into biofuels and satiate the global energy needs by effectively employing alternative fuels to the fuels derived from fossils. Ethanol and biodiesel are the two most common types of biofuels in use today, both of which represent the first generation of biofuel technology. Biofuels are biodegradable and non-hazardous. However, they do possess some drawbacks, like higher viscosity and density, high fuel consumption, high emissions, and poor cold flow properties, for example, cloud point, pour point and cold filter plugging point. These drawbacks lead to poor atomization of fuel, clogging of injector, restricted spray pattern of fuel in the combustion chamber and incomplete ignition [7–10]. As a solution to these shortcomings, several researchers inspected that without changing the standard engine, the properties of biofuels can be enhanced by blending some oxygenated, metal-based, antioxidant, lubricity improver and cetane number improver biofuel additives [11,12].

The additives play a vital role to meet the international fuel standards as well as real-time problems which are associated with biofuels. The fuel properties can be boosted by increasing the performance of biofuel and by reducing the harmful emissions from the engine. Interestingly, the selection of additives occurs based on their diverse properties such as flash point, viscosity, density, fire point, calorific value, solubility etc. [13]. Therefore, in the current demand list, the production of fuel additives is challenging, and can majorly be derived by converting the judiciously selected bioplatform molecules.

In 2004, the US Department Of Energy (USDOE) dictated the first original report on the selection of the top twelve bio-derived building blocks, such as 1,4-diacids (succinic acid, lactic acid, fumaric acid), itaconic acid, levulinic acid, polyols like sorbitol, glycerol and, xylitol, etc. [14]. Lately, in 2010 Bozell and Petersen [15] anticipated a revised list of platform chemicals comprising several above molecules, furans and bioethanol (Figure 3).

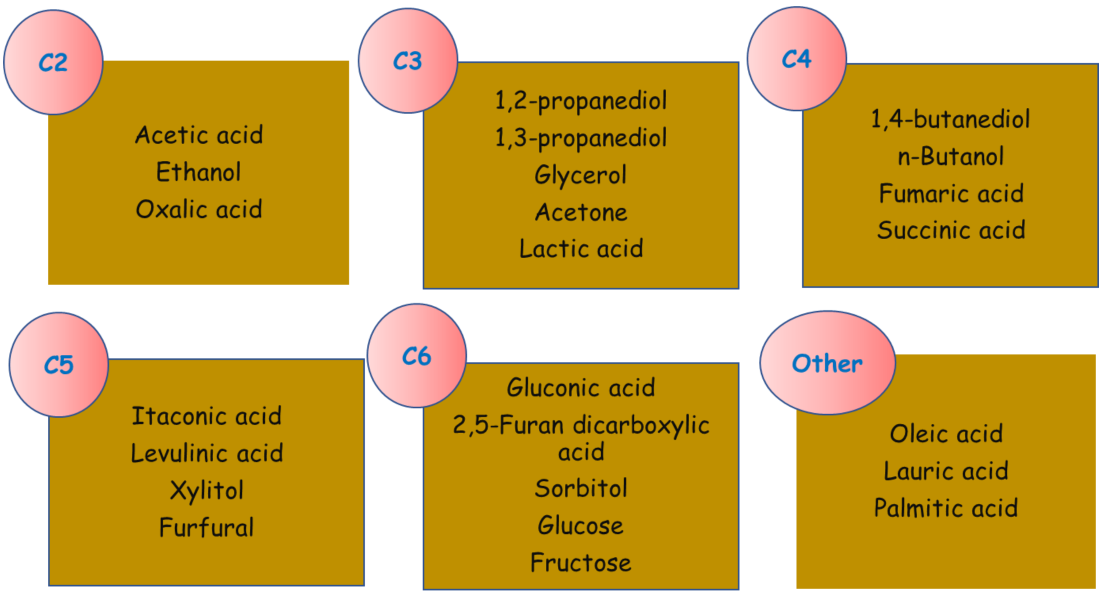

Figure 3 Bioplatform molecules/ building blocks

The potential multifunctionality of bioplatform chemicals opens new routes for speciality chemicals including fuel additives. The predominant transformations involved in the conversion of these bioplatform molecules to value added chemicals/fuel additives are chemical reduction, oxidation, dehydration, bond cleavage, and direct polymerization [14]. More specifically, a series of platform molecules such as levulinic acid, furans, glycerol, C6 sugars, 1,4-diacids, fatty acids, polyols, etc., are converted into a variety of fuel additives through catalytic transformations that include hydrogenation, esterification, etherification, acetalization, dehydration, hydrogenolysis, carboxylation, decarbonylation, and direct alcoholysis [16,17].

For the above transformations, numerous homogeneous as well as heterogeneous catalysts such as,

- Cyclic oligomers (calixarene based) [18,19]
- Ionic liquids [20,21]
- Metal organic frameworks [22,23]
- Acidic resins [24,25]
- Bimetallic catalysts [26,27]
- Carbon-based catalysts [28–35]
- Enzymes [36,37]
- Mesoporous materials [38–45]
- Metal oxides [46–48]
- Titanate nanotubes [49]
- Zeolites [50–54]
- Polyoxometalates [55–61]

have been utilized efficiently for the production of biofuel additives either by direct conversion of biomass fragments (lignin, cellulose, etc.) or by converting bioplatform molecules via the aforementioned routes (Figure 4).

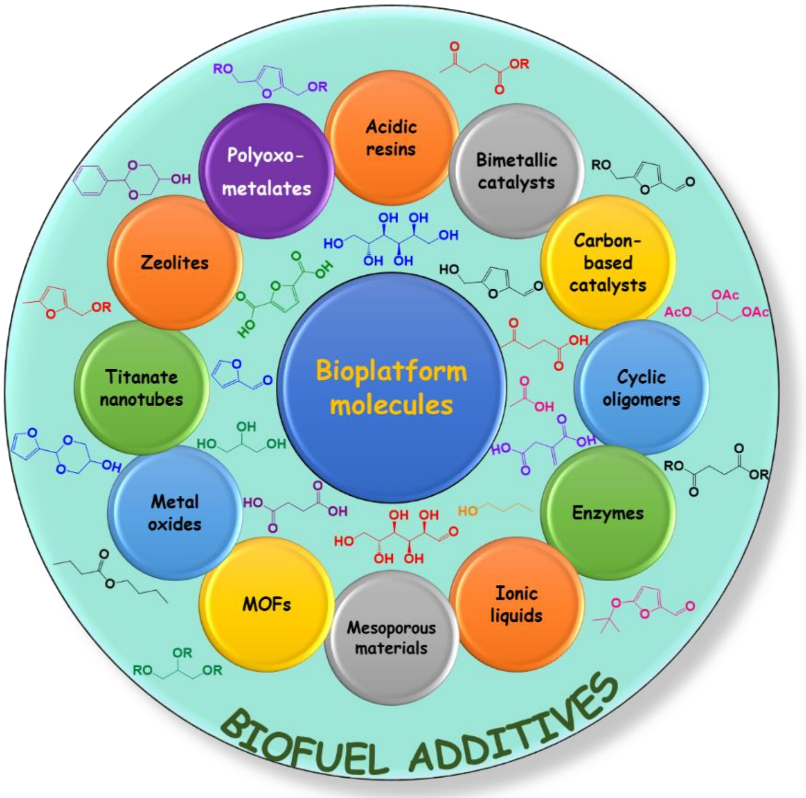

Figure 4 Different catalysts for conversion of bioplatform molecules into biofuel additives

Amongst all, an emerging research field with the development of polyoxometalates based catalysts has evoked tremendous revolution in providing excellent success to biomass conversions. They have several benefits as catalysts which makes them economically and environmentally attractive. They possess a unique set of physicochemical properties which are boons to catalysis. Amongst these properties, the most significant are well-defined structure and strong Bronsted acidity [62,63]. An additional appealing aspect of polyoxometalates in catalysis is their inherent stability toward oxygen donors [64–66].

Overview of Polyoxometalates

Polyoxometalates (POMs) are a discrete class of anionic metal oxygen clusters with exclusive properties of topology, size, electronic versatility as well as structural diversity. They have a general formula $[X_xM_mO_y]^{n-}$, where X is the hetero atom, generally, the main group element (e.g., P, Si, Ge or As), and M is the addenda atom, being a d-block element in a high oxidation state (V, Mo or W) [67–71]. These compounds possess high negative charge density, widely variable depending on their elemental composition and molecular structure (Figure 5).

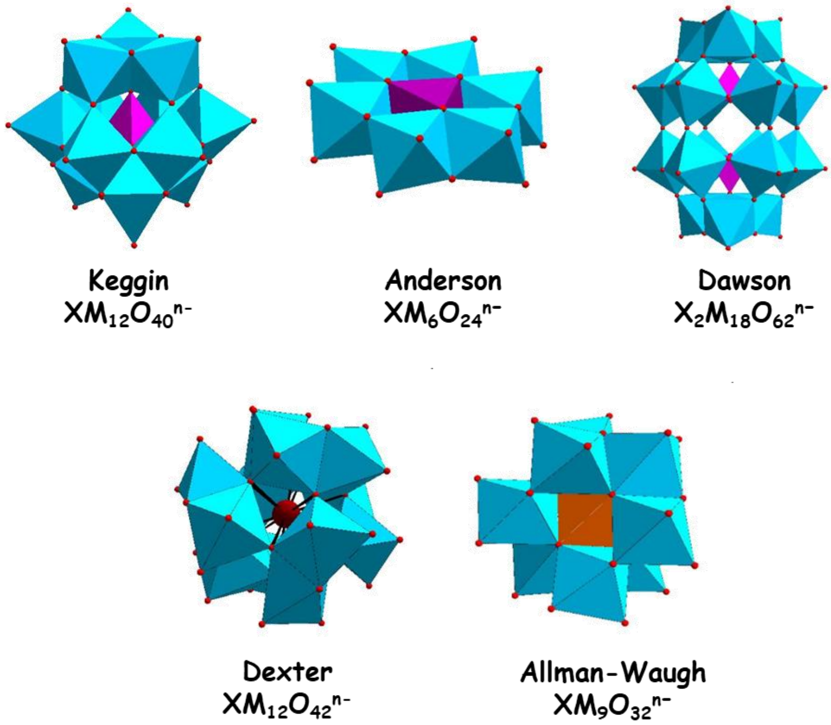

Figure 5 Polyhedral representation of classical POMs

History of POMs

The history of POMs started back in the early nineteenth century when Berzelius defined the formation of canary yellow precipitates of ammonium 12-phosphomolybdate on the addition of excess ammonium molybdate to phosphoric acid [72].

1. Around 20 years later, in 1848, Svanberg and Struve indicated that the insoluble ammonium salt of this complex could be used for the gravimetric analysis of phosphate [73].
2. The research on POM chemistry received motivation in 1862 when Marignac discovered silicotungstic acids and their salts. He successfully synthesized and analysed the two isomers namely, 12-tungstosilicic acid and 12- silicotungstic acid, today known as the α and β-isomers, respectively [74].

Thereafter, in the next 70 years, the field developed so rapidly that over 60 different types of heteropoly acids (giving rise to several hundred salts) had been defined.

3. According to the structural hypothesis of A. Miolati in 1908, the central heteroatom was assumed to have octahedral coordination with MO_4^{2-} or $M_2O_7^{2-}$ ligands [75]. This was further given a laboratory outlook by A. Rosenheim in the 1917 [76].
4. In 1929, Linus Pauling for the first time tried to elucidate the structure of a POM. He proposed a 12:1 complex structure based on the arrangement of 12 octahedra around a central XO_4 tetrahedron. According to his structural hypothesis, twelve WO_6 octahedra surround one PO_4 or SiO_4 tetrahedron to form 12-tungstoanions in which all polyhedron linkages would involve vertices sharing rather than edge-sharing to minimize electrostatic repulsion. Thus, the proposed structure would have 58 oxygen atoms and the molecular formula would be $[(PO_4)W_{12}O_{18}(OH)_{36}]^{3-}$ [77].
5. Later, in 1933, Keggin successfully explained the structure of $H_3[PW_{12}O_{40}].5H_2O$ and found that it was based on WO_6 octahedra which were linked by edges as well as corners [78,79]. Furthermore, the application of X-ray crystallography for the determination of polyoxometalate structures accelerated the development of POM chemistry.

6. In the following year, Signer and Gross confirmed that $H_4SiW_{12}O_{40}$, $H_5BW_{12}O_{40}$ and $H_6[H_2W_{12}O_{40}]$ were structurally isomorphic with Keggin's proposed structure [80].
7. Bradley and Illingworth confirmed Keggin's elucidation of $H_3[PW_{12}O_{40}].5H_2O$ from the studied crystal structure [81] and these results were also supported by single crystal experiments of Brown and co-workers [82].

Amongst all different types of POMs, the Keggin type is most extensively studied because of its ease in synthesis, and high thermal and chemical stability [64,67]. Considering this, the present thesis deals with Keggin type POMs only.

Keggin type Polyoxometalates

The Keggin type POMs have the general formula $[XM_{12}O_{40}]^{n-}$, where X belongs to the central heteroatom, usually, the main group element like P, Si, Ge and As and M is the addenda atom, a d-block element in their higher oxidation state (V^{IV}, V^{V}, Mo^{VI} or W^{VI}). They are formed by the condensation of different mononuclear oxoanions at lower pH as presented in the following equation (Eq 1).

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

The acidic form of POMs is known as Heteropolyacids (HPAs).

The ideal Keggin structure, $[XM_{12}O_{40}]^{3-}$ of α-type is shown in figure 6. It has a T*d* symmetry and consists of a central XO_4 tetrahedron (X = central heteroatom) surrounded by twelve MO_6 octahedra (M = addenda atom). The twelve MO_6 octahedral units form four groups of three edge-shared octahedra - M_3O_{13} triplet [78,79], which have a shared oxygen vertex connected to the central heteroatom. There are four classes of symmetry-equivalent oxygen atoms in this structure. X-O_a-$(M)_3$, M-O_b-M, connecting two M_3O_{13} units by corner sharing; M-O_c-M, connecting two M_3O_{13} units by edge-sharing; and terminal O_d-M, where M is the addenda atom and X the heteroatom.

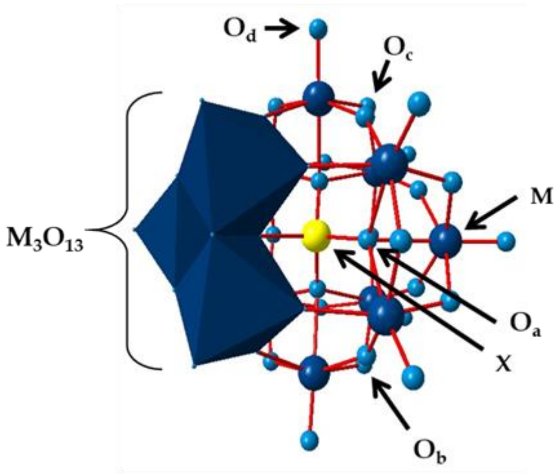

Figure 6 Structure of Keggin ion.

Important properties [64]

The pores of POMs are inter-particle and not intra-crystalline. Considering the size and shape of the Keggin anion and the crystal structure, there is no open pore through which nitrogen molecules can penetrate. Some of the significant properties of POMs are mentioned below,

1. ***Acidic properties -*** The acidic forms of POMs in the solid state are pure Bronsted acids which are stronger acids than the conventional inorganic solid acids. The acidic strength depends on the nature of heteroatom and addenda atoms. The order of acidic strength is,

$$H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiW_{12}O_{40} > H_4SiMo_{12}O_{40} > H_4GeMo_{12}O_{40}$$

2. ***The softness of anionic structure -*** The softness of the acidic form of POMs is an important characteristic relevant to catalysis. The effect of the softness becomes significant for reactions in aqueous solutions, in which the difference in the acid strength is less pronounced. The order of softness is,

$$H_4SiW_{12}O_{40} > H_3PW_{12}O_{40} > H_3PMo_{12}O_{40}$$

3. ***Thermal stability -*** In acidic form, the solid POMs are thermally stable. The thermal stability depends on the heteroatom, polyatomic and polyanionic structure. It follows the order,

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

4. ***Redox properties –*** The addenda atoms in their highest oxidation states are capable of acting as oxidizing agents. The oxidative ability decreases in the order $V^{-} > Mo^{-} > W^{-}$ containing anions.

There are a large number of articles available on POMs and looking at the bulk of the thesis we have included only the important books and reviews, as it is difficult to mention all the references, and we would like to excuse us if some of the references are not included.

An extensive literature on the synthesis, structure and properties of POMs has been constituted in the form of books as follows,

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8. S. Herrmann, New synthetic routes to polyoxometalate containing ionic liquids: an investigation of their properties. Springer, (2015).
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11. Y.F. Song, Polyoxometalate-Based Assemblies and Functional Materials, VII, 167, Springer Cham, (2018).

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Applications of POMs

POMs have very low surface area (1-10 m^2/g), and they are soluble in polar solvents. Due to the combination of their value added characteristics such as redox properties, large sizes, high negative charge and nucleophilicity, they play a prodigious role in various fields such as medicine [83–85], material science [86–89], photochromism [90,91], electrochemistry [92–94], magnetism [95–97] etc. However, the majority of their contribution is found in the field of catalysis, reported in the form of books and reviews [89,98–133] as well as patents [134–153].

Advantages of POMs as catalysts [64,154]

The advantages of POMs as catalysts are as follow,

1. **Designing at a molecular level**
    - *Acidic and redox properties:* These properties of the catalyst are governed by choosing appropriate elements i.e., type of polyanion, heteroatom counter-cation etc.
    - *Multifunctionality:* Acid-Redox, Acid-Base, multielectron transfer etc.
    - The tertiary structure, bulk type behaviour etc. for solid-state are well controlled by counter cations
2. **Molecular metal-oxide clusters**
    - Molecular designing of catalyst
    - Cluster models of mixed oxide catalysts and relationships between solution and solid catalysts
    - Description of catalytic processes at atomic/molecular level, spectroscopic study and stoichiometry are realistic, model compounds of reaction intermediates

3. Unique reaction fields

- *Surface type catalysis* - It is the most usual type of catalysis, where the reaction takes place on the surface of the solid catalyst and the rate of reaction is proportional to the surface area.
- *Bulk type I catalysis* - The reactant molecules are adsorbed in the interpolyanion spaces of the ionic crystal for reaction to occur and the formed products desorb. The classic example of this type is the acid-catalyzed reaction of polar molecules over the group I salts at relatively low temperatures. The solid behaves like a solution and the reaction surface becomes 3D, therefore it is termed "pseudoliquid" catalysis. Here, the rate of reaction depends on the volume of the catalyst, such as an acid-catalyzed reaction would depend on the bulk acidity of the catalyst.
- *Bulk type II catalysis* - Although the reaction progresses on the surface, there is a rapid migration of redox carriers like electrons and protons, because of which in principle, the bulk catalyst participates in the reaction. The classic examples of this are dehydrogenation and oxidation of hydrogen at high temperatures, and the reaction rate is proportional to the bulk volume of the catalyst. In the case of POMs, they behave as "pseudoliquids" and hence follow bulk type II catalysis, which provides a unique 3D environment, and make spectroscopic and stoichiometric studies feasible and realistic.

A diagrammatic representation of reaction fields of POMs is shown in figure 7.

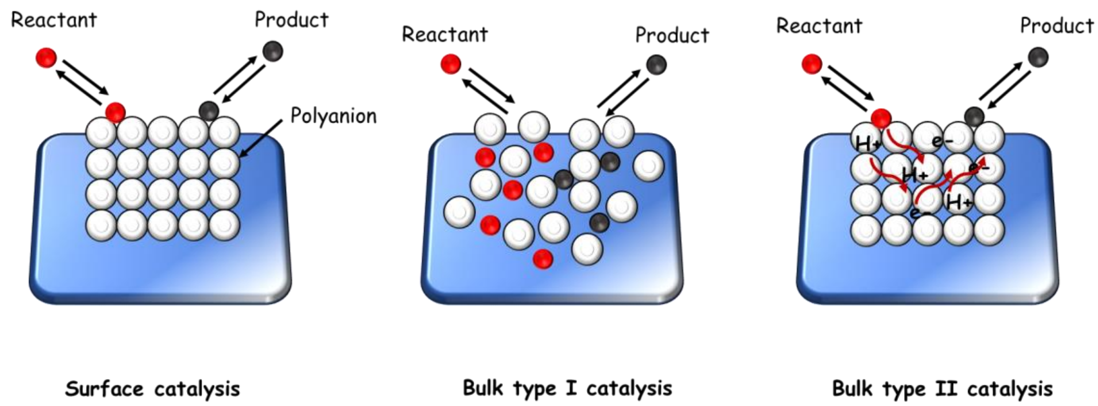

Figure 7 Modes of catalysis using POMs

4. Unique basicity of polyoxoanions

- It plays an important role in their high catalytic activity as they help in selective coordination as well as stabilization of reactive intermediates in solution, pseudoliquid and solid phases.

As shown earlier [Page no 17], the systematic approach of POMs in the field of catalysis began in the 1970s and made a huge contribution to the same. For more than the last decade, POM based catalysts have also started gaining importance in biomass conversion. Slowly the area is emerging with great attention and recent important achievements are summarized below,

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2. E. Brule et al., Process for converting a feedstock comprising a lignocellulosic biomass using a polyoxometalate salt comprising nickel and tungsten or nickel and molybdenum, WO2017084907A1, (2017).
3. R. Neumann et al., Catalytic formation of carbon monoxide (CO) and hydrogen (H2) from biomass, US9873612B2, (2018).
4. S. Gaur et al., Process and catalysts for the production of diesel and gasoline additives from glycerol, EP3814314A1, (2021)

The above literature survey directs that a majority of work has been reported on the exploration of phosphotungstates as catalysts for biomass conversion, and few studies are carried out using silicotungstates, even though it consists of unique advantages. Therefore, silicotungstates have been selected for the present work (Figure 8).

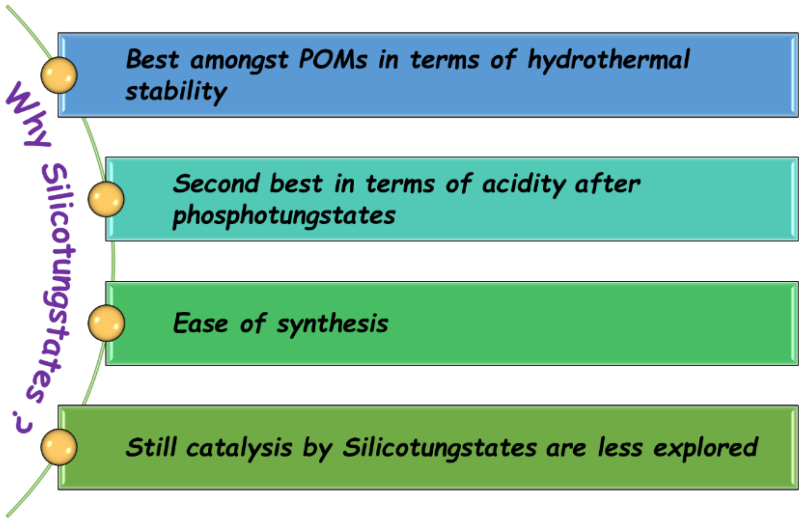


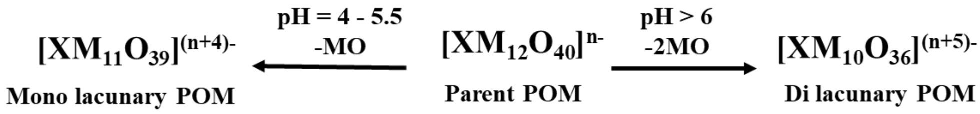
Figure 8 Advantages of Silicotungstates

As mentioned earlier, POMs can be modified at a molecular level to tune their acidic and redox properties. Amongst all, one of the most significant properties of modified precursors is their capability to reversibly accept and release specific numbers of electrons [67,108,109,114,116] These modifications of parent POMs are expected to aid in the development of new generation catalysts and therefore they are of potential importance in catalysis.

Amongst [65,70,155], one of the structural modifications at a molecular level can be achieved by creating a defect (lacuna) in the parent POMs, resulting in the formation of lacunary POMs.

What are Lacunary POMs?

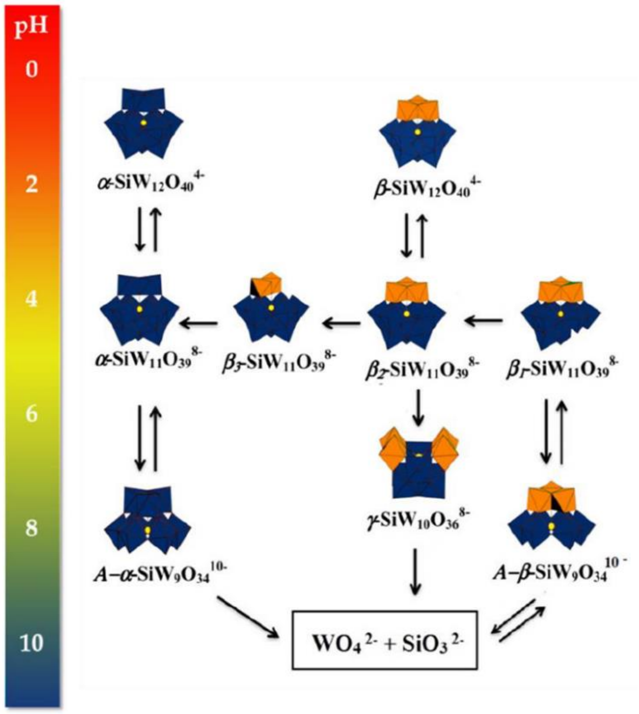
Lacunary Polyoxometalates (LPOMs) are a subclass of POMs possessing unique properties such as multidenticity, rigidity, and thermal and oxidative stability [62,64,67]. LPOMs can be easily synthesized, either by removing one or more M-O units (M = addenda atom) from the parent Keggin anion or by condensation of individual metal salts. Elimination of one, two and three MO units results in the formation of mono, di and tri lacunary anions, respectively, depending on the pH. For instance, mono lacunary POMs are obtained at pH 4-5.5 whereas the di and tri lacunary POMs are obtained at pH values >6 (Scheme 1) [156].



Scheme 1 Formation of mono and di lacunary POMs

Special attention for synthetic strategies of LPOMs must be paid in controlling the reaction conditions such as pH, temperature, buffer capacity, ionic strength, and cation size as they all possess the potential to exert a considerable effect on the polyanion equilibria and formation of products [109,157]. Generally, the most stable compounds, or least labile when they are metastable, are obtained with Si^{4+} as the hetero element. Silicotungstates are stable in acidic conditions and when the pH increases, hydrolytic cleavages of W-O bonds occur, leading to well-defined lacunary polyanions, with 11, 10, or 9 tungsten atoms [158].

Three parent silicotungstates, four mono lacunary silicotungstates [159], one di lacunary silicotungstate [160] and two tri lacunary silicotungstates [161] are known. They can be prepared following the general pH-dependent route (Scheme 2) [158,162].



Scheme 2 pH-dependent formation of Silicotungstates [161,162]

Furthermore, it is important to note that, identical to parent POMs, LPOMs also suffer from the traditional disadvantages of homogeneous catalysis such as,

- High solubility in a polar medium
- Lower surface area
- Difficult to separate from the reaction medium
- Limited stability

The above-mentioned drawbacks can be overcome by the development of heterogeneous catalysts i.e., by anchoring or supporting silicotungstates over suitable supports.

The supports provide an enlarged surface area for the dispersion of catalytic species depending on their nature. The catalyst molecules get distributed either on the surface of non-porous support or the surface as well as inside the channels of a porous support. The heterogeneous catalysts not only function mechanically as a homogeneous medium in solution but also operate as a separate phase. Thus, in one system the advantages of both homogenous as well as heterogeneous catalysts are retained.

Choice of the support

For the synthesis of heterogeneous catalysts, the choice of appropriate support is a crucial step. The nature of support also plays a critical role in determining the activity of catalyst. Acidic or neutral supports are found to be suitable for anchoring POMs and their catalytic activity was enhanced when a strong acidic support was used. The higher activity can be attributed to the synergistic relationship between the POMs and the support. However, it is well known that basic support, is not preferred for anchoring, as POMs get decomposed in the basic environment [163].

The features which affect the selection of appropriate support are highlighted in Figure 9.

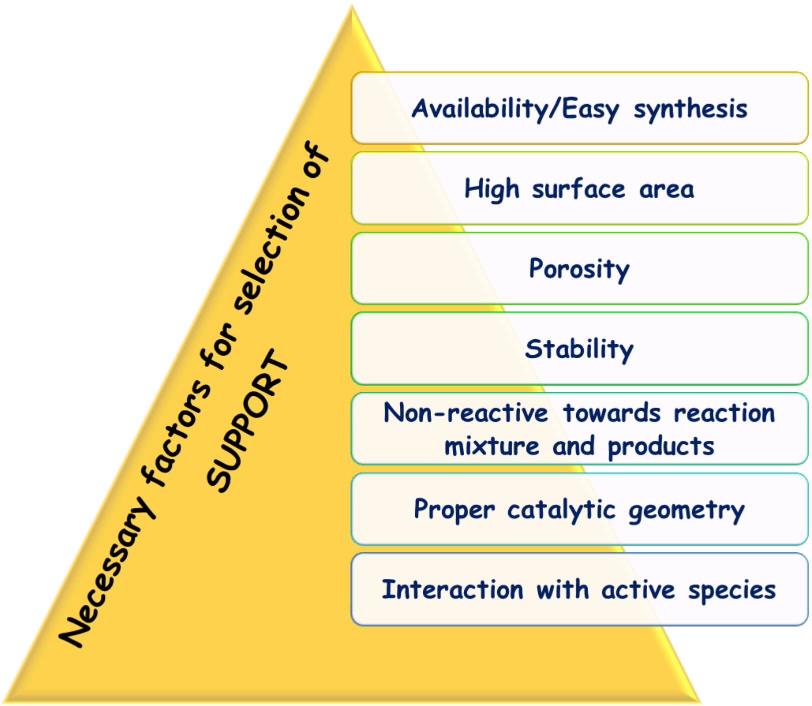


Figure 9 Considerations for selection of support

A thorough literature survey on the utilization of various supports for anchoring silicotungstates (for biomass conversion) in the past 15 years is summarized below,

Sr. No	Literature report	Support/s used
1.	E. Tsukuda, S. Sato, R. Takahashi, and T. Sodesawa, Production of acrolein from glycerol over silica-supported heteropoly acids, Catal. Comm., 8, 1349, (2007).	Al_2O_3, anatase-TiO_2, ZrO_2, SiO_2–Al_2O_3 (N632HN)
2.	K.M. Parida and S. Mallick, Silicotungstic acid supported zirconia: An effective catalyst for esterification reaction, J Mol Catal A Chem, 275, 77, (2007).	Hydrous Zirconia
3.	Esterification of free fatty acids with methanol using heteropolyacids immobilized on silica by C. S. Caetano, I. M. Fonseca, A. M. Ramos, J. Vital and J. E. Castanheiro, Catal. Comm., 9, 10, 1996, (2008).	Silica
4.	L. Cheng and X. Philip Ye, A DRIFTS Study of Catalyzed Dehydration of Alcohols by Alumina-supported Heteropoly Acid, Catal Lett, 130, 100, (2009).	Al_2O_3

5.	A. I. Tropecêlo, M. H. Casimiro, I. M. Fonseca, A. M. Ramos, J. Vital and J. E. Castanheiro, Esterification of free fatty acids to biodiesel over heteropolyacids immobilized on mesoporous silica, Appl. Catal. A., 390, 1-2, 183, (2010)	SBA-15
6.	P. Che, F. Lu, J. Zhang, Y. Huang, X. Nie, J. Gao and J. Xu, Catalytic selective etherification of hydroxyl groups in 5-hydroxymethylfurfural over $H_4SiW_{12}O_{40}$/MCM-41 nanospheres for liquid fuel production, Bioresour. Technol., 119, 433, (2012).	MCM-41
7.	M. H. Haider, N. F. Dummer, D. Zhang, P. Miedziak, T. E. Davies, S. H. Taylor, D. J. Willock, D. W. Knight, D. Chadwick and G. J. Hutchings, Rubidium- and caesium-doped silicotungstic acid catalysts supported on alumina for the catalytic dehydration of glycerol to acrolein, J. Catal., 286, 206, (2012).	α-Al_2O_3, (Delta + Theta) Al_2O_3
8.	K. Yan, G. Wu, J. Wen and A. Chen, One-step synthesis of mesoporous $H_4SiW_{12}O_{40}$-SiO_2 catalysts for the production of methyl and ethyl levulinate biodiesel, Catal. Commun., 34,58, (2013)	SiO_2
9.	S. Zhu, Yu. Zhu, X. Gao, T. Moa, Yi. Zhu and Y. Li, Production of bioadditives from glycerol esterification over zirconia supported heteropolyacids, Bioresour. Technol., 130, 45, (2013).	ZrO_2
10.	A. Patel and N. Narkhede, Biodiesel synthesis via esterification and transesterification over a new heterogeneous catalyst comprising lacunary silicotungstate and MCM-41, Catal. Sci. Technol., 3, 3317, (2013).	MCM-41
11.	N. Narkhede and A. Patel, Biodiesel Production by Esterification of Oleic Acid and Transesterification of Soybean Oil Using a New Solid Acid Catalyst Comprising 12-Tungstosilicic Acid and Zeolite Hβ, Ind. Eng. Chem. Res., 52, 38, 13637, (2013).	Zeolite Hβ
12.	N. Narkhede and A. Patel, Room temperature acetalization of glycerol to cyclic acetals over anchored silicotungstates under solvent free conditions, RSC Adv., 4, 19294, (2014).	MCM-41
13.	N. Narkhede, V. Brahmkhatri, A. Patel, Efficient	SBA-15

	synthesis of biodiesel from waste cooking oil using solid acid catalyst comprising 12-tungstosilicic acid and SBA-15, Fuel, 135, 253, (2014).	
14.	N. Narkhede and A. Patel, Efficient synthesis of biodiesel over a recyclable catalyst comprising a monolacunary silicotungstate and zeolite Hβ, RSC Adv., 4, 64379, (2014).	zeolite Hβ
15.	L. Liu B. Wang, Y. Du, Z. Zhong and A. Borgna, Bifunctional $Mo_3VO_x/H_4SiW_{12}O_{40}/Al_2O_3$ catalysts for one-step conversion of glycerol to acrylic acid: Catalyst structural evolution and reaction pathways, Appl. Catal., 174-175, 1, (2015).	Al_2O_3
16.	D. D. Bala, K. de Souza, M. Misra and D. Chidambaram, Conversion of a variety of high free fatty acid containing feedstock to biodiesel using solid acid supported catalyst, J. Clean. Prod., 104, 273, (2015).	KIT-6
17.	A. Talebian-Kiakalaieh and N. A. Saidina Amin, Kinetic modeling, thermodynamic, and mass-transfer studies of gas-phase glycerol dehydration to acrolein over supported silicotungstic acid catalyst, Ind. Eng. Chem. Res., 54, 33, 8113, (2015).	ZrO_2, Al_2O_3
18.	Y. Chen, Y. Cao, Y. Suo, G. Zheng, X. Guan and X. Zheng, Mesoporous solid acid catalysts of 12-tungstosilicic acid anchored to SBA-15: Characterization and catalytic properties for esterification of oleic acid with methanol, J Taiwan Inst Chem Eng, 51, 186, (2015).	SBA-15
19.	L. Liu, B. Wang, Y. Du and A. Borgna, Supported $H_4SiW_{12}O_{40}/Al_2O_3$ solid acid catalysts for dehydration of glycerol to acrolein: evolution of catalyst structure and performance with calcination temperature, Appl. Catal. A., 489, 32, (2015).	Al_2O_3
20.	A. Talebian-Kiakalaieh and N. A. Saidina Amin, Supported silicotungstic acid on zirconia catalyst for gas phase dehydration of glycerol to acrolein, Catal. Today, 256, 315, (2015).	ZrO_2
21.	S. Fu, J. Chu, X. Chen, W. Li and Y. Song, Well-Dispersed $H_3PW_{12}O_{40}/H_4SiW_{12}O_{40}$ nanoparticles on	Mesoporous polymer

	mesoporous polymer for highly efficient acid-catalyzed reactions, Ind. Eng. Chem. Res., 54, 46, 11534, (2015).	
22.	N. Narkhede and A. Patel, Facile synthesis of glycerol carbonate via glycerolysis of urea catalysed by silicotungstates impregnated into MCM-41, RSC Adv., 5, 52801, (2015).	MCM-41
23.	D. Unlu, O. Ilgen and N. D. Hilmioglu, Biodiesel additive ethyl levulinate synthesis by catalytic membrane: SO_4^{-2}/ZrO_2 loaded hydroxyethyl cellulose, Chem. Eng. J., 302, 260, (2016).	ZrO_2
24.	Chau T. Q. Mai and Flora T. T. Ng, Effect of metals on the hydrogenolysis of glycerol to higher value sustainable and green chemicals using a supported HSiW catalyst, Org. Process Res. Dev. 20, 1774, (2016).	Al_2O_3
25.	X. Kong, S. Wu, X. Li and J. Liu, Efficient conversion of levulinic acid to ethyl levulinate over silicotungstic acid modified commercially silica-gel sphere catalyst, Energy Fuels, 30, 8, 6500, (2016).	Silica gel sphere
26.	A. Talebian-Kiakalaieh, N. A. Saidina Amin, Z. Y. Zakaria, Gas phase selective conversion of glycerol to acrolein over supported silicotungstic acid catalyst, J Ind Eng Chem, 34, 300, (2016).	ZrO_2, γ-Al_2O_3
27.	M. Ramalingam, S. Manickam, K. R. Srinivasalu, M. B. Ismail and E. Deivanayagam, Ionic immobilization of silicotungstic acid on amine-functionalized zirconia: A mesoporous catalyst for esterification of maleic acid, Eur. J. Inorg. Chem., 1697, (2016).	ZrO_2
28.	Y. Chena, X. Zhang, M. Dong, Y. Wu, G. Zheng, J. Huang, X. Guan and X. Zheng, MCM-41 immobilized 12-silicotungstic acid mesoporous materials: Structural and catalytic properties for esterification of levulinic acid and oleic acid, J Taiwan Inst Chem Eng, 61, 147, (2016).	MCM-41
29.	S. Zhu, Y. Cen, J. Guo, J. Chai, J. Wanga and W. Fan, One-pot conversion of furfural to alkyl levulinate over bifunctional Au-$H_4SiW_{12}O_{40}/ZrO_2$ without external H_2, Green Chem.,18, 5667, (2016).	ZrO_2

30.	V. Simsek, L. Degirmenci and K. Murtezaoglu, Synthesis of a silicotungstic acid SBA-15 catalyst for selective monoglyceride production, Reac Kinet Mech Cat 117, 773, (2016).	SBA-15
31.	A. M. E. Caicedo, J. A. Rengifo-Herrera, P. Florian, M. N. Blanco, G. P. Romanelli and L. R. Pizzio, Valorization of biomass derivatives: Keggin heteropolyacids supported on titania as catalysts in the suitable synthesis of 2-phenoxyethyl-2-furoate, J Mol Catal A Chem, 425, 266, (2016).	TiO_2
32.	N. Narkhede and A. Patel, Sustainable valorisation of glycerol via acetalization as well as carboxylation reactions over silicotungstates anchored to zeolite Hβ, Appl. Catal. A, 515, 154, (2016).	zeolite Hβ
33.	D. Unlu and N. D. Hilmioglu, Applicability of a TSA/ZrO_2 catalytic membrane for the production of ethyl levulinate as raw material of gamma-valerolactone, Int. J. Hydrog. Energy, 42, 33, 21487, (2017).	ZrO_2
34.	K. V. Avramidou, F. Zaccheria, S. A. Karakoulia, K. S. Triantafyllidis and N. Ravasio, Esterification of free fatty acids using acidic metal oxides and supported polyoxometalate (POM) catalysts, Mol. Catal., 439, 60, (2017)	ZrO_2, 3.5% SiO_2-ZrO_2, SiO_2-Al_2O_3, SBA-15, Al-SBA-15
35.	A. Talebian-Kiakalaieh and N. A. Saidina Amin, Gas phase glycerol dehydration to acrolein using supported silicotungstic acid catalyst, Malaysian J. Anal. Sci, 21, 4, 849, (2017)	ɣ-Al_2O_3
36.	S. Gopinath, P. Vinoth Kumar, P. Sahaya Murphin Kumar, K. A. Yasar Arafath, S. Sivanesan and P. Baskaralingam, Cs-tungstosilicic acid/Zr-KIT-6 for esterification of oleic acid and transesterification of non-edible oils for green diesel production, Fuel, 234, 824, (2018).	Zr-KIT-6
37.	H. P. Winoto, Z. A. Fikri, J. M. Ha, Y. K. Park, H. Lee, D. J. Suh and J. Jae, Heteropolyacid supported on Zr-Beta zeolite as an active catalyst for one-pot transformation of furfural to ɣ-valerolactone, Appl. Catal. B, 241, 588, (2018).	Zr-Beta zeolite

38.	A. Gaurav, S. Dumas, C. T. Q. Mai and Flora T. T. Ng, A kinetic model for a single step biodiesel production from a high free fatty acid (FFA) biodiesel feedstock over a solid heteropolyacid catalyst, Green Energy Environ., 4, 3, 328, (2018).	Al_2O_3
39.	N. Lucas, L. Gurrala and A. Athawale, Heteropolyacids supported on mesoporous AlSBA-15 as efficient catalysts for esterification of levulinic acid, J. Porous Mater., 26, 1335, (2019).	AlSBA-15
40.	E. Kraleva and H. Atia, Keggin-type heteropolyacids supported on sol–gel oxides as catalysts for the dehydration of glycerol to acrolein, Reac Kinet Mech Cat, 126, 103, (2019).	Al_2O_3, TiO_2, ZrO_2, Three-mixed oxide AlTiZr
41.	P. Ganji and S. Roy, Conversion of levulinic acid to ethyl levulinate using tin modified silicotungstic acid supported on Ta_2O_5, Catal. Comm., 134, 105864, (2020).	Ta_2O_5
42.	Ö. D. Bozkurt, N. Bağlar, S. Çelebi, A. Uzun, Screening of solid acid catalysts for etherification of glycerol with isobutene under identical conditions, Catal. Today, 357, 483, (2020).	SiO_2, MCM-41, SBA-15
43.	N. García-Bosch, C. Especel, A. Guerrero Ruiz and I. Rodríguez-Ramos, Tracking the paths for the sucrose transformations over bifunctional Ru-POM/AC catalysts, Catal. Today, 357, 113, (2020).	Activated carbon
44.	Q. Zhang, B. Yang, Y. Tian, X. Yang, R. Yu, J. Wang, T. Deng and Y. Zhang, Fabrication of silicotungstic acid immobilized on Ce-based MOF and embedded in Zr-based MOF matrix for green fatty acid esterification, Green Process. Synth., 11, 184, (2022).	UiO-66(Zr)

From the above literature survey, it was observed that until now, no reports are available on the use of nano-porous MCM-48 and MCM-22 for anchoring silicotungstates.

Therefore, in this work, for the ***first time, we are introducing nano-porous MCM-48 and MCM-22 as new supports for anchoring silicotungstates*** (Figure 10).

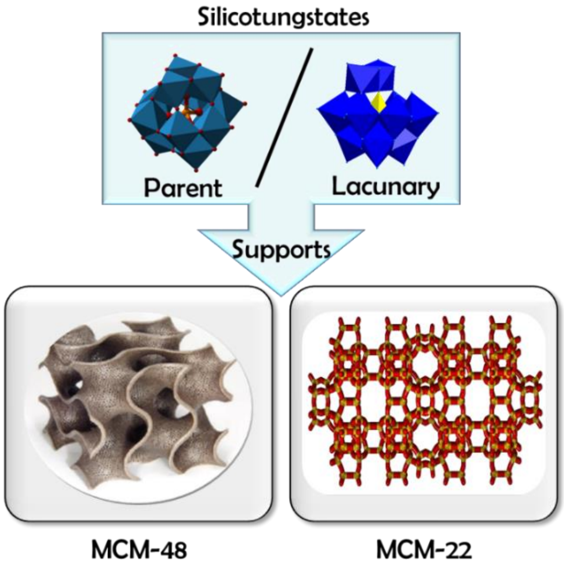


Figure 10 Supports for anchoring silicotungstates

A brief introduction and main reasons for selecting MCM-48 and MCM-22 as supports are as follow,

(i) **MCM-48 -** Mobil Composition of Matter No. 48 [164–166]

- It is a siliceous material, having three-dimensional cubic geometry.
- It possesses several attractive physical properties such as high thermal stability and high surface area in the range of 1000 – 1600 m^2/g with an interpenetrating mesoporous network.
- MCM-48 proves to be a more promising candidate as compared to other materials of its family, for catalytic applications due to its unique interwoven as well as branched pore network which assists favourable mass transfer kinetics in catalytic reactions.
- The cubic structure of MCM-48 delivers a large number of surface silanol groups that can bind and form a strong interaction with POMs.

- The advantageous structural, as well as chemical features of the MCM-48, would allow an accessible pathway toward catalytic sites for large molecules and effortlessly accommodates intermediates.

(ii) MCM-22 [167,168]

- MCM-22 forms a layered intermediate, which combines the potential of two classes of materials, i.e., zeolites and layered solids.
- It was synthesized in 1990 by Mobil Oil Corporation and the structure commission of the International Zeolite Association (IZA) designated this peculiar topology as MWW (Mobil Twenty Two).
- It is a hierarchical zeolite, possessing a crystalline three-dimensional structure, with hexagonal morphology, having two independent pore systems. One of the pores has 10 membered ring structure with 2D sinusoidal channels (0.4 nm diameter and 0.59 nm height) and the other is formed by stacked supercages having an internal diameter of 0.71 nm with 1.82 nm height.
- It has a secondary porosity level with a combination of improved pore size and inherent acidity which have levelled up remarkably the conversion and catalytic rate in many industries.
- This unique aluminosilicate framework provides surface silanol groups for interaction with POMs, as well as good thermal and chemical stability which will be well benefitted for catalytic transformations.

After a careful literature survey and from the viewpoint of valorization and upgradation of the bioplatform molecules, we have selected the following bioplatform as model molecules for their conversion into fuel additives and other value-added products.

- Levulinic acid
- Succinic acid
- Glycerol

Levulinic acid

Levulinic acid is one of the important intermediates and an originally bio-derived molecule that leads to ample valuable products. It holds an immense potential to generate biofuels, additives and value-added products such as alkyl levulinates, lactones, ɣ-valerolactone, ketals, pyrrolidinones, succinic acid, etc. [169,170] (Figure 11).

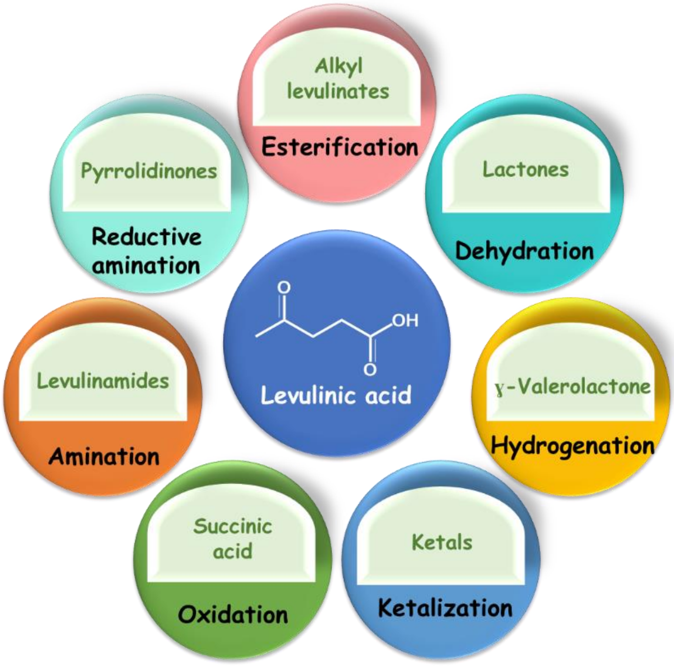


Figure 11 Potential transformations of levulinic acid

In this context, alkyl levulinates are of particular interest due to their specific physicochemical property and find their role in several applications including fuel additives, pharmaceutical agents, resin precursors, fragrance and flavouring agents. Particularly, they are more suitable as fuel blends in terms of having excellent lubricity, balanced flow property, low toxicity and constant flashpoint [132,171–173]. It is worthy to note that butyl levulinate, formed by the esterification of levulinic acid and n-butanol, has been proved to be more encouraging as a fuel additive compared to widely applicable ethyl levulinate due to its lower miscibility in water and it is persistent with diesel even at the diesel cloud point [174].

Succinic acid

Succinic acid has secured its place in both the original USDOE and Bozell's list of platform chemicals. It has proven to be one of the potential bioplatform and an essential starting material for producing valuable commodity chemicals. It is also a successful replacement for maleic anhydride. Several transformations are available to produce value added chemicals from succinic acid via esterification, reduction, reductive amination, etc. [175] (Figure 12).

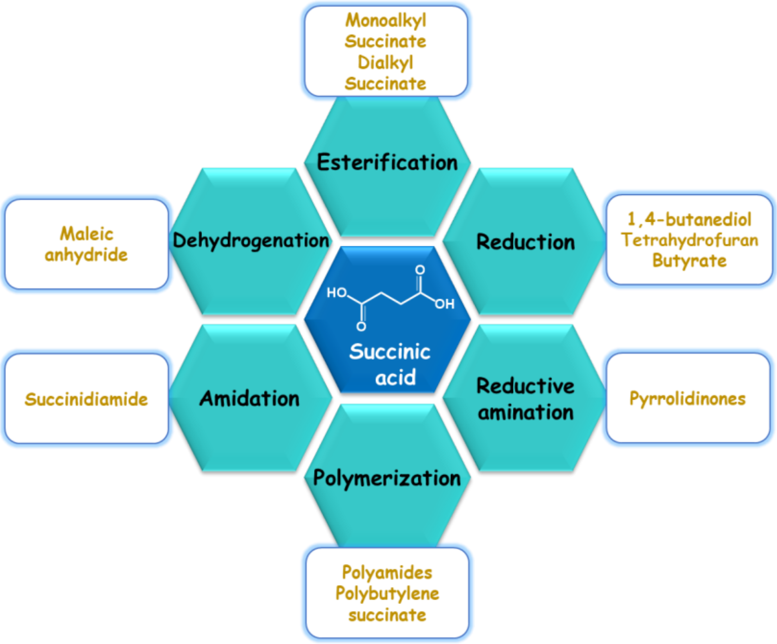


Figure 12 Potential transformations of succinic acid

However, the succinate esters are of particular interest due to their vast flora of industrial applications. They are obtained by esterification of succinic acid and n-butanol, monobutyl succinate and dibutyl succinate, find several synthetic industrial applications such as plasticizers, perfumery, scent in cosmetics and food products, diluents in paints and coatings, drug intermediate and dyes. Moreover, they possess high oxygen content. Therefore, they can be useful as a green solvent [176] and fuel components, especially dibutyl succinate, which works well as a promising fuel additive due to its lower water miscibility [177,178].

Glycerol

High value-added glycerol is a potential bioplatform molecule produced extensively as a major by-product (~10 wt % of total biodiesel formed) during the transesterification reaction of vegetable oil or animal fats with methanol. Raw glycerol finds varied uses and applications in several industries such as food additives, cosmetics, pharmaceuticals, polyesters, resins, etc. [179,180]. Collectively, these industries are unable to exploit all the glycerol formed from biodiesel manufacturing units, hence the present scenario demands the utilisation of this surplus glycerol. In a view of upgrading bio-platform molecules at the marketed level, several transformations of glycerol can be done through dehydration [181], hydrogenation [182], etherification [183], hydrogenolysis [184] etc. (Figure 13).

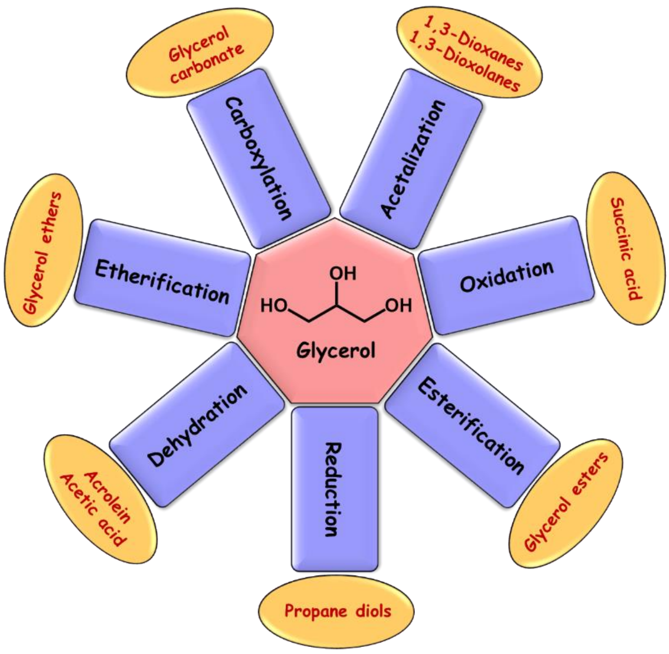


Figure 13 Potential transformations of glycerol

Amongst all, the best way to exploit the reactivity of three hydroxyl groups is through the acetalization reaction. It is one of the vital reactions from the viewpoint of varied applications. Glycerol acetals and ketals, which are potential biodiesel additives/blends [185,186] can be formed by condensation of glycerol with simple aldehydes & ketones using acid catalysts. In this direction, the acetalization of glycerol with furfural produces cyclic acetals, 1,3-dioxane (six-membered) and 1,3-dioxolane (five-membered), which have a tremendous contribution as antiknock additives and accelerators for ignition fuel, as fragrances, as food additives, in beverage, lacquer industries and Pharmaceuticals [186,187].

In the present work, we have selected the esterification of levulinic acid and succinic acid and acetalization of glycerol from the viewpoint of significant industrial transformations as well as important applications of the obtained products (Figure 14).

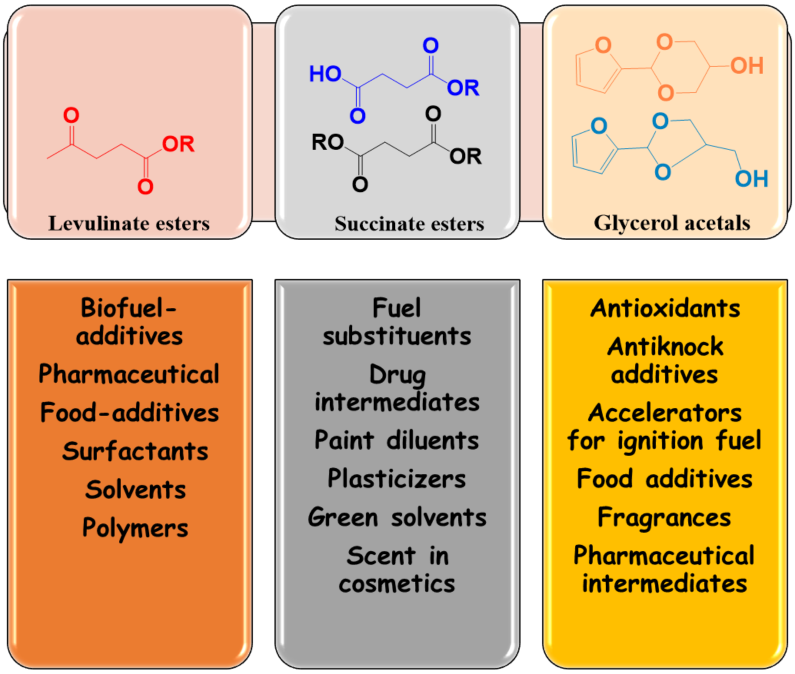


Figure 14 Importance and applications of products

Thus, based on the thorough literature survey, the objectives were set as follows:

1. To synthesize and characterize silica support, MCM-48
2. To tune the acidic properties of parent silicotungstic acid (SiW_{12}) by designing at a molecular level (formation of mono lacunary silicotungstate, (SiW_{11})
3. To synthesize heterogeneous catalysts by anchoring SiW_{12} and SiW_{11} onto different supports (Synthesized MCM-48 and commercially acquired MCM-22)
4. To characterize the synthesized catalysts by TGA, FT-IR, XRD, BET surface area and pore size distribution, TEM and acidic properties by n-butylamine and potentiometric titration
5. To carry out the potential transformations of bioplatform molecules such as levulinic acid, succinic acid, and glycerol into value added products via esterification and acetalization.
6. To identify the activation energy and to study the mechanistic pathway of the proposed reactions
7. To study the regeneration and recycling of the catalysts
8. To study the effect of active species as well as the support on the catalytic activity
9. To select the best catalyst based on the performance for the said reactions under similar reaction conditions

Organization of the Thesis

The set objectives were covered in two parts.

- **Part A: Silicotungstates anchored to MCM-48**
  - Chapter 1: Parent Silicotungstic acid (SiW_{12}) anchored to MCM-48: Synthesis, characterization and esterification as well as acetalization reactions
  - Chapter 2: Mono lacunary Silicotungstate (SiW_{11}) anchored to MCM-48: Synthesis, characterization and esterification as well as acetalization reactions

- **Part B: Silicotungstates anchored to MCM-22**
  - Chapter 1: Parent Silicotungstic acid (SiW_{12}) anchored to MCM-22: Synthesis, characterization and esterification as well as acetalization reactions
  - Chapter 2: Mono lacunary Silicotungstate (SiW_{11}) anchored to MCM-22: Synthesis, characterization and esterification as well as acetalization reactions

- **Annexure**: New Application: Catalytic degradation of some organic dyes over Silicotungstic acid anchored to MCM-22

A brief overview of each chapter

Part A: Silicotungstates anchored to MCM-48

Chapter 1 deals with the non-hydrothermal synthesis of nano-porous MCM-48 (nMCM-48) and a catalyst, parent Silicotungstic acid (SiW_{12}) anchored to nMCM-48, SiW_{12}/nMCM-48. Detailed characterization of catalyst using, acidity measurement, BET surface area measurements, elemental analysis (EDS), TGA, FT-IR, Powder XRD, ^{29}Si MAS NMR and TEM was carried out. The catalytic activity of the catalyst was evaluated for the esterification of levulinic and succinic acid with n-butanol as well as the acetalization reaction of glycerol with furfural. A detailed optimization study for all the reactions was carried out by keeping the experiments in varying reaction parameters, such as mole ratio of reactants, catalyst amount, reaction temperature and time. The regeneration and recycling studies were also carried out along with the characterization of regenerated catalysts. Furthermore, the activation energy of the reactions was identified and their mechanistic pathways were proposed.

Chapter 2 describes the synthesis of mono lacunary silicotungstate (SiW_{11}) and the catalyst, mono lacunary silicotungstate anchored to nMCM-48 (SiW_{11}/nMCM-48). It includes detailed characterization of catalyst using various physicochemical techniques and the catalytic efficiency of the catalyst was investigated for similar reactions, esterification as well as acetalization reactions of bioplatform molecules along with their thorough optimization study by varying different reaction parameters. To identify the sustainable nature of the catalyst, recycling experiments, as well as characterization of regenerated catalyst, were also carried out. Correspondingly, the activation energy for each reaction was identified by conducting kinetic experiments at different temperatures and time intervals. Moreover, a mechanism for each system was proposed and the effect of lacuna was studied.

Part B: Silicotungstates anchored to MCM-22

Chapter 1 demonstrates the synthesis of a catalyst comprising silicotungstic acid (SiW_{12}) and zeolitic support, MCM-22 (SiW_{12}/MCM-22) and its detailed characterization. The catalytic behaviour of the catalyst was investigated for the esterification as well as acetalization reaction of said bioplatform molecules and their detailed optimization study was carried out. The experiments in varying reaction parameters were screened and the optimum conditions were found, where maximum conversion of a substrate and the desired product was achieved. The sustainable nature and reliability of the catalyst were checked by recycling experiments as well as the characterization of regenerated catalyst. Kinetic experiments at different temperatures and time intervals were carried out to find the activation energy for all transformations. Also, a mechanism for each system was proposed.

Chapter 2 depicts the synthesis of catalyst, mono lacunary silicotungstate (SiW_{11}) anchored to MCM-22 (SiW_{11}/MCM-22) and characterized in detail by various physicochemical techniques. Similar catalytic applications, i.e., esterification and acetalization reactions of bioplatform molecules (levulinic acid, succinic acid and glycerol) were carried out. The reaction conditions to obtain the maximum conversion of the substrate and to achieve selectivity of desired products were determined by a detailed optimization study. The sustainability, as well as the true heterogeneous nature of the catalyst, was studied by recycling experiments and characterization of regenerated catalyst. The activation energy for all the reactions was determined from kinetic experiments and the probable mechanism was proposed.

Further, comparison of the activity of all the synthesized catalysts and a discussion on the effect of active species (SiW_{12}/SiW_{11}) as well as the effect of supports (nMCM-48/MCM-22) were also discussed. Based on this study, the best catalyst was proposed among the synthesized ones.

Annexure includes the new catalytic application of the parent silicotungstic acid anchored to MCM-22 (SiW_{12}/MCM-22) for the degradation of some organic dyes, present in the wastewater.

Characterization techniques used in the present work

Characterization of a heterogeneous catalyst is a fundamental part of catalyst development [188–190]. For a better understanding of the connection between the properties of the catalyst and its performance, as well as to know the intermediates present on the surfaces of the catalysts during the reaction, it is inevitable to elucidate their structures, compositions, and chemical properties of both the active species and the support (solid) used in heterogeneous catalysis. This acquaintance is vital to developing highly active, selective, and robust catalysts. Furthermore, information about the catalyst properties is also important to optimize a particular reaction condition for the desired products [191].

The types of acidic sites strength were determined by the potentiometric titration method.

Acidity measurement by potentiometric titration

The surface acid properties of a solid acid catalyst involve the determination of the acidic strength, types of acidic sites (very strong/strong/weak) and their density (number of acid centers per unit surface area of the solid). These descriptions are difficult to conquer, as the strength and the density of the sites are related to each other. Also, the distribution of the acid strength is usually heterogeneous.

Acidity measurements, in terms of acidic strength and sites, of the support and catalysts were measured using the potentiometric titration method as reported in the literature [192,193]. Suspension of 0.25 g of support/catalyst in 25 mL acetonitrile (ACN) was prepared. In this suspension, 0.1 mL of 0.05 N n-butylamine solution in ACN was added and allowed to stir for 3 h at 25 °C.

After that, the suspension was titrated against the same n-butylamine solution and the difference in the values of potential was measured by the digital pH meter. The acid strength of surface sites was designated according to the given scale: Ei>100 mV (very strong sites), 0<Ei<100 mV (strong sites), −100<Ei<0 mV (weak sites) and Ei<−100 mV (very weak sites).

A heterogeneous catalyst can be characterized by various tools involving different spectroscopic and physicochemical techniques. In recent times, many techniques have been developed for identifying the chemical composition, electronic properties and structure of the upper atomic layers of solids. These analytical techniques can be classified depending on the information obtained by them.

In the present work, the following characterization tools, as shown in Figure 15, have been used.

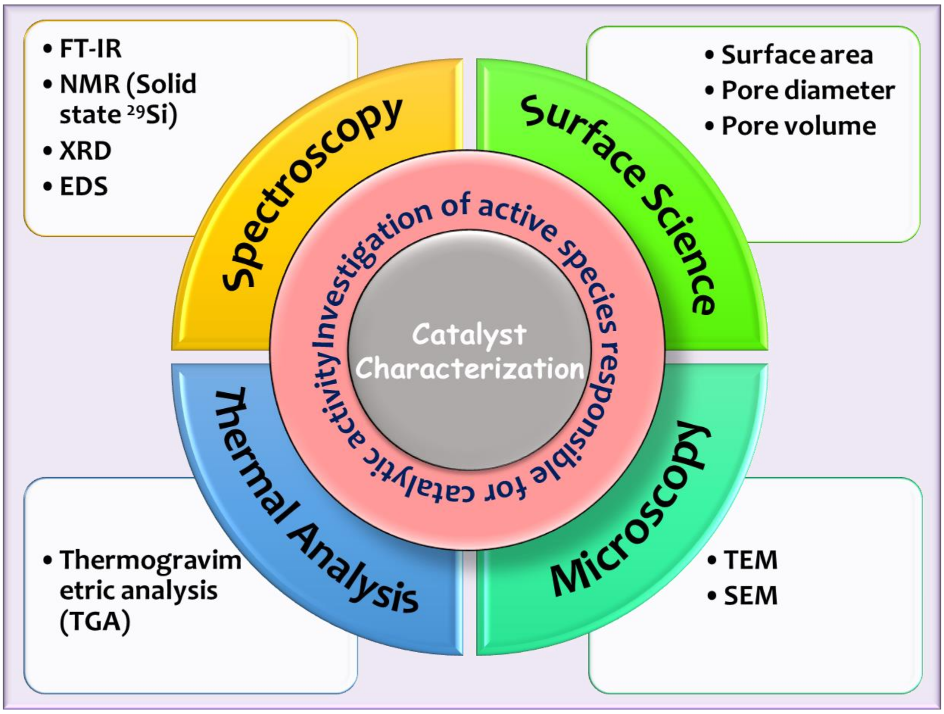


Figure 15 Tools for characterization techniques

BET surface area analysis [194]

Determination of the surface area of a heterogeneous catalyst becomes inevitable as the surface area of the catalyst is directly related to its catalytic activity. Also, it acquaints us with information about pore volume and pore size.

The Nitrogen adsorption-desorption isotherms of support and catalysts were recorded using a Micromeritics Surface Area analyzer (Model: ASAP 2010) with Nitrogen adsorption at 77 K. The samples were degassed under vacuum (5 – 10.3 mmHg) to evacuate the physisorbed moisture, at 150 °C for 4 h, before measurement. The specific surface area and pore size were calculated using Brunauer-Emmett-Teller (BET) method and the pore size distributions were calculated by Barrett-Joyner-Halenda (BJH) adsorption-desorption method.

Elemental Analysis: Energy-dispersive X-ray spectroscopy (EDS or EDX) [195]

Energy-dispersive X-ray spectroscopy (EDS or EDX) is one of the analytical tools, which gives information about the presence of elements (elemental analysis) or chemical characterization of a sample. It is the variant of X-ray fluorescence spectroscopy which depends on the examination of a sample through interactions between electromagnetic radiation and matter. It analyzes X-rays emitted by the matter in response to being hit with charged particles. The fundamental principle which governs its characterization capabilities is the fundamental fact that each element possesses a unique atomic structure, permitting X-rays that are characteristic of an element's atomic structure to be identified exclusively from one another.

The elemental analysis was performed by using the JSM-7100F (Model) EDX-SEM analyser for the quantitative determination of elements.

Thermogravimetric analysis (TGA) [194]

Thermogravimetric analysis is a useful tool for the measurement of the thermal stability of materials. Here, the substance is heated or cooled at a controlled rate and the weight is recorded as a function of time or temperature. For a supported catalyst, the profile of temperature-weight loss can provide important quantitative information on the presence of types of water in the sample. It differentiates loosely held "physisorbed" water and strongly bonded "chemisorbed" water, thus helping in determining the best conditions for removing the former.

Moreover, in the case of a less stable catalyst, the study of its decomposition can be done which helps in determining the maximum activation temperatures and the temperature range at which the supported species are stable to use in reactions.

TGA was performed under a nitrogen atmosphere with a flow rate of 2 mL min^{-1} at 25 – 600 °C and a ramp rate of 10 °C min^{-1} using Mettler Toledo Star SW 7.01 (Model)

Fourier Transform Infrared spectroscopy (FTIR) [194]

FT-IR spectroscopy is a powerful tool and widely used technique for the identification of functional groups present in materials/supported species. It usually provides the following useful information.

a. Determination of the surface species

b. Dispersion of the species over the support surface

c. Surface activity studies with the use of probe molecules

The common ways of preparing a sample for studying an insoluble solid are: 1) as a mull; 2) as a disc (using KBr), and 3) directly as a powder. These methods vary in terms of the extent of difficulty in obtaining spectra, ease of preparation of the sample, and reliability of the information obtained. The mull and disc methods are transmittance techniques.

The FT-IR spectra were recorded by preparing a disc of KBr and sample in a ratio of 10:1, on a Shimadzu instrument (IRAffinity-1S Model) in the range 4000-400 cm^{-1} at an average of 45 scans

Powder X-ray Diffraction (XRD) [195]

XRD is a useful tool that offers quick information on the forms (crystalline/amorphous) and phases of a solid reagent/material. It also measures the efficiency of dispersion of any supported reagent where the reagent generally exists in the crystalline form. In principle, XRD may correspondingly be useful for the identification of species formed during the preparation of a supported reagent.
The XRD patterns of the support and the catalyst were recorded using a D8 FOCUS X-ray Diffractometer (Model) from Bruker in the 2θ range of 0-80^o using CuKα radiation (λ = 1.54056 Å).

Solid state MAS NMR (^{29}Si) [194]

Magic Angle Spinning (MAS), in nuclear magnetic resonance, is a technique often used to perform experiments in solid-state NMR spectroscopy. By spinning the sample, usually at a frequency of 1 to 70 kHz at the magic angle θ_m (ca. 54.74°, where cos2θm=1/3) in the direction of the magnetic field, the normal broad lines become narrower and increase the resolution for better identification and analysis of the spectrum.
The chemical shifts of peaks in solid-state ^{29}Si NMR spectra were used for the characterization of solid materials using JOEL ECX 400 MHz High resolution multinuclear FT-NMR spectrometer (Model) for solid samples.

Transmission Electron Microscopy (TEM) [196]

TEM is a technique that utilizes a transmitted electron beam to image a particle sample. It is a preferred method to measure particle size, distribution of size and morphology. Additionally, it determines the elemental composition of the sample with high spatial resolution from the analysis of the X-ray produced by the interaction between the accelerated electrons and the sample.

TEM images were recorded on the JEOL TEM instrument JEM 2100 (Model) by applying an acceleration voltage of 200 kV using carbon coated 200 mesh Cu grid. The samples were dispersed by ultrasonication and coated on the grid, left overnight for drying in air.

Catalytic activity

Leaching test

The leaching of an active species from the support makes the catalyst unappealing. Therefore, it is inevitable to check the stability of heteropoly anions inside the porous supports. Heteropoly acids can be determined by developing heteropoly blue colour when they are treated with a mild reducing agent, such as ascorbic acid [197]. In this work, we have used a similar method to check the leaching of SiW_{12}/SiW_{11} from the supports, nMCM-48/MCM-22.
A series of 1-5 % solutions of SiW_{12}/SiW_{11} in water were prepared for standard samples. To 10 mL of the above samples, 1 mL of 10% ascorbic acid solution was added. The resulting mixture was diluted to 25 mL and scanned at a λ_{max} of 785 nm. A standard calibration curve was obtained by plotting values of absorbance with percentage solution. In a typical procedure, 1 g of the catalyst was taken in 10 mL of conductivity water and refluxed for 4 h. 1 mL of the supernatant solution was then treated with 10% ascorbic acid.
The same procedure was followed with all the acids and alcohol substrates and, the filtrates of the reaction mixtures (filtered in hot conditions) after the completion of the reaction.

The activity evaluation of the synthesized catalyst leads to the systematic development of new catalytic process by carefully undergoing a series of experimental steps. A diagrammatic representation for the catalyst development is shown in figure 16.

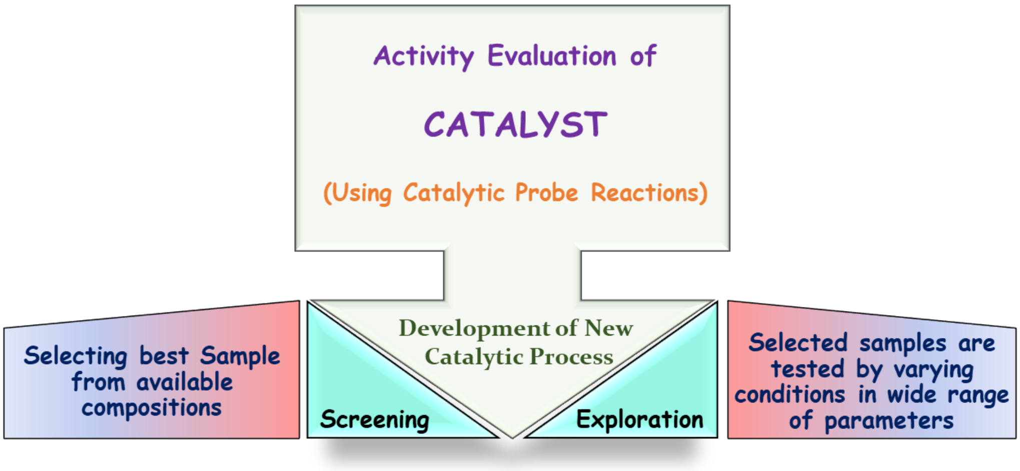


Figure 16 Tools for catalyst development

a) Esterification of levulinic acid with n-butanol

In a typical reaction procedure, levulinic acid (0.01 mol, 1.16 g), 1-butanol (0.02 mol, 1.482 g) and the required amount of catalyst were charged in a 50 mL batch reactor equipped with an air condenser, guard tube and a magnetic stirrer. The reaction was allowed to proceed at desired temperature and time. After completion of the reaction, the reaction mixture was gradually cooled at room temperature and the contents were diluted using 7-10 mL dichloromethane.

b) Esterification of succinic acid with n-butanol

The esterification reaction of succinic acid was performed in a 50 mL batch reactor equipped with a magnetic stirrer, an air condenser and a guard tube. Succinic acid (0.01 mol, 1.181 g), n-butanol (0.03 mol, 2.223 g) and the required amount of catalyst were charged in a glass reactor and allowed to react at the desired temperature. After completion of the reaction, the mixture was gradually cooled at room temperature and the contents were diluted with 10 mL methanol.

c) Acetalization of glycerol with furfural

The acetalization of glycerol was carried out in a 50 mL 2-neck batch reactor equipped with a magnetic stirrer under a nitrogen atmosphere. The reactor was charged with glycerol (0.01 mol, 0.92 g), furfural (0.01 mol, 0.96 g/0.02 mol, 1.92 g) and an essential amount of catalyst. The mixture was stirred vigorously at the required temperature under a nitrogen atmosphere and maintained for a certain interval of time. After the reaction, the contents of the mixture were diluted with 10-15 mL of 2-propanol.

For all the reactions, the reactant and products were analyzed using gas chromatography, Shimadzu 2014 GC. The obtained products were confirmed by comparing it with their respective standard samples.

Gas Chromatography (GC) [198]

GC is a type of chromatography used to separate and analyze the material, which is vaporized without decomposition. Its main applications include testing the purity of a compound and the separation of components of a mixture. In the present work, all the GC experiments were carried out on Shimadzu GC-2014 instrument using RTX-5 capillary column (internal diameter: 0.25 mm, length: 30 m) with nitrogen as carrier gas and flame ionization detector (FID).

All the reactions were carried out twice for the optimization of different reaction parameters and under the optimized reaction conditions, the reactions were repeated thrice. The results were reproducible with an error of ± 1 - 1.5%.

The conversion and selectivity for all the reactions were calculated by the following equations,

$$Conversion = \frac{(initial\ mol\%) - (final\ mol\%)}{(initial\ mol\%)}\ x\ 100$$

$$Selectivity = \frac{moles\ of\ product\ formed}{moles\ of\ substrate\ consumed}\ x\ 100$$

The Turnover Number (TON) and Turnover Frequency (TOF) were calculated by using the following equations,

$$TON = \frac{moles\ of\ product\ formed}{moles\ of\ catalyst}$$

$$TOF = \frac{TON}{reaction\ time}$$

The TON and TOF were calculated using the active amount of SiW_{12}/SiW_{11} present in the catalyst.

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