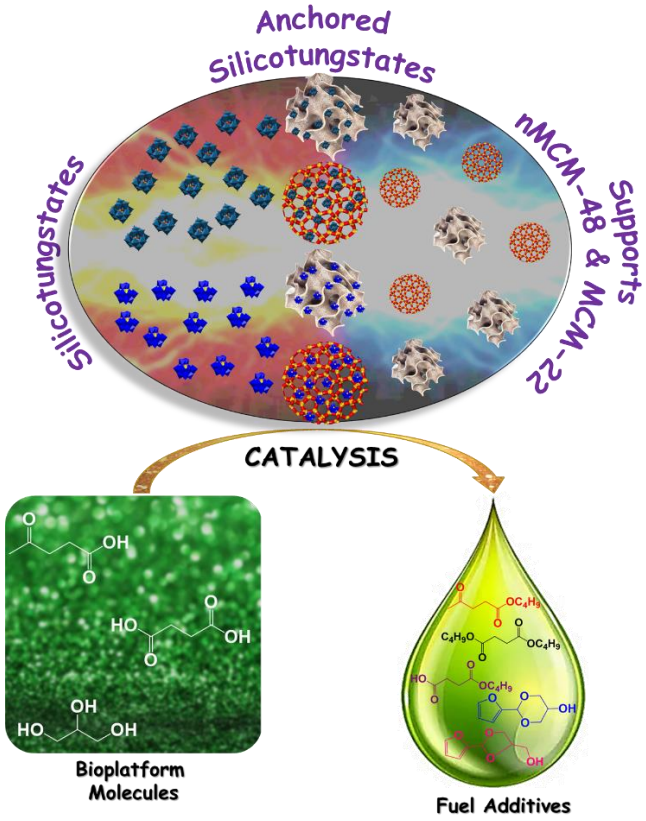
Summary of thesis entitled

Anchored Silicotungstates: Synthesis, Characterization and Conversion of some Bioplatform molecules into Value added products



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By

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

Crude oil and other liquids derived from fossil fuels are refined into petroleum products that mankind uses for numerous purposes. Historically, petroleum has been the key energy source for global energy consumption. The human race exploits petroleum products to propel vehicles, heat buildings, and produce electricity. While in the world of petrochemical industries, petroleum is used as a feedstock or a raw material to generate products such as plastics, soaps and detergents, solvents, drugs, fertilizers, pesticides, explosives, synthetic fibers and rubbers, paints, epoxy resins, and hundreds of other intermediates and end-user goods [1,2].

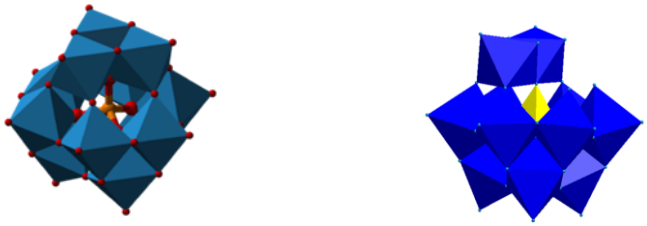
The upsurge in the demand of liquid fuel consumption and the diminishing fossil fuels to supply the global energy demand have attracted a worldwide mass of prospect scientists. This emerging research across the globe is driven by the rising shortage of fossil fuels, concerns regarding global warming and the increase in oil charges. Henceforth this challenging task can be addressed by replacing the non-renewable fossils by renewable biomass and inventing excellent sustainable technologies for production of biofuels biofuel additives and valuable chemicals from non-edible feedstock and judiciously selected bio-platforms, thus thereby building a base for future bio-based refineries[3].

The ultimate biorefinery concept is a germane research area, and these future findings hold their roots in an amazing capability of biomass, as an excellent alternative source to depleting non-renewable fossils. Nevertheless, the transformation of large biomass feedstock to simpler molecules is a challenging and developing domain. In this direction, valorization of platform chemicals, that are obtained from biomass can become a commencing objective for converting biobased feedstock to valuable chemicals, commodity materials and biofuels [4,5].

A biological material, biomass is a renewable energy source, derived from plants and animals or living organism. Future green and sustainable chemistry will rely on the creation of new product supply chains based on platform molecules derived from biomass. Although there is a large body of reported work on the production of these bioplatform molecules, it is very important to develop effective processes for adding value to these compounds through clean and efficient downstream chemistry. This can be achieved by catalysis which offers relevant possibility for sustainable production[6,7].

In the last two decades, the use of polyoxometalates (POMs) as catalysts has gained tremendous interest and open new expectations. By using polyoxometalates based catalysts, it is frequently possible to obtain higher selectivity and successfully solve ecological problems. They have several advantages as catalysts which make them economically and environmentally attractive. They have unique set of physicochemical properties that are of great value for catalysis. Among them the most important are well defined structure and strong Bronsted acidity. Their versatility and accessibility have led to many applications in various areas[8,9]. An additional attractive aspect of POMs in catalysis is their inherent stability toward oxygen donors [10–12]. The acidic as well as redox properties of POMs are a function of the nature of the metal atoms (addenda atoms) and of both the heteroatom and the counter ions. The structural reorganization of POMs occurs in the solution state depending on the conditions such as temperature, concentrations, and pH of the solution[8].

The replacement of one or more addenda atoms is expected to tune the acidic as well as redox properties, which may lead to the development of active and selective catalysts. These are called as lacunary POMs (LPOM). Removal of one MO units from the fully occupied POM silicotungstic acid **$[SiW_{12}O_{40}]^{4-}$** (SiW_{12})**,** giving rise to LPOM: mono lacunary **$[SiW_{11}O_{39}]^{8-}$** (SiW_{11}) (Figure 1).



$[SiW_{12}O_{40}]^{4-}$ $[SiW_{11}O_{39}]^{8-}$

Figure 1 Parent silicotungstic acid and Mono lacunary silicotungstate

Polyoxometalates are less corrosive and produce low amount of waste than conventional acid catalysts, they can be used as replacement in environmentally benign processes. As non-toxic crystalline substances, they are also preferable with regard to safety and ease of handling.

Keeping in mind these mentioned things; we have chosen silicotungstate based POMs for synthesis, characterization and catalytic applications because of some of its unique properties,

- Best amongst POMs in terms of hydrothermal stability
- Second best in terms of acidity after phosphotungstates
- Ease of synthesis
- Act as very good acid catalyst in homogeneous medium
- Still catalysis by Silicotungstates is less explored

Though, there are many advantages, the major disadvantages of polyoxometalates in homogeneous medium are solubility in polar medium, tedious separation of catalyst from reaction mixture and low thermal stability. The supporting of **POM** and **LPOM** on the suitable support is expected to overcome the above-mentioned problems.

Amongst various available supports, mesoporous and zeolitic supports are unique due to their interesting properties. MCM-48 and MCM-22 are of immense interest due to their unique pore networks, 3D cubic and 2D sinusoidal, respectively[13–16]. The pores are large enough to accommodate POMs in their channels. The loading of POMs on the mesoporous materials not

only allows transfer of POMs catalyzed reactions from homogeneous to heterogeneous medium but also effectively increases the surface area of POMs. The perfect pore size of these materials benefits the easy access of reactants and products.

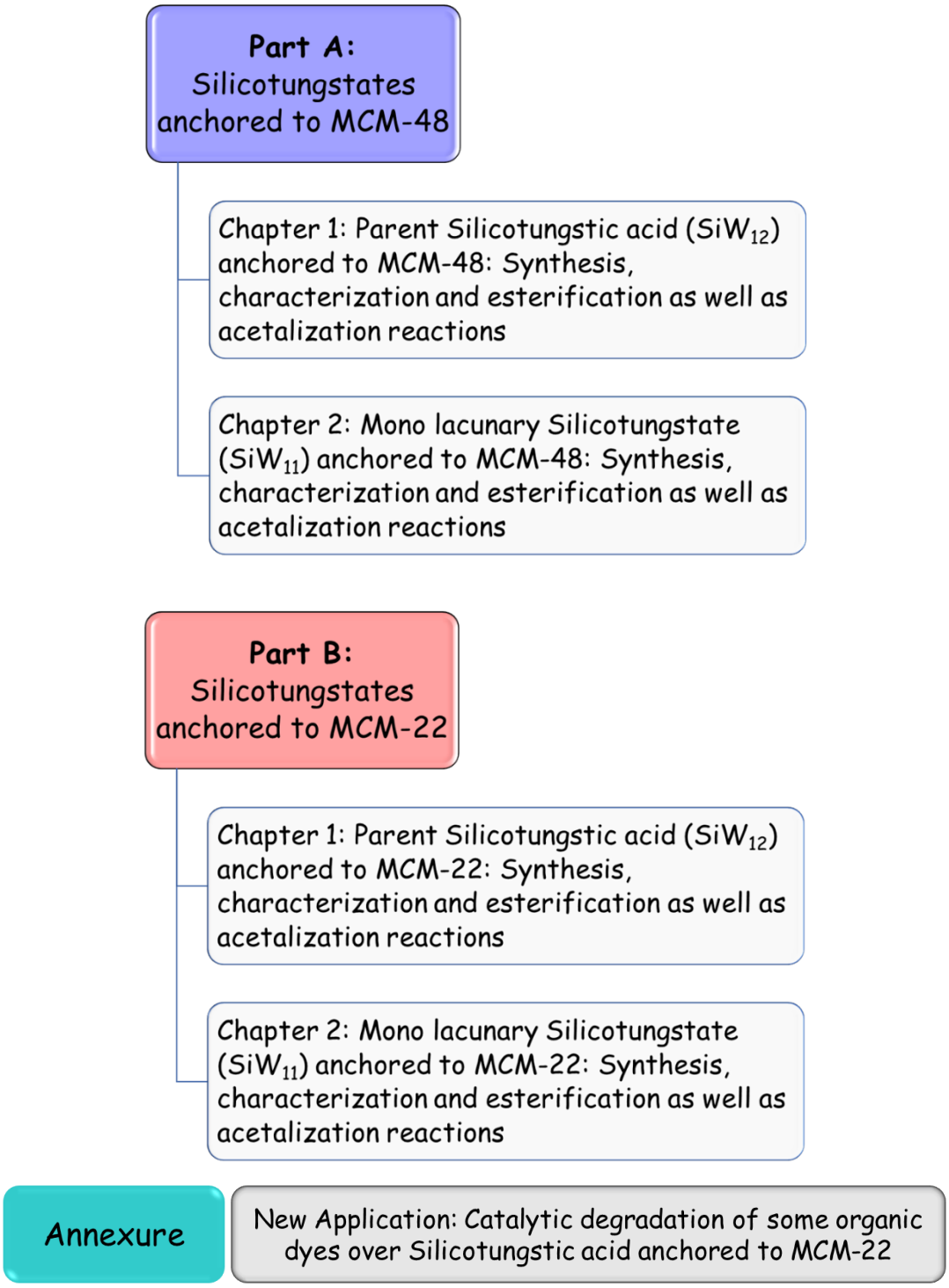
Keeping in mind the importance of conversion of Bioplatform molecules as well as development of new heterogeneous catalysts, it was thought to develop efficient heterogeneous catalysts comprising parent silicotungstic acid (SiW_{12}) as well as mono lacunary silicotungstate (SiW_{11}) and porous materials (MCM-48 and MCM-22), the objectives of this work are planned.

Objectives

1. To synthesize and characterize a silica support, MCM-48
2. To tune the acidic properties of parent silicotungstic acid (SiW_{12}) by designing at molecular level (formation of mono lacunary silicotungstate, (SiW_{11})
3. To synthesize heterogeneous catalysts by anchoring SiW12 and SiW11 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, SEM, 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

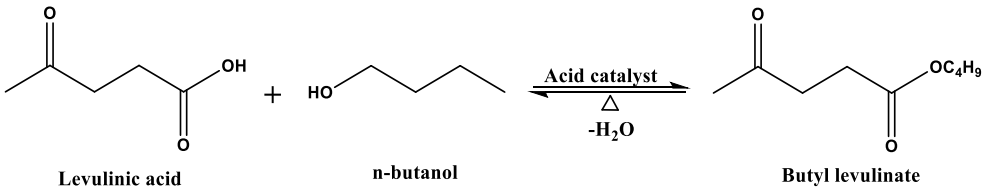
The set objectives were covered in two parts.



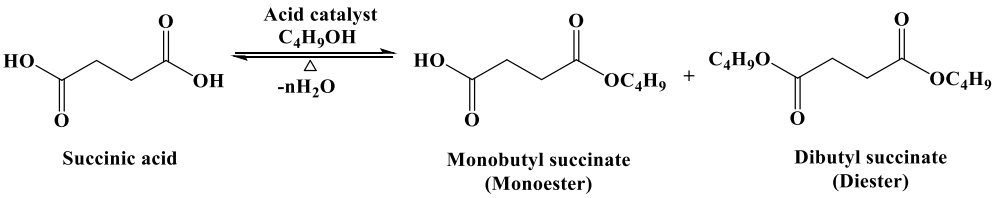
Part A: Silicotungstates anchored to MCM-48

Chapter 1 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 by a simple wet impregnation method. 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.

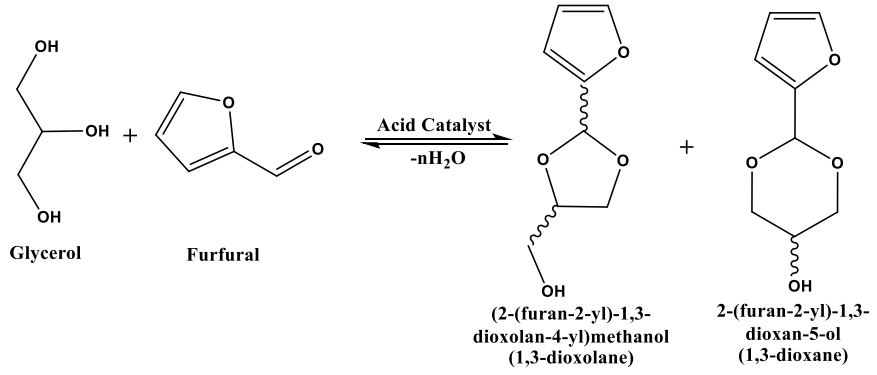
The catalytic activity of the catalyst was evaluated for the esterification of levulinic and succinic acid with n-butanol (Scheme 1 and Scheme 2) as well as the acetalization reaction of glycerol with furfural (Scheme 3)



Scheme 1 Esterification of levulinic acid with n-butanol



Scheme 2 Esterification of succinic acid with n-butanol



Scheme 3 Acetalization 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 optimized reaction conditions for all three reactions are as follow (Table 1),

Table 1 Optimized reaction conditions and obtained results over SiW_{12}/nMCM-48

Reaction	Optimized reaction conditions mole ratio/cat amount/temp/time	% Conv/Sel*	TON/TOF (h^{-1})
[a] Levulinic acid esterification	1:2/50mg/90 °C/4 h	99/100	2469/617
[b] Succinic acid esterification	1:3/100mg/80 °C/8 h	98/84	1227/153
[c] Glycerol acetalization	1:1/15mg/30 °C/40 min	89/69	7355/10978

*Selectivity of [a]Ester (Butyl levulinate), [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

The control experiments (Table 2) showed that the enhancement of acidic sites by Bronsted acidity present in SiW_{12} plays a significant role in promoting the reaction towards a forward direction, and also governs the formation of desired products. Overall, the concept of heterogenization of SiW_{12} by nMCM-48 offers an excellent catalytic system.

Table 2 Control experiments

Materials	% Conversion/%*Selectivity of desired product		
	[a]Levulinic acid esterification	[b]Succinic acid esterification	[c]Glycerol acetalization
nMCM-48	24/100	21/16	3.1/52
SiW_{12}	96/100	100/81	91/58
SiW_{12}/nMCM-48	99/100	98/84	89/69

Reaction conditions mole ratio [a]1:2, [b]1:3, [c]1:1; catalyst amount nMCM-48 [a]38.46 mg, [b] 77 mg, [c]11.5 mg; SiW_{12} [a]11.54 mg, [b]23 mg, [c]3.5 mg; SiW_{12}/nMCM-48 [a]50 mg, [b]100 mg, [c]15 mg; temperature [a]90 °C, [b]80 °C, [c]30 °C; time [a]4 h, [b]8 h, [c]40 min.
*Selectivity of [a]Butyl levulinate, [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

The regeneration and recycling studies were also carried out and the catalyst showed consistent activity for multiple runs. The characterization of regenerated catalysts intimated the sustainable nature of the catalyst and no change in its structure was observed. The comparative studies of esterification reactions under similar experimental conditions suggests that the activity of catalyst is more in levulinic acid esterification, as compared to succinic acid esterification.

Furthermore, the activation energy of the reactions was determined by carrying out experiments in different temperatures and time intervals. As observed from that the activation energy for all reactions exceeds 25 kJ/mol, indicating that the reactions are governed by a true chemical step and none of it follows a diffusion regime. It is noteworthy that amongst all the three transformations, the activation energy for esterification of levulinic acid was found to be the lowest (only 26 kJ/mol) (Table 3). This can be explained as levulinic acid is a monocarboxylic keto acid, which requires only one acid group to convert into the desired ester, whereas succinic acid possesses two carboxylic acid groups, a diacid requiring a higher number of catalytic sites as well as prolonged reaction time to undergo diesterification reaction, to obtain the desired diester and the obtained activation energy is in good agreement with it.

Table 3 Activation energy for all reactions over SiW_{12}/nMCM-48

Reaction	Temperature range (K)	Time intervals	Activation energy Ea (kJ/mol)
Levulinic acid esterification	323 – 353	2 – 6 h	26
Succinic acid esterification	343 – 373	4 – 8 h	55
Glycerol acetalization	293 - 323	20 – 60 min	35

Based on above observations, the mechanistic pathway for all three reactions was proposed. The probable mechanisms are shown below in Figure 2, Figure

3 and Figure 4 for esterification of levulinic acid, succinic acid and acetalization of glycerol, respectively.

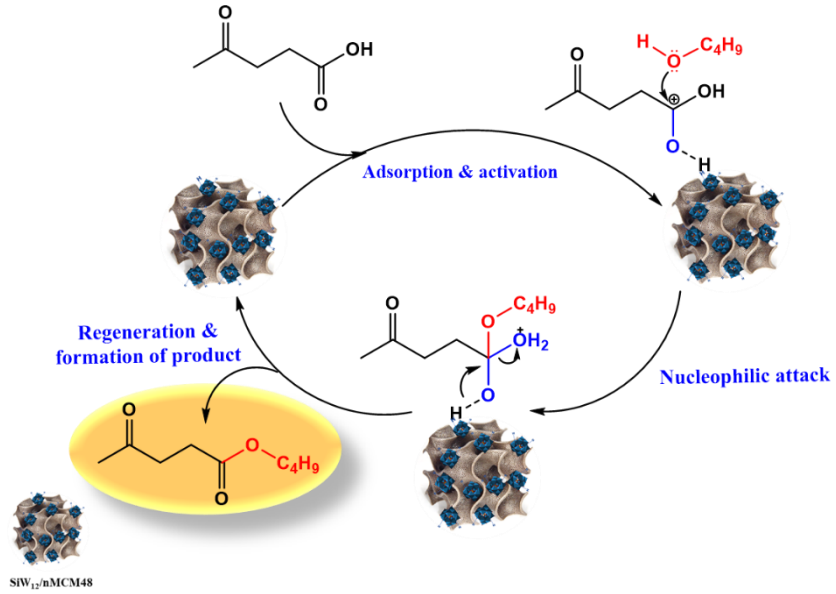


Figure 2 Plausible mechanism of esterification of levulinic acid with n-butanol over SiW_{12}/nMCM-48

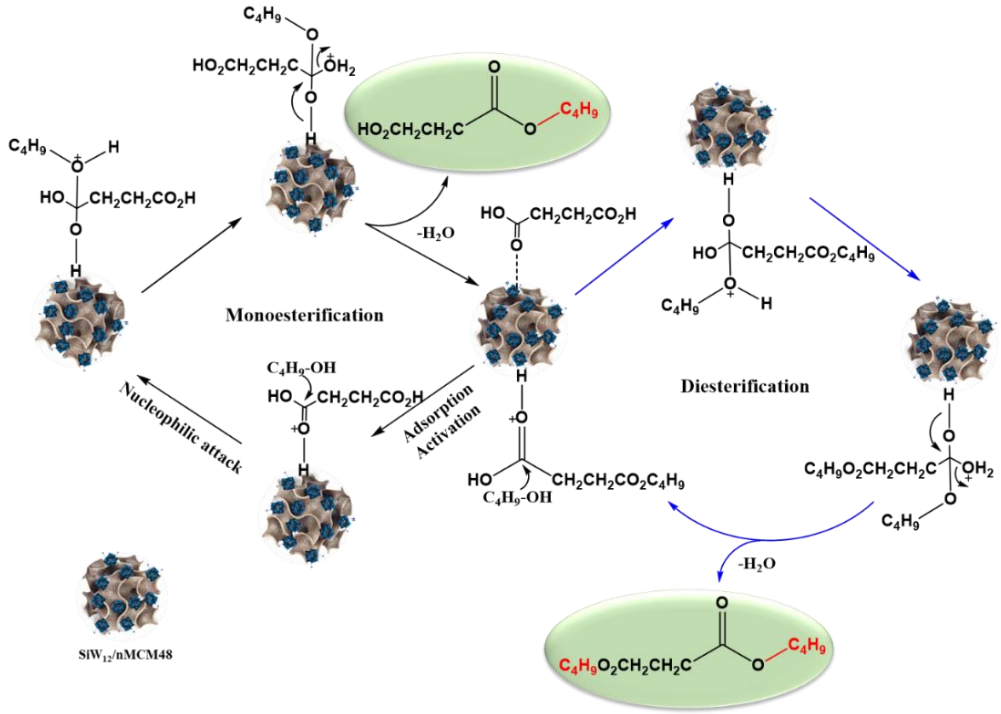


Figure 3 Plausible mechanism of esterification of succinic acid with n-butanol over SiW_{12}/nMCM-48

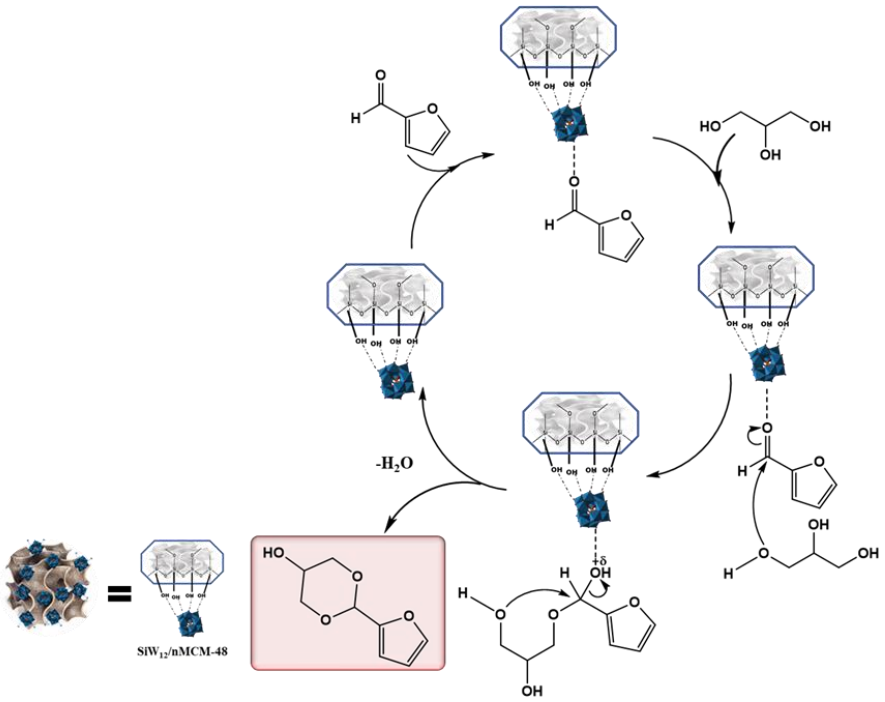


Figure 4 Plausible mechanism of acetalization of glycerol with furfural over SiW_{12}/nMCM-48

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) by impregnation method. It includes detailed characterization of SiW_{11} as well as catalyst using various physicochemical techniques.

To study the effect on catalytic efficiency of the catalyst by removal of one tungsten-oxygen unit, detailed optimization by varying different reaction parameters for similar reactions was carried out. The obtained results in the optimized reaction conditions over SiW_{11}/nMCM-48 are tabulated in Table 4.

Table 4 Optimized reaction conditions and obtained results over SiW_{11}/nMCM-48

Reaction	Optimized reaction conditions mole ratio/cat amount/temp/time	% Conv/Sel*	TON/TOF (h^{-1})
[a] Levulinic acid esterification	1:2/50mg/90 °C/4 h	49/84	1300/325
[b] Succinic acid esterification	1:3/75mg/90 °C/8 h	83/43	1466/183
[c] Glycerol acetalization	1:2/15mg/50 °C/40 min	66/65	5827/8697

*Selectivity of [a]Ester (Butyl levulinate), [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

The control experiments (Table 5) showed that compared to nMCM-48, SiW_{11} is a more active and responsible species for promoting the esterification reactions form but it is higher to a certain degree for acetalization reaction. Interestingly, the obtained results with the catalyst are appreciable to a greater extent when compared with the reactions with individual species. This suggests that the combined properties of SiW_{11}, as an active species and nMCM-48 as support forms a truly heterogeneous catalyst.

Table 5 Control experiments

Materials	%Conversion/%*Selectivity of desired product		
	[a]Levulinic acid esterification	[b]Succinic acid esterification	[c]Glycerol acetalization
nMCM-48	24/100	52/27	32/60
SiW_{11}	38/79	58/27	23/73
SiW_{11}/nMCM-48	49/84	83/43	66/65

Reaction conditions mole ratio [a]1:2, [b]1:3, [c]1:2; catalyst amount nMCM-48 [a]38.46 mg, [b] 57.7 mg, [c]11.54 mg; SiW_{11} [a]11.54 mg, [b]17.3 mg, [c]3.46 mg; SiW_{11}/nMCM-48 [a]50 mg, [b]75 mg, [c]15 mg; temperature [a]90 °C, [b]90 °C, [c]50 °C; time [a]4 h, [b]8 h, [c]40 min.
*Selectivity of [a]Butyl levulinate, [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

To identify the sustainable nature of the catalyst was established by the recycling studies, as well as characterization of regenerated catalyst. The activity of the catalyst was checked for esterification reactions under identical conditions and similar observation was found that esterification of levulinic acid is faster than that of succinic acid.

The activation energy for each reaction was identified and an observation similar to the previous chapter was found here also. The activation energy for all the reactions is exceeding 25 kJ/mol, which indicates that in SiW_{11}/nMCM-48, the reactions follow the kinetic regime and are truly chemical, at the expense of maximum efficiency of the catalyst. Furthermore, the activation energy for succinic acid esterification with the catalyst was quite high as compared to that of levulinic acid esterification. The explanation for this observation remains the same as given in previous chapter Table 6.

Table 6 Activation energy for all reactions over SiW_{11}/nMCM-48

Reaction	Temperature range (K)	Time intervals	Activation energy Ea (kJ/mol)
Levulinic acid esterification	343 – 373	2 – 6 h	29
Succinic acid esterification	343 – 373	6 – 10 h	75
Glycerol acetalization	303 – 333	20 – 60 min	65

For all three catalytic transformations using SiW_{11}/nMCM-48, we are expecting the same mechanism as shown in Part A Chapter 1 for SiW_{12}/nMCM-48.

Comparison of the activity of SiW_{12}/nMCM-48 and SiW_{11}/nMCM-48

The effect of active species (SiW_{12}/SiW_{11}) for esterification and acetalization reactions, experiments were carried out under identical reaction conditions over SiW_{12}/SiW_{11} anchored to the nMCM-48. From Table 7, it is apparent that the catalytic activity of SiW_{12}/nMCM-48 is much higher than that of SiW_{11}/nMCM-48 for all the reactions. The rate of conversion of substrates, selectivity of the desired product as well as TON and TOF for SiW_{12}/nMCM-48 catalyzed reactions are found to be excellent. The superiority in the activity of SiW_{12}/nMCM-48 can be directly correlated to its surface area.

Table 7 Comparison of activity of SiW_{12}/nMCM-48 and SiW_{11}/nMCM-48

Reaction	Catalyst	% Conv/Sel*	TON/ TOF (h^{-1})	Acidic strength (mV)	BET Surface area (m^2/g)
[a]Esterification of Levulinic acid	**SiW_{12}/nMCM-48**	**99/100**	**2469/617**	**700**	**588**
	SiW_{11}/nMCM-48	49/84	1300/325	460	516
[b]Esterification of Succinic acid	**SiW_{12}/nMCM-48**	**98/84**	**1227/153**	**700**	**588**
	SiW_{11}/nMCM-48	35/18	465/58	460	516
[c]Acetalization of Glycerol	**SiW_{12}/nMCM-48**	**89/69**	**7355/10978**	**700**	**588**
	SiW_{11}/nMCM-48	27/72	2389/3582	460	516

[a]**Esterification of Levulinic acid:** Reaction conditions- Mole ratio 1:2; catalyst amount 50 mg; temperature 90 °C; time 4 h.
[b]**Esterification of Succinic acid:** Reaction conditions- Mole ratio 1:3; catalyst amount 100 mg; temperature 80 °C; time 8 h.
[c]**Acetalization of Glycerol:** Reaction conditions- Mole ratio 1:1; catalyst amount 15 mg; temperature 30 °C; time 40 min.
*Selectivity of [a]Butyl levulinate, [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

From above observations, the catalytic activity order is:

SiW_{12}/nMCM-48 > SiW_{11}/nMCM-48

for both esterification as well as acetalization reactions.

Table 8 Activation energy

Reaction	**SiW_{12}/nMCM-48**	SiW_{11}/nMCM-48
Levulinic acid esterification	26 kJ/mol	29 kJ/mol
Succinic acid esterification	55 kJ/mol	75 kJ/mol
Glycerol acetalization	35 kJ/mol	65 kJ/mol

From **Table 8**, the activation energy order was found to be,

SiW_{12}/nMCM-48 < SiW_{11}/nMCM-48

for both esterification as well as acetalization reactions.

Part B: Silicotungstates anchored to MCM-22

Chapter 1 demonstrates the study of zeolitic support, MCM-22 for anchoring silicotunstic acid. The synthesis of a catalyst comprising silicotungstic acid (SiW_{12}) and MCM-22 (SiW_{12}/MCM-22), and its detailed characterization was carried out using similar physicochemical techniques as mentioned in Part A Chapter 1. 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 (Table 9).

Table 9 Optimized reaction conditions and obtained results over SiW_{12}/MCM-22

Reaction	Optimized reaction conditions mole ratio/cat amount/temp/time	% Conv/Sel*	TON/TOF (h^{-1})
[a] Levulinic acid esterification	1:2/50mg/90 °C/8 h	65/94	1621/203
[b] Succinic acid esterification	1:3/100mg/90 °C/10 h	97/59	1214/121
[c] Glycerol acetalization	1:2/30mg/30 °C/40 min	63/66	2625/3918

*Selectivity of [a]Esters (Butyl levulinate), [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

From the control experiments Table 10, it was observed that he alone support, MCM-22 is relatively less active, compared to alone SiW_{12}. After heterogenization by MCM-22, SiW_{12} plays a central role and the Bronsted acidity provided by it is the active species responsible to achieve the noticeable catalytic activity. For esterification reactions, along with the progress of the reaction, the selectivity also improves greatly by the presence of Bronsted acidity of SiW_{12} in the catalyst, but in acetalization reaction, the Al sites present in MCM-22 are expected to govern the selectivity of dioxane derivative. Thus, the overall observation of control experiments denotes that the combination of SiW_{12} and MCM-22 forms a true heterogeneous catalyst which synergistically works to bring out the best activity of the catalyst.

Table 10 Control experiments for SiW_{12}/MCM-22

Materials	% Conversion/%*Selectivity of the desired product		
	[a]Levulinic acid esterification	[b]Succinic acid esterification	[c]Glycerol acetalization
MCM-22	40/83	64/36	29/76
SiW_{12}	98/100	100/98	65/52
SiW_{12}/MCM-22	65/94	97/59	63/66

Reaction conditions mole ratio [a]1:2, [b]1:3, [c]1:2; catalyst amount MCM-22 [a]38.46 mg, [b] 77 mg, [c]23 mg; SiW_{12} [a]11.54 mg, [b]23 mg, [c]7.0 mg; SiW_{12}/MCM-22 [a]50 mg, [b]100 mg, [c]30 mg; temperature [a]90 °C, [b]90 °C, [c]30 °C; time [a]8 h, [b]10 h, [c]40 min.
*Selectivity of [a]Esters (Butyl levulinate), [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

The sustainable nature and reliability of the catalyst were checked by recycling experiments, giving consistent activity for multiple runs, and by the characterization of regenerated catalyst. Moreover, here also, the activity of catalyst for esterification of levulinic acid was found to be superior as compared to succinic acid in identical conditions.

The activation energy for all three reactions using SiW_{12}/MCM-22 was found to be exceeding 25 kJ/mol (Table 11), which indicated that all the reactions are truly governed by a chemical step and none of them follows a diffusion regime. Also, the present catalyst at its maximum efficiency is capable of lowering the activation energy for esterification of levulinic acid more as compared to that for esterification of succinic acid.

Table 11 Activation energy for all reactions over SiW_{12}/MCM-22

Reaction	Temperature range (K)	Time intervals	Activation energy Ea (kJ/mol)
Levulinic acid esterification	343 – 373	6 – 10 h	36
Succinic acid esterification	353 – 383	6 – 10 h	68
Glycerol acetalization	293 – 323	20 – 60 min	48

Also, a mechanism for each system was proposed based on above observations. The plausible mechanism is shown in Figure 5, Figure 6 and Figure 7.

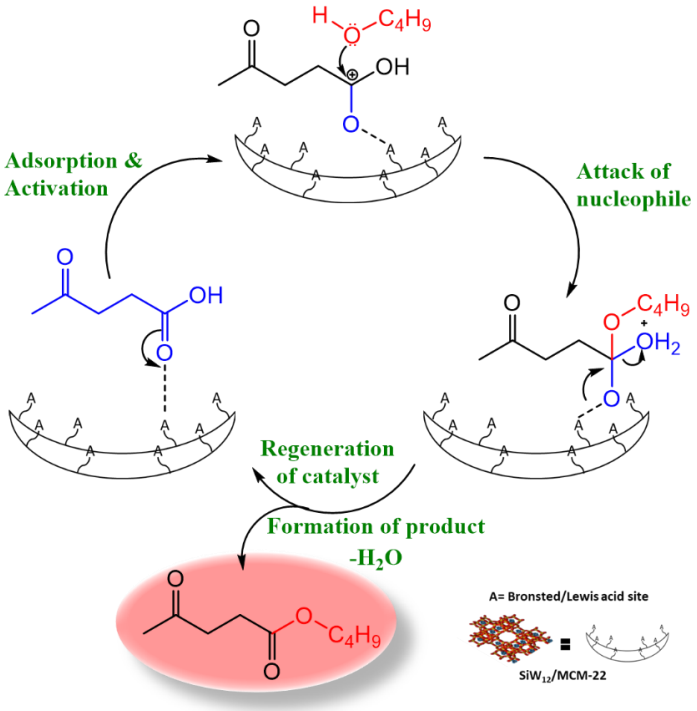


Figure 5 Plausible mechanism of esterification of levulinic acid with n-butanol over SiW_{12}/MCM-22

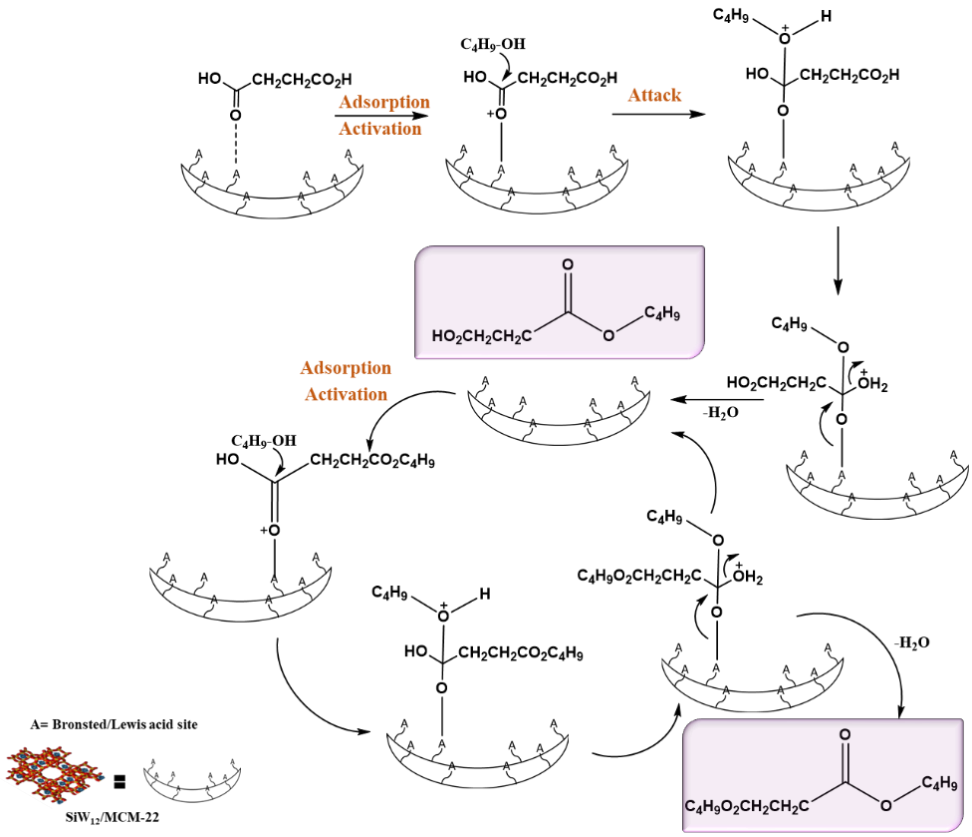


Figure 6 Plausible mechanism of esterification of succinic acid with n-butanol over SiW_{12}/MCM-22

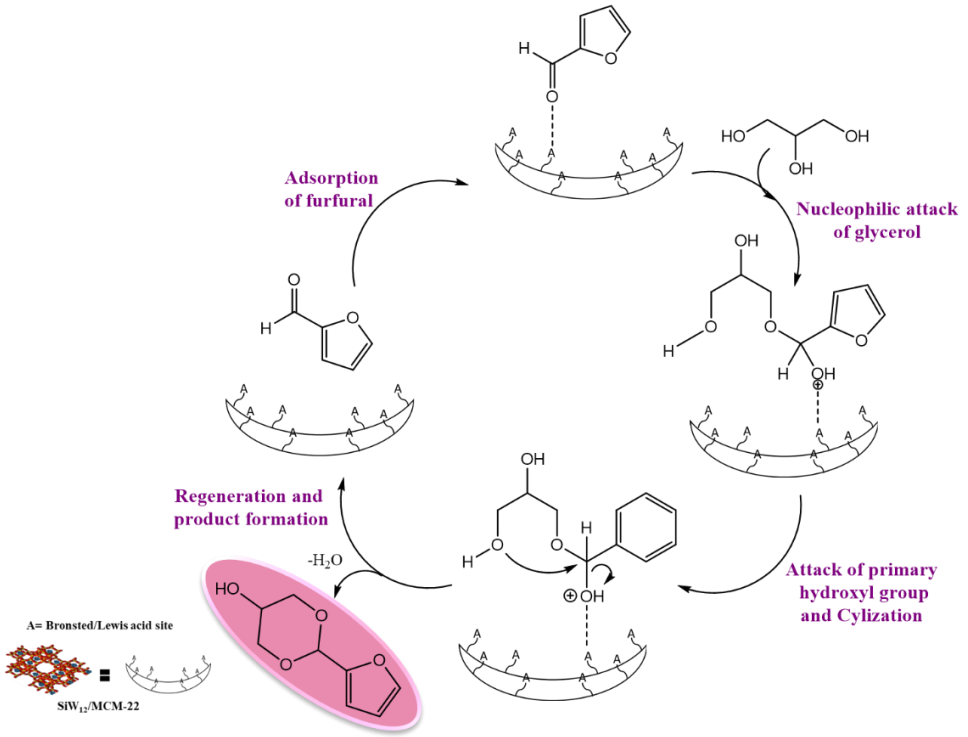


Figure 7 Plausible mechanism of acetalization of glycerol with furfural over SiW_{12}/MCM-22

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. The focus was driven to understand the combination of SiW_{11} and MCM-22 via studying the effect of addenda atom on the similar catalytic applications. 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.

Table 12 Optimized reaction conditions and obtained results over SiW_{11}/MCM-22

Reaction	Optimized reaction conditions mole ratio/cat amount/temp/time	% Conv/Sel*	TON/TOF (h^{-1})
[a] Levulinic acid esterification	1:2/50mg/90 °C/14 h	78/94	2069/148
[b] Succinic acid esterification	1:3/75mg/90 °C/8 h	76/41	1343/168
[c] Glycerol acetalization	1:2/30mg/50 °C/40 min	74/62	3267/4900

*Selectivity of [a]Ester (Butyl levulinate, [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

The control experiments depicts that the activity of MCM-22 is less as compared to that of SiW_{11}, except for acetalization of glycerol. While a majority of the active catalytic sites, in the form of Bronsted acidity, are provided by SiW_{11} and hence higher conversion was obtained alone SiW_{11}. This activity is imitated in the catalyst where the Bronsted acidity of SiW_{11} acts as active species and the support imparts successful heterogenization of it with enough surface area. Thus, the concerted effect of both SiW_{11} as well as MCM-22 gives better conversion and selectivity of desired products and proves a successful formation of a new heterogeneous catalyst.

Table 13 Control experiments for SiW_{11}/MCM-22

Materials	%Conversion/%*Selectivity of desired product		
	[a]Levulinic acid esterification	[b]Succinic acid esterification	[c]Glycerol acetalization
MCM-22	40/89	53/27	56/69
SiW_{11}	47/90	58/28	36/73
SiW_{11}/MCM-22	78/94	76/41	74/62

Reaction conditions mole ratio [a]1:2, [b]1:3, [c]1:2; catalyst amount MCM-22 [a]38.46 mg, [b] 57.7 mg, [c]23 mg; SiW_{11} [a]11.54 mg, [b]17.3 mg, [c]7.0 mg; SiW_{11}/MCM-22 [a]50 mg, [b]75 mg, [c]30 mg; temperature [a]90 °C, [b]90 °C, [c]50 °C; time [a]4 h, [b]8 h, [c]40 min.
*Selectivity of [a]Ester (Butyl levulinate, [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

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. As a general observation, equivalent to previous studies with a different catalyst, here also, the activation energy for all reactions was beyond 25 kJ/mol. This intimates that with SiW_{11}/MCM-22 also, all the reactions follow a kinetic regime and are governed truly by a chemical step, the reactions are not limited to a diffusion regime.

Table 14 Activation energy for all reactions over SiW_{11}/MCM-22

Reaction	Temperature range (K)	Time intervals	Activation energy Ea (kJ/mol)
Levulinic acid esterification	343 – 363	10 – 14 h	49
Succinic acid esterification	343 – 373	6 – 10 h	82
Glycerol acetalization	313 – 333	20 – 60 min	67

For all three catalytic transformations using SiW_{11}/MCM-22, we are expecting the same mechanism as explained in Part B Chapter 1 for SiW_{12}/MCM-22.

Comparison of activity of SiW_{12}/MCM-22 and SiW_{11}/MCM-22

The comparison of activity of SiW_{12}/SiW_{11} anchored to MCM-22 based catalysts was examined for esterification and acetalization in identical reaction conditions and the results are shown in

From the data (Table 15), the conversion of substrates, selectivity of desired product, TON and TOF of all the reactions in SiW_{12}/MCM-22 were found to be superior as compared to that in SiW_{11}/MCM-22. Moreover, the activity of both the catalysts corroborated to their acidic strength. Hence, the catalytic activity of MCM-22 based catalysts are directly related to their acidic strength and here also, the absence of one tungsten-oxygen unit lowers the catalytic activity.

Table 15 Comparison of activity of SiW_{12}/MCM-22 and SiW_{11}/MCM-22

Reaction	Catalyst	% Conv/Sel*	TON/ TOF (h^{-1})	Acidic strength (mV)	BET Surface area (m^2/g)
[a]Esterification of Levulinic acid	**SiW_{12}/MCM-22**	**65/94**	**1621/203**	**456**	**234**
	SiW_{11}/MCM-22	57/88	1510/189	383	324
[b]Esterification of Succinic acid	**SiW_{12}/MCM-22**	**97/59**	**1214/121**	**456**	**234**
	SiW_{11}/MCM-22	71/39	944/94	383	324
[c]Acetalization of Glycerol	**SiW_{12}/MCM-22**	**63/66**	**2625/3918**	**456**	**234**
	SiW_{11}/MCM-22	48/66	2120/3178	383	324

[a]**Esterification of Levulinic acid:** Reaction conditions- Mole ratio 1:2; catalyst amount 50 mg; temperature 90 °C; time 8 h.
[b]**Esterification of Succinic acid:** Reaction conditions- Mole ratio 1:3; catalyst amount 100 mg; temperature 90 °C; time 10 h.
[c]**Acetalization of Glycerol:** Reaction conditions- Mole ratio 1:2; catalyst amount 30 mg; temperature 30 °C; time 40 min.
*Selectivity of [a]Butyl levulinate, [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

From above studies, the activity order of MCM-22 based catalysts is

SiW_{12}/MCM-22 > SiW_{11}/MCM-22

for all three transformations

Table 16 Activation energy

Reaction	**SiW_{12}/MCM-22**	SiW_{11}/MCM-22
Levulinic acid esterification	36 kJ/mol	49 kJ/mol
Succinic acid esterification	68 kJ/mol	82 kJ/mol
Glycerol acetalization	48 kJ/mol	67 kJ/mol

From Table 2, the activation energy order was found to be,

SiW_{12}/MCM-22 < SiW_{11}/MCM-22

for both esterification as well as acetalization reactions.

Effect of supports nMCM-48/MCM-22 on esterification and acetalization reactions

It is observed from Table 17 that the catalysts with nMCM-48 as a support showed admirable catalytic activity as compared to that of MCM-22 based catalyst. This observed difference in the catalytic activity can be correlated to their unique structures, pore networks and acidic character.

Table 17 Effect of supports, nMCM-48 and MCM-22

Reaction	Catalyst	% Conv/Sel*	TON/ TOF (h^{-1})	Acidic strength (mV)	BET Surface area (m^2/g)
[a]Esterification of Levulinic acid	**SiW_{12}/nMCM-48**	**99/100**	**2469/617**	**700**	**588**
	SiW_{12}/MCM-22	38/94	948/237	456	234
	SiW_{11}/nMCM-48	**49/84**	**1300/325**	**460**	**516**
	SiW_{11}/MCM-22	32/78	847/212	383	324
[b]Esterification of Succinic acid	**SiW_{12}/nMCM-48**	**98/84**	**1227/153**	**700**	**588**
	SiW_{12}/MCM-22	67/34	839/105	456	234
	SiW_{11}/nMCM-48	**35/18**	**465/58**	**460**	**516**
	SiW_{11}/MCM-22	29/15	385/48	383	324
[c]Acetalization of Glycerol	**SiW_{12}/nMCM-48**	**89/69**	**7355/10978**	**700**	**588**
	SiW_{12}/MCM-22	21/69	1750/2623	456	234
	SiW_{11}/nMCM-48	**27/72**	**2389/3582**	**460**	**516**
	SiW_{11}/MCM-22	18/62	1593/2388	383	324

[a]**Esterification of Levulinic acid:** Reaction conditions- Mole ratio 1:2; catalyst amount 50 mg; temperature 90 °C; time 4 h.
[b]**Esterification of Succinic acid:** Reaction conditions- Mole ratio 1:3; catalyst amount 100 mg; temperature 80 °C; time 8 h.
[c]**Acetalization of Glycerol:** Reaction conditions- Mole ratio 1:1; catalyst amount 15 mg; temperature 30 °C; time 40 min.
*Selectivity of [a]Butyl levulinate, [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

The assistance order of support for esterification and acetalization reaction can be represented as

nMCM-48 > MCM-22

Effect of catalyst on activation energy

It is evident from the results (Table 18) that amongst all four catalysts, SiW_{12}/nMCM-48 provides excellent catalytic activity for all transformations in terms of % conversion of substrate as well as in obtaining the highest selectivity towards desired products. Relatively higher activation energy in other catalysts is also related to their less acidic strength where less acidic sites are available and so more energy is required to overcome the barrier, as compared to SiW_{12}/nMCM-48.

Table 18 Activation energy of esterification and acetalization reactions with all catalysts in their respective optimized conditions

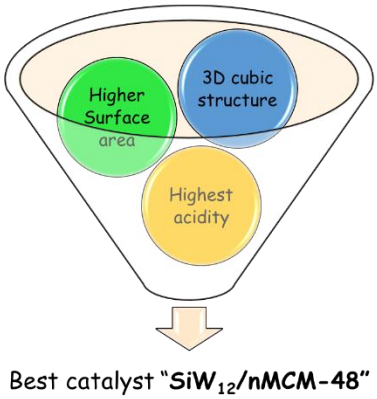
Reaction	Catalyst	% Conv/Sel*	TOF (h^{-1})	Acidic strength (mV)	Activation energy (kJ/mol)
[a]Esterification of Levulinic acid	**SiW_{12}/nMCM-48**	**99/100**	**617**	**700**	**26**
	SiW_{11}/nMCM-48	49/84	325	460	29
	SiW_{12}/MCM-22	65/94	203	456	36
	SiW_{11}/MCM-22	78/94	148	383	49
[b]Esterification of Succinic acid	**SiW_{12}/nMCM-48**	**98/84**	**153**	**700**	**55**
	SiW_{11}/nMCM-48	83/43	183	460	75
	SiW_{12}/MCM-22	97/59	121	456	68
	SiW_{11}/MCM-22	76/41	168	383	82
[c]Acetalization of Glycerol	**SiW_{12}/nMCM-48**	**89/69**	**10978**	**700**	**35**
	SiW_{11}/nMCM-48	66/65	8757	460	65
	SiW_{12}/MCM-22	63/66	3935	456	48
	SiW_{11}/MCM-22	74/62	4900	383	67

*Selectivity of [a]Ester (Butyl levulinate), [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

Thus, the order of catalysts in overcoming the energy barrier efficiently in terms of activation energy is as follow.

SiW_{12}/nMCM-48 > SiW_{12}/MCM-22 > SiW_{11}/nMCM-48 > SiW_{11}/MCM-22

Hence, the catalyst **SiW_{12}/nMCM-48** comes out to be the **best catalyst** amongst all the synthesized ones.



Substrate study of levulinic acid and succinic acid with different alcohols over SiW_{12}/nMCM-48

The study of different substrates holds enormous importance in developing an industrial catalytic process. The versatile nature of found best catalyst, SiW_{12}/nMCM-48 was explored for the esterification of levulinic acid and succinic acid with alcohols having varying carbon chains (unbranched and branched). The results for alkyl levulinates with C1 to C8 chain alcohols were obtained with excellent yields (>75%). Also, appreciable conversions (>80%) and expected trend in the results were observed for the esterification of succinic acid with C1 to C8 chain alcohols.

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 Figure 8. The maximum degradation efficiency was found to be 95% and 90% for Methylene Blue (MB) and Crystal Violet (CV) respectively in 60 min. Whereas the azo dye Chrysoidine Y (CY) exhibits lower degradation efficiency (84%) in similar conditions, that can be improved at higher time scale. The catalyst was recycled for four cycles and no significant decrease in activity was observed. Thus, the present material can be

a promising catalyst for the management of toxic organic dyes and other pollutants in the coloured wastewater effluents.

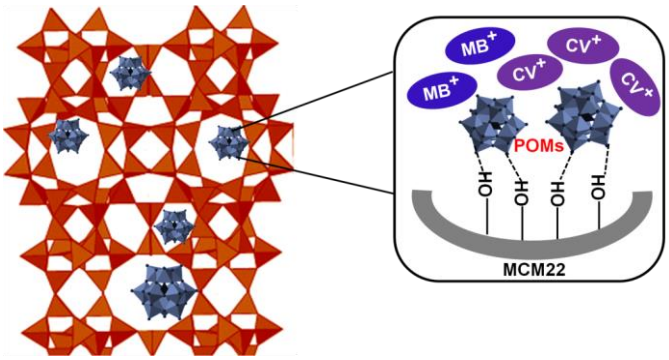


Figure 8 Proposed mechanism of dye degradation over SiW_{12}/MCM-22 catalyst

Main Conclusion

- Series of catalysts comprising SiW_{12}, SiW_{11}, nano-porous MCM-48 and MCM-22 were synthesized successfully.
- Synthesis of biofuel additives- Butyl levulinate, Dibutyl succinate and Glycerol acetals under mild reaction conditions via esterification and acetalization reactions of important bioplatform molecules were carried out effectively.
- All the processes are economic and environmental viable as the potential multifunctional nature of biomass derived platform molecules, were utilized to give value added products, thereby contributes commendably towards the energy transitions.
- The structure, geometry and inherent acidity of the support are important factors that matters in the catalytic activity.
- In all the transformations, the TON was found in the range 1214 – 7355 (exceeding 1000), indicating that all the catalysts are of industrial importance.

Novelty of the work

- For the first time, nano-porous MCM-48 and zeolitic MCM-22 were used as supports for anchoring silicotungstates.
- The challenging task and necessity for the production of alternative fuel additives by converting judiciously selected bioplatform molecules - levulinic acid, succinic acid and glycerol, was addressed.
- An evolution in the energy transition was directed for biomass conversion via green and ecofriendly catalytic routes.
- Green and sustainable catalytic routes for esterification and acetalization reactions were instituted with recycling ability, thus contributing effectively in the cost reduction of processes as well as making the overall procedures environmentally benign.

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