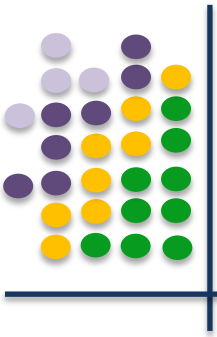


Chapter 2

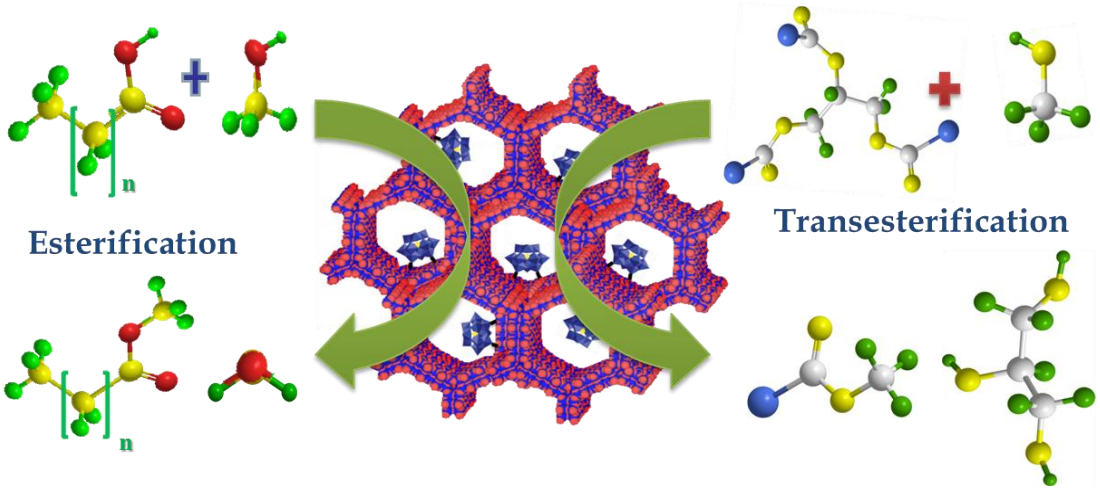
Catalytic Activity of SiW_{12}/SiW_{11} Anchored to MCM-41 for,

A) Biodiesel Synthesis via Esterification of Oleic acid and Transesterification of Soybean oil

B) Valorisation of Glycerol via Acetalization with Benzaldehyde and Carboxylation with Urea

CHAPTER 2A

BIODIESEL SYNTHESIS VIA ESTERIFICATION OF OLEIC ACID AND TRANSESTERIFICATION OF SOYBEAN OIL



Biodiesel is a non-petroleum based fuel that consists of alkyl esters derived from either the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with low molecular weight alcohols [1-3]. Biodiesel can be used as clean or as a mixture with conventional diesel fuel, which is stable and compatible in all ratios, termed as biodiesel blends. A blend of 80% petroleum diesel and 20% biodiesel (known as B20) can be used in unmodified diesel engines [3]. The use of biodiesel instead of conventional fuel does not require any large-scale technical interventions on the engine. Further it is biodegradable, less toxic and with lower exhaust emission of smoke, dust, CO_x (x = 1 or 2) and hydrocarbon comparing to fossil diesel which makes it an environmentally friendly fuel [7-8].

Biodiesel finds applications as fuel for domestic vehicular use, railways as well as in aircrafts in many countries. In 2007, McDonalds of UK announced it would start producing biodiesel from the waste oil, by-product of its restaurants. This fuel would be used to run its fleet [9]. British train operating company Virgin Trains claimed to have run the UK's first "biodiesel train", which was converted to run on 80% petroleum based diesel and 20% biodiesel [10]. Also in 2007, Disneyland began running the park trains on B98 (98% biodiesel). The program was discontinued in 2008 due to storage issues, but in January 2009, it was announced that the park would then be running all trains on biodiesel manufactured from its own used cooking oils. On November 7, 2011 United Airlines flew the world's first commercial aviation flight on a microbially derived biofuel using Solajet, Solazyme's algae-derived renewable jet fuel. This shows the progress in applications of biodiesel worldwide.

In biodiesel production process, raw materials account for almost 75% of total biodiesel cost. Basically all vegetable oils and animal fat can be used as feedstock for biodiesel production (Chart 1). Most of these oils and fats have a similar chemical composition however they consists different amounts of

individual fatty acids. The major fatty acids are those with a chain length of 16 and 18 carbons, whereas the chain could be saturated or unsaturated. Methyl esters produced from these fatty acids have very similar combustion characteristics in a diesel engine, as the major components in fossil diesel fuel are also straight chain hydrocarbons with a chain length of about 16 carbons (hexadecane/cetane). At present, the major feedstocks for the biodiesel production are rape seed oil (Canola), soybean oil, coconut oil, sunflower oil and palm oil [11-15].

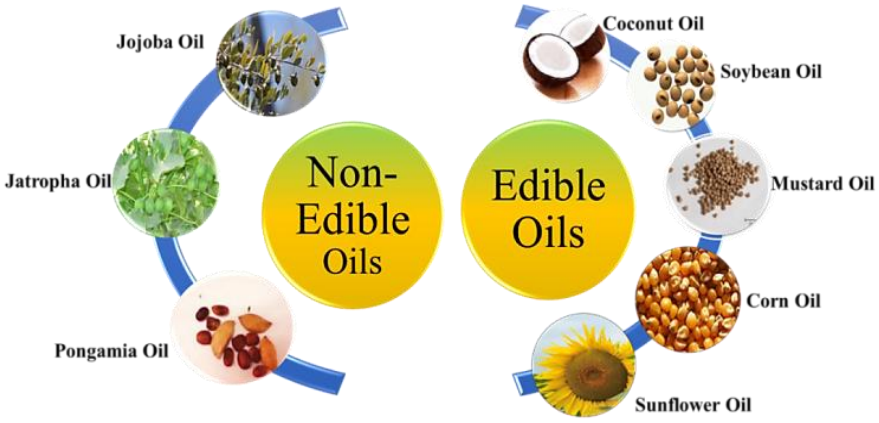


Chart 1. Different feedstocks for biodiesel production.

Several methodologies are available, which utilize homogeneous, heterogeneous as well as bio-catalysts for the synthesis of biodiesel. Although enzymatic catalysts are very selective and present high conversions using low oil to alcohol molar ratios [16], they are very expensive and show unstable activities [17]. Supercritical conditions require high temperature and hence increasing the overall cost of biodiesel production processes.

The conventional biodiesel production technology involves the use of alkaline homogeneous catalysts such as NaOH and KOH but sometimes CH_3ONa or CH_3OK are also employed [18-20] mainly in large-scale production plants. These are not compatible for feedstocks with large amounts of FFAs and moisture due to the formation of soaps that strongly affect the feasibility of

glycerol separation which is an important co-product of transesterification reaction. The traditional liquid acids such as HCl and H_2SO_4 were found to be more efficient [21] but they need very long reaction time and very high molar ratio of methanol to oil. Also corrosion of reaction vessels and problem of recycling are the key issues with traditional liquid acids. Therefore commercialization of biodiesel production is difficult due to the technological drawbacks such as separation and purification steps that increase the cost factor to maximum. Additionally, in order to meet the specified product quality, both the process involves a number of washing and purification steps producing a large amount of wastewater, which is environmentally unfavorable and requires appropriate treatment. The high amount of water used in washing and consequent treatment of the resulting large effluent increases the overall process cost. For these reasons, alternative methods have been developed for biodiesel synthesis.

Heterogeneous acid catalyzed transesterication reactions have the strong potential to replace liquid acid catalyst because of its obvious advantages such as their insensitiveness to FFA content, simultaneously occurrence of esterification and transesterification, avoiding washing step, easy separation as well as recycling of the catalyst and low product contamination [22-24].

A literature survey shows that esterification of FFAs to produce biodiesel involve use of different heterogeneous acid catalysts such as, clays [25], zeolite [26-28], ion exchange resin [28-30], carbon based material [28, 31], metal oxides as well as sulfated metal oxides [28,32-33], WO_3/ZrO_2 [34-35] and propylsulfonic acid functionalized mesoporous silica [36-37].

Recently, anchored POMs have got tremendous interest in biodiesel production due to their known advantages. As there are number of reports available for the same, for the sake of simplicity, we have categorized them on

basis of following class of supports: I) Metal oxides (Silica, Alumina, Zirconia, Niobia etc.), II) Clays, III) Carbons, IV) Zeolites and V) Mesoporous silica/MOFs.

I) POMs anchored to metal oxides supports (SiO_2, ZrO_2, Nb_2O_5, Al_2O_3 and Ta_2O_5).

Dalai and co-workers have reported the use of $H_3PW_{12}O_{40}$ impregnated on to four different supports such as hydrous zirconia, silica, alumina and activated carbon [38]. The synthesized catalysts were used for the biodiesel production from low quality canola oil. The $H_3PW_{12}O_{40}$ anchored to ZrO_2 showed best activity, but the reaction temperature was high affecting the cost factor in biodiesel production.

Castanheiro and co-workers synthesized series of $H_3PW_{12}O_{40}$, $H_4Si_{12}O_{40}$, $H_3PMo_{12}O_{40}$ anchored on to silica [39]. The synthesized materials were used in the esterification of palmitic acid with methanol. It was observed that the catalytic activity decreases in the series: PW-silica > SiW-silica > PMo-silica.

Essayem and group have reported $H_3PW_{12}O_{40}/SiO_2$ and $Cs_2HPW_{12}O_{40}$ for transesterification of rapeseed oil [40]. These catalysts possessed Brønsted acidity of high strength and catalytic activity, better than H_2SO_4 and H_3PO_4, however the acid strength didn't necessarily correlate with catalytic activity.

Zirconia is another metal oxide which has attracted much attention because of its thermal stability, stability under oxidizing and reducing conditions and amphoteric character of its surface hydroxyl groups. Halligudi and group have carried out the comparative study of zirconia anchored isopoly and heteropoly tungstate in transesterification of sunflower oil with methanol [41].

Guo et al. have reported synthesis of mesostructured Ta_2O_5 -based hybrid catalysts functionalized by both alkyl-bridged organosilica moieties and

Keggin-type POM. Different $H_3PW_{12}O_{40}$ loadings, ranging from 3.6 to 20.1 %, were obtained by a one-step sol-gel hydrothermal route in the presence of a triblock copolymer surfactant. The catalyst showed a promising activity in the esterification of lauric acid and myristic acid, in the transesterification of tripalmitin, as well as soybean oil [42-44].

Dias and co-workers have reported the synthesis, characterization and application of H_3PW/ZrO_2 catalyst for esterification of oleic acid with ethanol as a model reaction to produce long chain ester [45].

Sai Prasad and co-workers reported $H_3PW_{12}O_{40}$ anchored to hydrous zirconia for the esterification of palmitic acid with methanol [46]. The catalyst with 20wt% $H_3PW_{12}O_{40}$ calcined at 300 ^oC exhibited the highest activity. The pseudo-homogeneous (PH), Eley-Rideal (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic models were applied to correlate the experimental kinetic data and kinetic parameters were evaluated. The same group have reported $H_3PW_{12}O_{40}$ anchored to SnO_2 for the esterification of palmitic acid with methanol [47]. The catalyst with 15 wt% $H_3PW_{12}O_{40}$ was reported as the best composition of the catalyst, calcined at the temperature of 400 ^oC.

Niobium is an interesting and noteworthy catalyst as well as a support for different catalytic reactions. The catalytic applications of niobium compounds have increased in recent years [48-50]. Niobia can also be used as a promoter and also as a solid acid catalyst. Since it is reducible over a wide temperature range, niobia is also known as a typical strong metal support interacting with oxide. Sai Prasad and group have reported the catalytic activity $H_3PW_{12}O_{40}$ impregnated on niobium oxide for esterification of palmitic acid and transesterification of used cooking oil [48-50]. The esterification activity was correlated the acidity of the catalysts, which is dependent on the presence of

intact Keggin ions on the support. Effect of calcination temperature was studied and it was observed that the new phase WO_3 was observed for catalyst calcined above 500 ^oC.

Biodiesel synthesis from crude jatropha oil was carried out by Badday et al. using an ultrasound-assisted process [51]. Several γ-alumina anchored $H_3PW_{12}O_{40}$ catalysts were synthesized and characterized to elucidate their catalytic behaviours. Different design models such as full factorial design, Taguchi's algorithm and response surface methodology have been established for optimizing the data.

Abdullah and co-workers have carried out series of $H_3PW_{12}O_{40}$ and Cs exchanged $H_3PW_{12}O_{40}$ anchored to supports, ZrO_2 and SiO_2 [52]. The leaching of the active species during 1 h reaction, based upon final conversion at specified reaction conditions, fell in the following order: $20\%HPW/Al_2O_3$ = $20\%HPW/ZrO_2$ > $20\%WO_3/ZrO_2$ > $20\%HPW/SiO_2$ > CsHPW.

Gaigneaux et al. carried out synthesis of $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ anchored to silica which was previously grafted with zirconium butoxide [53]. The immobilization method promoted strong POM-support interaction and yielded 25 wt.% of well-dispersed POMs, thereby increasing the density of acid sites. The catalysts were active in the reaction of transesterification of methyl stearate with n-butanol and esterification of oleic acid with trimethylolpropane. The catalysts were stable toward leaching in a non-polar oleic acid medium. A discussion on circumventing the leaching in non-polar versus polar media was proposed in terms of interaction strength POMs-support. The stronger interaction (i.e., better resistance for leaching) was referred to the lower difference of electronegativity between Zr and W and the lower polarizability of the bonds Zr–O–W compared to Zr–O–Mo.

II) POMs anchored to clays

Yadav and co-workers reported the use of different lower and higher alcohols *viz*.; methanol, ethanol, n-propanol and n-octanol, for the synthesis of respective fatty acid esters by transesterification of vegetable oil (triglycerides) [54]. The superacids $H_3PW_{12}O_{40}$ as well as NH_4^+ salt of $H_3PMo_{12}O_{40}$ were used to increase the acidity and so the activity by loading on to K-10. The best catalyst (10% $H_3PW_{12}O_{40}$/Clay) was further investigated for the different refined, crude, cooked vegetable oil. The same group has also reported the use of $H_3PW_{12}O_{40}$ anchored to K-10 montmorillonite clay for transesterification of edible and non-edible oil at very high temperatures and pressure [55]. The activity decreases significantly during the fourth recycle and any post treatment cannot be given to regenerate the catalysts due to the alteration in clay pore structure, because of a collapse resulting in a severe reduction in surface area.

The esterification of FFA, oleic acid was carried out over $H_3PW_{12}O_{40}$ immobilized on the 3-aminopropyltriethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$) functionalized Palygorskite by Wang and group. 15% (w/w) $H_3PW_{12}O_{40}$ catalyst, HPW/APTES-Pa showed excellent activity and steady reusability up to four cycles [56].

Amazon kaolin flint was also successfully utilized by Barros and co-workers as a support for incorporation of $H_3PW_{12}O_{40}$ in different proportions, 20, 40 and 60 wt% via impregnation in aqueous solution (HCl 0.1 and 0.5 mol L^{-1}) and acetonitrile [57]. The catalytic results showed that HPW anchored on metakaolins with acid treatment promoted good conversion of oleic acid esterification, followed by a gradual increase with added support in HPW.

Bokade and group have reported the synthesis of methyl oleate biodiesel over $H_3PW_{12}O_{40}$ anchored montmorillonite K10 by response surface methodology

and kinetic modeling [58]. The 20% (w/w) $H_3PW_{12}O_{40}$/K10 follows green principles with potential advantages of complete oleic acid conversion, at milder operating conditions.

Pires and co-workers synthesized kaolin waste, MCM-41, MCM-48, MK700, and SBA-15 impregnated with $H_3PW_{12}O_{40}$ [59]. The obtained solid acid catalysts were characterized by various techniques. The surface acidities were measured by acid-base titrations with KOH. The catalytic activity of the catalysts were evaluated for the esterification of deodorized palm oil (DDPO) and 25%HPW/MK700 was found to be best with 83% conversion in 2h and 1:10 (DDPO: ethanol) molar ratio. From the results, it was concluded that the studied solids (MK700, MCM-4, MCM-48 and SBA-15) are promising supports for POMs and appear to be attractive heterogeneous catalysts for preparation of esters from low quality oils and fats.

III) POMs anchored on Carbon

Activated carbon fibre (ACF) has also been used as a support for heterogenizing $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ by Alcaniz-Monge et al [60]. They further demonstrated that washing with ethanol and H_2SO_4 provides an acidic medium which reduces POMs leaching and H^+ coming from the H_2SO_4 regenerate the active sites and thereby maintains the catalytic activity for a higher number of cycles.

Badday et al. have reported optimization of biodiesel production process from jatropha oil catalyzed by activated carbon-anchored $H_3PW_{12}O_{40}$ catalyst under application of ultrasonic energy [61]. Influence of ultrasonic energy on different process was elucidated. Also they have not observed any leaching which revealed that the reaction was predominately heterogeneous in nature. Very recently the same group reported ultrasound-assisted transesterification of crude Jatropha oil by activated carbon-anchored $H_3PW_{12}O_{40}$ catalyst [62].

They have elucidated the effect of water and FFA contents in the jatropha oil on the reaction. The catalysts showed moderate water tolerance to a limit of 1% w/w water content.

IV) POMs anchored to Zeolites

Dalai and co-worker have demonstrated the use of H-Y, H-β and H-ZSM-5 zeolites as supports for $H_3PW_{12}O_{40}$ [63]. The catalysts were characterized extensively using BET, XRD, FTIR, Raman, XPS and NH_3-TPD. Their catalytic activity was tested for esterification of FFA present in the green seed canola (GSC) oil, and transesterification of GSC oil using a stirred tank reactor for biodiesel production. In this study, $H_3PW_{12}O_{40}$ impregnated HY zeolite showed higher catalytic activity for esterification, and $H_3PW_{12}O_{40}$ impregnated Hβ zeolite showed higher catalytic activity for the transesterification reaction compared to other catalysts. A catalyst, 55%TPA/H-β showed optimum catalytic activity for both esterification and transesterification. Further, the catalyst was also used for etherification of by-product glycerol with 100% conversion. Further, the same group reported application of $H_3PW_{12}O_{40}$ impregnated HY zeolite for esterification of FFA of GSC oil [64]. The changes in the catalyst structural properties and catalytic activity with the $H_3PW_{12}O_{40}$ impregnation have been correlated with the help of artificial neural network (ANN). A 10.2% $H_3PW_{12}O_{40}$ loaded HY zeolite showed optimum catalytic activity in esterification of oleic acid. The reaction conversion of 99.3 % (for oleic acid) and 97.2% (for FFA) were achieved, with 13.3 wt.% catalyst and 20:1 methanol to FFA molar ratio at 120 ^oC and reaction time of 7.5 h.

V) POMs anchored to Mesoporous silica/MOFs

The discovery of the M-41S family of mesoporous materials has greatly increased the range of supports for preparing heterogeneous catalysts. The advantage of using ordered mesoporous silica especially MCM-41 and SBA-15

as supports in heterogeneous catalysis are their relatively large pores which facilitate mass transfer and the very high surface area which allows a high concentration of active sites per mass of material [65-67]. Further the amorphous pore walls give mesoporous silica a great deal of flexibility in terms of their composition and pore channel structure and allow post-synthesis modifications which may be performed for pore size control framework stabilisation, compositional modifications or the formation of mesoporous/ zeolite composite materials [68].

Castanheiro et al. reported a detailed study on esterification of palmitic acid for biodiesel production over $H_3PW_{12}O_{40}$ immobilized on SBA-15 [69]. They observed small leaching of the $H_3PW_{12}O_{40}$ from SBA-15 to liquid phase during the reaction. Hameed et al. studied single-step esterification of crude non-edible karanj (Pongamia pinnata) oil to fatty acid methyl esters over mesostructured SBA-16 anchored $H_3PMo_{12}O_{40}$ catalyst [70]. The catalyst with 15 wt.% MP exhibited a peerless catalytic activity. The catalyst could be reused up to four cycles without any loss in the conversion.

Yan et al have recently reported mesoporous $H_4SiW_{12}O_{40}$-SiO_2 for production of methyl and ethyl levulinate biodiesel. The catalyst 20 wt% $H_4SiW_{12}O_{40}$-SiO_2 exhibited the best activity in the synthesis of both methyl levulinate [71]. ICP analysis showed 1.0% leaching of $H_4SiW_{12}O_{40}$ during 1st run, but for subsequent run 4 no further leaching of tungsten was detected.

Dalai and coworkers have reported $H_3PW_{12}O_{40}$ anchored by using organic functional group and was incorporated into the SBA-15 [72]. Catalytic activity of these catalysts was tested for esterification and transesterification of canola oil. They observed that organically functionalized $H_3PW_{12}O_{40}$ anchored to SBA-15 shows higher catalytic activity for esterification of FFA, whereas

$H_3PW_{12}O_{40}$ incorporated into SBA-15 shows higher catalytic activity for transesterification of waste green seed canola oil.

Recently, our group has reported synthesis and characterization of catalysts comprising $H_3PW_{12}O_{40}$ anchored to MCM-41 [73] and SBA-15 [74] for esterification of palmitic acid and oleic acid, respectively with methanol. The transesterification reaction of waste cooking oil was also carried out with 65% conversion for MCM-41 based catalyst and 75% conversion for SBA-15 based catalyst. Both the catalysts showed good recyclability up to four cycles without any loss in the activity. The excellent catalytic performance was attributed to the large surface area and pore diameter of the mesoporous supports as well as the Bronsted acid strength of $H_3PW_{12}O_{40}$. A catalyst comprising $H_3PW_{12}O_{40}$ anchored on to MCM-48 was used for the first time for biodiesel synthesis via esterification of oleic acid [75]. The excellent catalytic activity over TPA_3/MCM-48 was extended to transesterification reaction for biodiesel production from waste cooking oil, WCO and jatropha oil, JO, as low cost feedstocks with very high conversion of 95% and 93%, respectively. Further the next acidic species in the Keggin family, $H_4SiW_{12}O_{40}$ was used to synthesize an active heterogeneous catalyst TSA_3/MCM-41 [76]. The application of the catalyst was carried out for esterification of oleic acid as well as transesterification of JO. The large surface area, high value of total acidity and availability of more Bronsted acid sites, all together imply the excellent catalytic activity of TSA_3/SBA-15 as compared to that of TSA_3/MCM-41. Catalytic results demonstrated that the pore diameter as well as pore volume plays a crucial role in catalyst performance. Recently, we reported transesterification of WCO and esterification of oleic acid over $H_4SiW_{12}O_{40}$ anchored on SBA-15 [77]. The detailed kinetic study for esterification of oleic acid was also carried out and showed activation energy of 50 kJ mol^{-1}. The catalyst was recycled up to four times after simple work up with minimal of 2% loss in the conversion form the fresh cycle with 86% conversion.

Fazaeli et al. synthesized $H_3PW_{12}O_{40}$ anchored to Al–functionalized SBA-15 mesoporous molecular sieve featuring a well-defined three-dimensional (3D) mesoporosity [78]. The prepared catalyst (PW_{12}/Al–SBA-15) was tested for the esterification process of palmitic acid to produce methyl palmitate. The effects of the methanol/oil ratio, catalyst amounts, reaction time, and reaction temperature on the conversion are also reported in this paper. By using a 35 wt% of PW_{12}/Al–SBA-15 with methanol/oil molar ratio of 20:1 at reflux of methanol, the oil conversion of 98% after 8 h of reaction was achieved over the solid catalyst for at least 6 cycles under mild conditions.

Zheng and group have carried out synthesis of $H_4SiW_{12}O_{40}$ anchored to mesoporous molecular sieves SBA-15 [79]. The results showed that the HSiW/SBA-15 retained the hexagonal mesoporous structure and the Keggin characteristic, although the textural parameters decreased with increasing loading of HSiW. The catalytic results showed that the environmentally benign mesoporous solid acid catalysts were efficient in the esterification of oleic acid for the synthesis of biodiesel. The catalyst with 30 wt. % HSiW loading exhibited the best activity under the reaction conditions.

Chidambaram and his group reported the use of $H_4SiW_{12}O_{40}$ anchored to mesoporous siliceous support, KIT-6 [80]. Efficiency of the catalyst in the production of biodiesel from a variety of high free fatty acid containing feedstock was evaluated. The composition of free fatty acids in all the feedstock oils (algae oil, coffee oil, palmitic acid and used cooking oil) and their biodiesel resulting from the feedstock were also analyzed. Compared with other solid acid catalysts, the resulting materials show stable and highly efficient catalytic performance in biodiesel production with the highest conversion of 99%. A catalyst 26 wt% $H_4SiW_{12}O_{40}$ anchored to KIT-6 was found to be the most active catalyst for esterification at 70 °C with an alcohol/acid volume ratio of 2 and 1.5 wt% of catalyst amount for 3 h.

Our group has already carried out esterification of oleic acid over parent SiW_{12}/MCM-41 [81]. In the present chapter, anchored lacunary silicotungstate SiW_{11}/MCM-41 has been utilized for biodiesel synthesis via esterification of oleic acid. In addition, transesterification of soybean oil over catalysts comprising of SiW_{12}/SiW_{11} anchored to MCM-41 was also carried out. Influence of various reaction parameters (catalyst concentration, acid/ alcohol molar ratio, reaction time and temperature) on catalytic performance was studied to optimize the conditions for obtaining maximum conversions. Both the catalysts were regenerated and reused up to four cycles and regenerated catalysts were characterized for acidic strength, BET surface area and FT-IR analysis. Further, mechanism for esterification as well as transesterification was also proposed. The quality of biodiesel synthesized by transesterification of soybean oil was checked by ^{1}H-NMR, FT-IR, acid value, flash point, pour point and viscosity.

EXPERIMENTAL

Materials

All used chemicals were of A.R. grade. Oleic acid and methanol were purchased from Merck. All the oil samples were procured from the local market and used without any pre-treatment.

Reaction Procedure

Esterification of oleic acid

The esterification of oleic acid with methanol was performed in a 50 mL batch reactor provided with a double walled air condenser, magnetic stirrer, Dean-Stark apparatus and a guard tube. A Dean-Stark apparatus was connected to a round-bottom flask to separate the water formed during the reaction. Oleic acid (0.01 mol) was esterificated with 0.4 mol methanol in presence of 100 mg of catalyst at 60 ^{o}C for 10 h. The obtained products were evaluated on a gas chromatograph (Nucon-5700) using a BP1 capillary column (30 m length, 0.25 mm internal diameter). Gas Chromatograph programming parameters were: Injector temperature = 240 ^{o}C, Detector temperature = 260 ^{o}C, Column temperature = 80-250 ^{o}C with rate 10 ^{o}C/min. Product identification was done by comparison with standard authentic sample, methyl oleate.

Transesterification of soybean oil

The typical transesterification reaction was carried out in a 100 mL glass reactor, provided with mechanical stirring, thermometer and condenser. In a typical run 5 g oil was added to the reactor vessel followed by methanol (20 g) followed by catalyst addition 200 mg and the reaction mixture was refluxed at 65 °C for 8 h with constant stirring in order to keep the system uniform in temperature and suspension. After the reaction was completed, the mixture

was rotary evaporated at 50 °C to separate excess methanol. The conversion of FFA to biodiesel was calculated by means of the acid value (AV) of the oil layer with the following equation,

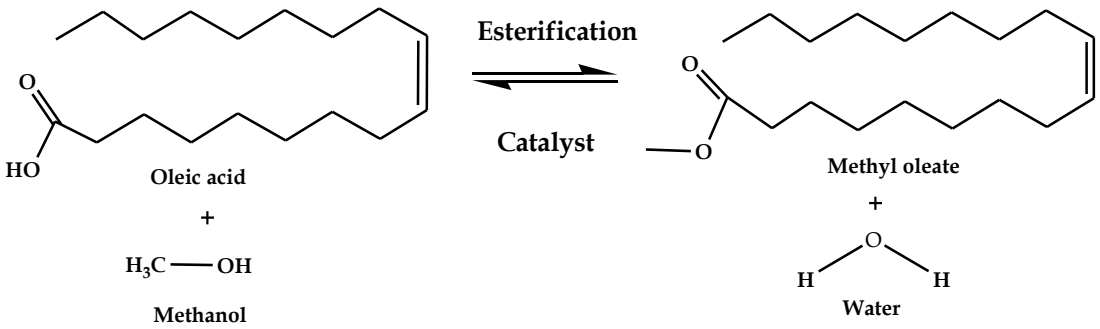
$$\text{Conversion}(\%) = \left(1 - \frac{\text{AV}_{\text{BD}}}{\text{AV}_{\text{SO}}}\right) \times 100$$

Where, AV_{BD} is acid value of biodiesel (oil layer) and AV_{SO} refers to acid value of soybean oil [82-85].

RESULTS AND DISCUSSION

I) Esterification of oleic acid with methanol

The esterification reaction of long chain carboxylic acids such as oleic acid is interesting in the context of biodiesel production. Oleic acid is present in different extension in vegetable oils like Soybean, Jatropha Curcas, Sunflower, Rapeseed, Pongamia, Palm and Sea Mango. The esterification reaction is an equilibrium-limited reaction (Scheme 1). In order to overcome the equilibrium limitation of the esterification of oleic acid, the reaction was carried out by taking methanol in excess.



Scheme 1. Esterification of oleic acid with methanol.

The effect of various reaction parameters such as % loading of SiW_{11}, oleic acid/alcohol molar ratio, amount of catalyst, reaction time and temperature were studied to optimize the conditions for maximum conversion.

Effect of % loading of SiW_{11}

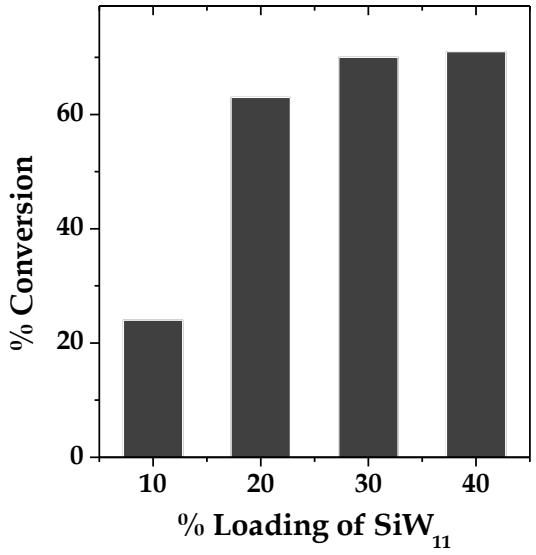


Figure 1. Effect of % loading of SiW_{11} onto MCM-41, Reaction conditions: mole ratio of oleic acid /methanol, 1:40; amount of catalyst, 100 mg; reaction temperature, 60 ^{o}C; reaction time, 10 h.

To study the effect of % loading (Figure 1) esterification reaction was performed with 10% SiW_{11}/MCM-41, 20% SiW_{11}/MCM-41, 30% SiW_{11}/MCM-41 and 40% SiW_{11}/MCM-41. The conversion of oleic acid increases on increasing SiW_{11} loading. The enhanced activity could be assigned to the increase in SiW_{11} content. For 40% loaded catalyst showed no significant increase in the conversion. Therefore, 30% SiW_{11}/MCM-41 was considered for further studies.

Effect of mole ratio of acid to alcohol

To see the effect of the mole ratio, the esterification reaction was performed by varying the mole ratio of oleic acid to methanol, with 0.1 g of the catalyst for 10 h at 60 °C (Figure 2). According to the chemical dynamics, the esterification could be enhanced by increasing the amounts of methanol. It can be observed from Figure 2 that the oleic acid conversion increases with an increase in the

oleic acid/methanol ratio and reaches to 70% at the oleic acid/methanol mole ratio of 1:40. With a further increase in the molar ratio, there is only a slight increase in conversion. Hence, the molar ratio of 1:40 was considered to be optimum for obtaining high conversion.

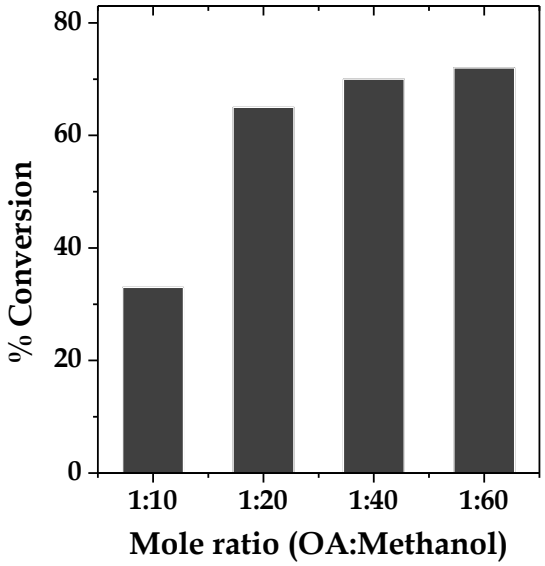


Figure 2. Effect of OA/methanol mole ratio. Reaction conditions: amount of catalyst, 100 mg; reaction temperature, 60 ^{o}C; reaction time, 10 h.

Effect of amount of catalyst

The effect of the amount of catalyst on oleic acid conversion was studied by varying catalyst amount in the range 25-150 mg. As shown in Figure 3, the oleic acid conversion was increased with increase in the amount of 30% SiW_{11}/MCM-41 and touches an optimum of 70% conversion. The increase in the conversion could be attributed to an increase in the number of available catalytically active sites. Hence, 100 mg of the catalyst was considered to be optimum for the maximum conversion.

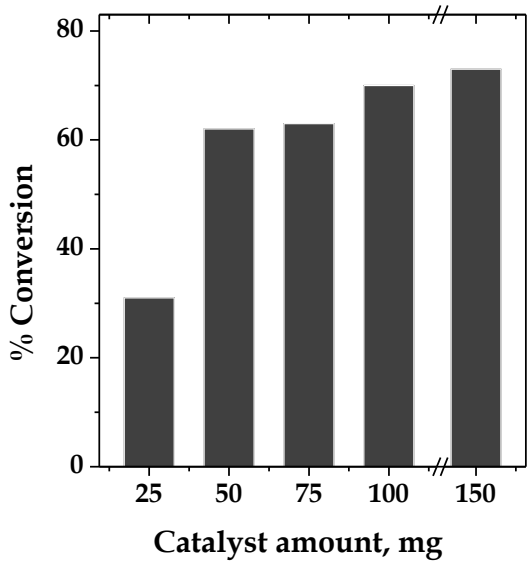


Figure 3. Effect of catalyst amount. Reaction conditions: mole ratio of oleic acid/methanol, 1:40; reaction temperature, 60 ^{o}C; reaction time, 10 h.

Effect of reaction time

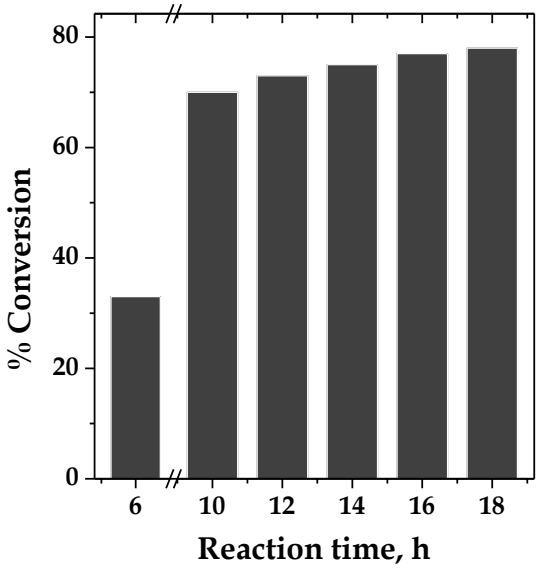


Figure 4. Effect of reaction time. Reaction conditions: mole ratio of oleic acid /methanol, 1:40; amount of catalyst, 100 mg; reaction temperature, 60 ^{o}C.

The effect of reaction time was studied by varying the reaction time in the range 6 to 18 h (Figure 4). The oleic acid conversion was increased with an increase in the reaction time up to 16 h. The oleic acid conversion was 77% at

16 h of reaction time. After 16 h, no significant increase in the conversion was observed. As a result 16 h of the reaction time was considered to be optimum for the esterification reaction.

Effect of reaction temperature

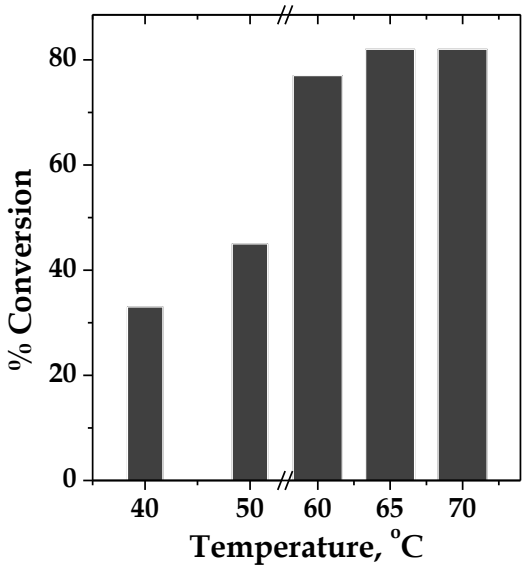


Figure 5. Effect of temperature. Reaction conditions: mole ratio of oleic acid /methanol, 1:40; amount of catalyst, 100 mg; reaction time, 16 h.

The effect of reaction temperature on the oleic acid conversion was investigated in the temperature range of 40 to 70 °C. As illustrated in Figure 5, the reaction temperature strongly affected the conversion. There was a gradual increase in the conversion upon increasing reaction temperature from 40 to 65 °C. Maximum of 81% conversion was achieved at 65 °C. The high reaction temperature results in high reaction rate. However, the further increase in reaction temperature from 65 to 70 °C results slight decrease in the conversion because of attaining the boiling point of methanol. Hence 65 °C was considered to be optimum for the esterification reaction.

The optimized conditions for oleic acid (81% conversion) esterification over 30% SiW_{11}/MCM-41 are: mole ratio of acid to alcohol 1:40; concentration of catalyst 100 mg; reaction temperature 65 °C, and reaction time 16 h.

Control experiments for esterification of oleic acid

The control experiment by MCM-41 support was carried out under the optimized conditions. It is seen from the Table 1 that MCM-41 is not much active towards the esterification of oleic acid indicating catalytic activity is fairly due to SiW_{11} only. Identical TON values shows catalytic activity of SiW_{11} is retained after heterogenization in to the mesoporous channels of MCM-41. Thus, we were successful in synthesizing a heterogeneous catalyst and in overcoming the traditional problems of homogeneous catalyst.

Table 1. Control experiments for esterification of oleic acid.

Catalyst	% Conversion	TON	TOF, h^{-1}
MCM-41[a]	8	-	
SiW_{11}[b]	79	971	60.6
30% SiW_{11}/MCM-41[a]	81	998	62.4

[a]*Amount of catalyst, 0.1 g; mole ratio of oleic acid/alcohol, 40; reaction temperature, 65 °C; reaction time, 16 h.* [b]*catalyst quantity of 23 mg. TON= moles of product/ moles of catalyst and TOF= TON/ reaction time.*

Heterogeneity test

Rigorous evidence of heterogeneity can be gained only by filtering the catalysts before completion of the reaction and analysing the filtrate for activity [86]. A test was performed by filtering the catalyst from the reaction mixture at 65 °C after 8 h, and the filtrate was allowed to react up to 16 h. The

reaction mixture of 16 h and the filtrate were analysed by gas chromatogram. There was no change in the % conversion, which indicates the present catalyst falls into the category C [86]. On the basis of these results, it can be concluded that there is no leaching of SiW_{11} from the support, and the catalyst is truly heterogeneous in nature.

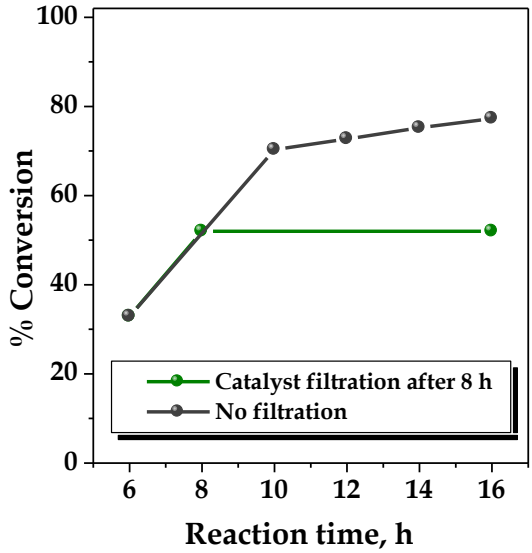


Figure 6. Heterogeneity test for esterification of oleic acid. Reaction conditions: Amount of catalyst, 0.1 g; mole ratio of oleic acid/alcohol, 40; reaction temperature, 65 °C.

Regeneration and recycling of the catalyst

Catalytic activity of regenerated catalysts

The catalyst was recycled in order to examine its activity as well as stability. After the reaction, the catalyst was separated from the reaction mixture by simple centrifugation; the first washing was given with methanol to remove the products, then the subsequent washings were done by conductivity water and then dried at 100 °C, and the recovered catalyst was charged for the further run. No appreciable decrease in the conversion was observed up to four cycles (Figure 7).

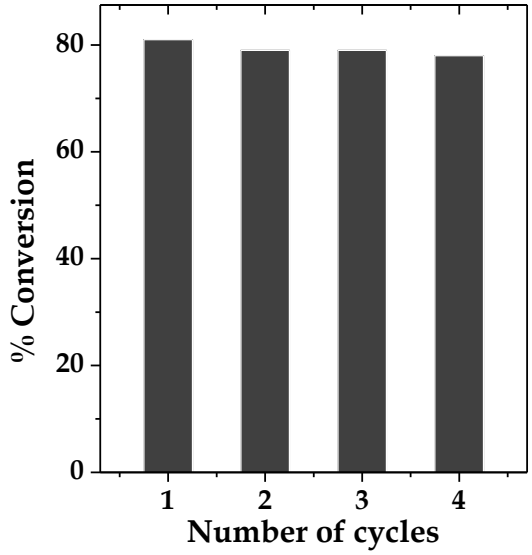


Figure 7. Recycling of the catalyst. Reaction conditions: amount of catalyst, 100 mg; acid to alcohol mole ratio, 1:40; reaction temperature, 65 °C; reaction time, 16 h.

Characterization of Regenerated catalysts

The regenerated catalyst was further characterized by FT-IR, XRD, EDX and surface area measurement in order to see any structural change. FT-IR spectra of the used catalyst (Figure 8a) shows retention of bands at 960 cm^{-1} and 900 cm^{-1} corresponding to the symmetric stretching of $W=O_d$ and $Si-O_a$ bonds of SiW_{11}. This shows that the structure of SiW_{11} in regenerated catalyst remains unchanged. An XRD pattern of the regenerated catalyst (Figure 8b) shows reflection of (100) which confirms retention of hexagonal channel system and support the above conclusion. The EDX elemental analysis of the reused catalyst shows W (15%) and Si (27.9%), which are comparable with fresh catalyst (W = 15.2%; Si = 27.6%). BET surface area and pore diameter of the reused catalyst were found to be 526.2 m^2/g and 3.85 nm, respectively, which are comparable with the fresh catalyst (Surface area: 536 m^2/g; pore diameter: 3.96 nm). The slight decrease in the values may be due to the pore blocking.

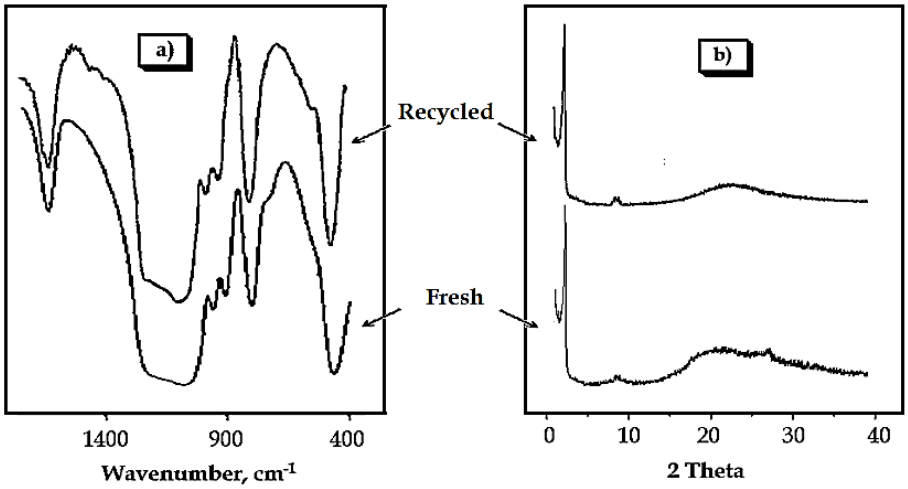


Figure 8. a) FT-IR and b) XRD of fresh and recycled catalysts.

Kinetic study

A detailed study on the kinetic behaviour was tested for esterification of oleic acid over 30% SiW_{11}/MCM-41. In all the experiments, reaction mixtures were analysed at a fixed interval of time. Esterification of oleic acid with methanol was carried with a 1:40 molar ratio; since methanol was taken in large excess, the rate law is expected to follow first-order dependence.

The plot of ln (Co/C) versus time (Figure 9) shows a linear association of oleic acid consumption with respect to time. With an increase in the reaction time, there is a gradual increase in the oleic acid conversion over the present catalyst. This observation indicates that esterification of oleic acid follows first-order dependence with respect to time.

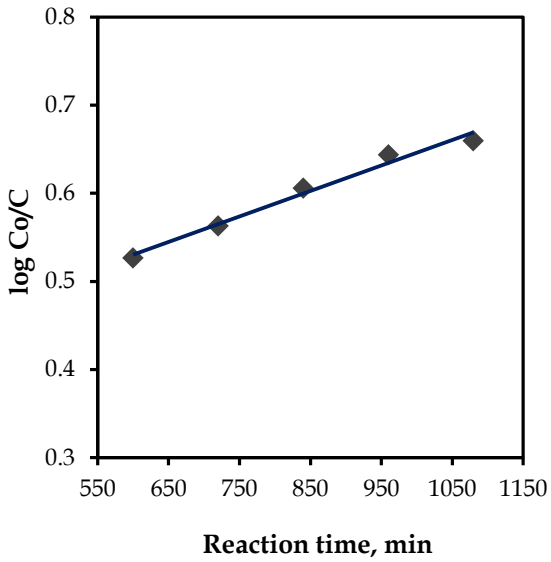


Figure 9. First-order plot for esterification of oleic acid with methanol over 30% SiW_{11}/MCM-41.

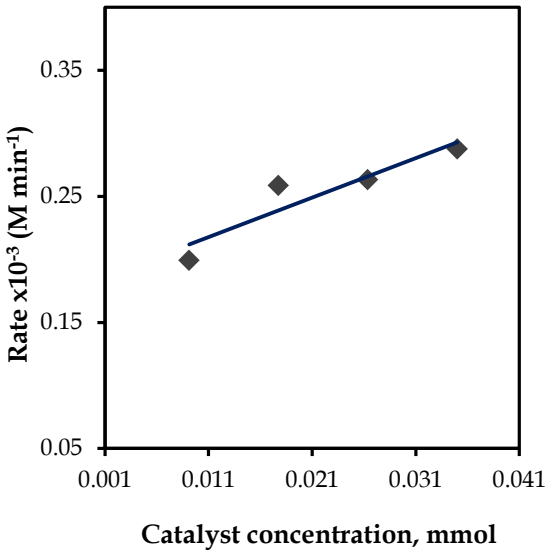


Figure 10. Plot of reaction rate vs. catalyst concentrations.

This was further anchored by the study of the effect of catalyst amount on the rate of esterification of oleic acid. The catalyst amount was varied from 9×10^{-3} to 35 $\times 10^{-3}$ mmol at a fixed substrate concentration of 10 mmol and at a temperature of 65 °C. It can be observed from Figure 10 that the rate of reaction increases linearly with an increase in the catalyst amount.

Estimation of activation energy (Ea)

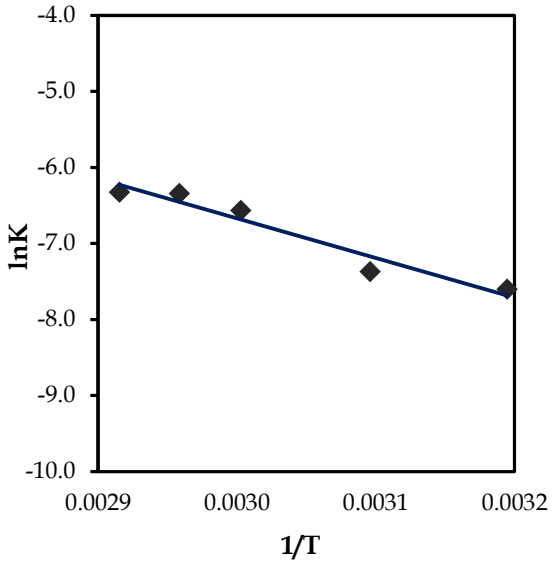


Figure 11. Arrhenius plot for determination of activation energy.

The graph of ln k versus 1/T was plotted (Figure 11) and the value of activation energy (Ea) and the pre-exponential factor (A) was calculated from the plot using the Arrhenius equation. The rate constant, k for the esterification of oleic acid with methanol by using 30% SiW_{11}/MCM-41 at 60 °C was found to be 1.6×10^{-3} min^{-1}. The pre-exponential factor (A) and activation energy (Ea) were found to be 8.7×10^{4} min^{-1} and 49.8 kJ mol^{-1}, respectively.

It is important to know whether the reaction rate is diffusion limited/mass transfer limited or it is truly directed by the chemical step where the catalyst is being used at its maximum capacity. It is reported that Ea for diffusion limited process is as low as 10-15 kJ mol^{-1}, and reactions whose rate is governed by a truly chemical step show activation energy higher than 25 kJ mol^{-1} [87]. In the present system, the activation energy is 49.8 kJ mol^{-1}, and therefore, the rate is truly governed by the chemical step and the reaction is not surface type diffusion limited catalysis.

Esterification of oleic acid over SiW_{12}/MCM-41 [81]

The optimized conditions for esterification of oleic acid with methanol over 30% SiW_{12}/MCM-41 (conversion of oleic acid 99%) are as follows,

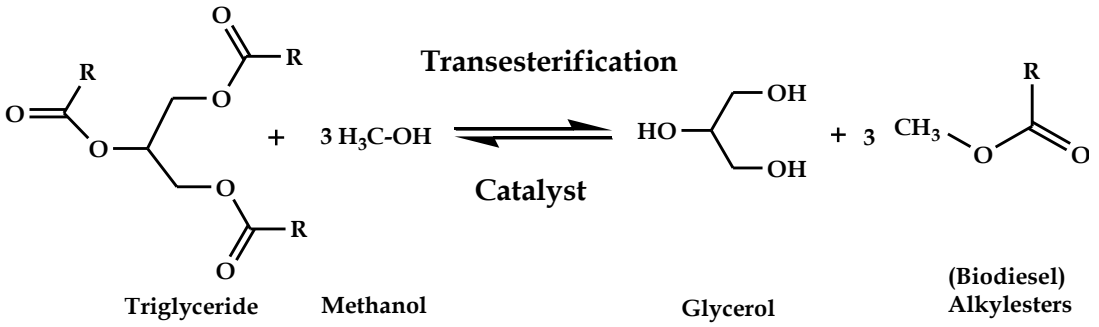
Mole ratio of acid to alcohol: 1:40

Amount of catalyst : 0.1 g

Reaction temperature : 60 ^{o}C

Reaction time : 10 h

II) Transesterification of triglycerides (Soybean oil)



Scheme 2. Biodiesel production from transesterification of triglyceride.

Transesterification is a universal and established method for biodiesel production from vegetable and other fatty oils (Scheme 2). Soybean oil is a vegetable oil extracted from the seeds of the soybean (Glycine max). It is one of the most widely consumed cooking oils. As a drying oil, processed soybean oil is also used as a base for printing inks (soy ink) and oil paints. The main FFA constituents of soybean oil are Palmitic acid (11 %), Stearic acid (4%), Oleic acid (23%), Linoleic acid (54%) and Linolenic acid (8%) [88]. This suggests that soybean oil possesses triglyceride esters of both saturated and unsaturated FFA and is perfect feedstock to study the catalytic behaviour.

Application of the present catalysts was extended for transesterification of soybean oil with methanol. The properties such as acid value, saponification value, iodine value and average molecular weight of soybean oil are given in Table 2. Acid values and saponification values were determined by acid-base titration and from these values average molecular weight was determined using following equation,

$$\mathrm{M} = \left(\frac{56.1 \times 1000 \times 3}{\mathrm{SV} - \mathrm{AV}}\right)$$

Where, SV denotes saponification value and AV denotes to acid value.

Table 2. Properties of soybean oil.

Properties	Values
Colour	Pale yellow
Acid value, mg KOH/g	0.467
Saponification value, mg KOH/g	178.3
Iodine value, g I_2/100g oil	121.4
Average Molecular weight, g/mol	946.5

The effect of reaction parameters such as SiW_{12}/SiW_{11} content, oil/alcohol ratio, catalyst amount, reaction time and temperature were studied to optimize the conditions for maximum soybean oil conversion.

Effect of % loading of SiW_{12}/SiW_{11}

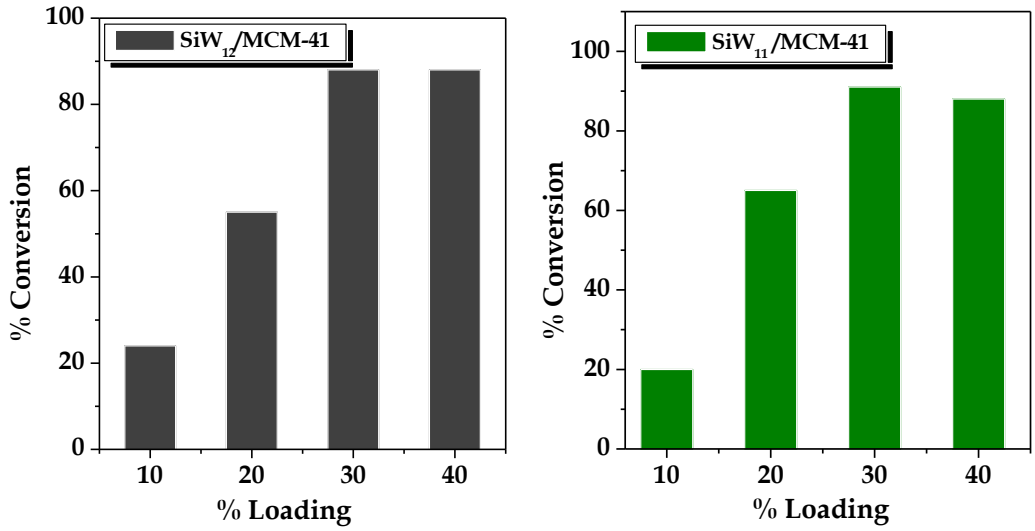


Figure 12. Effect of % loading of SiW_{12}/SiW_{11}; Reaction conditions: w/w ratio of oil to alcohol 1:4; amount of catalyst 200 mg; reaction temperature 65 °C and reaction time 8 h for 30% SiW_{12}/MCM-41 and 16 h for 30% SiW_{11}/MCM-41.

To study the effect of % loading of SiW_{12}/SiW_{11} transesterification reaction was carried out with 10-40% loaded catalysts. The obtained results are shown in Figure 12. It was observed that with increase in the % loading of SiW_{12}/SiW_{11}, % conversion was also increased up to 30% loading. The enhanced activity could be assigned to the increase in the active sites. For 30 and 40% loadings, the difference in the conversion was not significant. Hence, 30% SiW_{12}/MCM-41 and 30% SiW_{11}/MCM-41 were selected for carrying out detailed study.

Effect of wt. ratio of oil to alcohol

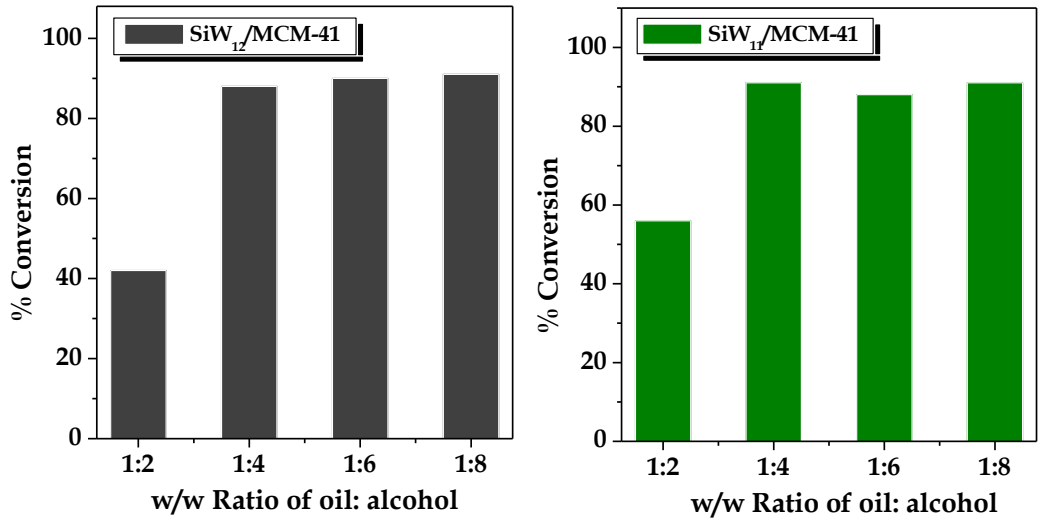


Figure 13. Effect of weight ratio of oil/alcohol; Reaction conditions: amount of catalyst 200 mg; reaction temperature 65 °C and reaction time 8 h for 30% SiW_{12}/MCM-41 and 16 h for 30% SiW_{11}/MCM-41.

Transesterification reaction consists of a series of consecutive reversible reactions to produce three moles of esters and one mole of glycerol. Effect of w/w ratio of oil to methanol was studied from 1:2 to 1:8 (Figure 13) and it was seen that by increasing the methanol content the viscosity of the reaction mixture decreases. This promotes better mixing between reactants and catalyst, which enhances the rate of mass transfer. This eventually results in a higher conversion within a fixed reaction time. The percentage conversion

accordingly increases with the increase in methanol ratio up to 1:4. On further increasing the molar ratio, no significant increase in conversion was observed, which might be due to the saturation of active sites with methanol molecules rather than oil and hindering the completion of oil being protonated at the active sites. Under the oil: methanol ratio of 1:4 w/w, the optimum conversions were achieved for both the catalysts.

Effect of amount of catalyst

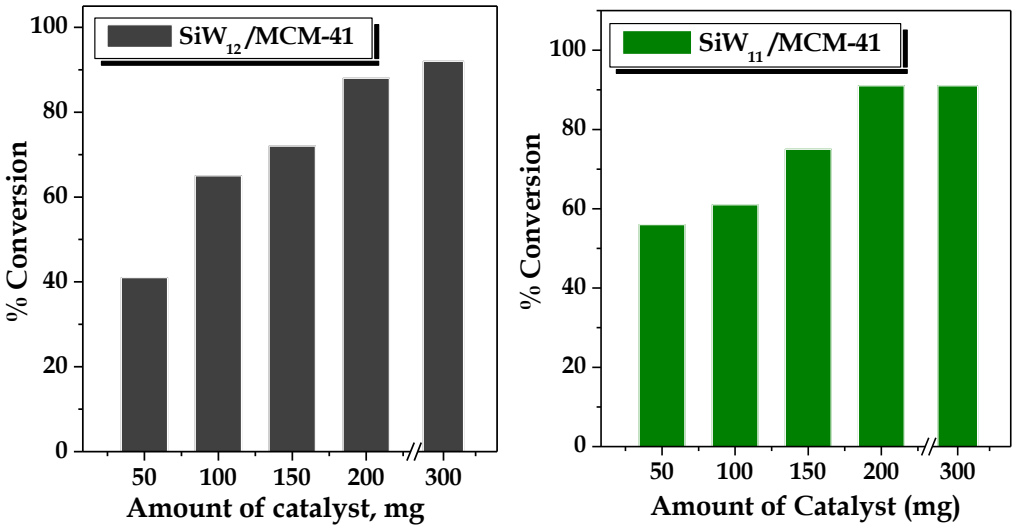


Figure 14. Effect of amount of catalyst; Reaction conditions: w/w ratio of oil to alcohol 1:4; reaction temperature 65 °C and reaction time 8 h for 30% SiW_{12}/MCM-41 and 16 h for 30% SiW_{11}/MCM-41.

The effect of the catalyst amount on the oil conversion is shown in Figure 14. Experiments were carried out by varying the amount of the catalyst between 50-300 mg keeping the oil to methanol ratio of 1:4 at 65 ^{o}C. An increase in the conversion of oil was noticed when the amount of the catalyst was increased up to 200 mg and acid-catalyzed process attains optimum conversion at 200 mg of the catalyst. The increase in the oil conversion with an increase in the catalyst amount can be attributed to an increase in the availability and number

of catalytically active sites. With further increasing the amount of catalyst, saturation in the oil conversion was observed.

Effect of reaction time

Reaction time always plays a significant role in the transesterification reaction, especially in reactions catalyzed by heterogeneous catalyst, mainly due to mass transfer limitations. Therefore, long reaction time has become one of the vital factors to drive the reaction to completion. The conversion of soybean oil for 30% SiW_{12}/MCM-41 increases with increase in the reaction time from 2 h up to 8 h (Figure 15). At 8 h 88% conversion was observed, however on further increasing the reaction time the conversion was not increased. This may be due to the blocking of active sites by glycerol molecules formed during the reaction. Hence, reaction time of 8 h was considered to be optimum for 30% SiW_{12}/MCM-41. Similarly, 16 h of reaction time comes out to be optimum for 30% SiW_{11}/MCM-41.

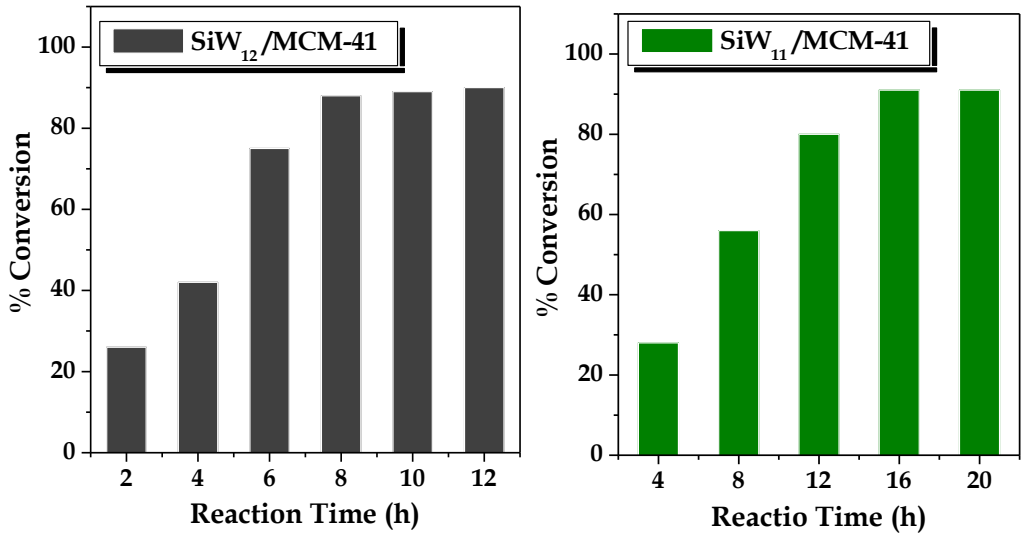


Figure 15. Effect of reaction time; Reaction conditions: w/w ratio of oil to alcohol 1:4; amount of catalyst 200 mg; reaction temperature 65 °C.

Effect of reaction temperature

The effect of temperature on the conversion was studied and it was seen that the temperature evidently affects both the reaction rate and conversion of soybean oil into biodiesel (Figure 16). With subsequent increase in the temperature, percentage conversion was also increased. It can be seen that at 65 ^{o}C optimum conversions were obtained for both the catalysts. On the other hand, the conversion levels off for temperatures beyond 65 ^{o}C which can be ascribed to attainment of boiling point of methanol. Hence, 65 ^{o}C was considered as optimum temperature for the transesterification reaction.

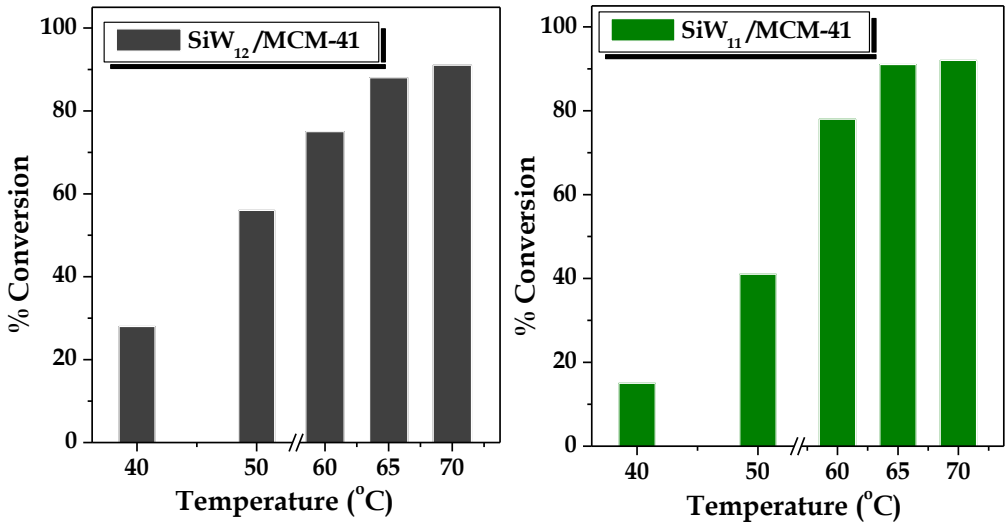


Figure 16. Effect of reaction temperature; Reaction conditions: w/w ratio of oil to alcohol 1:4; amount of catalyst 200 mg and reaction time 8 h for 30% SiW_{12}/MCM-41 and 16 h for 30% SiW_{11}/MCM-41.

The optimized conditions for transesterification of soybean oil are shown in Table 3. The activity of 30% SiW_{12}/MCM-41 was higher than 30% SiW_{11}/MCM-41 under similar reaction conditions. The activity of the catalysts was found to be depending on the acidic strength of the catalysts (438 mV for 30% SiW_{12}/MCM-41 and 260 mV for 30% SiW_{11}/MCM-41). It is known that the acidic character of POMs is mainly due to the acidic addenda atoms, i.e.

tungsten in the present case and removal of one tungsten-oxygen unit from the parent SiW_{12} is expected to decrease the acidity and activity of the SiW_{11}. The obtained order of the catalytic activity, 30% SiW_{12}/MCM-41 > 30% SiW_{11}/MCM-41, is as expected.

Table 3. Optimized conditions for transesterification of soybean oil.

Catalysts	Reaction time, h	w/w ratio of oil to alcohol	Catalyst amount, mg	Temp., ^{o}C	% Conversion
30% SiW_{12}/MCM-41	8	1:4	200	65	88
30% SiW_{11}/MCM-41	8	1:4	200	65	58
30% SiW_{11}/MCM-41	16	1:4	200	65	91

Control experiments

Table 4. Control experiments for transesterification of soybean oil under optimized conditions.

Catalyst	% Conversion	TON	TOF, h^{-1}
MCM-41[a]	11	-	
SiW_{12} [b]	97	319	39.9
SiW_{11} [b]	93	298	18.6
30% SiW_{12}/MCM-41 [a]	88	290	36.2
30% SiW_{11}/MCM-41 [a]	91	292	18.2

Reaction condition: Catalyst amount [a] 200 mg and [b] 46 mg; mole ratio oil to alcohol 1:4; reaction temperature 65 ^{o}C; reaction time 8 h for 30% SiW_{12}/MCM-41 and 16 h for 30% SiW_{11}/MCM-41. TON= moles of product/ moles of catalyst and TOF= TON/ reaction time.

The control experiments with MCM-41 and SiW_{12}/SiW_{11} were also carried out under optimized conditions. It can be seen from Table 4 that MCM-41 was not much active towards the transesterification of triglycerides indicating the catalytic activity is mainly due to SiW_{12}/SiW_{11}. The same reaction was carried out by taking the active amount of SiW_{12}/SiW_{11} (46 mg). It is clear from the Table 4 that the catalytic activities of SiW_{12}/SiW_{11} have been retained in the respective catalysts (identical TONs) indicating that SiW_{12}/SiW_{11} stays the real active species. Thus, we were successful in anchoring silicotungstates to MCM-41 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Heterogeneity test

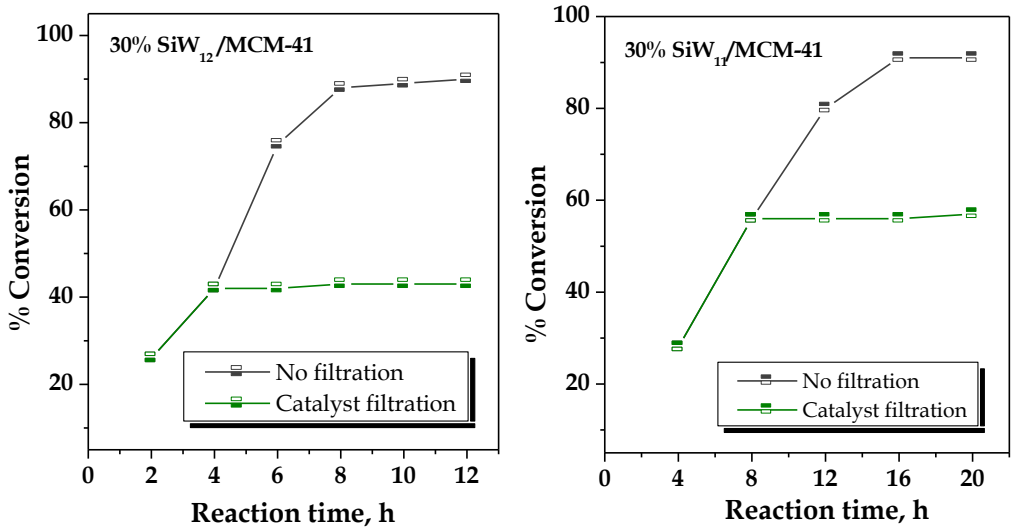


Figure 17. Heterogeneity test for transesterification of soybean oil. Reaction conditions: w/w ratio of oil to alcohol 1:4; amount of catalyst 200 mg; reaction temperature 65 °C.

Rigorous evidence of heterogeneity can be gained only by filtering the catalysts before completion of the reaction and analysing the filtrate for activity [86]. A test was performed by filtering the catalyst from the reaction mixture at 65 °C after 4 h for 30% SiW_{12}/MCM-41 and 8 h for 30% SiW_{11}/MCM-41, and the

filtrate was allowed to react up to optimized reaction time. The final reaction mixture and midway filtered were analysed for conversion. There was no change in the % conversion, which indicates the present catalyst falls into the category C [86]. On the basis of these results, it can be concluded that there is no leaching of SiW_{12}/SiW_{11} from the support, and the catalyst is truly heterogeneous in nature.

Regeneration and recycling of the catalyst

Catalytic activity of regenerated catalysts

Transesterification of soybean oil was carried out with the recycled anchored catalysts, under the optimized conditions. After the reaction, the catalysts were separated from the reaction mixture by simple centrifugation; the first washing was done with methanol to remove the products, then the subsequent washings were done by distilled water and then dried at 100 °C, and the recovered catalyst was charged for the further run. No appreciable decrease in the conversion was observed after two cycles (Table 5).

Table 5. Recycling studies under the optimised conditions.

Catalyst	Number of cycles (Conv. %)		
	Fresh	1st	2nd
30% SiW_{12}/MCM-41	88	86	85
30% SiW_{11}/MCM-41	91	90	88

Reaction condition: Catalyst amount 200 mg; mole ratio oil to alcohol 1:4; reaction temperature 65 ^{o}C; reaction time 8 h for 30% SiW_{12}/MCM-41 and 16 h for 30% SiW_{11}/MCM-41.

The recycling study was carried out using single reaction batch and the catalysts were recovered by centrifugation. The catalyst quantity recovered was charged for the next run. Hence there is handling loss of the catalyst which

prevents further use of the catalyst. However, the use of catalyst can be extended for further runs.

Characterization of Regenerated catalysts

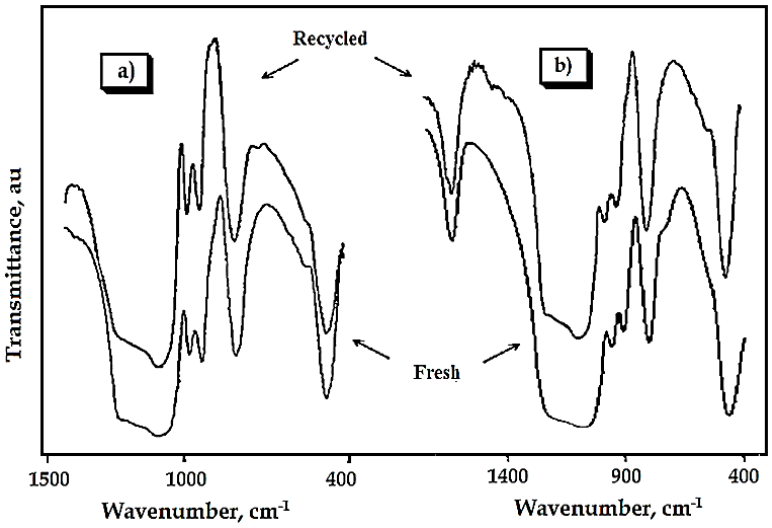


Figure 18. FT-IR spectra of fresh and recycled catalysts, (a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41.

Further the recycled catalysts were characterized for acidic strength, FT-IR and BET surface area analysis in order to see any structural change. The acidic strengths of fresh and recycled catalysts are comparable (for 30% SiW_{11}/MCM-41: fresh=260 mV and recycled= 255 mV and for 30% SiW_{12}/MCM-41: fresh=438 mV and recycled= 434 mV). The FT-IR spectrum of recycled 30% SiW_{12}/MCM-41 showed the retention of typical bands for SiW_{12}, at 979 cm^{-1} and 923 cm^{-1} corresponding to $W=O_d$ and $Si-O_a$ symmetric stretching, respectively. The FT-IR spectrum of the used catalyst 30% SiW_{11}/MCM-41 (Figure 18) shows retention of bands at 960 cm^{-1} ($W=O_d$) and 900 cm^{-1} ($Si-O_a$) suggesting that the structure of SiW_{11} is intact in the regenerated catalyst. The BET surface area values of the recycled catalysts (520 for 30% SiW_{11}/MCM-41 and 332 for 30% SiW_{12}/MCM-41) are comparable with the fresh ones (536 for 30% SiW_{11}/MCM-41 and 349 for 30% SiW_{12}/MCM-41).

Characterization of biodiesel derived from transesterification of soybean oil

The biodiesel sample from transesterification of soybean oil was characterized by FT-IR and ^{1}H-NMR analysis. The biodiesel i. e. fatty acid ester obtained by transesterification reaction was designated by BDSO.

FT-IR analysis for fatty acid methyl esters

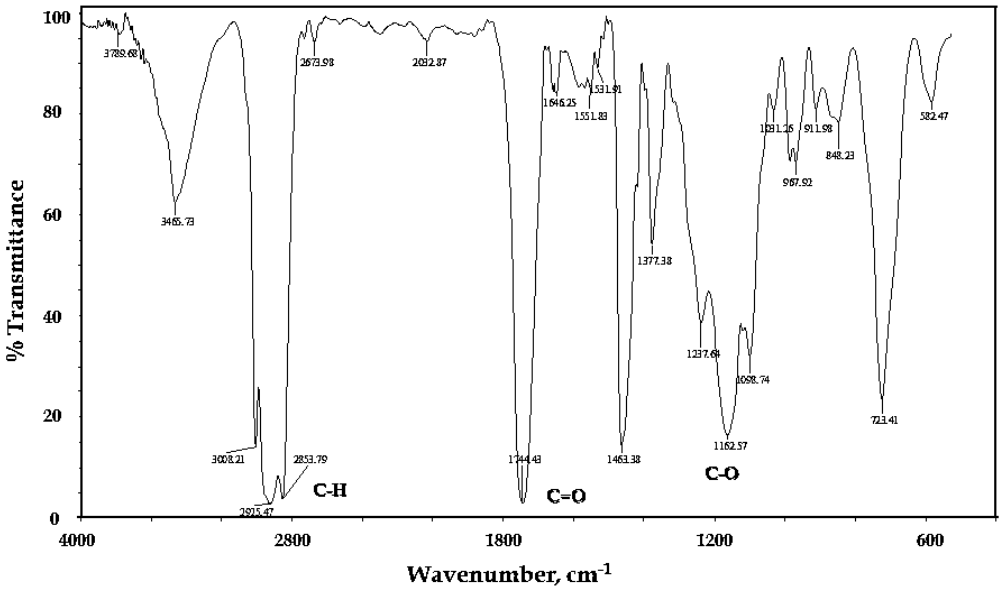


Figure 19. FT-IR spectrum of biodiesel samples, BDSO.

The FT-IR spectra have been used to identify functional groups and the bands corresponding to various stretching and bending vibrations in the sample of biodiesel derived from soybean oil (Figure 19). The position of carbonyl group in FT-IR is sensitive to substituent effects and to the structure of the molecule. The methoxy ester carbonyl group in BDSO was appeared at 1744 cm^{-1}. The band appeared at 3465 cm^{-1} showed the overtone of ester functional group. The C-O stretching vibration in BDSO showed two asymmetric coupled vibrations at 1162 cm^{-1} and 1098 cm $^{-1}$ due to C-C(=O)-O and 1031 cm^{-1} due to O-C-C.

^{1}H NMR of biodiesel samples

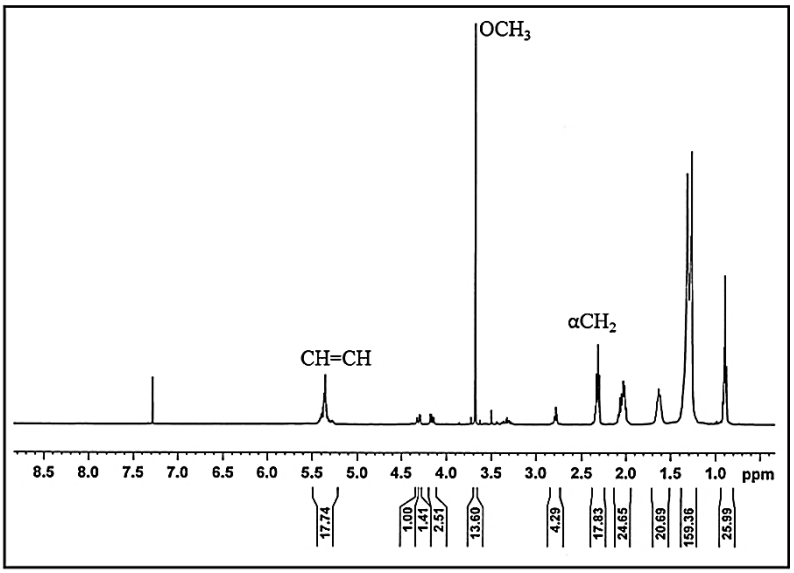


Figure 20. ^{1}H-NMR of biodiesel sample, BDSO.

Biodiesel sample BDSO was characterized by ^{1}H-NMR spectroscopy (Figure 20). The characteristic peak of methoxy protons was observed as a singlet at 3.678 ppm and a triplet of CH_2 protons at 2.296 ppm. These two peaks are the distinct peaks for the confirmation of methyl esters present in biodiesel.

Properties of biodiesel produced

The physical and chemical properties of biodiesel from soybean oil were studied. The biodiesel was prepared in the laboratory scale. The biodiesel sample SOBD was analysed for various properties. The properties measured were compared with the ASTM specifications and the results are presented in Table 6.

Table 6. Properties of BDSO.

Property	Testing procedure	ASTM D6751 Standard for Biodiesel	ASTM D 975 Standard for diesel fuel	BDSO
Acid Value, mg KOH/g	ASTM D1980-87	0.5	-	<0.05
Viscosity at 40 ^{o}C	ASTM D446	1.9 to 6	1.3 to 4.1	5.1
Flash point(^{o}C)	-	100 to 170	60 to 80	164
Pour point(^{o}C)	ASTM D97	-15 to 10	(-35) to 15	4

Acid value is a measure of the FFA content of the biodiesel. Free fatty acids in the oil indicate incomplete transesterification or oxidative degradation where fatty acid methyl ester molecules are regenerated during shelving. Acid numbers higher than 0.8 mg KOH/g have been associated with fuel system deposits and reduced life of fuel pumps and filters [89-90]. The acid value of BDSO was found to be quite below the required limit. The kinematic viscosity indicates the flow capability of any fuel and it was found that it was within the limits of ASTM standards for BDSO. Flash point is the lowest temperature at which vapours from a fuel will ignite on application of a small flame under standard test conditions. The flash point of BDSO sample was 164 ^{o}C which falls within the limits of ASTM standard. Biodiesel is safer than petro-diesel to handle and store because it has a little bit higher flash point than petro-diesel.

The pour point of BDSO was 4, which may be due to the higher content of unsaturated fatty acid in raw soybean oil. The result was found to be within the specified limit and BDSO was suitable not only for the tropical region but also for moderate temperate region. However, further research and development on additional fuel properties and the effects of biodiesel on the engine are necessary.

Mechanism of esterification – transesterification reaction

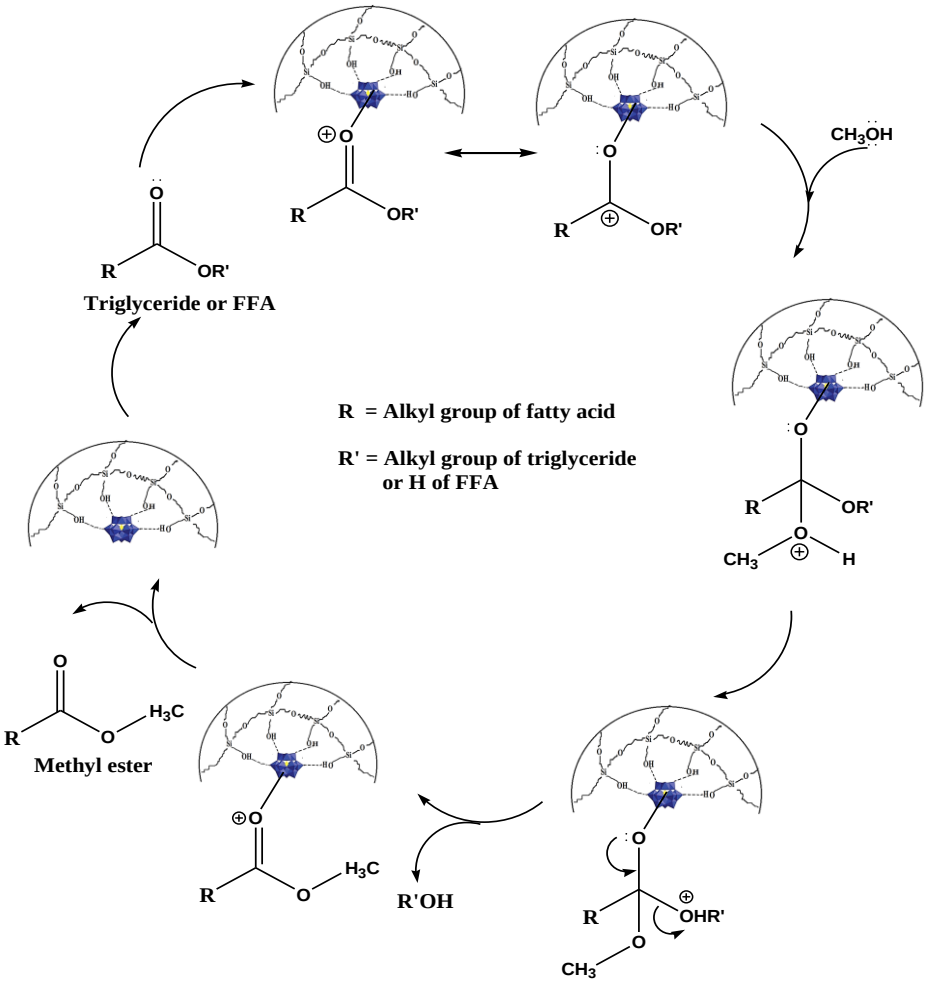


Figure 21. Mechanism of esterification–transesterification reactions.

The reaction mechanism for transesterification of triglyceride or esterification of FFA is shown in Figure 21. The transesterification takes place between triglyceride and alcohol, in the present case soybean oil and methanol. Very

high surface area and large pore dimensions of the present catalyst plays an important role in diffusion of large triglyceride molecules on to the surface of the catalyst. The interaction of the carbonyl oxygen of free fatty acid with acidic sites of the catalyst forms carbocation. POMs are known to stabilise carbocation intermediate thereby assisting the rate of the reaction [5]. The nucleophilic attack of alcohol to the carbocation produces a tetrahedral intermediate [38]. During esterification reaction the tetrahedral intermediate eliminates water molecule to form the alkyl ester of fatty acids (Biodiesel). The transesterification mechanism can be extended to tri- and di-glyceride. It is well known that transesterification is a stepwise reaction. In the reaction sequence, the triglyceride is converted stepwise to di- and monoglyceride and finally glycerol. The tetrahedral intermediate formed during reaction eliminates di-, monoglyceride and glycerol when tri-, di- and monoglyceride come in contact with the acidic sites, respectively, to give one mole of ester ($RCOOCH_3$) in each step.

Conclusions

- The present catalysts showed *excellent activities* for biodiesel synthesis via *esterification of FFA, oleic acid*.
- *Kinetic studies* show that esterification of oleic acid *follows first* order rate law without any diffusion or mass transfer limitation.
- The present catalysts also exhibits *outstanding activities* for the *transesterification of triglyceride* feedstock, *soybean oil* with methanol under mild conditions.
- The EDS, BET as well as FT-IR of *reused catalysts* shows *no structural changes* indicating catalytic systems are stable.
- The *recycling studies* showed that both the catalysts can be reused several times without any significant loss in the activity.
- The 30% SiW_{12}/MCM-41 shows *superior catalytic activity* as compared to 30% SiW_{11}/MCM-41 for both esterification as well as transesterification reaction under similar conditions.
- The *reaction mechanism* for both the reactions has been demonstrated.
- The higher activities enables the catalysts to be used for *feedstocks that are rich in FFAs*.
- We have successfully developed *environmentally benign heterogeneous catalysts* for biodiesel production from soybean oil.

References

1. Z. Helwani, M. R. Othman, N. Aziz, W. J. N. Fernando and J. Kim, Fuel Process. Technol., 90, 1502, (2009).
2. A. Demirbas, Energy Convers. Manage., 50, 14, (2009).
3. B. Buczek, L. Czepirski, Inform AOCS, 15,186, (2004).
4. M. T. Pope, Inorganic Chemistry Concepts Vol. 8: Heteropoly and Isopoly Oxometalates, Springer, Berlin, (1983).
5. T. Okuhara, N. Mizuno, M. Misono, Adv. Catal., 41, 113, (1996).
6. I. V. Kozhevnikov, Catalysts for fine chemical synthesis, Catalysis by polyoxometalates Wiley, Chichester, vol 2, (2002).
7. A. Demirbas, Energy Convers. Manage., 44, 2093, (2003).
8. C. Stavarache, M. Vinatoru, R. Nishimura, Y. Maeda, Ultrason. Sonochem., 12, 367, (2005).
9. P. V. Tekade, O. A. Mahodaya, G. R. Khandeshwar, B. D. Joshi, Sci. Revs. Chem. Commun., 2(3), 208, (2012).
10. G. Pahl, Biodiesel: Growing a New Energy Economy. Chelsea Green Publication Company, US, (2004).
11. S. Peter, E. Weidner, Eur. J. Lipid Sci. Technol., 109, 11, (2007).
12. Z. Tang, L. Wang, J. Yang, Eur. J. Lipid Sci. Technol., 110, 747, (2008).
13. N. Dizge, C. Aydiner, D. Y. Imer, M. Bayramoglu, A. Tanriseven, B. Keskinler, Bioresource Technol., 100, 1983, (2009).
14. V. B. Veljkovic, O. S. Stamenkovic, Z. B. Todorovic, M. L. Lazic, D. U. Skala, Fuel., 88, 1554, (2009).
15. C. C. M. Silva, N. F. P. Ribeiro, M. V. M. Souz, D. A. G. Aranda, Fuel Process. Technol., 91, 205, (2010).
16. M. A. Jackson, J. W. King, J. Am. Oil Chem. Soc., 73, 353, (1996).
17. Y. Zhang, M. A. Dube, D. D. McLean and M. Kates, Bioresour. Technol., 89, 1, (2003).
18. D. Y. C. Leung, Y. Guo, Fuel Process. Technol., 87, 883, (2006).

19. M. Y. Koh, T. I. M. Ghazi, Renew. Sustain. Energy Rev., 15, 2240, (2011).
20. G. Mendow, N. S. Veizaga, C. A. Querini, Biores. Technol., 102, 6385, (2011).
21. S. V. Ghadge, H. Raheman, Biomass Bioenerg., 28, 601, (2005).
22. V. P. Amish, N. Subrahmanyam, P. A. Payal, Fuel, 88, 625, (2009).
23. S. H. Shuit, Y. T. Ong, K. T. Lee, B. Subhash S. H. Tan, Biotechnol. Adv., 30, 1364, (2012)
24. G. C. Martins, T. Sergio, M. L. Ledo, U. Schuchardt, Biores. Technol., 99, 6608, (2008).
25. L. S. do Nascimentoa, L.M.Z. Titoa, R. S. Angélicab, C. E.F. da Costaa, J. R. Zamiana, G. N. da Rocha Filhoa, Appl. Catal. B: Env., 101, 495, (2011).
26. K-H. Chung, B-G. Park, J. Ind. Eng. Chem.15, 388, (2009).
27. S.R. Kirumakki, N. Nagaraju, S. Narayanan, Appl. Catal. A: Gen., 273, 1, (2004).
28. A. A. Kiss, A. C. Dimian, G. Rothenberg, Adv. Synth. Catal., 348, 75, (2006).
29. M. A. Harmer, W. E. Farneth, Q. Sun, J. Am. Chem. Soc. 118, 7708, (1996).
30. M. A. Harmer, Q. Sun, A. J. Vega, W. E. Farneth, A. Heidekum, W. F. Hoelderich, Green Chem. 2, 7, (2000).
31. T. Okuhara, Catal. Today. 73, 167 (2002).
32. Y. Wang, Y. Liu, C. Liu, Energy. Fuels. 22, 2203, (2008).
33. A. A. Kiss, A. C. Dimian, G. Rothenberg, Energy Fuels, 22,598, (2008)
34. Y. -M. Park, D. -W. Lee, D. -K. Kim, J. -S. Lee, K. -Y. Lee, Catal. Today, 131, 238, (2008).
35. Y. -M. Park, J. Y. Lee, S. -H. Chung, I. S. Park, S. -Y. Lee, D. -K. Kim, J. -S. Lee, K. -Y. Lee, Bioresour. Technol., 101, S59, (2010).
36. J. A. Melero, L. F. Bautista, G. Morales, J. Iglesias, D. Briones, Energy Fuels, 23, 539, (2009).

37. I. K. Mbaraka, K. J. McGuire, B .H. Shanks, Ind. Eng. Chem. Res., 45, 3022 (2006).
38. M. G. Kulkarni, R. Gopinath, L. C. Meher, A. K. Dalai, Green Chem., 8, 1056, (2006).
39. C. S. Caetano, I. M. Fonseca, A. M. Ramos, J. Vital, J. E. Castanheiro, Catal. Comm., 9, 1996, (2008).
40. B. Hamad, R. O. L. Souza de, G. Sapaly, M. G. C. Rocha, P. G. P. Oliveira de, W. A. Gonzalez, Catal. Comm., 10, 92, (2008).
41. G. Sunita, B. M. Devassy, A. Vinu, D. P. Sawant, V. V. Balasubramanian, S. B. Halligudi, Cat. Comm., 9, 696, (2008).
42. L. Xu, W. Li, J. Hu, X. Yang, Y. Guo, Appl. Catal. B, 90, 587, (2009).
43. L. Xu, Y. Wang, X. Yang, J. Hu, W. Li and Y. Guo, Green Chem., 11, 314, (2009).
44. L. Xu, W. Li, J. Hu, K. Li, X. Yang, F. Ma, Y. Guo, X. Yu, Y. Guo, J. Mater. Chem., 19, 8571, (2009).
45. C. F. Oliveira, L. M. Dezaneti, F. A. C. Garcia, Julio L. de Macedo, J. A. Dias, S. C. L. Dias, K. S. P. Alvim, Appl. Catal A, 372, 153, (2010).
46. K. Srilatha, N. Lingaiah , P. S. Sai Prasad, B. L. A. Prabhavathi Devi, R. B. N. Prasad, Reac. Kinet. Mech. Cat., 104, 211, (2011).
47. K. Srilatha, Ch. Ramesh Kumar, B. L. A. Prabhavathi Devi, R. B. N. Prasad, P. S. Sai Prasada, N. Lingaiah, Catal. Sci. Technol., 1, 662, (2011).
48. K. Srilatha, N. Lingaiah, B. L. A. P. Devi, R. B. N. Prasad, S. Venkateswar, P. S. S. Prasad, Appl. Catal. A, 365, 28, (2009).
49. K. Srilatha, B. L. A. Prabhavathi Devi, N. Lingaiah, R. B. N. Prasad, P. S. Sai Prasad, Bioresour. Technol., 119, 306, (2012).
50. K. Srilatha, T. Issariyakul, N. Lingaiah, P. S. Sai Prasad, J. Kozinski, A. K. Dalai, Energy Fuel., 24, 4748, (2010).
51. A. S. Badday, A. Z. Abdullah, K. T. Lee, Appl. Energy, 105, 380, (2013).

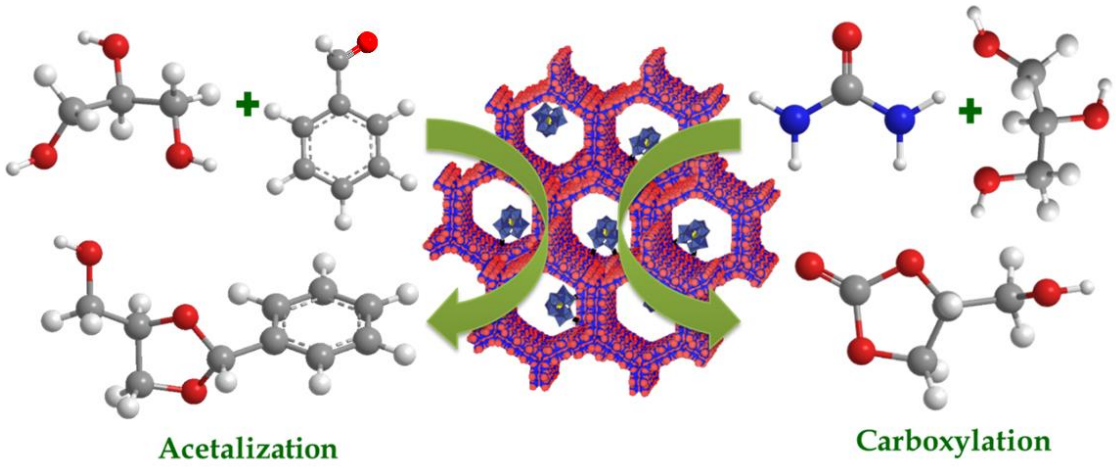
52. R. Sheikh, M. S. Choi, J. S. Im, Y. H. Park, J. Ind. Eng. Chem., 19, 1413, (2013).
53. M Kuzminska, T. V. Kovalchuk, R. Backov, E. M. Gaigneaux, J. Catal., 320, 1, (2014).
54. V. V. Bokade, G. D. Yadav, Process Saf. Environ. Prot., 85 (B5), 372, (2007).
55. V. V. Bokade, G. D. Yadav, Ind. Eng. Chem. Res., 48, 9408, (2009).
56. L. X. Zhang, Q. Z. Jin, J. H. Huang, Y. F. Liu, L. Shanl, X. G. Wang, Energ. Source. Part A, 34, 1037, (2012).
57. O. da Silva Lacerda J, R. M. Cavalcanti, T. M. de Matos, R. S. Angélica, G. N. da Rocha Filho, I. de C. Lopes Barros, Fuel, 108, 604, (2013).
58. K. Y. Nandiwale, V. V. Bokade, Ind. Eng. Chem. Res., 53 (49), 18690, (2014).
59. L. H. O. Pires, A. N. de Oliveira, O. V. Monteiro Jr., R. S. Angélica, C. E. F. da Costa, J. R. Zamian, L. A. S. do Nascimento, G. N. R. Filho, Appl. Catal. B: Env., 160-161, 122, (2014).
60. J. Alcaniz-Monge, G. Trautwein, J. P. Marco-Lozar, Appl. Catal. A, 468, 432, (2013).
61. A. S. Badday, A. Z. Abdullah, K. T. Lee, Renew. Energy, 50, 427, (2013).
62. A. S. Badday, A. Z. Abdullah, K. T. Lee, Renew. Energy, 62, 10, (2014).
63. C. Baroi, S. Mahto, C. Niu, A.K. Dalai, Appl. Catal. A, 469, 18, (2014).
64. C. Baroi, A. K. Dalai, Appl. Catal. A: Gen., 485, 99, (2014).
65. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, Nature, 359, 710, (1992).
66. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, J. Am. Chem. Soc., 114, 10834, (1992).
67. T. Vralstad, G. Oye, J. Sjoblom, M. Stocker, J. Dispersion Sci. Technol., 27, 489, (2006).
68. A. Tuel, Micropor. Mesopor. Mater., 27, 151, (1999).

69. I. Tropecelo, M. H. Casimiro, I. M. Fonseca, A. M. Ramos, J. Vital, J. E. Castanheiro, Appl. Catal. A, 390, 183, (2010).
70. M. S. Khayoon, B.H. Hameed, Fuel Process. Technol., 114, 12, (2013).
71. K. Yan, G. Wu, J. Wen, A. Chen, Catal. Commun., 34, 58, (2013).
72. C. Baroi, A. K. Dalai, Catal. Today, 207, 74, (2013).
73. V. Brahmkhatri, A. Patel, Ind. Eng. Chem. Res., 50, 6620, (2011).
74. V. Brahmkhatri, A. Patel, Appl. Catal. A, 403, 161, (2011).
75. S. Singh, A. Patel, J. Clean. Prod., 72, 46, (2014).
76. V. Brahmkhatri, A. Patel, Ind. Eng. Chem. Res., 50, 13693, (2011).
77. N. Narkhede, V. Brahmkhatri, A. Patel, Fuel, 135, 253, (2014).
78. R. Fazaeli , H. Aliyan, Rus. J. Appl. Chem., 88, 676, (2015).
79. Y. Chen, Y.Cao, Y. Suo, G-P Zheng, X-X Guan, X-C Zheng, J. Taiwan Inst. Chem. Eng., (2015), 51, 186-192.
80. D. D. Bala, K. de Souz, M. Misra, D. Chidambar, J. Cleaner Prod., 104, 273, (2015).
81. V. Brahmkhatri, A. Patel, Environmentally Benign Catalysts Based on Heteropolyacids for Clean Organic Transformations, (Eds.) A. Patel, Springer Inc., New York, pp. 189, (2013).
82. A. Talebian-Kiakalaieh, N. A. S. Amin, A. Zarei, I. Noshadi, Appl Energy, 102, 283, (2013).
83. J. M. Marchetti, V. U. Miguel, A. F. Errazu, Fuel, 86, 906, (2007).
84. G. Corro, U. Pal, N. Tellez, Appl. Catal. B: Env., 129, 39, (2013).
85. V. Brahmkhatri, A. Patel, Appl. Catal. A: Gen., 403, 161, (2011).
86. R. A. Sheldon, M. Walau, I. W. C. E. Arends, U. Schuchurdt, Acc. Chem. Res., 31, 485, (1998).
87. G. C. Bond, Heterogeneous Catalysis: Principles and Applications, Oxford Chemistry Series; Clarendon Press: Oxford, Ch. 3, p 49, (1974).
88. A. K. Endalew, Y. Kiros, R. Zanzi, Biomass Bioenergy, 35, 3787, (2011).

89. US Department of Energy. Energy efficiency and renewable energy. Biodiesel handling and use guidelines. 3. Edition. DOE/GO-102006-2358, (2006).
90. D. Y. C. Leung, B. C. P. Koo, Y. Guo, Bioresour. Technol., 97, 250, (2006).

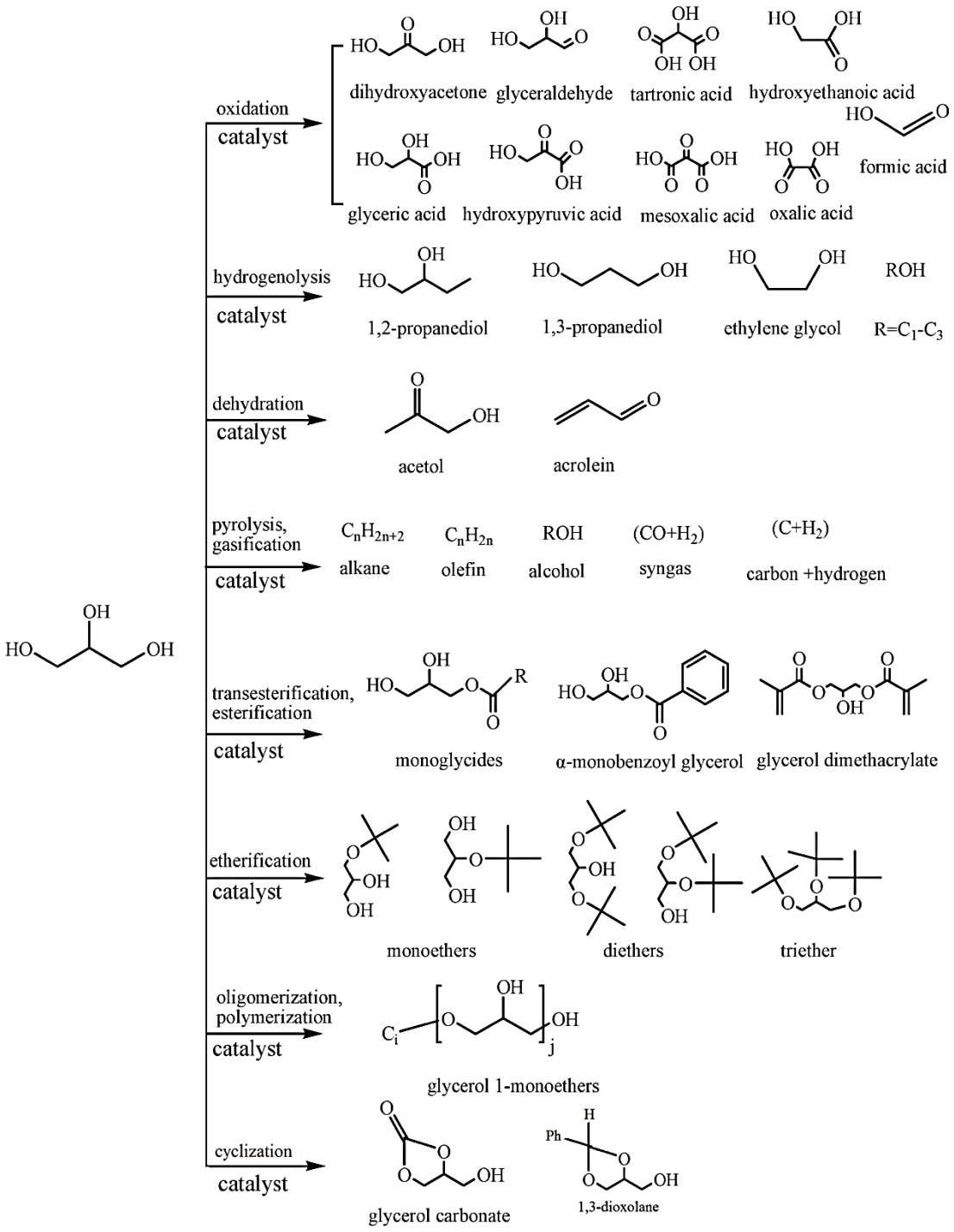
CHAPTER 2B

VALORISATION OF GLYCEROL VIA ACETALIZATION WITH BENZALDEHYDE AND CARBOXYLATION WITH UREA



Glycerol is generated at the rate of 1 mol of glycerol for every 3 mol of methyl esters synthesized, approximately 10 wt% of the total product [1]. Biodiesel production is accompanied by the formation of glycerol as a by-product and thus the availability of glycerol has tripled within the last ten years due to the increased biodiesel production [2]. In addition as countries like America and Brazil target increased biofuel usage in future, the glycerol availability will still increase [3]. The use of glycerol is limited now, being mainly confined to pharmaceuticals and cosmetics. Hence new processes are needed that can convert the surplus glycerol to value-added chemicals. In addition to low price of glycerol, this will also improve the economic viability of biodiesel manufacture.

The different reaction procedures for conversion of glycerol to value-added chemicals including oxidation, dehydration, hydrogenolysis, pyrolysis, etherification, esterification, steam reforming, acetalization, polymerization, and oligomerization are presented in Scheme 1. [2, 4-8].



Scheme 1. Pathways of catalytic conversion of glycerol into useful chemicals (With addition from Ref. 2).

Amongst, the cyclization of glycerol via acetalization reaction is one of the most important procedures for the synthesis of green and cost-effective bio-

additive chemicals from glycerol. Glycerol reacts with simple carbonyl compounds to provide isomeric 1,3-dioxane and dioxolane products as novel fine chemical intermediates. These cyclic acetals are potential precursors for the manufacture of green platform chemicals 1,3-dihydroxyacetone and 1,3-propanediol [9]. The acetalization reaction is many times necessary for protection of carbonyl groups during the manipulation of multifunctional organic molecules [10] as well as it has direct applications as fragrances, in cosmetics, food and beverage additives, pharmaceuticals, in detergents, in lacquer industries and as ignition accelerators and antiknock additives in combustion engines [11] and in port wine production [12]. Glycerol acetals can also be used as the basis for surfactants [13].

Traditionally, the acetalization of glycerol was carried out over mineral acids as homogeneous catalysts [14]. However, the effluent disposal leads to environmental problems and economical inconveniences. These problems can be overcome by use of heterogeneous catalysts such as Alumina [15], mesoporous aluminosilicates [16], ion-exchange resins [17], transition metal complexes [18-20] and mixed metal oxides [22-22] have also been employed.

Carboxylation of glycerol is also important class of reaction to produce glycerol carbonate. Glycerol carbonate has excellent properties such as low toxicity, good biodegradability and a high boiling point which make it a very attractive chemical for a variety of applications such as a high boiling polar solvent, an intermediate in organic synthesis [23] and in the synthesis of polycarbonates [24], polyurethanes [25] and in cosmetic and medical institutes as they have low toxicity, volatility, combustibility and good moisturizing ability [26]. Besides, they also play a major role as a component of surfactants, paints, coatings and gas-separation membranes [27]. Additionally, there is a general consensus that the potential of glycerol carbonate as an anti-explosive additive

for gasoline and diesel will result in an unprecedented growth in the coming years [28-30].

The traditional route for the synthesis of glycerol carbonate (GlyC) is the transesterification of glycerol with acyclic organic carbonates [31-32]. However, the carbonates utilised during the transesterification are also typically generated *via* phosgene utilisation which suffers from the drawback of being a dangerous and environmentally unfriendly reactant or energy intensive routes employing epoxides. The direct reaction of glycerol with CO_2 appears very attractive, but it has serious thermodynamic limitations [33]. One of the practical routes for carbonylation of glycerol is the use of urea as a carbonate source [30]. The major advantage of this method over other processes is that urea is readily available and cheap. Literature survey shows that catalysts with Lewis acid sites such as ZnO [34], Co_3O_4/ZnO [35], $ZnCl_2$ [36], γ-zirconium phosphate [27], HTc–Zn derived from hydrotalcite [32] Sm-exchanged heteropoly tungstate [37], gold supported ZSM-5 [30] manganese sulfate [30] and metal oxides [38] produce high glycerol carbonate yields.

The literature survey shows that the reports on glycerol valorisation via acetalization or carboxylation reaction using anchored polyoxometalates (POMs) are comparatively few.

Castanheiro et al. have reported the synthesis and characterization of silica immobilized $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ for acetalization of glycerol with acetone [39]. All catalysts tested on acetalization of glycerol showed high selectivity to solketal (97% near complete conversion). Further recycling studies showed that after the fourth cycle, the catalysts lost only 10-13% of its initial activity.

Lingaiah at al. have carried out Sm^{3+} and Zn^{2+} exchanged $H_3PW_{12}O_{40}$ for glycerolysis of urea [40-41]. It was reported that catalyst retains its Keggin

structure even after exchange with metal ions. The catalytic studies showed that Zn-TPA comes out to be better catalyst amongst the two. Both the catalysts were recycled successfully up to three times.

Zhang et al. have synthesized $H_3PW_{12}O_{40}$ encapsulated mesoporous metal-organic framework (MOF), MIL-100(Fe), by a simple low-temperature, HF-free incorporation route via the reaction of ferric nitrate and trimesic acid in the presence of $H_3PW_{12}O_{40}$ [42]. The characterization results indicate that the $H_3PW_{12}O_{40}$ molecules were successfully incorporated within the mesoporous cages of the MIL-100(Fe) as non-coordinating guests, thus maintaining the integrity of the protonic acidity of $H_3PW_{12}O_{40}$. The resulting HPW@MIL-100(Fe) catalyst exhibits high activity and excellent reusability in the esterification reactions with no evidence for agglomeration, leaching, or deactivation of the $H_3PW_{12}O_{40}$ during several repeated uses of the catalyst. The catalyst also shows excellent catalytic properties in the acetalization of benzaldehyde and ethanediol. The unique characteristics of MIL-100(Fe) and the well dispersion of $H_3PW_{12}O_{40}$ molecules within the mesoporous cages of the MIL-100(Fe) matrix may account for the high catalytic activity and recyclability of the HPW@MIL-100(Fe) catalyst.

With a focus on recent developments in the conversion of glycerol into value-added chemicals, we describe in this paper the sustainable route towards solvent free valorisations of glycerol via acetalization of glycerol with benzaldehyde as well as glycerolysis of urea over MCM-41 anchored silicotungstates. The effects of different reaction variables such as catalyst concentration, mole ratio and reaction time were studied to optimize the conditions for maximum conversion. The catalysts were also recycled up to four times without any significant loss in the conversion.

EXPERIMENTAL

Materials

All used chemicals were of A.R. grade. Silicotungstic acid, benzaldehyde, tetraethylorthosilicate, glycerol, sodium tungstate, sodium silicate, acetonitrile, n-butylamine, urea and acetone were purchased from Merck.

Reaction Procedure

Acetalization reaction

A typical acetalization reaction of glycerol with aldehydes was carried out in a 50 ml two-necked round bottom flask under inert atmosphere. The flask was charged with glycerol (10 mmol), benzaldehyde (12 mmol) and 50 mg of catalyst. The reaction mixture was vigorously stirred at room temperature (28-30 ^{o}C) under N_2 atmosphere for 60 min. The products were analysed using Shimadzu 2014 GC equipped with RTX-5 capillary column (internal diameter: 0.25 mm, length: 30 m).

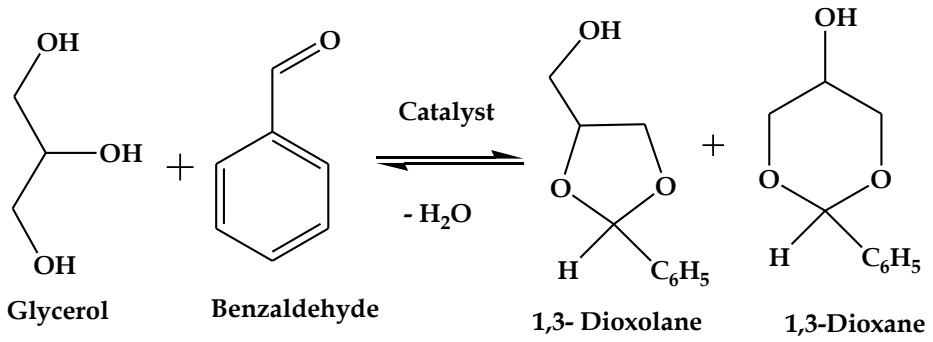
Carboxylation reaction

In a typical carboxylation reaction, glycerol (10 mmol) and urea (10 mmol) were placed in a 50 mL round bottom flask and the catalyst (100 mg) was added. The reaction was performed at 140 ^{o}C and N_2 was purged in the reaction mixture. After completion of the reaction, methanol was added to the reaction mixture and the catalyst was separated by centrifugation. The products were analysed by using Shimadzu 2014 Gas Chromatography instrument equipped with RTX-5 capillary column (internal diameter: 0.25 mm, length: 30 m). The products were identified by comparison with the standard samples.

RESULTS AND DISCUSSION

I) Acetalization of glycerol with benzaldehyde

Acetalization of glycerol with benzaldehyde (Scheme 2) produces two main products; 1,3-dioxolane and 1,3-dioxane, whose relative formation depends on the acetalization position within the glycerol molecule. The glycerol acetalization reaction favours the formation of kinetically favoured product, 1,3-dioxolane.



Scheme 2. Acetalization of glycerol with benzaldehyde.

Effect of % loading of SiW_{12}/SiW_{11}

The effect of percentage loading of SiW_{12}/SiW_{11} was studied by carrying out acetalization reaction over 10% to 40% loaded catalysts for both the systems (Figure 1). Low conversions were obtained for low loadings of SiW_{12}/SiW_{11}. The optimum of 91% conversion with 74% 1,3-dioxolane selectivity was obtained by using 30% SiW_{12}/MCM-41 and 85% conversion with 82% 1,3-dioxolane selectivity was obtained by using 30% SiW_{11}/MCM-41. The enhanced activity can be assigned to the increase in SiW_{12}/SiW_{11} content. Further increase in loading beyond 30% loading no significant increase in the conversion was observed. As a result, 30% loading was optimum and considered for the further studies.

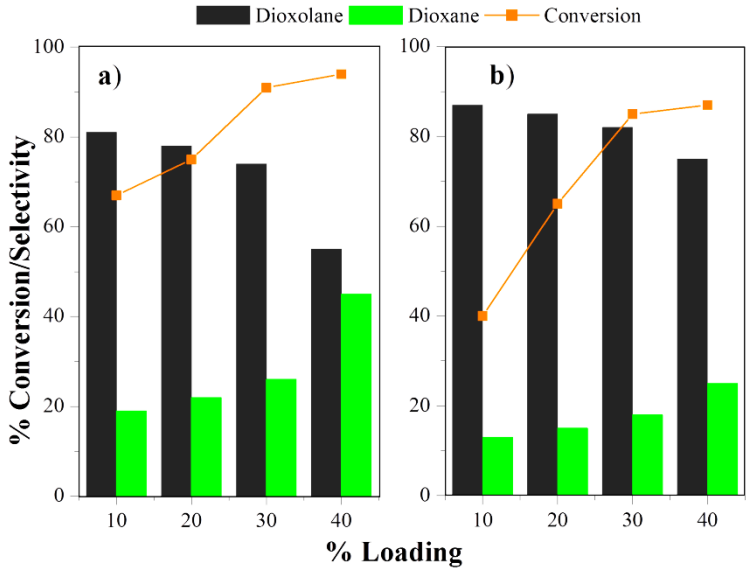


Figure 1. Effect of loading on acetalization of glycerol over a) SiW_{12}/MCM-41 and b) SiW_{11}/MCM-41. Reaction conditions: mole ratio G/B: 1/1.2; time: 60 min; temperature: 30 ^{o}C; catalyst amount: 100 mg.

Effect of mole ratio of glycerol to benzaldehyde

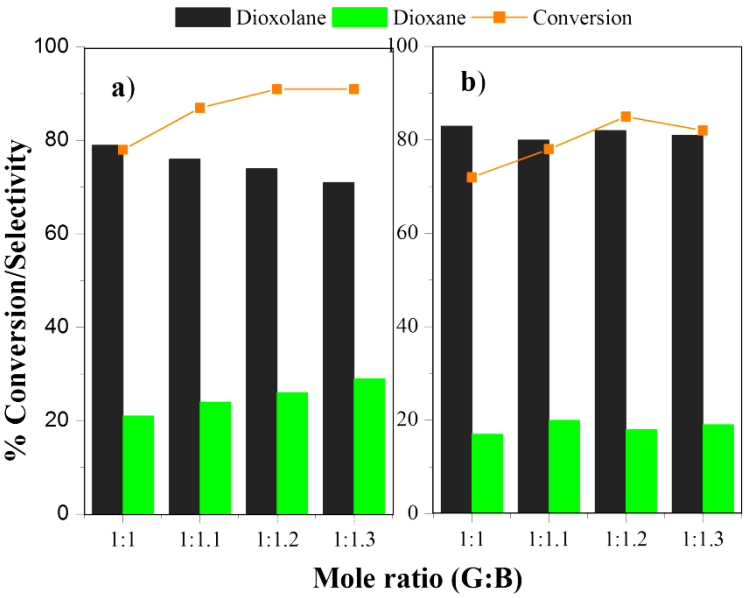


Figure 2. Effect of mole ratio on acetalization of glycerol over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: time: 60 min; temperature: 30 ^{o}C; catalyst amount: 100 mg.

The effect of glycerol to benzaldehyde mole ratio was studied by varying ratio from 1:1 to 1:1.3 over both the catalysts (Figure 2). The glycerol conversion was found to be increasing with increase in the mole ratio. However the selectivity remains almost the same for both the catalysts. The optimum mole ratio of glycerol: benzaldehyde was found to be 1:1.2 for both catalysts.

Effect of amount of catalyst

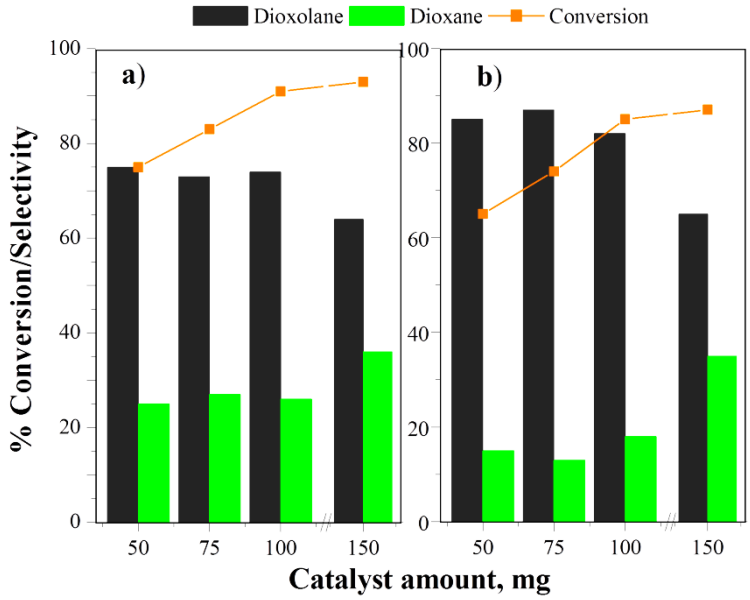


Figure 3. Effect of catalyst amount on acetalization of glycerol over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: mole ratio G/B: 1/1.2; time: 60 min; temperature: 30 ^{o}C.

The effect of the amount of catalysts on glycerol conversion was studied by varying catalyst amount in the range 50-150 mg. As shown in Figure 3, initial increase in the catalyst concentration increases the conversion of glycerol with almost similar selectivity to dioxolane and reaches saturation conversion at 100 mg of the catalyst amount. Similar trend was observed for both the catalysts. The increase in the conversion can be attributed to an increase in the number of available catalytically active sites. Hence, 100 mg of the catalyst was considered to be optimum for the maximum conversion.

Effect of reaction time

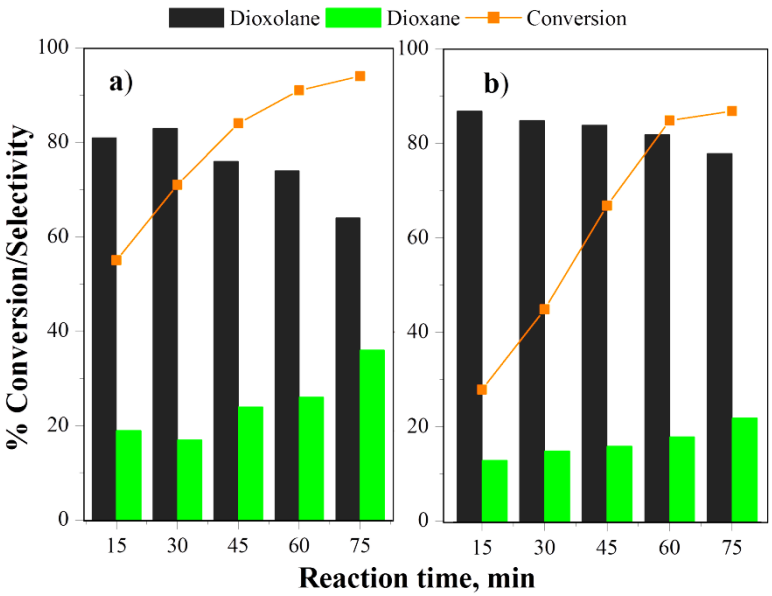
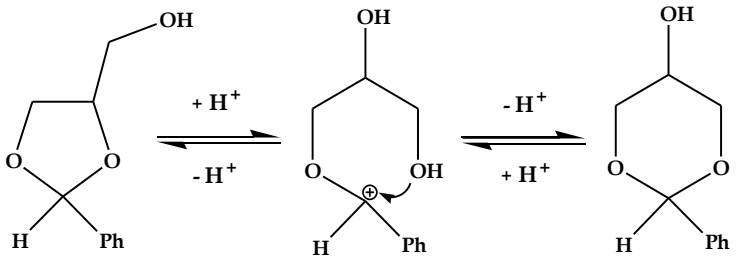


Figure 4. Effect of reaction time on acetalization of glycerol over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: mole ratio G/B: 1/1.2; temperature: 30 ^{o}C; catalyst amount: 100 mg.

In order to examine the variation of glycerol conversion and products selectivity with time, we have studied acetalization of glycerol at different time intervals (reaction time varied from 15 to 75 min). The conversion of glycerol was increased with increase in the reaction time. It was observed from the Figure 4 that the kinetically favoured product dioxolane was formed initially as major product and with increase in time the selectivity towards thermodynamically more stable product, dioxane increases slowly. At 60 minutes of the time 91% conversion with 74% selectivity to dioxolane was observed for 30% SiW_{12}/MCM-41 and 85% conversion of glycerol with 82% selectivity to dioxolane was observed for 30% SiW_{11}/MCM-41.

The optimized conditions for maximum conversion (91% for 30% SiW_{12}/MCM-41 and 85% for 30% SiW_{11}/MCM-41) are: mole ratio G/B: 1/1.2; time: 60 min; temperature: 30 ^{o}C; catalyst amount: 100 mg.

Among both the catalysts, 30% SiW_{11}/MCM-41 showed better selectivity of dioxolane than 30% SiW_{12}/MCM-41. There exists equilibrium between dioxolane and dioxane in the presence of strong acid sites via key intermediate benzyl cation (Scheme 3). The catalyst 30% SiW_{12}/MCM-41 possesses very strong acid sites (438 mV) than 30% SiW_{11}/MCM-41 (260 mV). The strength of the acid sites leads to the ring transformation and hence relatively low selectivity was observed for 30% SiW_{12}/MCM-41. By looking at the industrial importance of the dioxolane derivative, 30% SiW_{11}/MCM-41 will be the choice of better catalyst.



Scheme 3. Acid catalyzed transformation between dioxolane and dioxane obtained in glycerol acetalization with benzaldehyde.

Control experiments

The acetalization of glycerol was carried out without catalyst as well as using MCM-41, and active species (SiW_{12} and SiW_{11}). It is clear from the Table 1 that the support MCM-41 is not much active towards the acetalization and the activity of the species SiW_{12}/SiW_{11} has been retained in the catalysts. The results suggest that we were successful in heterogenizing homogeneous catalysts SiW_{11}/SiW_{12} on MCM-41 support.

Table 1. Control experiments for acetalization of glycerol with benzaldehyde.

Catalyst	% Conversion	% Selectivity[c]	TON	TOF, h^{-1}
No catalyst	15	90	-	
MCM-41	28	85	-	
SiW_{12}[a]	95	65	1188	1188
SiW_{11}[a]	90	70	1048	1048
30% SiW_{12}/MCM-41[b]	91	74	1139	1139
30% SiW_{11}/MCM-41[b]	85	82	989	989

Reaction conditions: mole ratio G/B: 1/1.2; time: 60 min; temperature: 30 °C; catalyst amount: [a]23 mg / [b]100 mg, [c]Dioxolane selectivity. TON= moles of product / moles of catalyst, TOF= TON/ reaction time.

Regeneration and recycling of the catalyst

Table 2. Recycling studies under the optimised conditions.

Catalyst	Number of cycles (Conv. %)				
	Fresh	1st	2nd	3rd	4th
30% SiW_{12}/MCM-41	91	89	88	89	87
30% SiW_{11}/MCM-41	85	85	84	85	82

Reaction conditions: mole ratio G/B: 1/1.2; time: 60 min; temperature: 30 °C; catalyst amount: 100 mg.

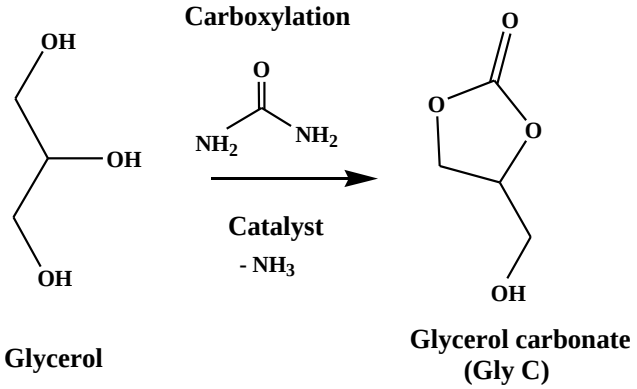
The catalysts were recycled for four times in order to test their activity in successive runs. The catalysts were separated from the reaction mixture by simple centrifugation, washed with 5 mL methanol and then with 5 mL distilled water, dried at 100 °C in an oven for 10 h and the recovered catalysts

were charged for the further runs. No appreciable decrease in the conversion was observed up to four cycles (Table 2).

Further the recycled catalysts were characterized for acidic strength, FT-IR analysis and BET surface area in order to see any structural change. The results are similar to the previously presented in *Chapter 2a* hence are not included.

II) Carboxylation of glycerol

The activity of synthesized catalysts, 30% SiW_{12}/MCM-41 and 30% SiW_{11}/MCM-41 was evaluated for the synthesis of glycerol carbonate by solvent free carboxylation of glycerol (Gly) with urea (Scheme 4). The effect of different reaction parameters on the conversion as well as selectivity for GlyC was evaluated.



Scheme 4. Synthesis of glycerol carbonate from glycerolysis of urea.

Effect of % loading of SiW_{12}/SiW_{11}

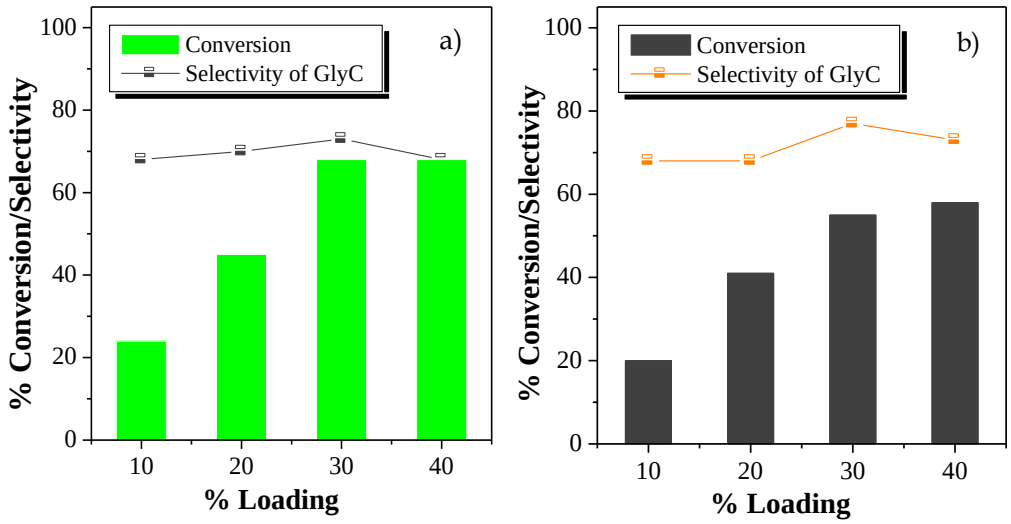


Figure 5. Effect of % loading on carboxylation of glycerol over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: mole ratio Gly/Urea: 1/1; time: 8 h; temperature: 140 ^{o}C; catalyst amount: 100 mg.

The effect of percentage loading of SiW_{12}/SiW_{11} on the conversion of glycerol was studied by varying the loading from 10-40% (Figure 5). It is clear that the increase in the loading of SiW_{12}/SiW_{11} linearly increases the conversion of glycerol up to 30% loading. This can be correlated with the increase in the catalytically active acidic sites. For higher loadings, both conversion as well as selectivity decreases which may be due to adsorption of liberated NH_3 molecules at acidic SiW_{12}/SiW_{11} species on the surface of catalysts. The selectivity of GlyC was not affected much by the increase in the % loading. The optimum glycerol conversion of 55% for 30% SiW_{11}/MCM-41 and 68% for 30% SiW_{12}/MCM-41 was achieved with 30% loading and further increase in the loading does not influence the conversion. Hence, 30% loaded catalysts were selected for the further studies.

Effect of mole ratio of glycerol to urea

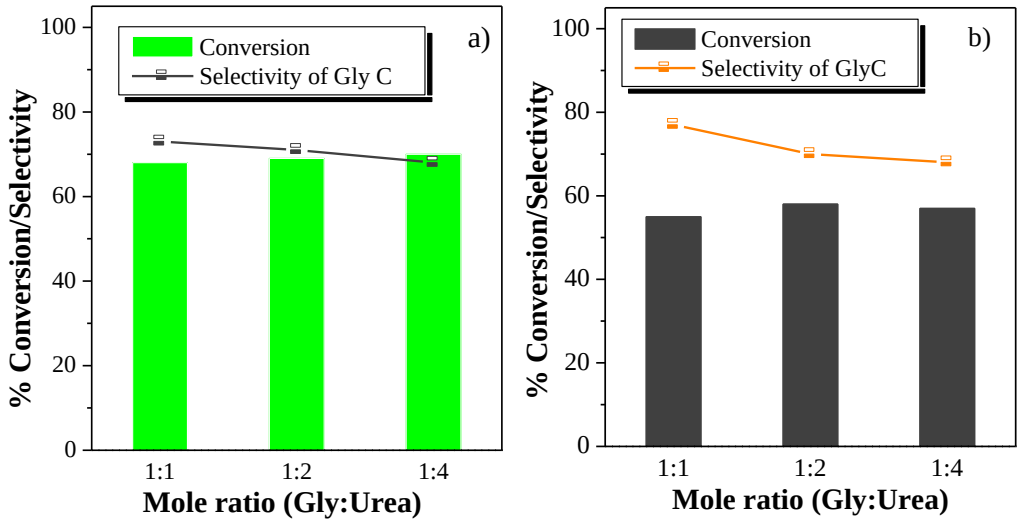


Figure 6. Effect of Gly: Urea mole ratio on carboxylation of glycerol over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: time: 8 h; temperature: 140 ^oC; catalyst amount: 100 mg.

Figure 6 shows the influence of glycerol to urea mole ratio on the conversion of glycerol and selectivity of the GlyC. It can be noted that with G: U molar ratio

of 1:1, the conversion of glycerol was 55% with 77% selectivity towards glycerol carbonate for 30% SiW_{11}/MCM-41. However, further increase in the mole ratio did not increase the conversion of the glycerol. It was interesting to note that with increase in the mole ratio selectivity of GlyC was decreased for both the catalysts. This is due to the fact that at higher concentration of urea, there is a possibility of formation of by-product by reaction of free hydroxyl group of glycerol with excess urea. As a result 1:1 ratio was considered as optimum mole ratio for maximum selectivity of GlyC.

Effect of amount of the catalyst

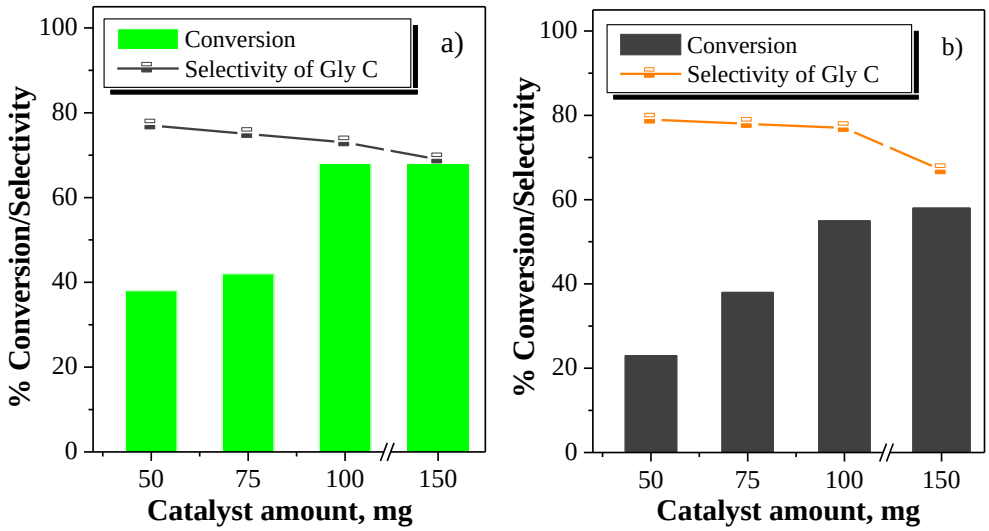


Figure 7. Effect of catalyst amount on carboxylation of glycerol over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: mole ratio G/U: 1/1; time: 8 h; temperature: 140 ^{o}C.

The studies of effect of catalyst amount on the conversion (Figure 7) of glycerol suggest that with increase in catalyst amount the conversion of glycerol also increases linearly. However, for higher catalyst concentration, the selectivity of GlyC was decreased. The excess catalyst might be favouring the reaction between the product GlyC and urea to yield, 5-hydroxymethyloxazolidine-2-one. Hence, 100 mg of catalyst amount was considered to be optimum.

Effect of reaction time

The effect of reaction time on the conversion of glycerol (Figure 8) suggests that increase in the reaction time increases the conversion of the glycerol as well as selectivity of GlyC. Further it was observed that catalytic activity of both the catalysts was limited to 62% for 30% SiW_{11}/MCM-41 and 75% for 30% SiW_{12}/MCM-41 at 140 °C and 8 h. This may be due to the fact that liberated NH_3 forms ammonium salt with the silicotungstates and thereby poisoning the catalyst even after purging the reaction mixture with N_2 in order to remove the excess of NH_3 formed. With further increase in the reaction time, the coke formation starts.

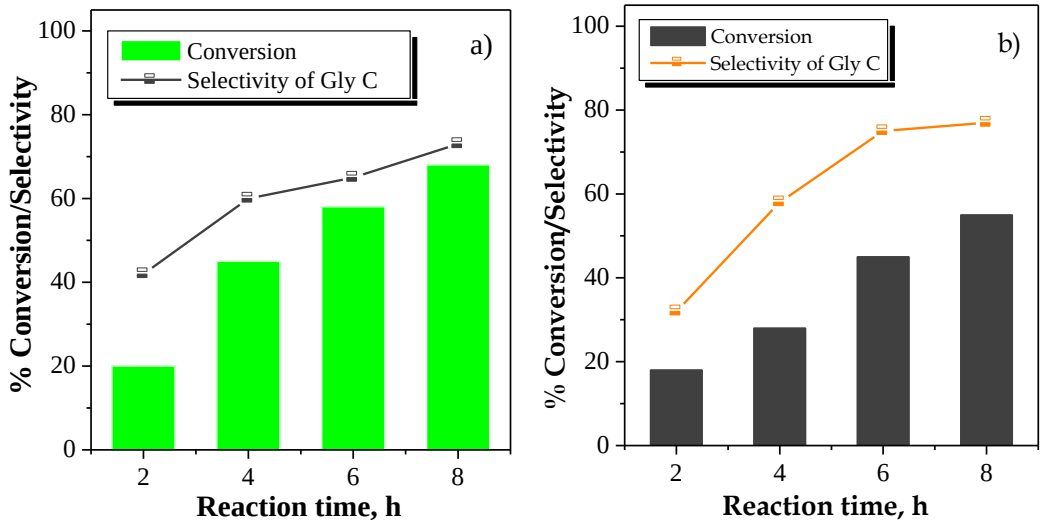


Figure 8. Effect of reaction time on carboxylation of glycerol over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: mole ratio G/U: 1/1; temperature: 140 °C; catalyst amount: 100 mg.

Effect of reaction temperature

The temperature variation study was carried out by varying the temperature in the range of 100 °C to 150 °C (Figure 9). With increase in the reaction temperature, both conversion as well as selectivity was increased drastically. This is due to the fact that high temperatures are required to break the urea

molecules. Further, higher temperatures facilitate desorption of accumulated NH_3 molecules from the catalyst surface. Maximum glycerol conversion of 62% for 30% SiW_{11}/MCM-41 and 75% for 30% SiW_{12}/MCM-41 was achieved at 150 ^oC which was considered to be optimum temperature for glycerolysis of urea.

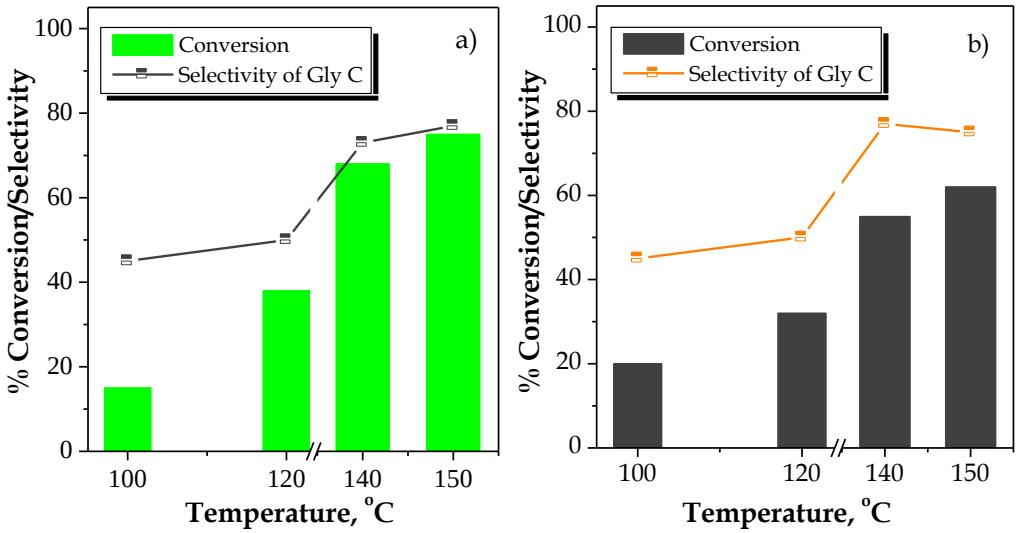


Figure 9. Effect of temperature on carboxylation of glycerol over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: mole ratio G/U: 1/1; time: 8 h; catalyst amount: 100 mg.

The optimized conditions (maximum conversion; 75%, and selectivity; 77%) for 30% SiW_{12}/MCM-41 are, mole ratio Gly/Urea: 1; temperature: 150 ^oC; catalyst amount: 100 mg; reaction time: 8 h. Similarly, the final optimized conditions (maximum conversion; 62%, and selectivity; 75%) for 30% SiW_{11}/MCM-41 are, mole ratio Gly/Urea: 1; temperature: 150 ^oC; catalyst amount: 100 mg; reaction time: 8 h.

Among the two catalysts, 30% SiW_{12}/MCM-41 was better in terms of activity as well as selectivity. The results are quite consistent with the acidic strength of both the catalysts. Further it was observed that catalytic activity of both the catalysts was limited to 75% for 30% SiW_{12}/MCM-41 and 62% for 30% SiW_{11}/MCM-41. This may be due to the fact that liberated NH_3 forms

ammonium salt with the silicotungstates and thereby poisoning the catalyst even after purging the reaction mixture with N_2 in order to remove the excess of NH_3 formed.

Control experiments

The carboxylation of glycerol was carried out without catalyst as well as using support, and active species (Table 3). The support was not much active towards the carboxylation and activities of active species are quite comparable with those of the catalysts. Thus, we were successful in heterogenizing SiW_{12}/SiW_{11} on to the mesoporous support without losing its catalytic activity.

Table 3. Control experiments for carboxylation of glycerol with urea.

Catalyst	% Conversion	% Selectivity[c]	TON	TOF
No catalyst	19	36	-	
MCM-41[b]	24	45	-	
SiW_{12}[a]	71	75	889	111.1
SiW_{11}[a]	65	70	820	102.5
30% SiW_{12}/MCM-41[b]	75	77	939	117.3
30% SiW_{11}/MCM-41[b]	62	75	782	97.7

Reaction conditions: mole ratio Gly/Urea: 1/1; time: 8 h; temperature: 150 ^oC; catalyst amount: [a]23 mg / [b]100 mg. TON was calculated from the formula, TON= moles of product/moles of catalyst. [c] glycerol carbonate selectivity. TOF=TON/ reaction time.

Heterogeneity test

For the rigorous proof of heterogeneity, a test was carried out by filtering catalyst (30% SiW_{11}/MCM-41) from the reaction mixture after 4 h and allowed the filtrate to react up to 8 h. The reaction mixture of 4 h and filtrate was analysed by Gas Chromatography. Both the samples showed same conversion

of 26%. Similar results were obtained for 30% SiW_{12}/MCM-41. It has been reported by Sheldon et al. that there are three categories for a catalyst to behave as a true heterogeneous catalyst in context of leaching of metal from the support a) the metal leaches but is not active homogeneous catalyst, b) metal leaches to form an active homogeneous catalyst and c) the metal does not leach is a true heterogeneous catalyst. The results indicate that the present catalyst fall into category C [43]. On the basis of these results, it can be concluded that there is no any leaching of the SiW_{12}/SiW_{11} from the support and the present catalysts are truly heterogeneous in nature.

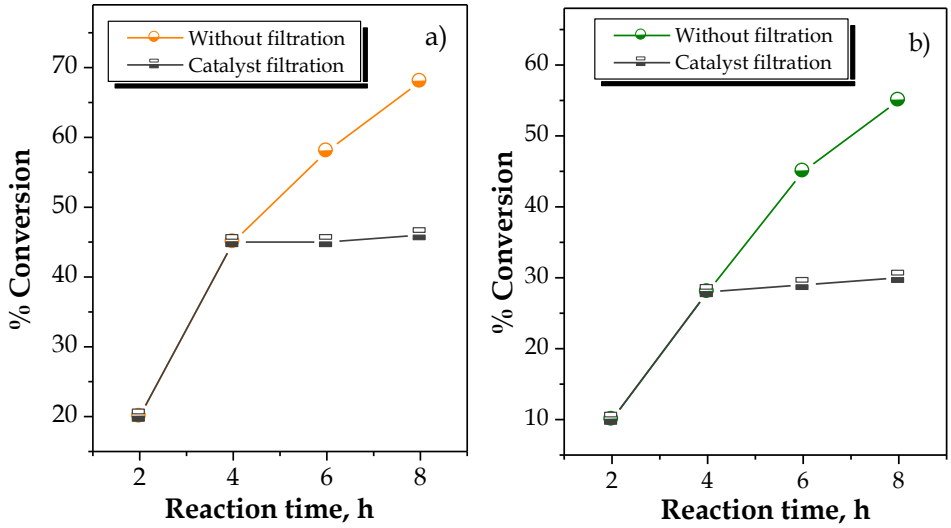


Figure 10. Heterogeneity test for glycerolysis of urea over a) 30% SiW_{12}/MCM-41 and b) 30% SiW_{11}/MCM-41. Reaction conditions: mole ratio Gly/Urea: 1; time: 8 h; temperature: 140 ^{o}C; catalyst amount: 100 mg.

Regeneration and recycling of the catalyst

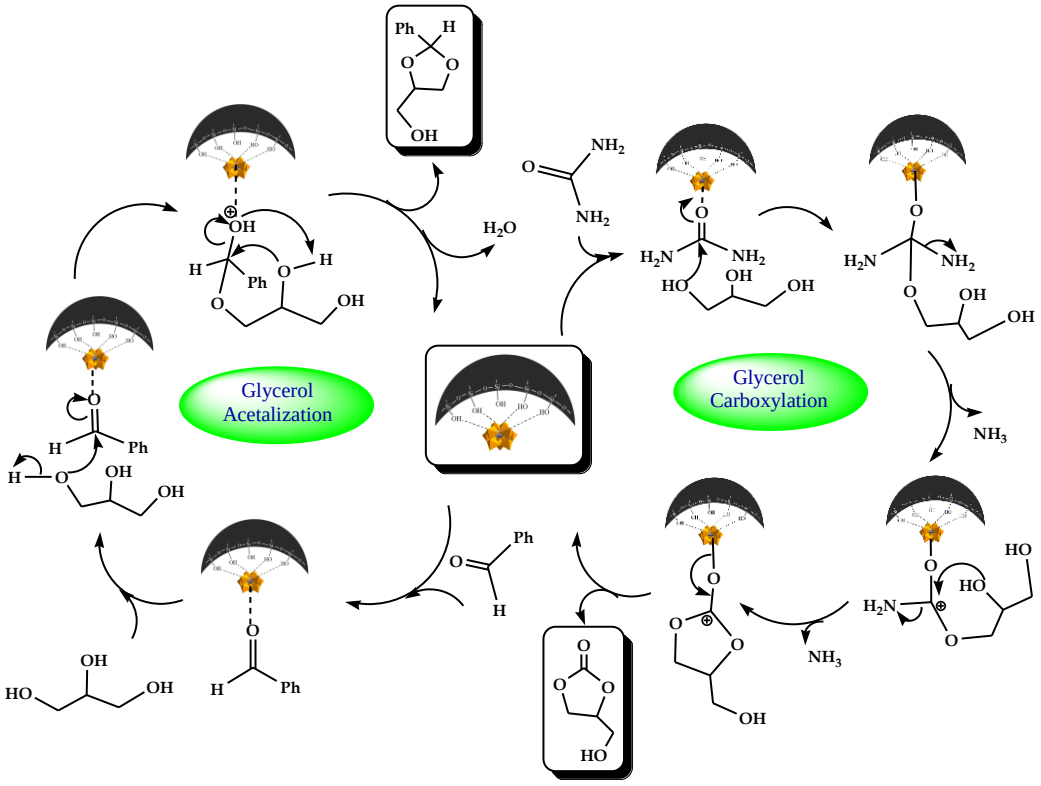
The catalysts were recycled up to four times in order to test their activity in successive runs. The catalysts were separated from the reaction mixture by simple centrifugation, washed with 5 mL methanol and then with 5 mL distilled water, dried at 100 ^{o}C in an oven for 10 h and the recovered catalysts were charged for the further runs. The conversion of glycerol observed up to

four successive runs for 30% SiW_{11}/MCM-41 are 62%, 60%, 58% and 57% and for 30% SiW_{12}/MCM-41 are 75%, 72%, 71% and 70%. Thus, the catalysts can be reused up to four cycles with minimal loss in the activity.

Characterization of Regenerated catalysts

Further the recycled catalysts were characterized for acidic strength, FT-IR analysis and BET surface area in order to see any structural change. The results are similar to the previously presented in *Chapter 2a* hence are not included.

Reaction mechanism for acetalization as well as carboxylation of glycerol



Scheme 5. Reaction mechanism for glycerol acetalization as well as carboxylation reactions.

The probable mechanism for acetalization as well as carboxylation of glycerol is shown in Scheme 5. Very high surface area and pore dimension of the

present catalyst plays an important role in diffusion of large substrate molecules on to the surface of the catalyst.

For glycerolysis of urea, a tetrahedral intermediate is formed by nucleophilic attack of hydroxyl group of glycerol to the carbonyl carbon of urea. The subsequent release of two ammonia molecules leads to the formation of GlyC [40]. The leaving off of the product molecule is again a steric effect in the heterogeneous catalysis and the present catalyst contains large pore diameter that facilitates the escape of product molecule.

In the case of glycerol acetalization, the first step is the coordination and activation of the carbonyl group of the benzaldehyde [32]. Then, the carbon atom of the carbonyl group can be attacked by the primary alcoholic group of glycerol followed by the formation of a bond between the carbonyl oxygen atom and the β-carbon of the glycerol. Finally, the dehydration process leads to the formation of dioxolane.

Conclusions

- The present catalysts show *very high conversion and selectivity* for *acetalization* of glycerol with benzaldehyde. Very short reaction time, room temperature and solvent free conditions make the process *environmentally benign.*
- *30% SiW_{12}/MCM-41* exhibited *91%* conversion of glycerol with *74%* selectivity of 1,3-dioxolane whereas *85%* conversion with *82%* selectivity was observed by using *30% SiW_{11}/MCM-41.*
- By tuning acidic strength of the parent silicotungstate, the selectivity of the 1,3-dioxolane was increased from *74%* to *82%*.
- The present catalysts also showed outstanding activities for *carboxylation of glycerol* with urea to synthesize GlyC.
- *75%* conversion with *77%* selectivity of GlyC was achieved with *30% SiW_{12}/MCM-41* and *62%* conversion with *75%* selectivity was achieved by using *30% SiW_{11}/MCM-41*.
- EDS, BET as well as FT-IR of reused catalysts show *no structural changes* indicating catalytic systems are stable.
- The catalysts were *regenerated and reused* successfully up to four cycles without significant loss in the activity.
- The 30% SiW_{12}/MCM-41 shows *superior catalytic activities* as compared to 30% SiW_{11}/MCM-41.
- A *reaction mechanism* for valorisation of glycerol via acetalization as well as carboxylation reactions has been discussed.

References

1. M. McCoy, Chem. Eng. News, 84, 7, (2006).
2. C.-H. Zhou, J. N. Beltramini, Y.-X. Fan, G. Q. Lu, Chem. Soc. Rev., 37, 527, (2008).
3. G. S. Nair, E. Adrijanto, A. Alsalme, I. V. Kozhevnikov, D. J. Cooke, D. R. Brown, N. R. Shiju, Catal. Sci. Technol., 2, 1173, (2012).
4. A. Brandner, K. Lehnert, A. Bienholz, M. Lucas, P. Claus, Top. Catal., 52, 278 (2009).
5. L. C. Meher, D. Vidya Sagar, S. N. Naik, Renew. Sus. Energ. Rev., 10, 248, (2006).
6. J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel, C. Rosier, Green Chem., 6, 359, (2004).
7. J.-M. Clacens, Y. Pouilloux, J. Barrault, Appl. Catal. A: Gen., 227 (1-2), 181, (2002).
8. K. Gottlieb, H. Neitsch, R. Wessendorf, Chem.-Ing. Tech., 66 (1), 64, (1994).
9. A. J. Showler, P.A. Darley, Chem. Rev., 67, 427, (1967).
10. T. W. Green, P.G.M. Wuts, Protective Groups in Organic Synthesis, vol. 4, 2nd ed., Wiley, New York, p. 212 (1991).
11. M. J. Climent, A. Corma, A. Velty, Appl. Catal. A: Gen., 263, 155, (2004).
12. A. Cesar, D.S. Ferreira, J.C. Barbe, A. Bertrand, J. Agric. Food Chem. 50, 2560, (2002).
13. M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, Angew. Chem. Int. Ed. 46, 4434, (2007).
14. S. B. Umbarkar, T. V. Kotbagi, A. V. Biradar, R. Pasricha, J. Chanale, M. K. Dongare, A. –S. Mamede, C. Lancelot, E. Payen, J. Mol. Catal. A: Chem., 310, 150, (2009).
15. T. Vu Moc and P. Maitte, Bull. Soc. Chim. Fr., 9, 2558, (1975).
16. M. J. Climent, A. Corma, S. Iborra, M. C. Navarro, J. Primo, J. Catal., 161, 783, (1996).

17. J. Deutsch, A. Martin, H. Lieske, J. Catal., 245, 428, (2007).
18. P. Sudarsanam, B. Mallesham, A. N. Prasad, P. S. Reddy, B. M. Reddy, Fuel Process. Technol., 106, 539, (2013).
19. C. Crotti, E. Farnetti, N. Guidolin, Green Chem., 12, 2225, (2010).
20. M. Cataldo, E. Nieddu, R. Gavagnin, F. Pinna, G. Strukul, J. Mol. Catal. A: Chem., 142, 305, (1999).
21. B. Mallesham, P. Sudarsanam, G. Raju and B. M. Reddy, Green Chem., 15, 478, (2013).
22. M. S. Khayoon and B. H. Hameed, Appl. Catal. A: Gen., 465, 191, (2013).
23. A. C. Simao, B. Lynikaite-Pukleviciene, C. Rousseau, A. Tatibouet, S. Cassel, A. Sackus, A. P. Rauter P. Rollin, Lett. Org. Chem., 3, 744, (2006).
24. G. Rokicki, P. Rakoczy, P. Parzuchowski and M. Sobiecki, Green Chem., 7, 529, (2005).
25. L. Ubaghs, N. Fricke, H. Keul and H. Hocker, Macromol. Rapid Commun., 25, 517, (2004).
26. V. Plasman, T. Caulier, Plast. Addit. Compd., 7, 30, (2005).
27. M. Aresta, A. Dibenedetto, F. Nocito, C. Ferragina, J. Catal., 268, 106, (2009).
28. M. A. Pacheco, C. L. Marshall, Energy Fuel, 11, 2, (1997).
29. A. Dibenedetto, A. Angelini, M. Aresta, J. Ethiraj, C. Fragale, F. Nocito, Tetrahedron, 67, 1308, (2011).
30. B. Hammond, J. A. Lopez-sanchez, A. R. Mohd Hasbi, N. Dimitratos, R. L. Jenkins, A. F. Carley, Q. He, C. J. Kiely, D. W. Knight, G. J. Hutchings, Dalton. Trans., 40, 3927, (2011).
31. J. R. O. -Gomez, O. G. -J. -Aberasturi, B. M. -Madurga, A. P. -Rodriguez, C. R. -Lopez, L. L. -Ibarreta, J. T. -Soria, M. C. illaran-Velasco, Appl. Catal. A: Gen., 366, 315, (2009).
32. M. J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Concepcion, J. Catal., 269, 140, (2010).

33. J. B. Li, T. Wang, J. Chem. Thermodyn., 43, 731, (2011).
34. J. W. Yoo, Z. Mouloungui, Stud. Surf. Sci. Catal., 146, 757, (2003).
35. F. R. Marcos, V. C. Casilda, M. A. Banares, J. F. Fernandez, J. Catal., 275, 288, (2010).
36. J. H. Park, J. S. Choi, S. K. Woo, S. D. Lee, M. Cheong, H. S. Kim and H. Lee, Appl. Catal., A, 433-434, 35, (2012).
37. C. R. Kumar, K. Jagadeeswaraiah, P. S. S. Prasad, N. Lingaiah, Chem. Cat. Chem., 4, 1360, (2012).
38. K. Jagadeeswaraiah, C. R. Kumar, P. S. S. Prasad, S. Loridant, N. Lingaiah, Appl. Catal., A, 469, 165, (2014).
39. P. Ferreira, I. M. Fonseca, A. M. Ramos, J. Vital, J. E. Castanheiro, Appl. Catal. B: Env., 98, 94 (2010).
40. C. R. Kumar, K. Jagadeeswaraiah, P. S. S. Prasad, N. Lingaiah, Chem. Cat. Chem., 4, 1360, (2012).
41. K. Jagadeeswaraiah, C. R. Kumar, P. S. S. Prasad, N. Lingaiah, Catal. Sci. Technol., 4, 2969, (2014).
42. F. Zhang, Y. Jin, J. Shi, Y. Zhong, W. Zhu, M. Samy El-Shall, Chem. Eng. J., 269, 236 (2015).
43. R. A. Sheldon, M. Walau, I. W. C. E. Arends, U. Schuchurdt, Acc. Chem. Res., 31, 485, (1998).