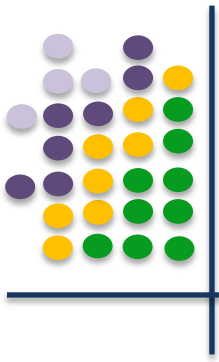


Chapter 4

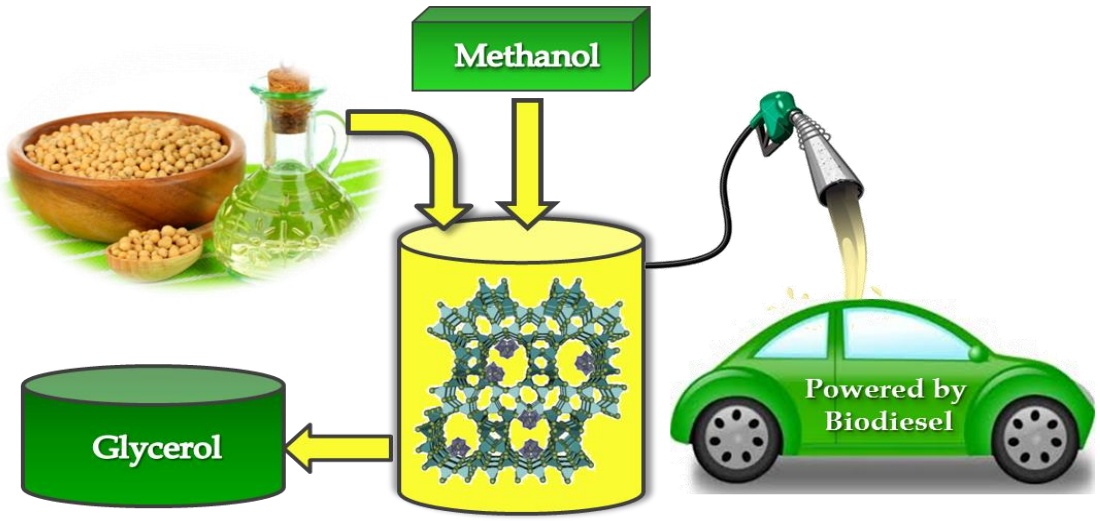
Catalytic Activity of SiW_{12}/SiW_{11} Anchored to Hβ for,

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 4A

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



The present chapter deals with the application of synthesized catalysts, $SiW_{12}/H\beta$ as well as $SiW_{11}/H\beta$ towards biodiesel synthesis. The esterification of oleic acid was carried out in order to find the optimized conditions for maximum conversion. The kinetic studies were carried out to calculate the Activation energy and Arrhenius constant. The heterogeneity test was carried out in order to confirm the truly heterogeneous nature of the catalysts. Further, catalysts were recovered and recycled to check their recyclability. The recycled catalysts were further characterized for acidic strength, FT-IR, elemental analysis and BET surface area.

EXPERIMENTAL

Materials

All used chemicals were of A.R. grade. Oleic acid and methanol were purchased from Merck. Soybean oil sample was 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 0.2 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 soybean 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 [1-4].

RESULTS AND DISCUSSION

I) Esterification of oleic acid with methanol

The esterification reaction is an equilibrium-limited reaction. In order to overcome the equilibrium limitation of the esterification of oleic acid, the reaction was carried out by taking methanol in excess.

The effect of various reaction parameters such as % loading of SiW_{12}/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_{12}/SiW_{11}

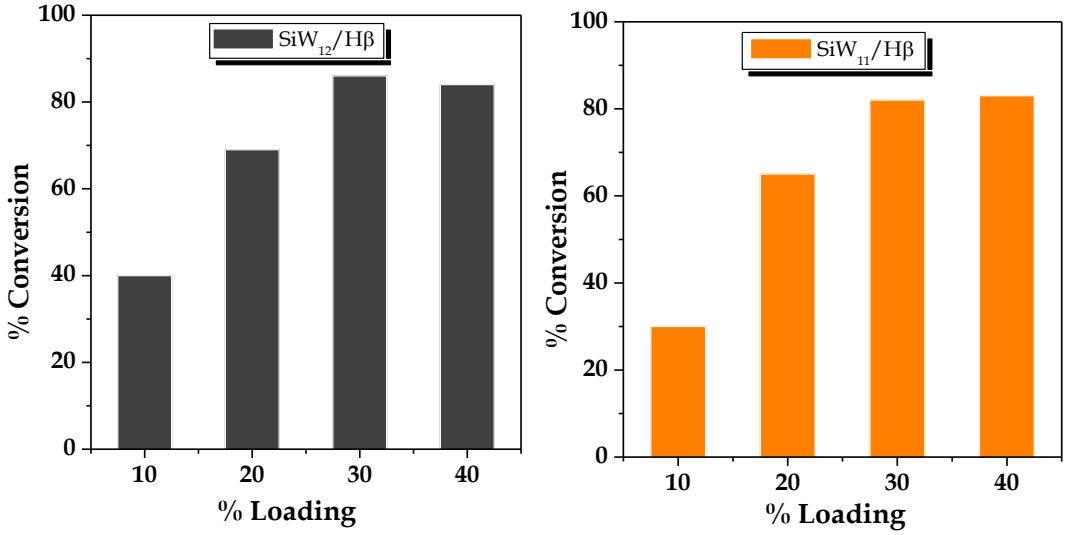


Figure 1. Effect of % loadings of SiW_{12}/SiW_{11} onto Hβ, Reaction conditions: mole ratio of oleic acid/methanol, 1:20; amount of catalyst, 100 mg; reaction temperature, 60 ^{o}C; reaction time, 10 h.

To study the effect of % loading (Figure 1) esterification reaction was performed with 10-40% loaded catalysts. The conversion of oleic acid increases with increase in percentage loading. The enhanced activity could be assigned to the increase in SiW_{12}/SiW_{11} content. Further, 40% loaded catalysts showed no significant increase in the conversion. It is well known that increasing %

loading by impregnation method can lead to a poorer dispersion, which in turn could result in the formation of larger aggregates of the active species at the expense of smaller, more active clusters [5]. Hence, 30% loading was considered to be optimum for the esterification reaction.

Effect of mole ratio of oleic acid to methanol

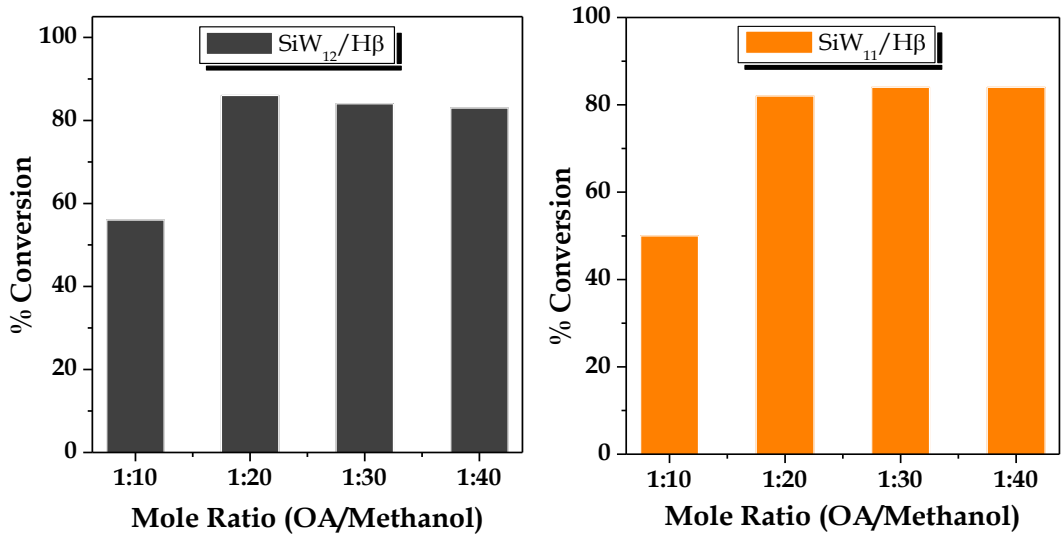


Figure 2. Effect of oleic acid to methanol mole ratio. Reaction conditions: amount of catalyst, 100 mg; reaction temperature, 60 ^{o}C; reaction time, 10 h.

To see the effect of the mole ratio, the esterification reaction was performed by varying the mole ratio of oleic acid to methanol from 1:10 to 1:40, with 100 mg 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 that the oleic acid conversion increases with an increase in the oleic acid/methanol ratio and reaches optimum at the oleic acid/methanol mole ratio of 1:20 for both the catalysts. With a further increase in the molar ratio, there is no significant increase in the conversion. As a result, the oleic acid to methanol molar ratio of 1:20 was considered to be optimum for obtaining high conversion.

Effect of amount of catalyst

The effect of the amount of catalysts on oleic acid conversion was studied by varying catalyst amounts in the range 50-150 mg. As shown in Figure 3, the oleic acid conversion was increased with increase in the amount of both the catalysts and touches an optimum of 86% for 30% SiW_{12}/Hβ and 82% for 30% SiW_{11}/Hβ with 100 mg catalyst amount. 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.

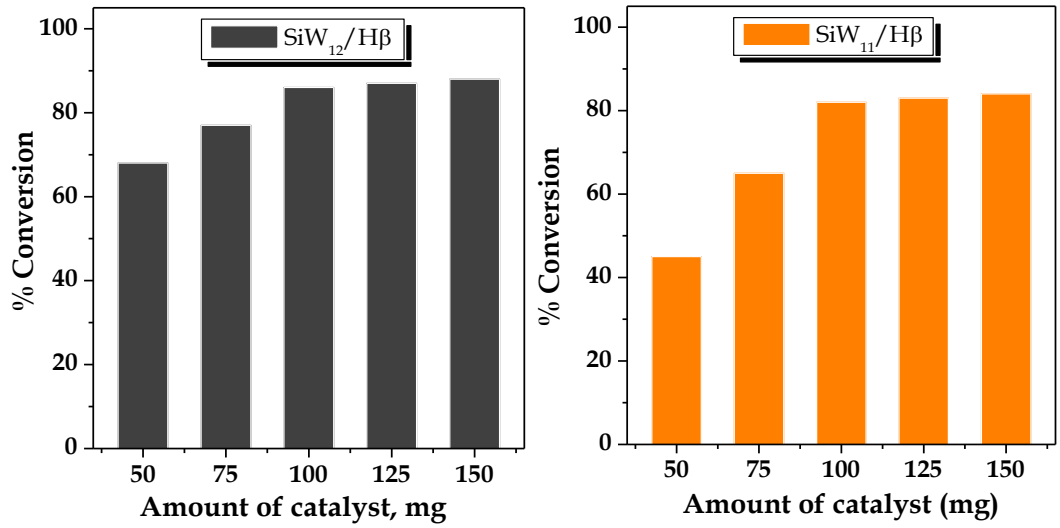


Figure 3. Effect of catalyst amount. Reaction conditions: mole ratio of oleic acid/methanol, 1:20; reaction temperature, 60 ^{o}C; reaction time, 10 h.

Effect of reaction time

The effect of reaction time was studied by varying the reaction time in the range 4 to 12 h (Figure 4). The oleic acid conversion was increased with an increase in the reaction time up to 10 h for both the catalysts. The oleic acid conversion was 86% and 82% respectively, for 30% SiW_{12}/Hβ and 30% SiW_{11}/Hβ at 10 h of reaction time. With further increase in the reaction time,

no significant increase in the conversion was observed. As a result 10 h of the reaction time was considered to be optimum for the esterification of oleic acid.

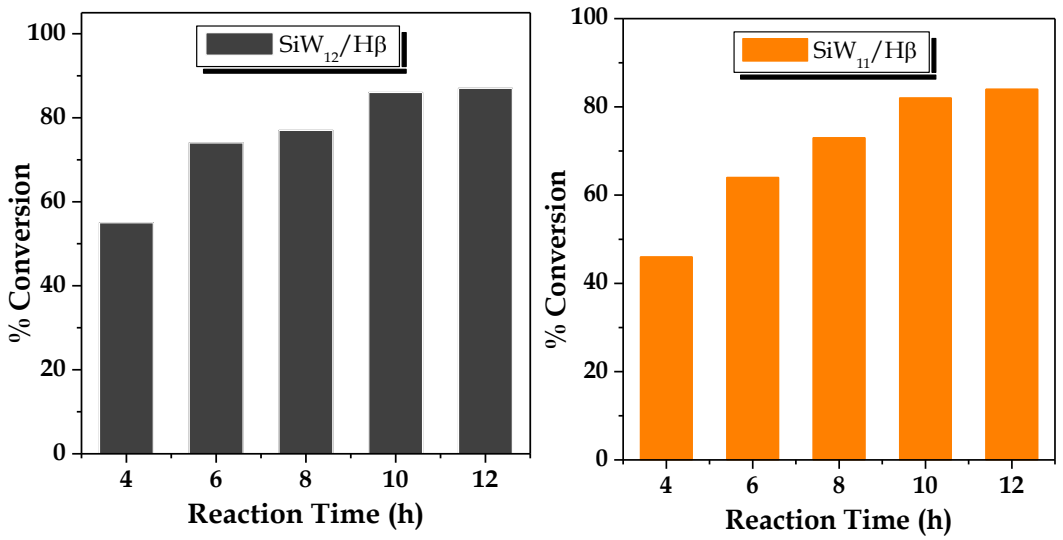


Figure 4. Effect of reaction time. Reaction conditions: mole ratio of oleic acid/methanol, 1:20; amount of catalyst, 100 mg; reaction temperature, 60 °C.

Effect of reaction temperature

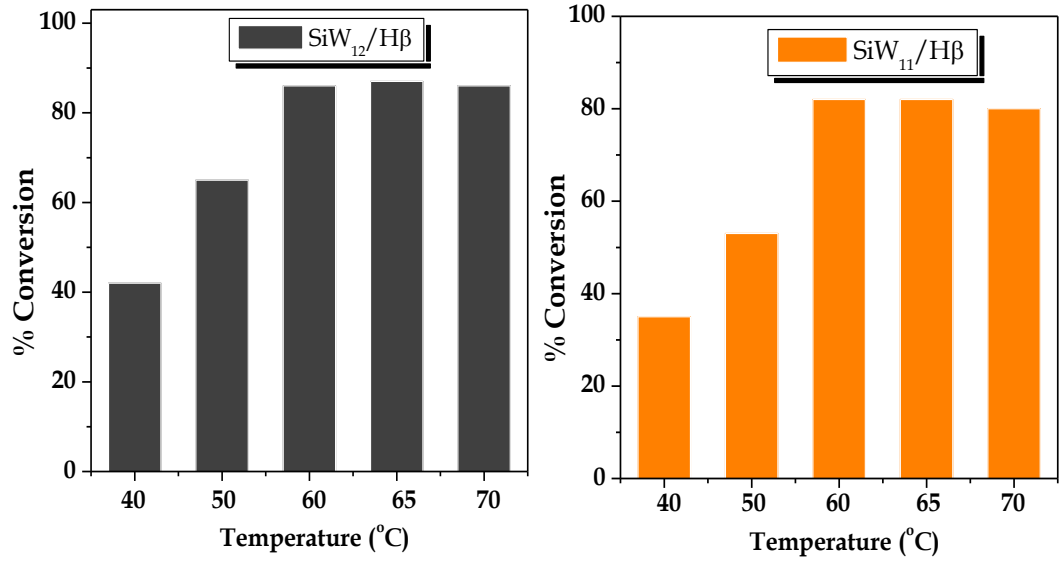


Figure 5. Effect of temperature. Reaction conditions: mole ratio of oleic acid/methanol, 1:20; amount of catalyst, 100 mg; reaction time, 10 h.

The effect of reaction temperature on the oleic acid conversion was investigated in the temperature range of 40 to 70 ^{o}C. As illustrated in Figure 5, the reaction temperature strongly affected the conversion for both the catalysts. There was a gradual increase in the conversion upon increasing reaction temperature from 40 to 60 °C. This might be due to increased reaction rate at high reaction temperature. However, the further increase in the reaction temperature from 60 to 70 °C does not affect the conversion because of attaining the boiling point of methanol. Hence 60 °C was considered to be optimum for the esterification reaction.

The optimized conditions for oleic acid esterification over 30% SiW_{12}/Hβ (maximum conversion 86%) and 30% SiW_{11}/Hβ (maximum conversion 82%) are: mole ratio of acid to alcohol 1:20; concentration of catalyst 100 mg; reaction temperature 60°C, and reaction time 10 h.

The trend in the activity of the catalysts was found to be depending on the acidic strength of the catalysts (657 mV for 30% SiW_{12}/Hβ and 390 mV for 30% SiW_{11}/Hβ). 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 as a result activity of the SiW_{11}. The order of the catalytic activity was 30% SiW_{12}/Hβ > 30% SiW_{11}/Hβ.

Control experiments for esterification of oleic acid

The control experiment using SiW_{12}, SiW_{11} as well as Hβ was carried out under the optimized conditions. It is seen from the Table 1 that Hβ is not much active towards the esterification of oleic acid indicating catalytic activity is truly due to SiW_{12}/SiW_{11} only. The TON values show that catalytic activity of SiW_{12}/SiW_{11} has been retained after introduction in to the framework of Hβ.

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}
Hβ [a]	23	-	
SiW_{12} [b]	90	1126	112.6
30% SiW_{12}/Hβ [a]	86	1075	107.5
SiW_{11} [b]	79	971	97.1
30% SiW_{11}/Hβ [a]	82	1008	100.8

[a]*Amount of catalyst, 100 mg; mole ratio of oleic acid/methanol, 1/20; reaction temperature, 60 °C; reaction time, 10 h.* [b]*catalyst quantity of 23 mg. TON= moles of product/moles of catalyst, 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. A test was performed by filtering the catalysts from the reaction mixture at 60 °C after 6 h, and the filtrate was allowed to react up to10 h. The reaction mixture of 10 h and the filtrate of 6 h were analysed by gas chromatography. There was no change in the percentage conversion. According to Sheldon et al., there are three categories for a catalyst to act as a true heterogeneous 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 show that the present catalytic systems fall into category c [6]. 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 present catalysts are truly heterogeneous in nature.

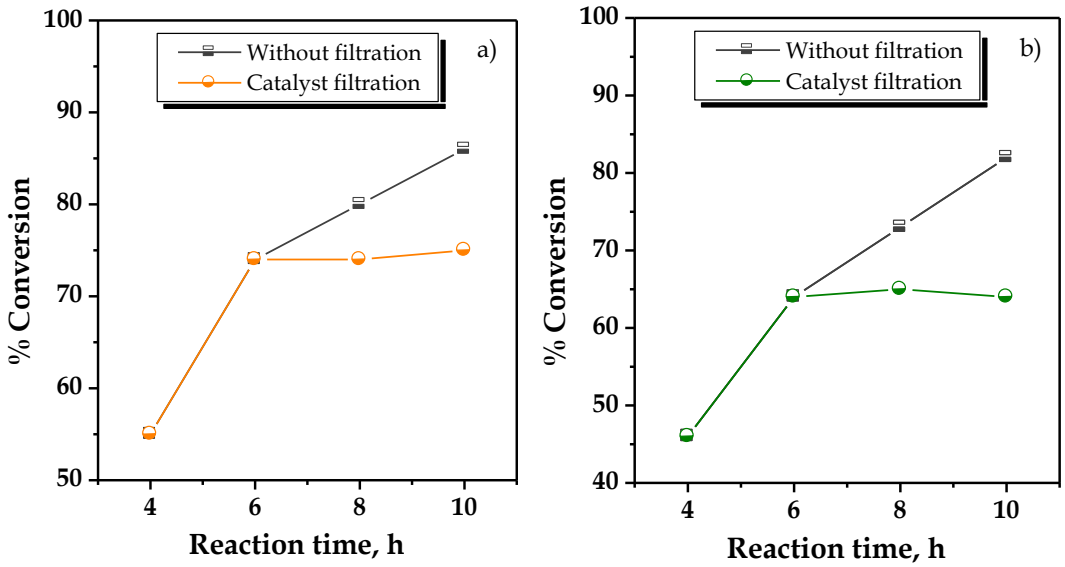


Figure 6. Heterogeneity test for esterification of oleic acid over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$. Reaction conditions: Amount of catalyst, 100 mg; mole ratio of oleic acid/alcohol, 1/20; reaction temperature, 60 °C.

Regeneration and recycling of the catalyst

Catalytic activity of regenerated catalysts

The catalysts were recycled in order to examine 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 catalysts were charged for the further run. No appreciable decrease in the conversion was observed up to four cycles (Figure 7).

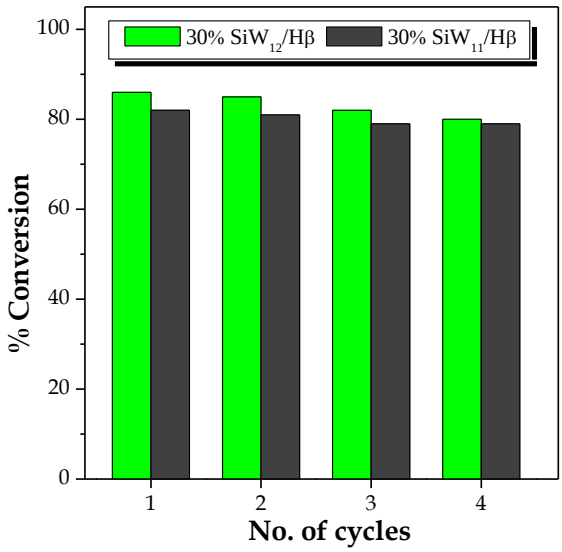


Figure 7. Recycling study of the catalysts for esterification of oleic acid. Reaction conditions: amount of catalyst, 100 mg; oleic acid to methanol mole ratio, 1:20; reaction temperature, 60 °C; reaction time, 10 h.

Characterization of Regenerated catalysts

The regenerated catalyst was further characterized by FT-IR, XRD, acidic strength and surface area measurement in order to see any structural change. The acidic strength of recycled catalysts was comparable to that of the fresh one (for 30% SiW_{12}/Hβ: fresh= 657 mV, recycled 650 mV; for 30% SiW_{11}/Hβ: fresh= 390 mV, recycled 386 mV). Further in order to confirm the retention of the SiW_{12}/SiW_{11} species on to the support, FT-IR analysis was carried out for the reused catalysts. The FT-IR spectrum of recycled 30% SiW_{12}/Hβ (Figure 8a) showed the retention of typical bands for SiW_{12}, at 920 cm^{-1} corresponding to symmetric Si-O_a stretching. The FT-IR spectrum of the used catalyst 30% SiW_{11}/Hβ (Figure 8b) shows retention of bands at 942 cm^{-1} (Si-O_a), 860 cm^{-1} (W-O_b-W) and 715 cm^{-1} (W-O_c-W) suggesting that the structure of SiW_{11} is intact in the regenerated catalyst.

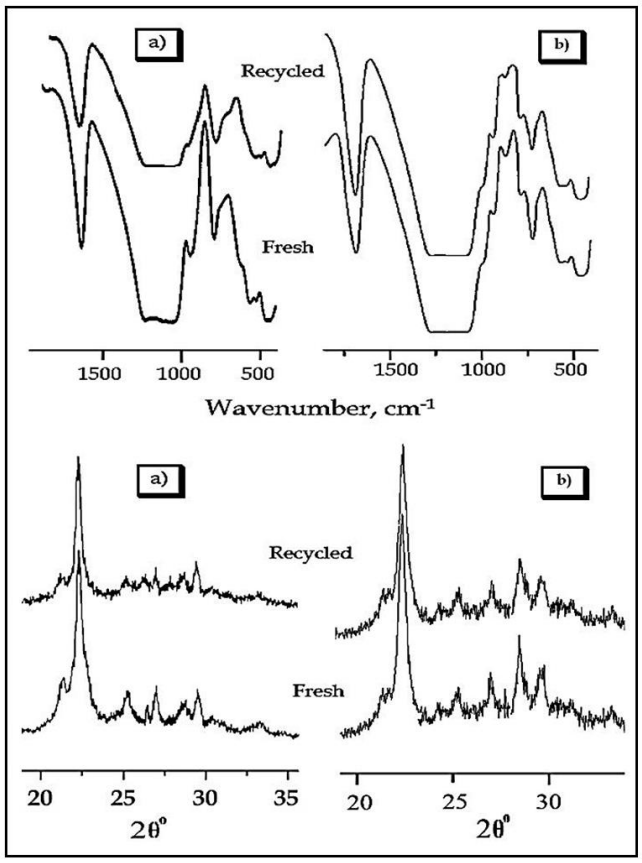


Figure 8. FT-IR and XRD of fresh and recycled catalysts, a) 30% SiW_{12}/Hβ and b) 30% SiW_{11}/Hβ.

The XRD patterns (Figure 8) of the recycled catalysts were identical with the fresh one suggesting the retention of both zeolite framework as well as Keggin unit in the recycled catalysts. The BET surface area values of the recycled catalysts (412 m^2/g for 30% SiW_{12}/Hβ, 424 m^2/g for 30% SiW_{11}/Hβ) are comparable with the fresh ones (419.2 m^2/g for 30% SiW_{12}/Hβ, 439.8 m^2/g for 30% SiW_{11}/Hβ).

Kinetic study

A detailed study on the kinetic behaviour was tested for esterification of oleic acid over 30% $SiW_{12}/H\beta$ as well as 30% $SiW_{11}/H\beta$. In all the experiments, reaction mixtures were analysed at a fixed interval of time. Esterification of oleic acid with methanol was carried with a 1:20 molar ratio; since methanol was taken in large excess, the rate law is expected to follow first-order dependence.

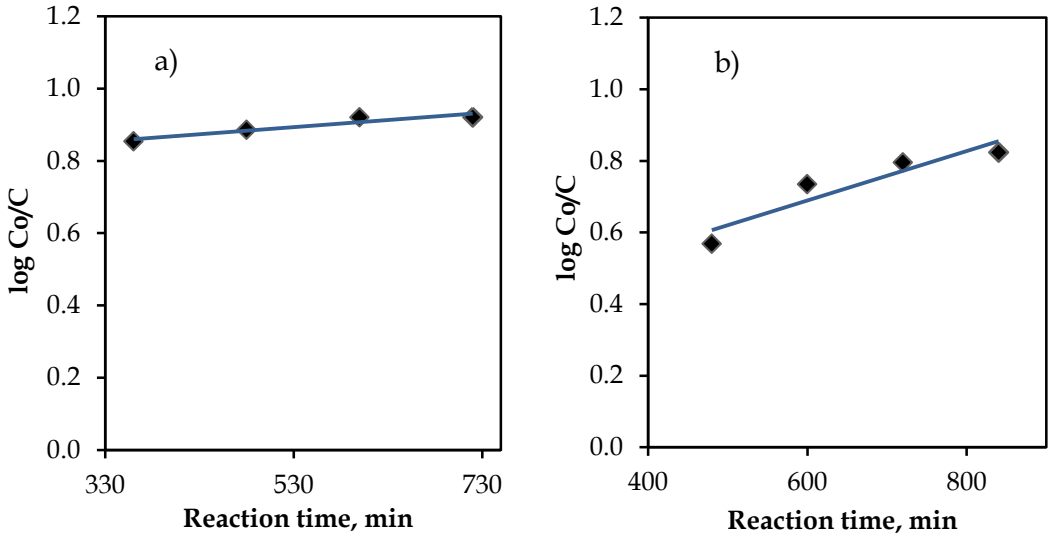


Figure 9. First-order plot for esterification of oleic acid with methanol over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$.

The plot of ln (Co/C) versus time (Figure 9) shows a linear association of oleic acid consumption with respect to time for both the catalysts. This observation indicates that esterification of oleic acid follows first-order dependence with respect to time.

The first order dependence was further confirmed by the study of the effect of amounts of 30% $SiW_{12}/H\beta$ and 30% $SiW_{11}/H\beta$ on the rate of esterification of oleic acid with methanol. The catalyst amount was varied in different time interval at a fixed substrate concentration of 10 mmol and at a temperature of 60 °C. It can be observed from Figure 10 that the rate of reaction increases

linearly with an increase in the catalyst amount for both the catalysts confirming that the present catalytic reaction follows first order kinetics which was as expected.

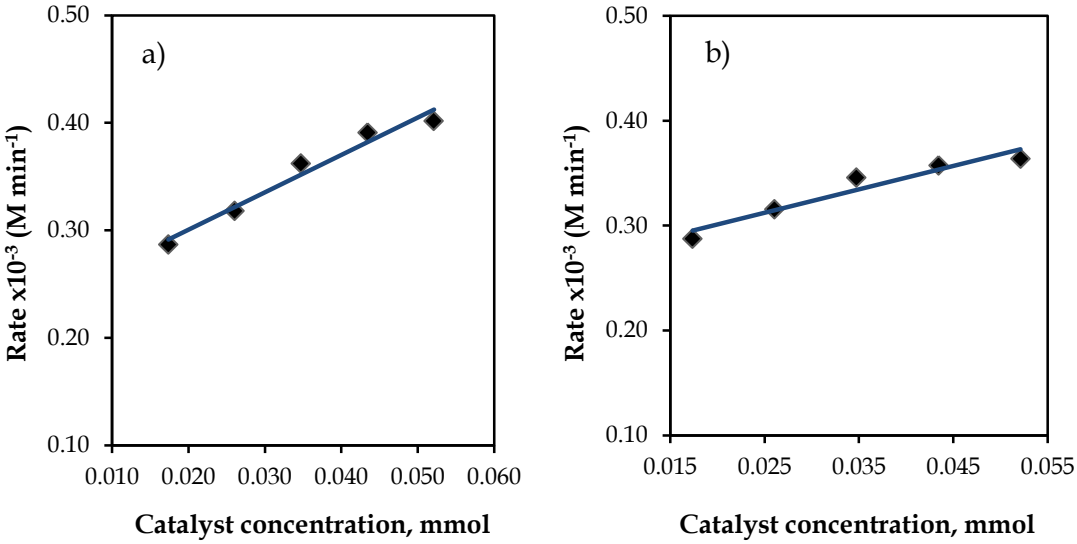


Figure 10. Plot of reaction rate vs. catalyst concentrations for esterification of oleic acid over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$.

Estimation of activation energy (Ea)

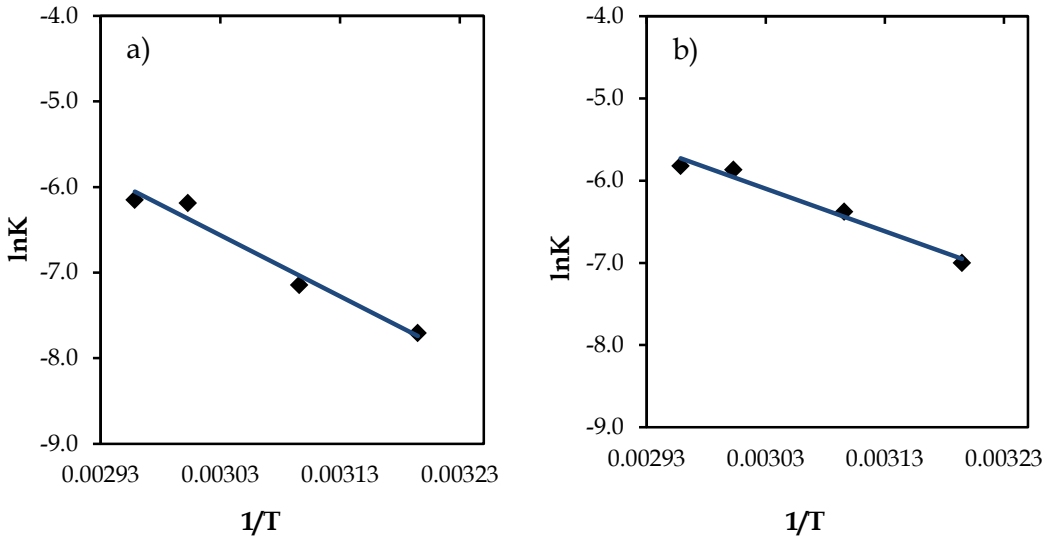


Figure 11. Arrhenius plots for determination of activation energy for esterification of oleic acid over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$.

The graph of lnk 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), pre-exponential factor (A) and activation energy (Ea) for the esterification of oleic acid with methanol over both the catalysts are presented in Table 2.

Table 2. Kinetic parameters for esterification of oleic acid with methanol.

Catalyst	Kinetic parameters		
	Rate constant at 60 ^{o}C (k), min^{-1}	Arrhenius constant (A), min^{-1}	Activation energy, $kJmol^{-1}$
30% $SiW_{12}/H\beta$	2.9×10^{-3}	2.3×10^{4}	49.8
30% $SiW_{11}/H\beta$	2.6×10^{-3}	1.5×10^{4}	43

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} [7]. In the present catalytic systems, the activation energies are >25 kJ mol^{-1}, and therefore, it can be concluded that the reaction rate is truly governed by the chemical step and the reaction is not surface type diffusion limited catalysis.

II) Transesterification of triglycerides (Soybean oil)

The effect of reaction parameters such as SiW_{12}/SiW_{11} content, oil/alcohol weight 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}

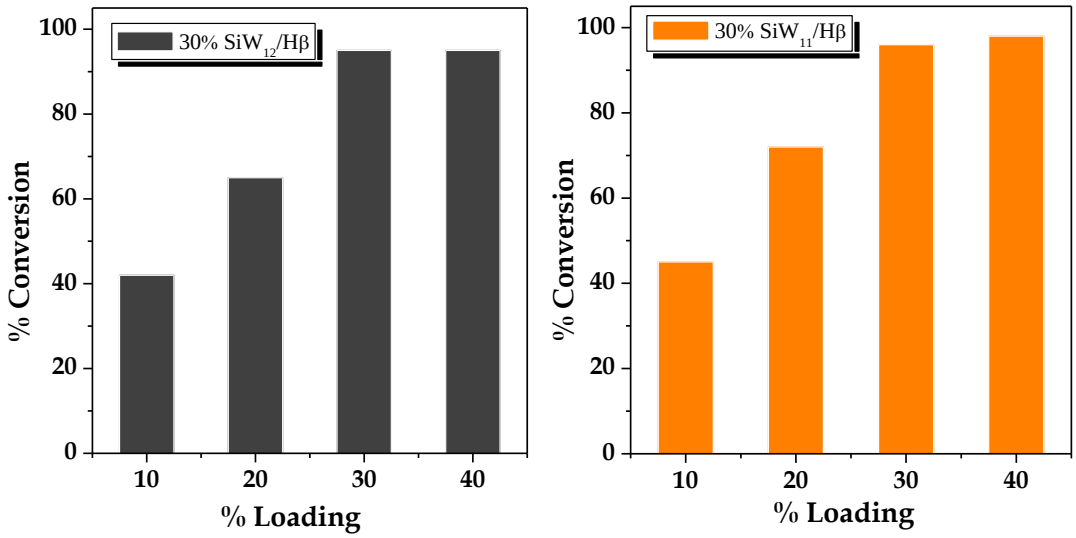


Figure 12. Effect of % loading of SiW_{12}/SiW_{11}; Reaction conditions: weight ratio of oil to methanol, 1:4; amount of catalyst, 200 mg; reaction temperature, 65 °C and reaction time, 8 h.

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% $SiW_{12}/H\beta$ and 30% $SiW_{11}/H\beta$ were selected for carrying out detailed study.

Effect of wt. ratio of oil to alcohol

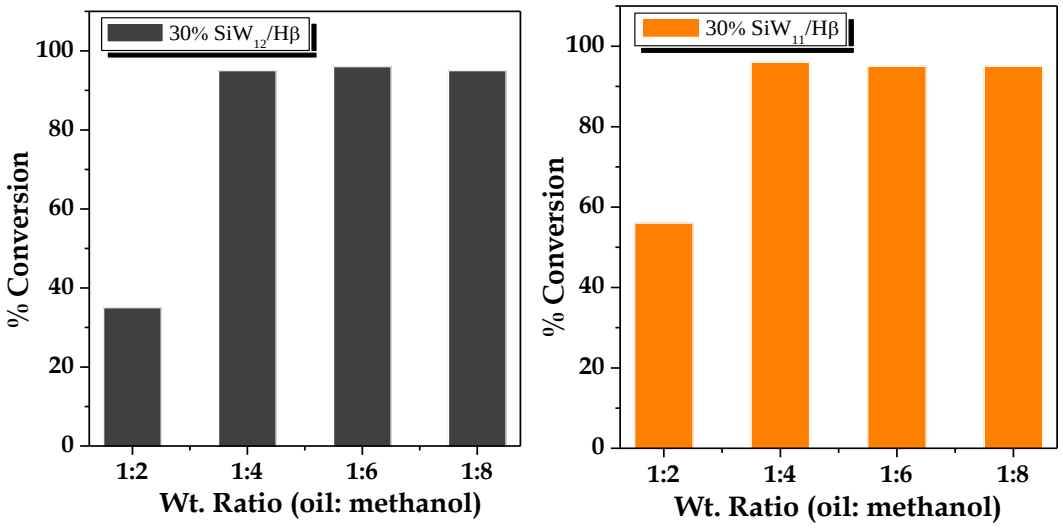


Figure 13. Effect of weight ratio of oil/alcohol; Reaction conditions: amount of catalyst, 200 mg; reaction temperature, 65 °C and reaction time, 8 h.

To see the effect of the oil/alcohol ratio, the transesterification reaction was performed by varying the weight ratio of soybean oil to methanol from 1:2 to 1:8 using 200 mg of the catalysts for 8 h at 65 °C. It was observed from Figure 13 that the soybean oil conversion increases with an increase in the oil/methanol ratio and reaches to ~96% at the oil/methanol ratio of 1:4. However, the further increase in ratio beyond 1:4 results no increase in the conversion of soybean oil. When too much excess methanol is used for the transesterification reaction, the alcohol will tend to increase the solubility of glycerol. This can lead to unfavorable glycerolysis reaction of biodiesel to occur and thereby decreases the conversion. Hence, the ratio of 1:4 is optimum for obtaining high conversion.

Effect of amount of catalyst

The effect of the catalyst amount on the soybean oil conversion is shown in Figure 14. Experiments were carried out by varying the amount of the catalyst

between 50-300 mg keeping the soybean oil to methanol ratio of 1:4 at 65 °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 could 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.

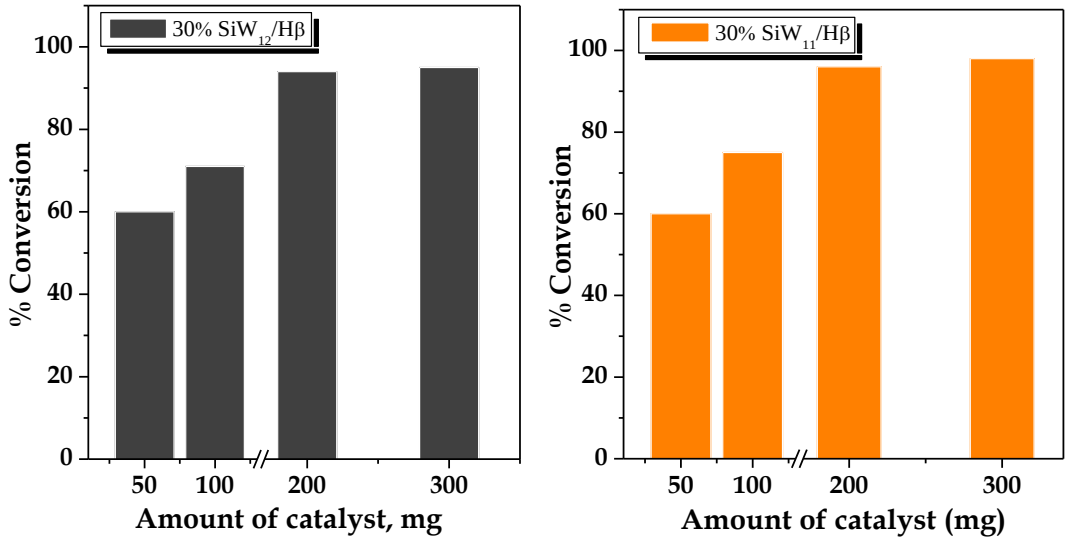


Figure 14. Effect of amount of catalyst; Reaction conditions: w/w ratio of oil to alcohol, 1:4; reaction temperature, 65 °C and reaction time, 8 h.

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 increases with increase in the reaction time from 2 h up to 8 h (Figure 15) for both the catalysts. 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 maximum conversion.

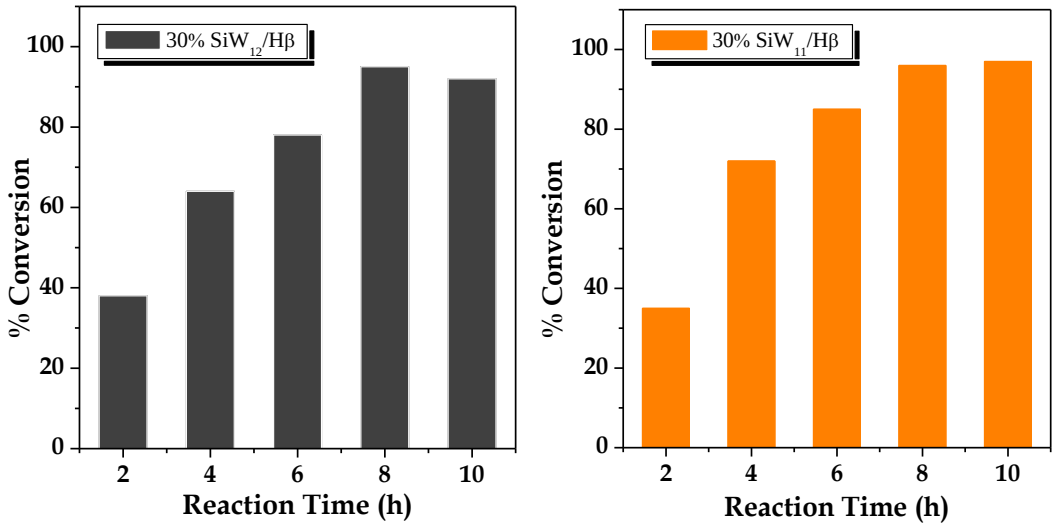


Figure 15. Effect of reaction time; Reaction conditions: w/w ratio of oil to alcohol, 1:4; amount of catalyst, 200 mg; reaction temperature, 65 °C.

Effect of reaction temperature

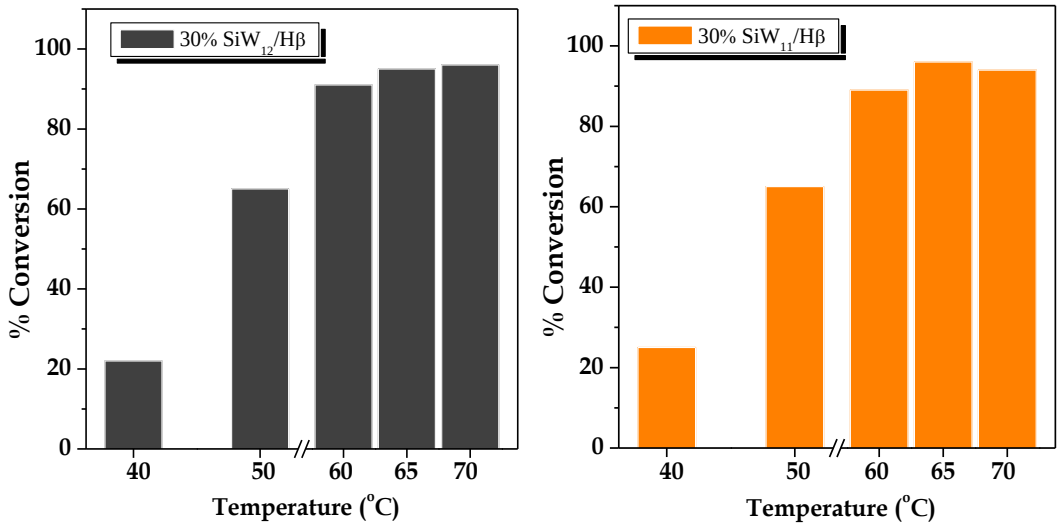


Figure 16. Effect of reaction temperature; Reaction conditions: w/w ratio of oil to alcohol, 1:4; amount of catalyst, 200 mg and reaction time, 8 h.

The effect of temperature on the soybean oil 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.

The optimized conditions for 30% SiW_{12}/Hβ (maximum conversion 95%) as well as 30% SiW_{11}/Hβ (maximum conversion 96%) are as follows: w/w ratio of oil to alcohol, 1:4; amount of catalyst, 200 mg; and reaction temperature, 65 °C; reaction time, 8 h.

The activities of both the catalysts were almost similar under the similar reaction condition for transesterification of soybean oil. This may be due to the strong acidic character of the support which enhances the overall activity of the catalyst.

Control experiments

Table 3. Control experiments for transesterification of soybean oil.

Catalyst	% Conversion	TON	TOF, h^{-1}
Hβ [a]	31	-	
SiW_{12} [b]	97	322	40.2
SiW_{11} [b]	93	307	38.4
30% SiW_{12}/Hβ [a]	95	315	39.4
30% SiW_{11}/Hβ [a]	96	317	39.6

Reaction condition: Catalyst amount [a] 200 mg and [b] 46 mg; mole ratio soybean oil to methanol, 1:4; reaction temperature, 65 ^{o}C; reaction time, 8 h. TON= moles of product/moles of catalyst, TOF= TON/reaction time.

The control experiments with Hβ and SiW_{12}/SiW_{11} were carried out under optimized conditions. It can be seen from Table 3 that support 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) and it was observed that catalytic activities of SiW_{12}/SiW_{11} have been retained in the respective catalysts indicating that SiW_{12}/SiW_{11} behaves as real active species. Thus, we were successful in anchoring silicotungstates to Hβ without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Heterogeneity test

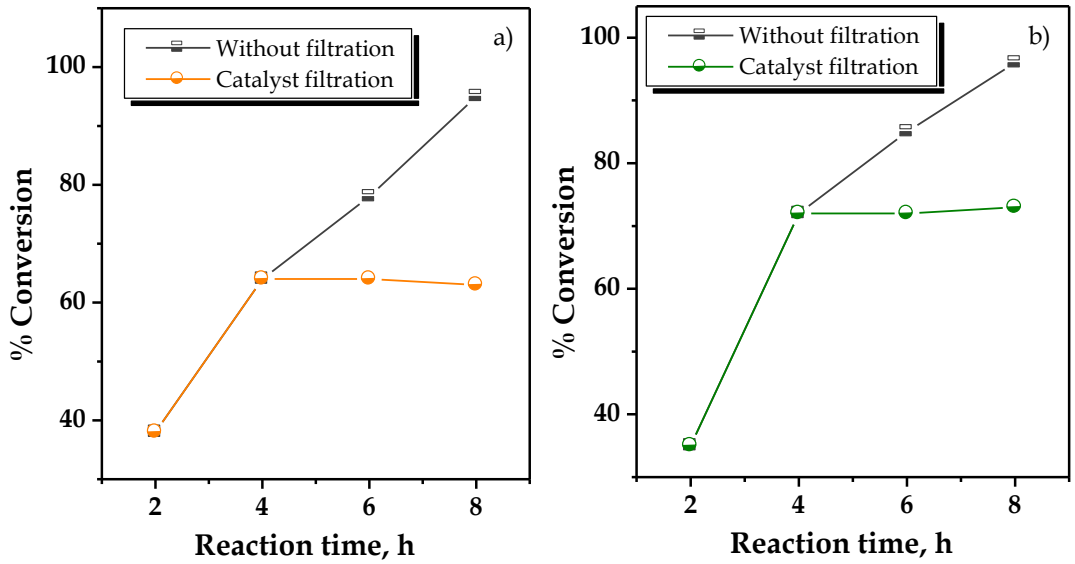


Figure 17. Heterogeneity test for transesterification of soybean oil over a) 30% SiW_{12}/Hβ and b) 30% SiW_{11}/Hβ. Reaction conditions: w/w ratio of oil to alcohol, 1:4; amount of catalyst, 200 mg; reaction temperature, 65 °C.

A heterogeneity test was performed by filtering both the catalysts from the reaction mixture at 65 °C after 4 h and the filtrate was allowed to react up to 8 h. The final reaction mixture of 8 h shows the conversion similar to the 4 h sample. 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 catalysts are truly heterogeneous in nature.

Recycling and characterization of the regenerated catalyst

Catalytic activity of regenerated catalysts

Transesterification of soybean oil was carried out with the recycled 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 catalysts were charged for the further run. No appreciable decrease in the conversion was observed after three cycles (Table 4).

Table 4. Recycling studies under the optimised conditions.

Catalyst	Number of cycles (Conv. %)			
	Fresh	1st	2nd	3rd
30% $SiW_{12}/H\beta$	95	95	94	93
30% $SiW_{11}/H\beta$	96	95	94	92

Reaction condition: Catalyst amount 200 mg; mole ratio oil to alcohol 1:4; reaction temperature 65 ^{o}C; reaction time 8 h.

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

Possible industrial scheme for biodiesel production

The transesterification of soybean oil was successfully scaled up for biodiesel synthesis using up to 300 g feedstock over 30% $SiW_{12}/H\beta$ with 92% conversion under optimized conditions as compared to batch scale. Depending on the requirements, the size of the unit can be scaled up to get higher production capacity. A possible scheme of this integrated process using heterogeneous acid catalysts is shown in Figure 18. After completion of transesterification reaction settling can be used to separate the two products, i.e. crude glycerol and biodiesel. After settling, crude glycerol is washed with water to remove impurities and the traces of the catalyst. In heterogeneous catalysis, the reaction mainly takes place on the surface of active sites. Hence, after the completion of the reaction, the unreacted as well as the by-product molecules must be removed from the surface in order to activate the catalyst for the next run.

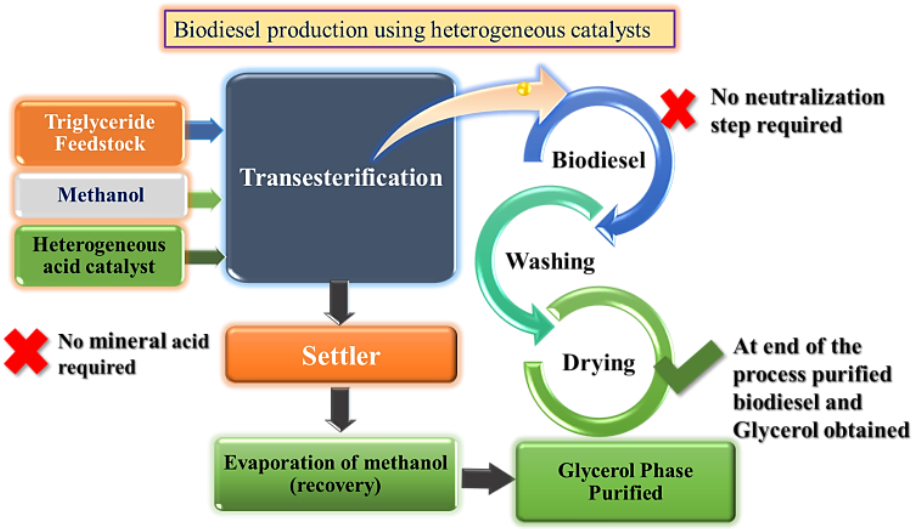


Figure 18. Process for biodiesel production over heterogeneous acid catalysts.

Conclusions

- The present catalysts showed *excellent activities* for biodiesel synthesis via *esterification of FFA, oleic acid*.
- *Kinetic studies* showed that esterification of oleic acid follows *first order* rate law without any diffusion or mass transfer limitation.
- *30% $SiW_{12}/H\beta$* showed *86%* conversion of oleic acid whereas *30% $SiW_{11}/H\beta$* gives *82%* conversion of oleic acid.
- The present catalysts also exhibits *outstanding activities* for the *transesterification* of triglyceride feedstock, *soybean oil* with methanol under mild conditions.
- *30% $SiW_{12}/H\beta$* showed *95%* conversion of soybean oil whereas *30% $SiW_{11}/H\beta$* showed *96%* conversion of soybean oil.
- The EDS, BET as well as FT-IR of *reused catalysts* showed *no structural changes* indicating catalytic systems are stable.
- The catalysts *recycling studies* showed thaat both the catalysts can be reused several times without significant loss in the activity.
- The 30% $SiW_{12}/H\beta$ showed *superior catalytic activity* as compared to 30% $SiW_{11}/H\beta$.
- The higher activities for both esterification as well as transesterification reactions enables the catalysts to be used for *feedstocks that are rich in FFAs*.
- We have also demonstrated *the industrial process* for biodiesel production.

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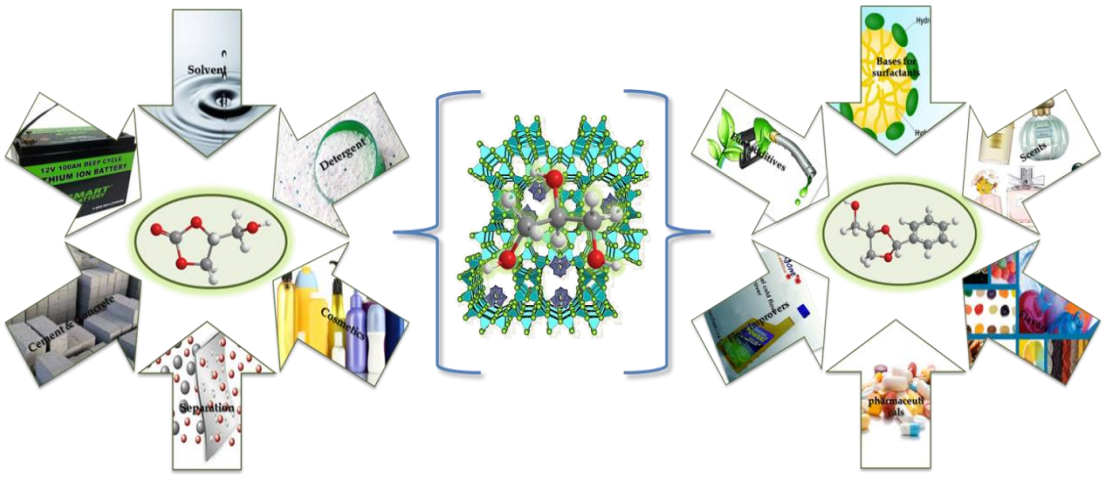
CHAPTER 4B

VALORISATION OF GLYCEROL VIA ACETALIZATION WITH BENZALDEHYDE AND CARBOXYLATION WITH UREA



In the present work, synthesized catalysts, SiW_{12}/SiW_{11} anchored to zeolite Hβ were evaluated for the acetalization of glycerol with benzaldehyde as well as carboxylation of glycerol with urea. The effects of different reaction variables such as catalyst concentration, mole ratio, temperature and reaction time were studied to optimize the conditions for maximum conversion. Also, the catalysts were regenerated after simple workup procedure and successfully reused up to four cycles.

EXPERIMENTAL

Materials

All used chemicals were of A.R. grade. 12-Tungstosilicic 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 (10 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 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.

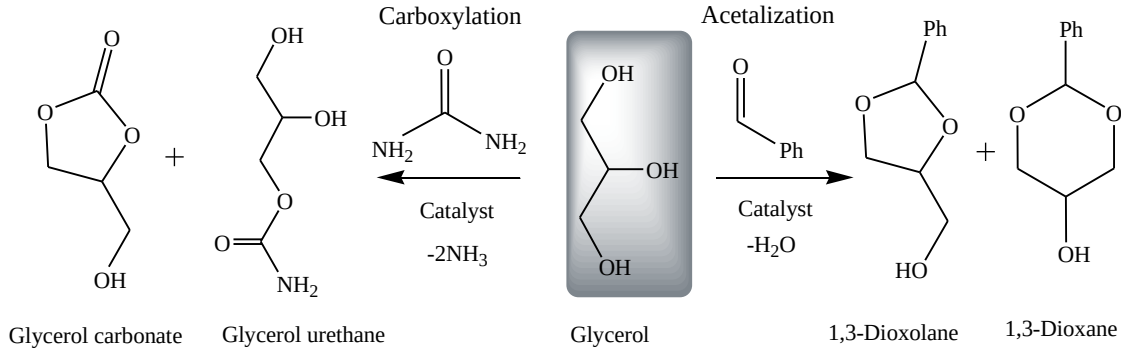
Carboxylation reaction

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 Gas Chromatography.

RESULTS AND DISCUSSION

This study is focused on a) solvent free room temperature acetalization of glycerol with benzaldehyde and b) carboxylation of glycerol with urea (Scheme 1).



Scheme 1. Glycerol valorisation via acetalization as well as carboxylation.

a) Acetalization of glycerol with benzaldehyde

Acetalization of glycerol with benzaldehyde 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 1).

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}.

With increase in the loading, % conversion was increased however selectivity of the dioxolane was decreased. The reason being increased catalytically active sites which favour the acid catalysed transformation of dioxolane to dioxane. This is in good agreement with the literature result [1]. For $SiW_{11}/H\beta$ optimum of 95% conversion of glycerol with 78% selectivity of 1,3-dioxolane was obtained. Further increase in the loading beyond 30% produces no significant change in the conversion. As a result, 30% loading was considered as optimum for both the systems and used for the further studies.

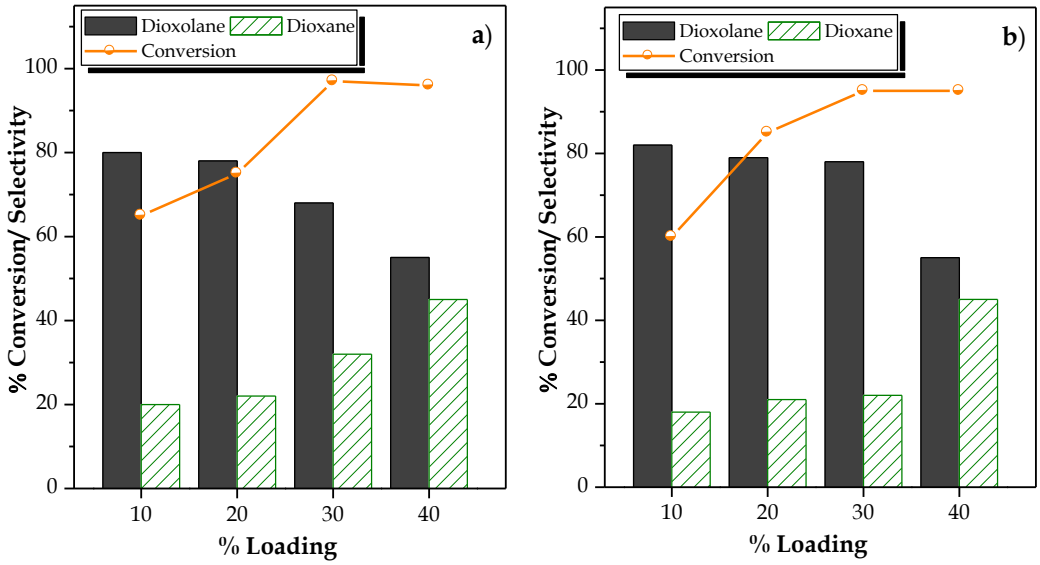


Figure 1. Effect of loading on acetalization of glycerol over a) $SiW_{12}/H\beta$ and b) $SiW_{11}/H\beta$. Reaction conditions: mole ratio of glycerol/benzaldehyde, 1/1; time, 60 min; temperature, 30 ^{o}C; catalyst amount, 50 mg, N_2 atmosphere.

Effect of mole ratio of glycerol to benzaldehyde

The effect of glycerol to benzaldehyde mole ratio was studied by varying ratio from 1:1 to 1:1.4 over both the catalysts (Figure 2). Surprisingly, the conversion of glycerol was not affected on variation of the mole ratio rather the selectivity of dioxolane was decreased slightly due to the formation of six membered dioxane derivatives. Hence, the mole ratio of 1:1 was considered as optimum.

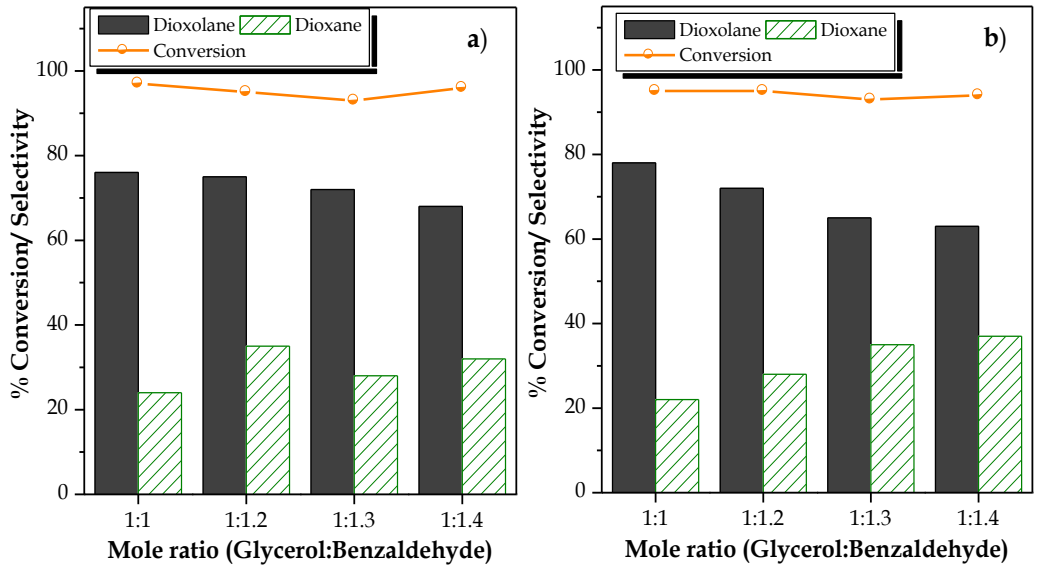


Figure 2. Effect of glycerol to benzaldehyde mole ratio on acetalization of glycerol over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$. Reaction conditions: time, 60 min; temperature, 30 °C; catalyst amount, 50 mg, N_2 atmosphere.

Effect of amount of catalyst

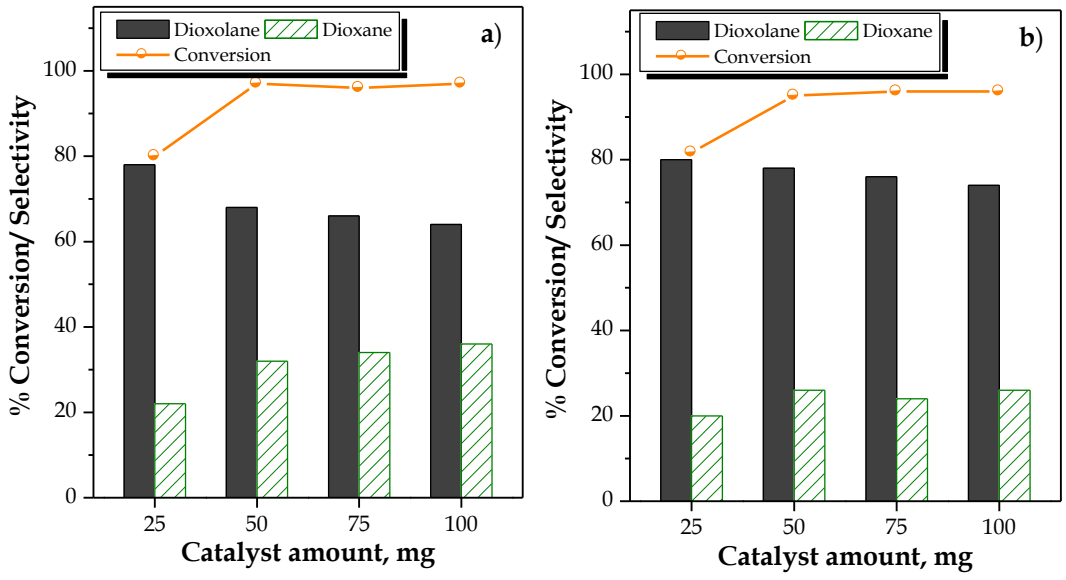


Figure 3. Effect of catalyst amount on acetalization of glycerol over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$. Reaction conditions: mole ratio of glycerol/benzaldehyde, 1/1; time, 60 min; temperature, 30 °C, N_2 atmosphere.

The effect of the amount of catalysts on glycerol conversion was studied by varying catalyst amount in the range 25-100 mg. As shown in Figure 3, initial increase in the catalyst concentration increases the conversion of glycerol and reaches saturation conversion at 50 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. Further increase in the catalyst amount from 50-100 mg shows saturation in the conversion however selectivity decreases. The excess strong acidic sites of the catalyst are responsible for ring transformation from five membered dioxolane to the six membered dioxane. As a result, 50 mg of the catalyst was considered to be optimum for the maximum glycerol conversion.

Effect of reaction time

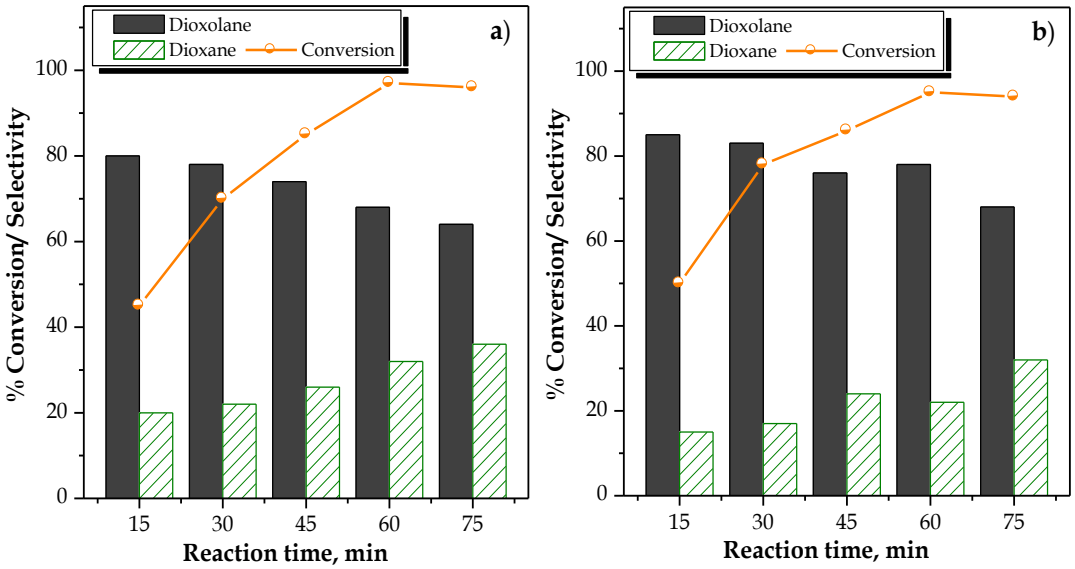


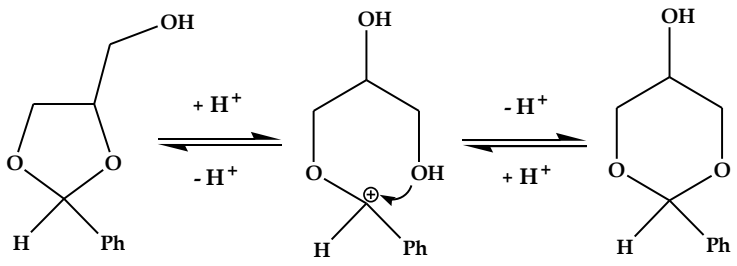
Figure 4. Effect of reaction time on acetalization of glycerol over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$. Reaction conditions: mole ratio of glycerol/benzaldehyde, 1/1; temperature, 30 ^{o}C; catalyst amount, 50 mg, N_2 atmosphere.

In order to examine the variation of glycerol conversion and products selectivity with time, we have studied acetalization of glycerol by varying

reaction time 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. The evolution of dioxolane to dioxane at longer reaction times was also reported by Gonzalez-Arellano et al [2]. At 60 minutes of the time optimum conversion as well as selectivity was observed over both the catalysts.

The optimized conditions for both the catalysts are as follows, for 30% $SiW_{11}/H\beta$ maximum conversion 95% and selectivity of 78% of dioxolane and for 30% $SiW_{12}/H\beta$ maximum conversion of 97% and selectivity of 68% was achieved under the optimized conditions: mole ratio of glycerol/ benzaldehyde, 1/1; temperature, 30 ^oC; catalyst amount, 50 mg; time, 60 min.

Among both the catalysts, 30% $SiW_{11}/H\beta$ showed better selectivity of dioxolane than 30% $SiW_{12}/H\beta$ with almost similar conversion. There exists equilibrium between dioxolane and dioxane in the presence of strong acid sites via key intermediate benzyl cation (Scheme 2). The catalyst 30% $SiW_{12}/H\beta$ (657 mV) possesses very strong acid sites than 30% $SiW_{11}/H\beta$ (390 mV). The strength of the acid sites leads to the ring transformation in the case of 30% $SiW_{12}/H\beta$. Hence, relatively low selectivity was observed for 30% $SiW_{12}/H\beta$.



Scheme 2. Acid catalyzed transformation between dioxolane and dioxane obtained in glycerol acetalization with benzaldehyde.

Control experiments

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

Catalyst	% Conversion	% Selectivity[c]	TON	TOF, h^{-1}
No catalyst	17	60	-	
Hβ	28	85	-	
SiW_{12}[a]	93	65	1164	1164
30% SiW_{12}/Hβ[b]	97	68	1214	1214
SiW_{11}[a]	90	70	1048	1048
30% SiW_{11}/Hβ [b]	95	78	1106	1106

Reaction conditions: mole ratio glycerol/benzaldehyde: 1/1; time: 60 min; temperature: 30 °C; catalyst amount: [a]12 mg/[b]50 mg, N_2 atmosphere. [c]Dioxolane selectivity. TON= moles of product / moles of catalyst, TOF= TON/reaction time.

The acetalization of glycerol was carried out without catalyst as well as using Hβ, and active species (SiW_{12}/SiW_{11}). It is clear from the Table 1 that the support Hβ is not much active towards the acetalization and the activity of the species SiW_{12}/SiW_{11} has been retained in the catalysts.

Regeneration and recycling of the catalyst

Catalytic activity of regenerated catalysts

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 °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 (Figure 5).

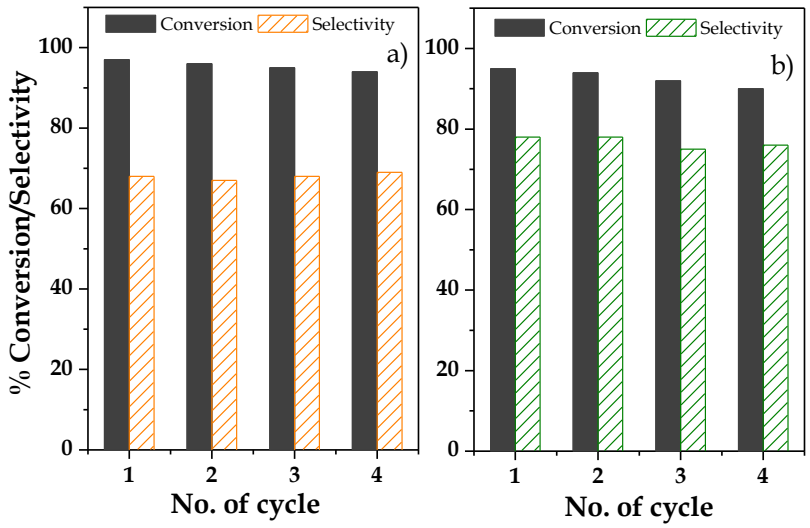


Figure 5. Recycling test for acetalization of glycerol over a) 30% SiW_{12}/Hβ and b) 30% SiW_{11}/Hβ. Reaction conditions: mole ratio of glycerol/benzaldehyde, 1/1; temperature, 30 ^{o}C; catalyst amount, 50 mg; time, 60 min.

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 4a* hence are not included.

b) Carboxylation of glycerol

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

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

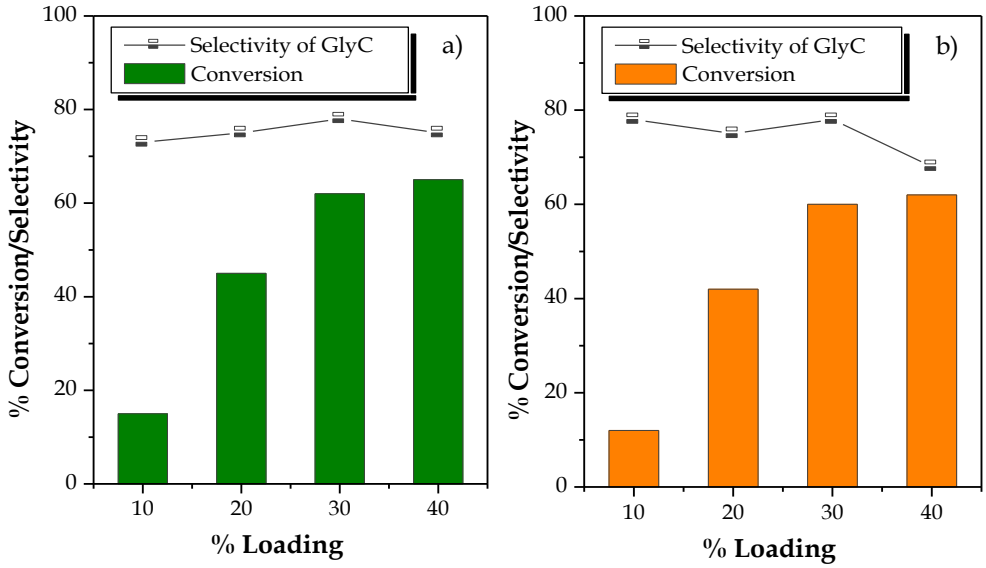


Figure 6. Effect of % loading on carboxylation of glycerol over a) 30% SiW_{12}/Hβ and b) 30% SiW_{11}/Hβ. Reaction conditions: mole ratio G/U: 1/1; time: 8 h; temperature: 140 ^{o}C; catalyst amount: 100 mg; N_2 purging.

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 6). It is clear that the increase in the % loading of SiW_{12}/SiW_{11} linearly increases the conversion of glycerol. This can be associated with the increased catalytically active acidic sites. The optimum conversion was achieved with 30% loading over both the catalysts. The higher loadings of SiW_{12}/SiW_{11} up to 40% did not result in the increase in the activity and the conversions are practically unchanged. It is well known that increasing % loading via impregnation technique leads to poorer

dispersion, which results in the development of larger aggregates of the active species at the expense of more active smaller clusters [3]. As a result, 30% loaded catalysts were selected for the further studies.

Effect of mole ratio of glycerol to urea

Figure 7 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, maximum selectivity towards glycerol carbonate was observed for both the catalysts. 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 formation of (2-oxo-1,3-dioxolan-4-yl) methyl carbamate via reaction of free hydroxyl group present in the GlyC with excess urea. This is in good agreement with the previous reports [4-5]. As a result 1:1 ratio was considered to be optimum for maximum conversion and selectivity of GlyC.

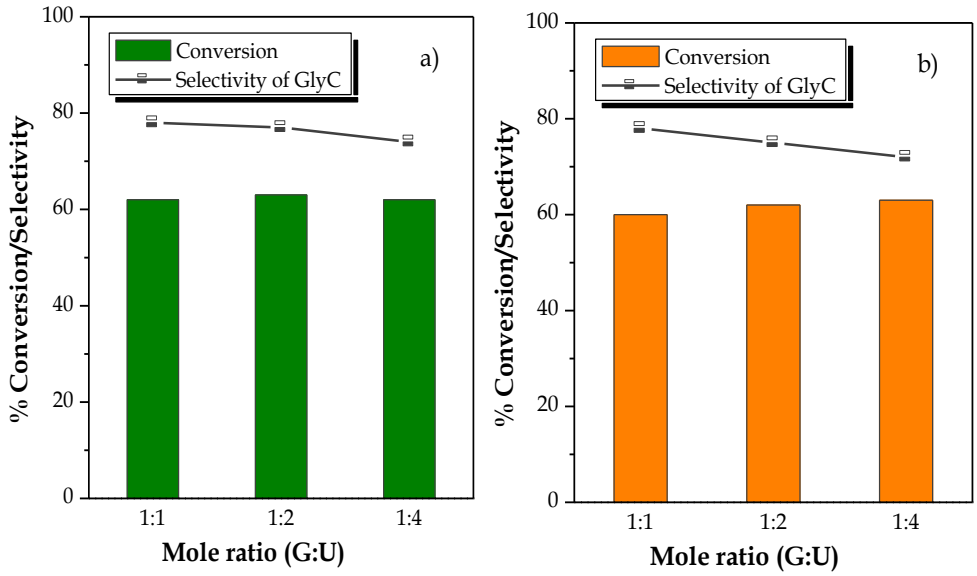


Figure 7. Effect of G:U mole ratio on carboxylation of glycerol over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$. Reaction conditions: time: 8 h; temperature: 140 ^{o}C; catalyst amount: 100 mg; N_2 purging.

Effect of amount of the catalyst

The effect of catalyst amount on the conversion and selectivity was studied by varying the amount of catalyst in the range of 50-150 mg (Figure 8). It was observed that with increase in the catalyst amount, the conversion of glycerol also increases linearly. At low catalyst amount the selectivity of by-product, glycerol urethane was high and with increase in the amount, there is drastic increase in the selectivity of GlyC. On increasing the catalyst amount, the catalytically active acidic site also increases and hence the intermediate product, glycerol urethane further loses NH_3 to give desired product, GlyC. Hence, 100 mg of catalyst amount was considered to be optimum for carboxylation of glycerol over both the catalysts.

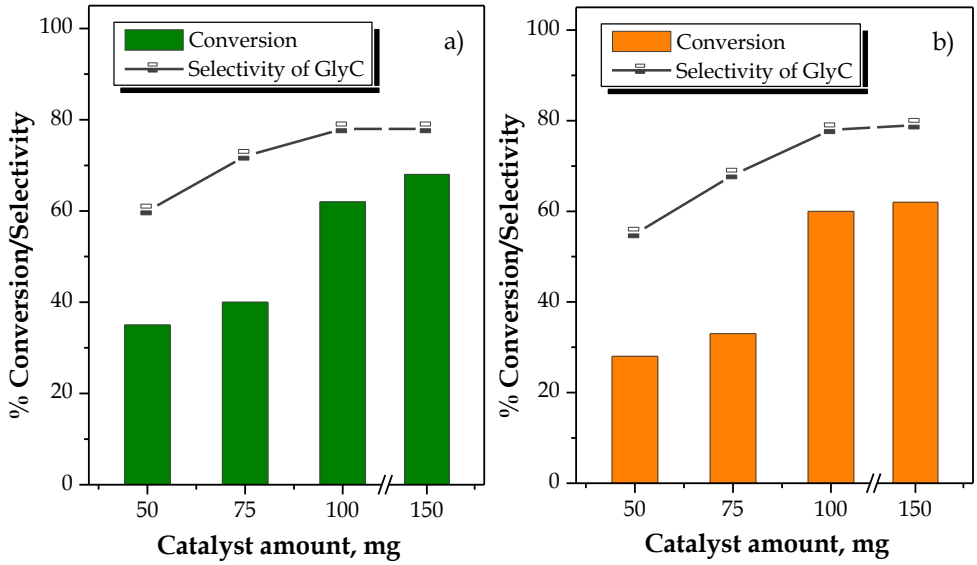


Figure 8. Effect of catalyst amount on carboxylation of glycerol over a) 30% SiW_{12}/Hβ and b) 30% SiW_{11}/Hβ. Reaction conditions: mole ratio G/U: 1/1; time: 8 h; temperature: 140 ^oC; N_2 purging.

Effect of reaction time

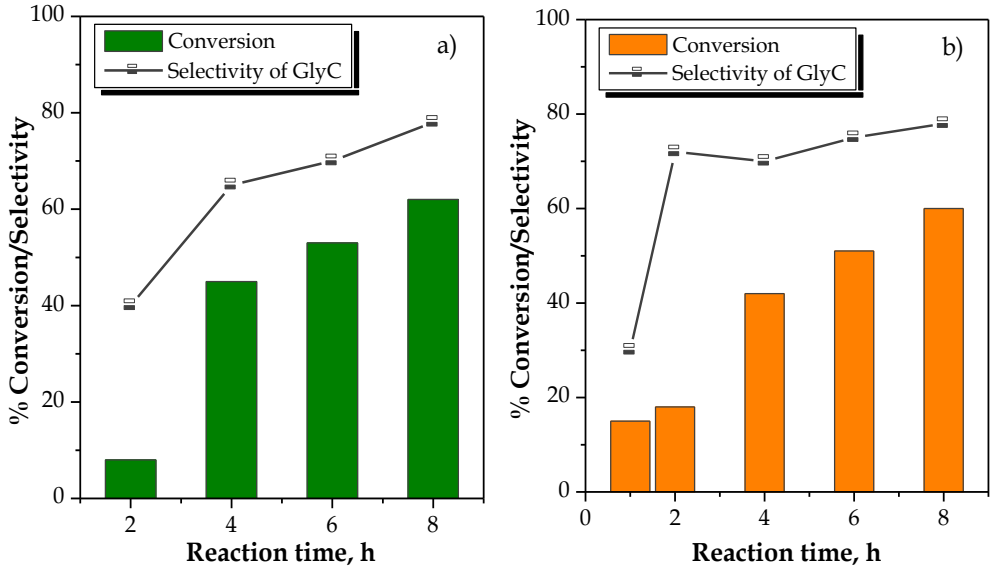


Figure 9. Effect of reaction time on carboxylation of glycerol over a) 30% SiW_{12}/Hβ and b) 30% SiW_{11}/Hβ. Reaction conditions: mole ratio G/U: 1/1; temperature: 140 ^{o}C; catalyst amount: 100 mg; N_2 purging.

Reaction time is an important parameter and long reaction times were adopted usually for the carbonylation of glycerol to obtain reasonable conversion [6]. The effect of reaction time was studied from 2 h to 8 h over both the catalysts and the results are shown in Figure 9. It was interesting to note down that initially the selectivity towards glycerol urethane was high and with increase in the reaction hours, the selectivity towards GlyC was increased. This indicates that glycerol urethane is quickly formed intermediate which is then slowly converted in to the GlyC, which is further confirmed by FT-IR of the reaction mixture at different reaction hours (Figure 10). After 8 h of the reaction time coke formation of the reaction mixture starts.

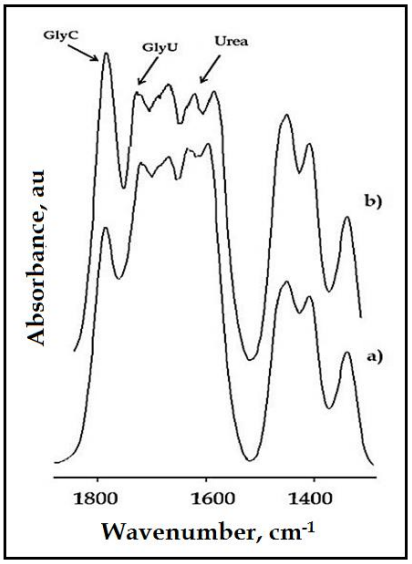


Figure 10. FT-IR spectra of the reaction solution after a) 2h and b) 8 h. (~1785 cm^{-1}: carbonyl stretching of glycerol carbonate (GlyC); ~1720 cm^{-1}: carbonyl stretching of glycerol urethane (GlyU)).

Effect of reaction temperature

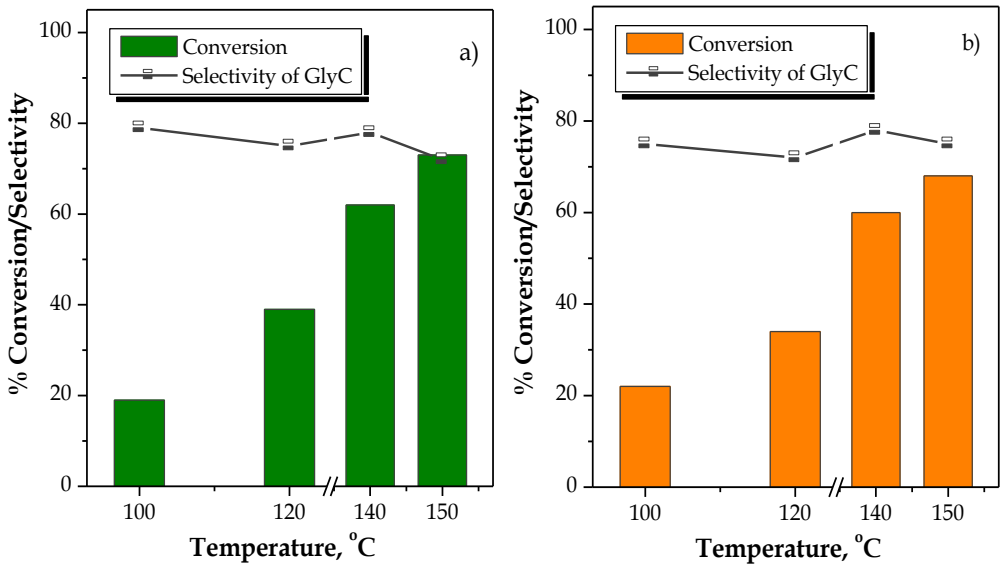


Figure 11. Effect of temperature on carboxylation of glycerol over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$. Reaction conditions: mole ratio G/U: 1/1; time: 8 h; catalyst amount: 100 mg; N_2 purging.

The temperature variation study was carried out by varying the temperature in the range of 100 ^{o}C to 150 ^{o}C (Figure 11). The conversion of glycerol was very low when the reactions were carried out below 120 ^{o}C. With increase in the reaction temperature, the conversion 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 conversions were achieved at 150 ^{o}C for both the catalysts which was considered to be optimum temperature for glycerolysis of urea. Further increase in the temperature showed coke formation of the reaction mixtures.

For 30% SiW_{12}/Hβ maximum conversion of 73 % and selectivity of 72% and for 30% SiW_{11}/Hβ maximum conversion, 68% and selectivity of 75% of GlyC was achieved under optimized conditions of, mole ratio G:U, 1:1, temperature: 150 ^{o}C, catalyst amount: 100 mg, reaction time: 8 h.

Better activity was observed for 30% SiW_{12}/Hβ as compared to 30% SiW_{11}/Hβ. The trend in activity was consistent with the acidity of both the catalysts as described in the Chapter 4a, page no. 177. Further, it was observed that catalytic activity of both the catalysts was limited to 73% for 30% SiW_{12}/Hβ and 68% for 30% SiW_{11}/Hβ. This may be due to the formation of ammonium salt with the silicotungstates by liberated NH_3 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 (SiW_{12} and SiW_{11}). It is clear from the Table 2 that the support was not much active towards the carboxylation and the activities of the species SiW_{12}/SiW_{11} have been retained in the catalysts. The activity of

30% SiW_{12}/Hβ was higher than 30% SiW_{11}/Hβ. The results are quite consistent with the acidity of both the catalyst suggesting *pseudo-liquid type (I)* behaviour of the catalysts [7].

Table 2. Control experiments for carboxylation of glycerol with urea.

Catalyst	% Conversion	% Selectivity[c]	TON	TOF, h^{-1}
No catalyst	19	36	-	
SiW_{12}[a]	71	75	889	111.1
SiW_{11}[a]	65	70	820	102.5
Hβ[b]	39	52	-	
30% SiW_{12}/Hβ[b]	73	72	914	114.2
30% SiW_{11}/Hβ[b]	68	75	858	107.2

Reaction conditions: mole ratio G/U: 1/1; time: 8 h; temperature: 150 °C; catalyst amount: [a]23 mg / [b]100 mg, [c]glycerol carbonate selectivity. TON= moles of product/moles of catalyst, TOF= TON/ reaction time.

Heterogeneity test

For adequate proof of heterogeneity, a test was performed by removing the catalysts from the reaction mixture after 4 h by centrifugation and allowed the substrates to react up to 8 h. The reaction mixture of 4 h and filtrate was analysed by Gas Chromatography. Both samples showed same conversion of 42% (Figure 12a) for 30% SiW_{12}/Hβ. Similar results were observed for 30% SiW_{11}/Hβ (Figure 12b). In another experiment after 4 h of the reaction time, the catalysts were filtered by centrifugation and new reactant, glycerol (10 mmol) and urea (10 mmol) was added to the filtrate and reactions were further continued up to 8 h. The conversion of final sample was similar to that of the 4

h sample. According to Sheldon et al., there are three categories for a catalyst to act 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 [8]. The results show that the present catalytic systems fall into category c. 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 present catalysts are truly heterogeneous in nature.

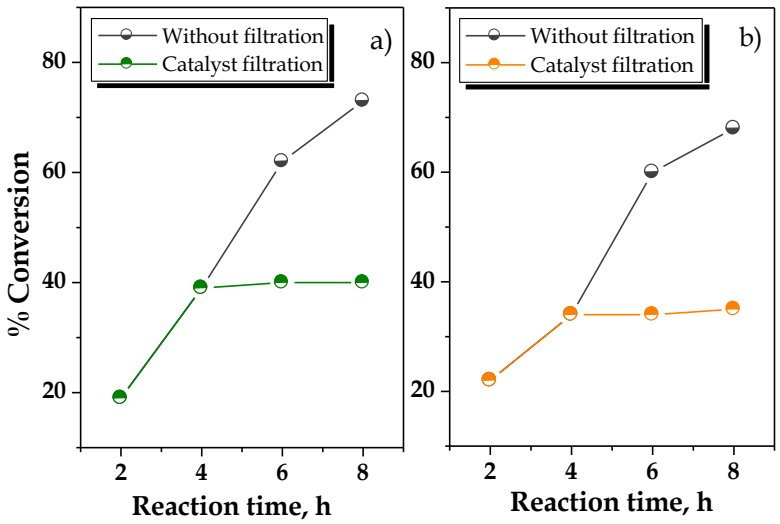


Figure 12. Heterogeneity test for glycerolysis of urea over a) 30% $SiW_{12}/H\beta$ and b) 30% $SiW_{11}/H\beta$. Reaction conditions: mole ratio Gly/Urea: 1/1; time: 8 h; temperature: 150 ^{o}C; catalyst amount: 100 mg; N_2 purging.

Regeneration and recycling of the catalyst

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 characterized for acidic strength, FTIR and BET in order to see any structural change. The results are similar to the previously presented in *Chapter 4a*. The catalysts were recycled up to four times in order to test their activity in

successive runs (Figure 13). There was no appreciable loss in the activity of the catalysts and catalysts can be reused up to four cycles.

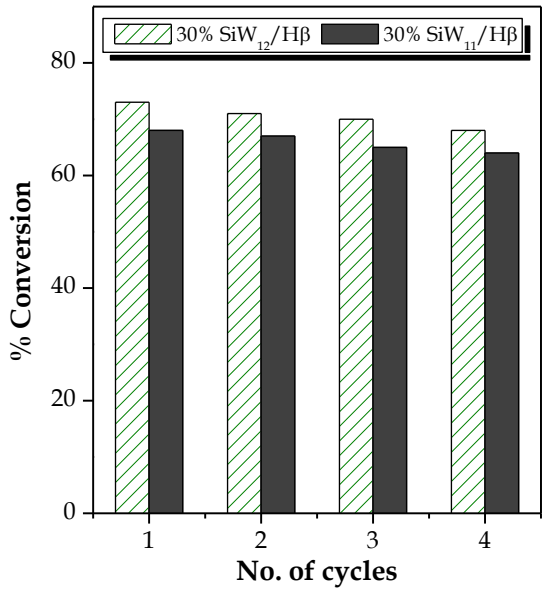


Figure 13. Recycling study for glycerolysis of urea over 30% SiW_{12}/Hβ and 30% SiW_{11}/Hβ. Reaction conditions: mole ratio Gly/Urea: 1/1; time: 8 h; temperature: 150 ^{o}C; catalyst amount: 100 mg; N_2 purging.

Conclusions

- The present catalytic systems 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.
- By *tuning acidic strength* of the parent silicotungstate, the selectivity of the 1,3-dioxolane was increased from *68%* for 30% SiW_{12}/Hβ to *78%* for 30% SiW_{11}/Hβ.
- The present catalysts also exhibits outstanding activities for *carboxylation of glycerol with urea* to synthesize GlyC.
- Maximum of *73%* conversion with *72%* selectivity of GlyC was achieved with 30% SiW_{12}/Hβ and *68%* conversion with *75%* selectivity was achieved by using 30% SiW_{11}/Hβ.
- 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}/Hβ* shows superior catalytic activities as compared to *30% SiW_{11}/Hβ*.

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