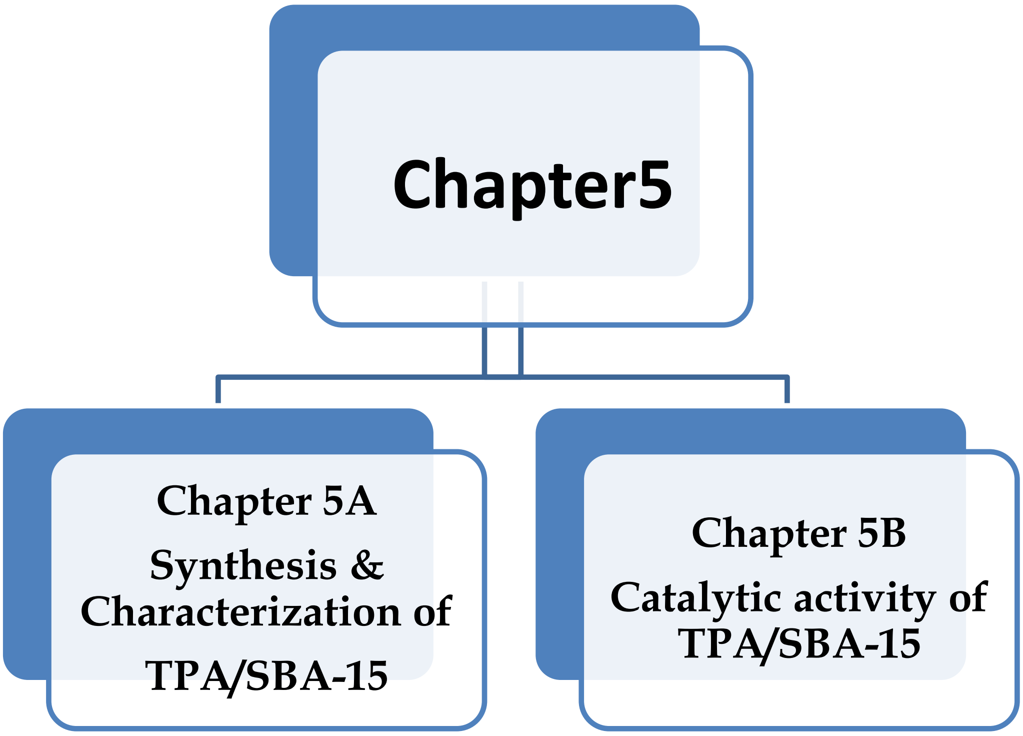
Chapter5



Chapter5

Chapter 5A
Synthesis & Characterization of TPA/SBA-15

Chapter 5B
Catalytic activity of TPA/SBA-15

Chapter 5A

Synthesis & Characterization of

- **SBA-15**
- **12-tungstophosphoric acid anchored to SBA-15 (TPA/SBA-15)**

Papers Published

Appl. Catal. A: Gen. 403 (2011) 161-172.

Applied Catalysis A: General 403 (2011) 161–172

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

12-Tungstophosphoric acid anchored to SBA-15: An efficient, environmentally benign reusable catalysts for biodiesel production by esterification of free fatty acids

Varsha Brahmkhatri, Anjali Patel*

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Vadodara 390002, India

ARTICLE INFO

Article history:
Received 30 March 2011
Received in revised form 20 June 2011
Accepted 29 June 2011
Available online 6 July 2011

Keywords:
12-Tungstophosphoric acid
SBA-15
Oleic acid
Waste cooking oil
Biodiesel

ABSTRACT

12-Tungstophosphoric acid anchored to SBA-15 was synthesized and characterized by various physico-chemical techniques such as TGA, FT-IR, DRS, XRD, N_2 adsorption–desorption, solid state NMR (^{31}P and ^{29}Si), SEM and TEM. The use of synthesized catalyst was explored for biodiesel production by esterification of free fatty acid, oleic acid with methanol. Influence of various reaction parameters (such as catalyst concentration, acid/alcohol molar ratio and reaction temperature) on catalytic performance was studied. The catalyst shows high activity in terms of conversion of oleic acid as well as high turnover frequency of 9.3 min^{-1}. It also shows potential of being used as recyclable catalyst material after simple regeneration. Kinetic investigation reveals that the esterification reaction of oleic acid with methanol follows a first order dependency on the concentration of the oleic acid and the catalyst. The influence of temperature on rate constant was also studied and the activation energy was found to be 44.6 kJ mol^{-1}. As an application, preliminary study was carried out for biodiesel production from waste cooking oil, as feedstock without any pre-treatment, with methanol. Studies show that the catalyst can be used for biodiesel production from waste cooking oil under mild conditions.

Why SBA-15?

- SBA-15 is one of the most important candidate among the mesoporous silica materials.
- It Possess thick pore walls and large pore diameters as compared to MCM-41.
- It exhibits high hydrothermal stability as compared to MCM-41.
- They found extended the applications in catalysis and separation because it has the advantage in the diffusion and transport of large molecules.

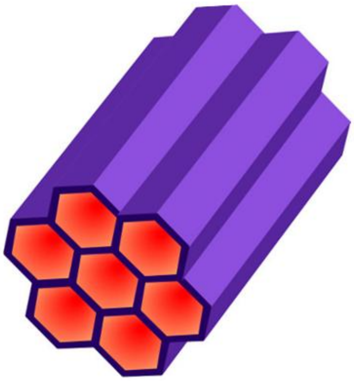


Figure 82. Structure of SBA-15

SBA-15 is a mesoporous silica which has cylindrical pores arranged in a hexagonal order (figure 82) synthesized with the Pluronic triblock-copolymer P123. For this material, the pore size refers to the width of the cylindrical pores which can be tuned between 4-26 nm [1-4] even though pore sizes above 12 nm are rare. The length of the pores varies from ~200 nm [5, 6] to several microns. Around each mesopore is a microporous network called the corona [7-11]. This network interconnects the mesopores with each other and is responsible for the high surface area of SBA-15 [12].

The present chapter describes synthesis and physico-chemical and spectroscopic characterization of support, SBA-15 and the catalyst containing different loadings of TPA anchored to SBA-15. The support and the catalysts were characterized by different physico-chemical techniques such as elemental analysis (EDS), thermo gravimetric analysis (TGA-DTG), Fourier Transform Infrared Spectroscopy (FT-IR), Laser-Raman Spectroscopy, Diffuse Reflectance Spectroscopy (DRS), X-ray diffraction (XRD), surface area measurement (BET method), pore size, pore volume and ^{31}P and ^{29}Si MAS-NMR studies. Further, the surface morphology of support and catalyst was studied by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The total acidity was determined by n-butylamine titration. The types of acidic sites (acidic strength) were determined by potentiometric titration.

Experimental Section

Materials

All chemicals used were of A.R. grade. $H_3PW_{12}O_{40}$. nH_2O (Loba chemie, Mumbai), pluronic123 (Aldrich), tetraethyl orthosilicate (TEOS), oleic acid and methanol were used as received from Merck.

Synthesis of SBA-15

The synthesis of SBA-15 was carried out as reported in literature [1]. The SBA-15 synthesis (Figure 83) was carried out without hydrothermal conditions. In a typical preparation, 4 g of Pluronic P123 was dissolved in 30ml water and 120 mL, 2M HCl with stirring at 35 °C .Then 8.5 g of TEOS was added into the solution with stirring at 35 °C for 20 h. Then the mixture was aged at 80 °C for 48 h without hydrothermal conditions. The solid product was recovered, washed and air dried at room temperature. The calcination was carried out at 500 °C for 6 h.

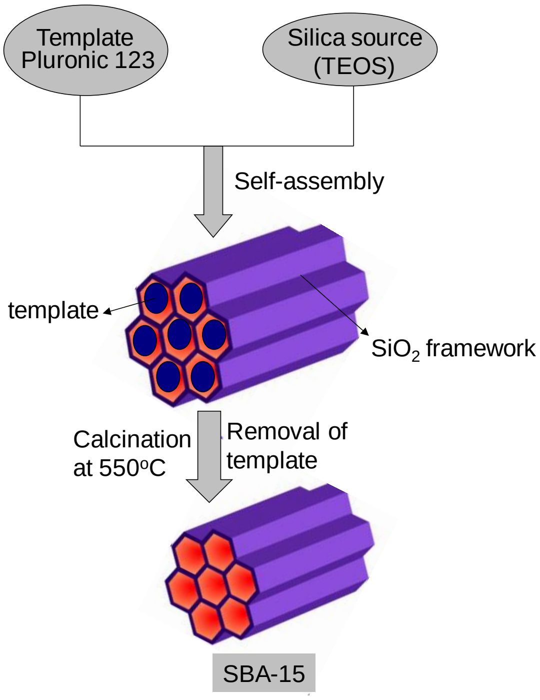


Figure 83. Synthesis of SBA-15

Synthesis of the catalyst

Anchoring of TPA onto SBA-15

TPA was anchored to SBA-15 by dry impregnating method. 1 g of SBA-15 was impregnated with an aqueous solution of TPA (0.1g/10 mL of double distilled water). The water from the suspension was allowed to evaporate at 100 °C in an oven. Then the resulting mixture was dried at 100 °C with stirring for 10 h. The material thus obtained was designated as TPA_1/SBA-15. Same procedure was followed for the synthesis of a series of TPA anchored catalyst (0.2-0.4 g/20-40 mL of conductivity water). The obtained materials were designated as TPA_2/SBA-15, TPA_3/SBA-15 and TPA_4/SBA-15 respectively.

RESULTS AND DISCUSSION

(a) Characterization of the support, SBA-15

The support, SBA-15 was successfully synthesized and characterized by various spectroscopic techniques. Only the main characterization techniques such as XRD, SEM, TEM and BET surface area measurements are presented here and the rest of the techniques will be discussed along with the catalyst.

XRD pattern of SBA-15 is shown in Figure 84. The XRD patterns of parent SBA-15 show three well resolved peaks at 0.89^0, 1.50^0 and 1.72^0 which are indexed to (1 0 0), (1 1 0) and (2 0 0) reflections of ordered hexagonal mesophase as reported earlier[1].

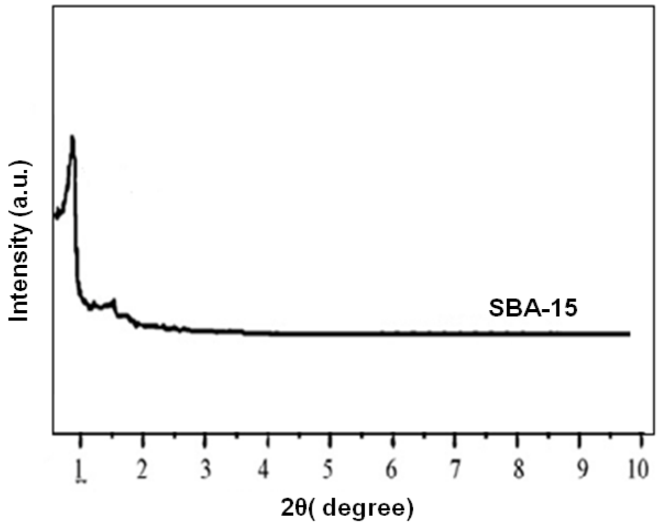
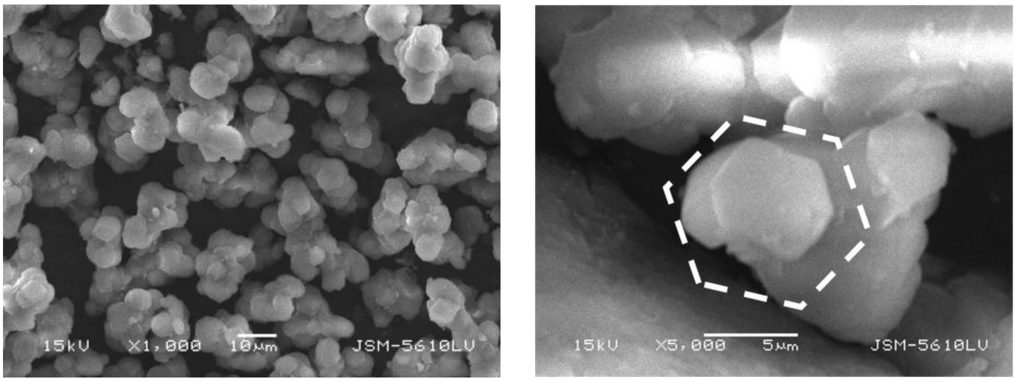


Figure 84. X-ray diffraction pattern of SBA-15

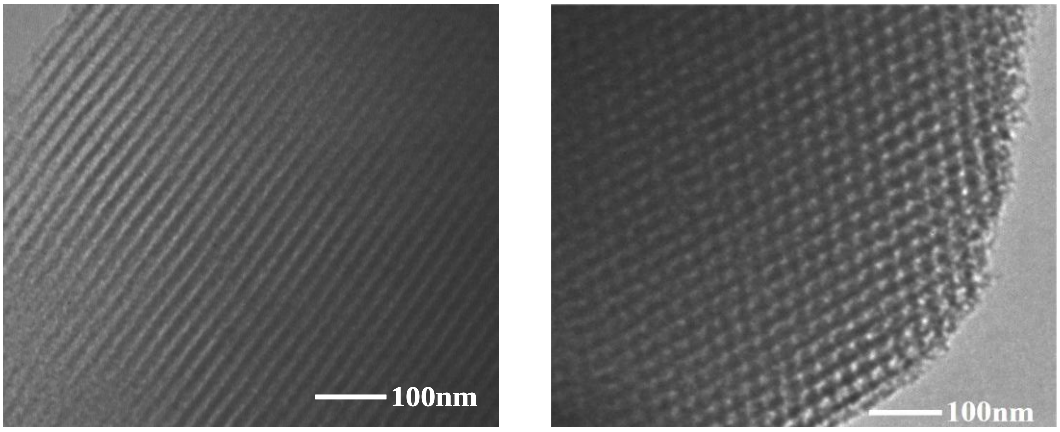
Figure 85 (a) and (b) shows the SEM images of SBA-15 at various magnifications. The SEM images showed the uniform growth of hexagonal morphology and the aggregates of the hexagonal particles. These hexagonal particles try to aggregate and remain stacked over each other.



(a) (b)

Figure 85. SEM images of SBA-15

The figure 86 shows TEM images of SBA-15. The TEM images of SBA-15, figure (a) shows the morphology of 2-D hexagonal arrays of channels with uniform pore size. Figure 4 (b) clearly shows hexagonal mesopores. This confirms the formation of SBA-15 with long range order.



(a) (b)

Figure 86.TEM images of SBA-15

The surface area of SBA-15 was found to be 834 m^2/g with 6.8 nm pore diameter.

(b)Characterization of TPA/SBA-15

Chemical Stability

Chemical stability of a catalyst plays an important role. The materials which have a high solubility in water and/or in acidic media may not be very useful. It is advisable to have a rough guide of the solubility of the material being used as a catalyst. The stability of all the synthesized materials have to be check in different acids and bases.

The supported catalysts were evaluated for chemical stability and the present catalysts, shows no change in colour or form on heating with water. The materials are stable in different mineral acids like HCl, H_2SO_4, HNO_3 and bases like NaOH, Na_2O_3 etc. up to ~ 2M concentration.

Leaching test

Any leaching of the active species from the support makes the catalyst unattractive and hence it is necessary to study the stability as well as leaching of TPA from the support. TPA can be quantitatively characterized by the heteropoly blue colour, which is observed when it reacted with a mild reducing agent such as ascorbic acid [13]. In the present study, this method was used for determining the leaching of TPA from the support. Standard samples containing 1–5% of TPA in water were prepared. To 10 ml of the above samples, 1 ml of 10% ascorbic acid was added. The mixture was diluted to 25 ml. The resultant solution was scanned at λmax of 785 cm^{-1} for its absorbance values. A standard calibration curve was obtained by plotting values of absorbance against % concentration. 1 g of catalyst with 10 ml conductivity water was refluxed for 24 h. Then 1 ml of the supernatant solution was treated with 10% ascorbic acid. Development of blue colour was not observed indicating that there was no leaching. The same procedure was repeated with alcohols and the filtrate of the reaction mixture after completion of reaction in order to check the presence of any leached TPA. The absence of blue colour indicates no leaching of TPA.

Elemental analysis (EDS)

Elemental analysis (EDS) for TPA_3/SBA-15 catalyst is shown in Table 42. The obtained results were close to the theoretical values.

Table 42. Elemental analysis (EDS)

Catalyst	Elemental analysis (weight %)					
	O	Si	W		P	
			By EDS	Theoretical	By EDS	Theoretical
TPA_3/SBA-15	53.93	27.8	17.97	19	0.30	0.32

Thermal Analysis (TGA-DTG)

Figure 87 shows the TGA-DTA curves of pure TPA, SBA-15 and TPA_3/SBA-15.The unsupported pure TPA exhibits weight loss in three stages at 100, 200 and 485 °C as indicated by the DTA curve. These can be attributed to initial weight due to adsorbed water, second weight loss due to loss of water of crystallization near 200 °C to give the Keggin structure, which is stable on heating up to 350 °C. The endothermic peak observed on DTA curve at 485 °C may be attributed to the decomposition of the Keggin structure of TPA into the simple oxides [14].

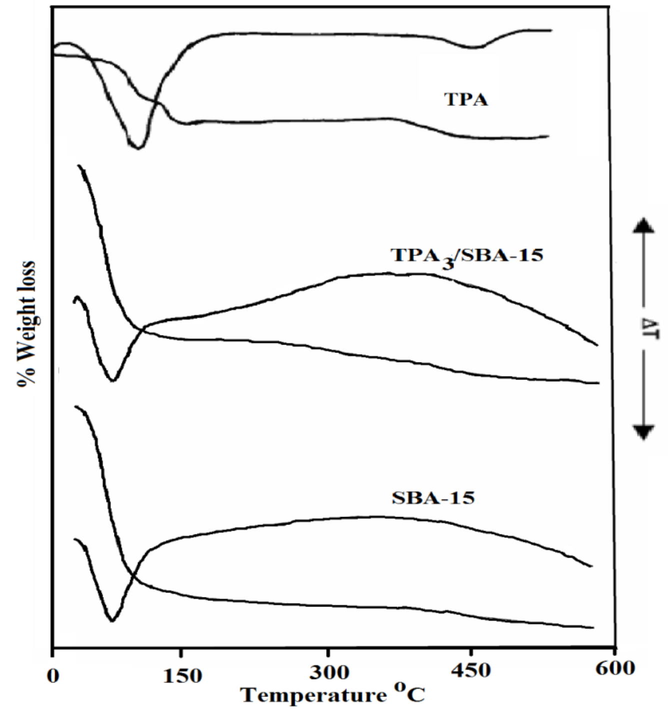


Figure 87. TGA-DTA of pure TPA, SBA-15 and TPA$_3$/SBA-15

SBA-15 showed (figure 87) initial weight loss of 8.4% which was accompanied by a broad band on the DTA curve, appearing as an endothermic peak at 80 °C. This may be due to the loss of adsorbed water molecules. The final 3.22 % weight loss above 450 °C may be due to the condensation of silanol groups to form siloxane bonds. After that absence of any weight loss indicates that support is stable up to 600 °C. TPA$_3$/SBA-15 (figure 87) shows initial weight loss of 16.76% due to the loss of adsorbed water. Second weight loss of 4.54% between 150-250 °C corresponds to the loss of water of crystallization of Keggin ion. After that another gradual weight loss was also observed from 250-500°C due to the difficulty in removal of water contained in TPA molecules inside the channels of SBA-15. This type of inclusion causes the stabilization of TPA molecules inside the channels of SBA-15. As compared to the pure TPA, absence of any endothermic peak on DTA curve at 485°C indicates the stability of TPA up to 550 °C over SBA-15 support.

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR of SBA-15 (Figure 88) shows a broad band around 1100 and 1165 cm^{-1} corresponding to asymmetric stretching of Si-O-Si. The band at 801 and 458 cm^{-1} are due to symmetric stretching and bending vibration of Si-O-Si respectively. The band at 966 cm^{-1} corresponds to symmetric stretching vibration of Si-OH. The broad absorption band around 3448 cm^{-1} is the absorption of Si-OH on surface, which provides opportunities for forming the hydrogen bond. FT-IR spectra of TPA$_3$/SBA-15 (Figure 88) were almost the same as that of the support, SBA-15. The typical bands for TPA, at 987 cm^{-1} and 897cm^{-1} corresponding to (ν_{asym} W=O), and stretching vibrations of (W-O$_c$-W) that corresponds to corner sharing oxygens respectively, are clearly observed in TPA$_3$/SBA-15. The presence of these bands strongly reveals that the primary structure of TPA Keggin anion is preserved even after anchoring to SBA-15 support.

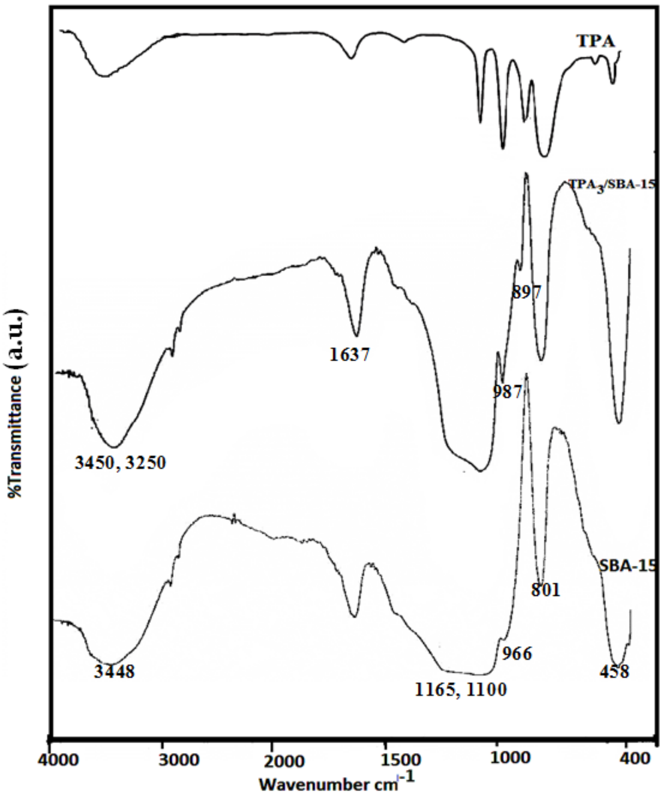


Figure 88. FT-IR spectra of TPA, SBA-15 and TPA$_3$/SBA-15

The absence of vibration band at 1080 cm^{-1} of TPA may be because of very low concentration of TPA, or the TPA bands may be superimposed with those of support. In addition to the characteristic band for TPA, FT-IR spectra of TPA_3/SBA-15 also shows the infra-red absorption peaks at 1637 and 3450 cm^{-1} with a shoulder at 3250 cm^{-1}, probably corresponds to the bending and stretching vibrations of bridging hydroxyl, respectively, because of the interaction of TPA anions and surface silanol groups of SBA-15.

Laser Raman Spectroscopy (LRS)

Raman spectra of TPA and TPA_3/SBA-15 are shown in Figure 89. The Raman spectrum of TPA shows bands at 1010, 990, 900, 550, and 217 cm^{-1} , which have already been assigned to v_s (W-O_d), v as (W-O_d), v_{as} (W-O_b-W), v_s (W-O_c-W), and v_s (W-O_a), respectively (Figure 89) where O_a, O_b, O_c , and O_d correspond to the oxygen atoms linked to phosphorus, to oxygen atoms bridging two tungsten (from two different triads for O_b and from the same triad for O_c), and to the terminal oxygen W=O, respectively [14].

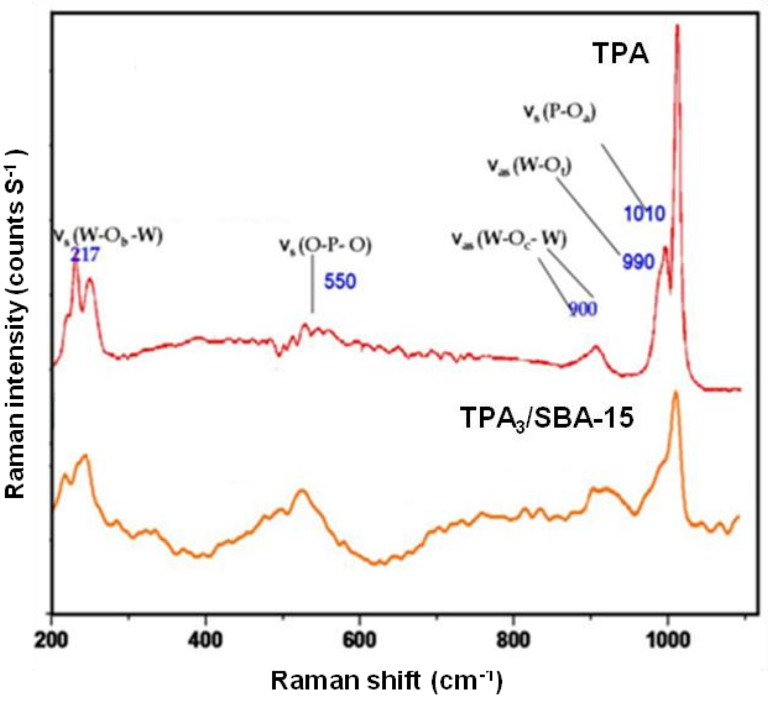


Figure 89. Raman spectra of TPA and TPA_3/SBA-15

In case of anchored catalysts, TPA_3/SBA-15 the absence of a significant band shifts in the spectra indicates that the environment of the Keggin unit is similar to that of TPA which confirms the retainment of the Keggin structure even after anchoring to support SBA-15.

Diffuse Reflectance Spectroscopy (DRS)

The DRS spectra of SBA-15, TPA and TPA_3/SBA-15 are shown in Figure 90. A broad band from 260 to 275 nm was observed for TPA. This characteristic band can be assigned to the oxygen-metal charge transfer of tungstophosphate anion $PW_{12}O_{40}^{3-}$ which is in agreement with a previous report [15]. The DRS spectra of TPA_3/SBA-15 show λmax at 260 nm giving evidence of presence of the stable Keggin ion species in SBA-15.

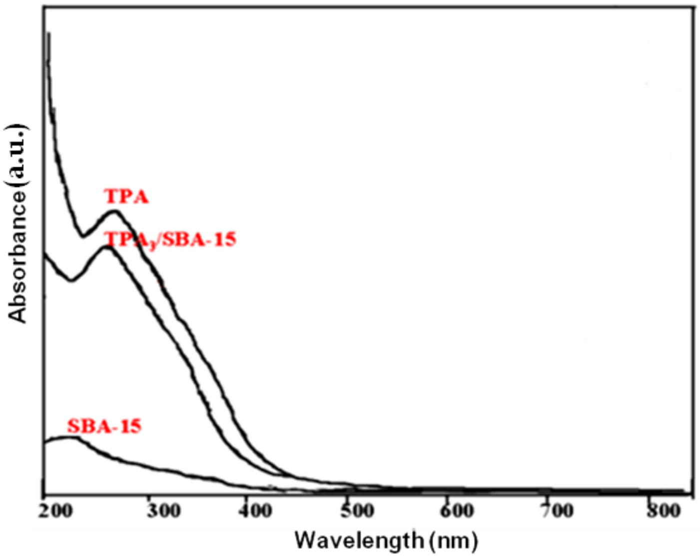
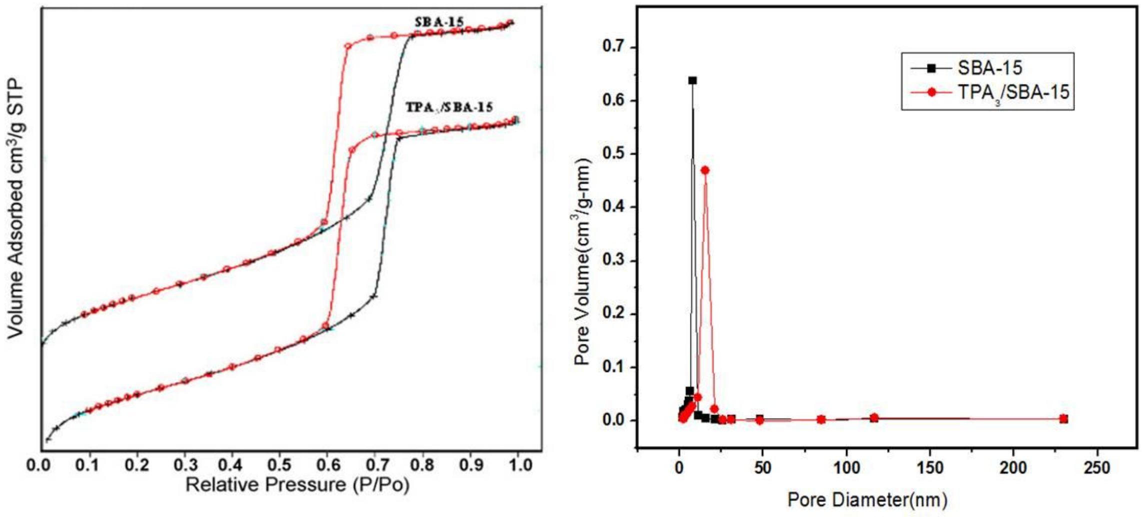


Figure 90. DRS spectra of SBA-15, TPA and TPA_3/SBA-15

N_2 sorption isotherms

The adsorption–desorption isotherms of N_2 for pure SBA-15 and TPA_3/SBA-15 are shown in Figure 91(a). All the N_2 adsorption–desorption isotherms are of type IV in nature according to the IUPAC classification and exhibited an H1 hysteresis loop which is a characteristic of mesoporous solids [16]. The adsorption branch of each isotherm showed a sharp inflection, which means a typical capillary condensation within uniform pores and considerable adsorption amounts indicate that, there is considerable volume of nanospaces even after the introduction of TPA. The position of the inflection point is clearly related to the diameter of the mesopore, and the sharpness of this step indicates the uniformity of the mesopore size distribution. In addition narrow pore size distribution was observed (Figure 91b) for both SBA-15 as well as TPA_3/SBA-15 indicates long range order over large scales. The decrease in pore diameter in the catalyst TPA_3/SBA-15 (62 Å) is due to the presence of TPA.



(a) (b)

Figure 91. (a) Nitrogen sorption isotherms of SBA-15 and TPA_3/SBA-15 (b) Pore size distribution.

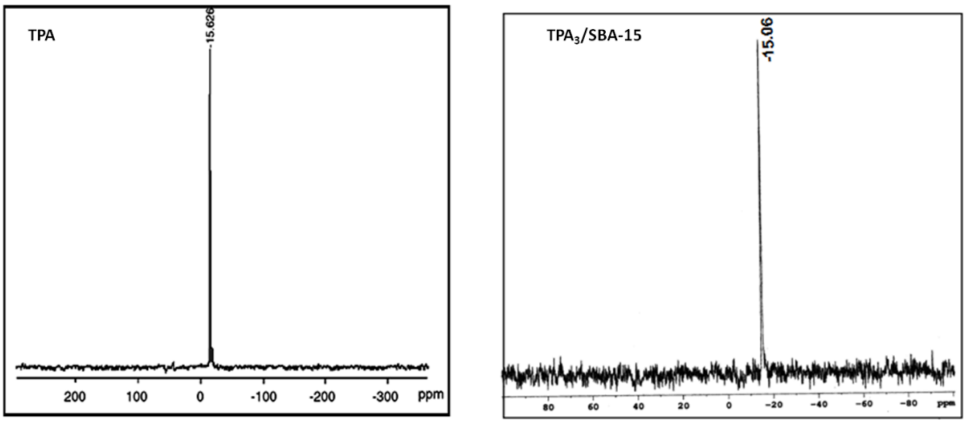
The results for surface area, pore size and pore volumes are presented in Table 43. As the TPA loading increases surface area, pore diameter and pore volume all strongly decreases relative to the support, SBA-15. The reason being, as the TPA species enters the mesopores of SBA-15 it decrease the pore diameter, and also probably some TPA species appear in the mesoporous channels that decrease the average pore volume as well as the surface area. Specific surface area, porosity and pore diameter, all strongly decreased for TPA_3/SBA-15 relative to the starting support, SBA-15.

Table 43. Textural properties of support and catalysts

Catalyst	Surface area(m^2/g)	Pore diameter d(Å)	Mesopore volume (cm^3/g)
SBA-15	834	68	1.26
TPA_1/SBA-15	784	63.98	1.18
TPA_2/SBA-15	746	62.72	1.14
TPA_3/SBA-15	714	62	1.11
TPA_4/SBA-15	699	61.65	1.02

^{31}P MAS- NMR studies

^{31}P NMR is the most important method to study chemical environment around the phosphorous in heteropoly compounds. The ^{31}P NMR spectra of TPA and TPA_3/SBA-15 are shown in Figure 92. The value of chemical shift for TPA is -15.626 ppm and is in good agreement with the reported value [17]. The value of chemical shift for TPA_3/SBA-15 is -15.06 ppm. No appreciable change in chemical shift value reveals that the surrounding environment of the TPA does not change when anchored SBA-15. In other words the Keggin ion structure is retained even after anchoring to SBA-15.



(a) (b)

Figure 92. ^{31}P NMR spectra of (a) TPA and (b) TPA_3/SBA-15

^{29}Si MAS- NMR studies

^{29}Si MAS-NMR is the most important method to study chemical environment around the silicon nuclei in mesoporous silica materials. Figure 93 shows the ^{29}Si MAS-NMR spectra of the SBA-15 and TPA_3/SBA-15. A broad peak between -90 and -125 ppm was observed which can be attributed to three main components with chemical shifts at -90, -100 and -109.74 ppm. These signals are resulted from Q2(-90ppm) , Q3 (-100ppm) and Q4 (-109.47ppm) silicon nuclei, where Qx corresponds to a silicon nuclei with x siloxane linkages, i.e., Q2 to disilanol Si-(O-Si)2(-O-X)2, where X is H or TPA , Q3 to silanol (X-O)-Si-(O-Si)3 and Q4 to Si-(O-Si)4 in the framework [18, 19]. The spectra of TPA_3/SBA-15 were relatively broad as compared SBA-15 which may be due the presence of TPA. Also the intensity of the Q^2 and Q^3 peaks decreases when the support, SBA-15 is loaded with TPA .i.e., in catalysts TPA_3/SBA-15. This may be due to the presence of TPA inside the hexagonal channels.

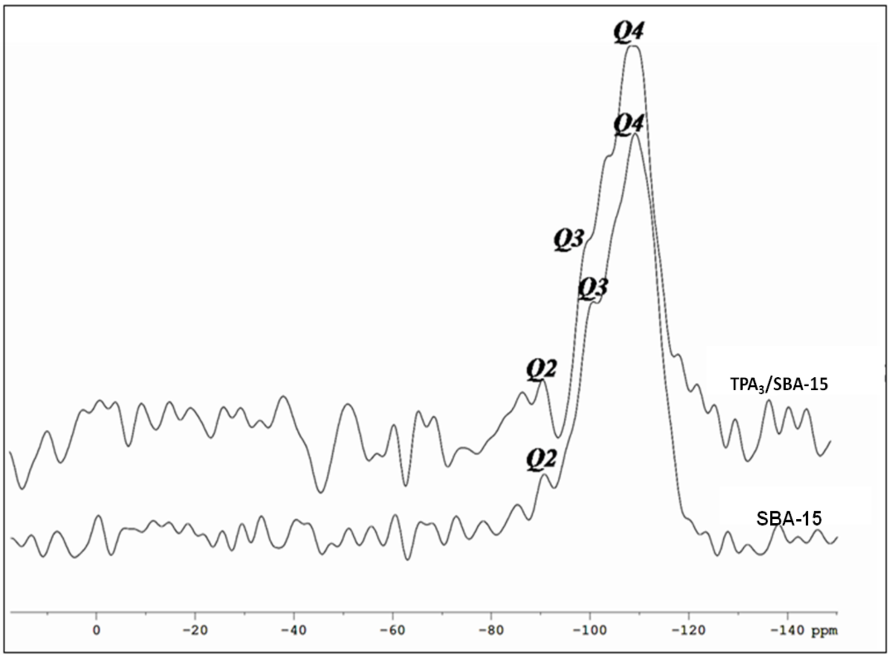


Figure 93. ^{29}Si MAS-NMR spectra of SBA-15 and TPA_3/SBA-15

The fractions of Q^2, Q^3 and Q^4 units and their relative values derived from the figure 93 are given in table 44. If the values of $(Q^3+Q^2)/Q^4$ for SBA-15 and TPA_3/SBA-15 were compared, the greater value obtained for TPA_3/SBA-15 catalyst indicates strong interaction between SBA-15 frameworks with TPA.

FT-IR, DRS and ^{31}P NMR spectra shows that Keggin ion structure of TPA remains intact even after anchoring to SBA-15. ^{29}Si NMR data and FT-IR studies shows that there is a strong interaction, hydrogen bonding between terminal oxygens of TPA with the surface silanol groups of SBA-15.

Table 44. ^{29}Si NMR data

Catalyst	^{29}Si NMR data			
	Q^4%	Q^3%	Q^2%	$(Q^3+Q^2)/Q^4$
SBA-15	74	21	3	0.32
TPA_3/SBA-15	67.5	27	5.5	0.48

To study the dispersion of TPA species into SBA-15, materials were further characterized for XRD, SEM and TEM.

X-ray diffraction (XRD)

XRD patterns of TPA, SBA-15, and TPA_3/SBA-15 of are shown in Figure 94. The XRD patterns of parent SBA-15 show three well resolved peaks at 0.89°, 1.50° and 1.72° which are indexed to (100), (110) and (200) reflections of ordered hexagonal mesophase. It is interesting to note that, in TPA_3/SBA-15, the intensity of peaks corresponding to (110) and (200) planes of SBA-15 decreases. Further, the comparison of the XRD patterns of SBA-15 and TPA_3/SBA-15 reveals that the mesoporous structure is rather intact even after the TPA loading. This indicates high dispersion of TPA on the support. As compared to the other supports, SBA-15 could accommodate more discrete TPA species because of its large pore volume and high surface area. The XRD patterns of TPA_3/SBA-15 show, the appearance of very small peaks of TPA but all the typical characteristic diffraction peaks of crystalline phase of TPA were not observed as compared to the XRD of bulk phase of TPA. Further the absence of characteristic peaks of crystalline phase of TPA indicates that TPA is highly dispersed inside the hexagonal channels of SBA-15[20].

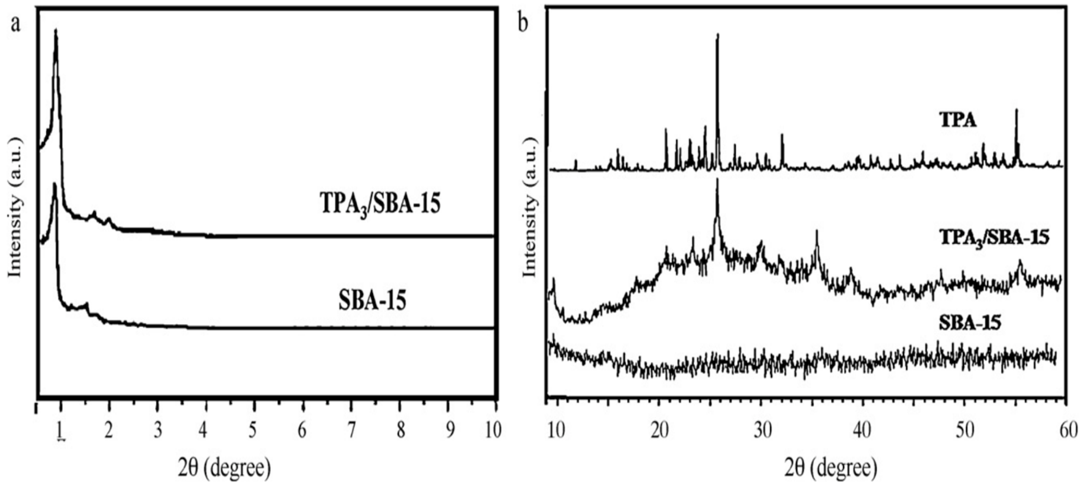
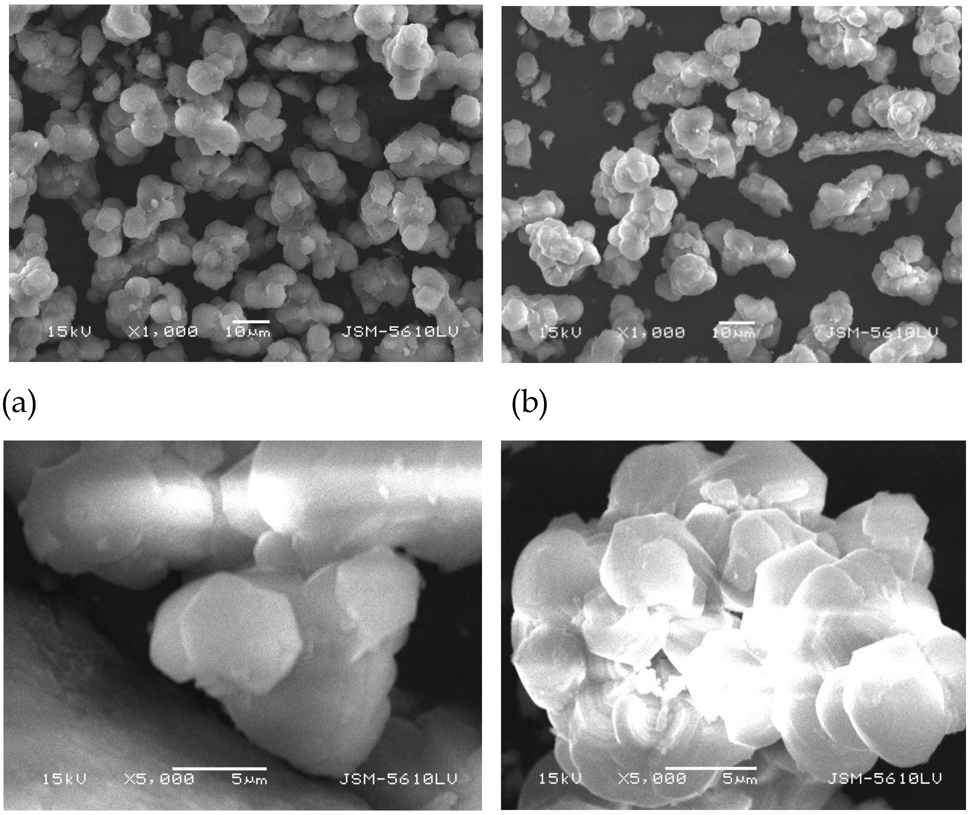


Figure 94. (a) Small angle XRD of SBA-15and TPA_3/SBA-15 (b) XRD patterns of TPA, SBA-15 and TPA_3/SBA-15

Scanning Electron Microscopy (SEM)

Figure 95 (a) and (c) shows the SEM images of SBA-15 and TPA_3/SBA-15. The SEM images showed the uniform growth of hexagonal morphology and the aggregates of the hexagonal particles. These hexagonal particles try to aggregate and remain stacked over each other. The surface morphology of the catalyst is almost identical to that of pure SBA-15. No change in surface morphology of both indicates TPA species are well dispersed inside the hexagonal pores. Further no separate crystallites of bulk phase of TPA were found in TPA_3/SBA-15 (figure 95 b, d).



(a) (b)

(c) (d)

Figure 95. SEM images of SBA-15(a, c) and TPA_3/SBA-15(b, d)

Transmission Electron Microscopy (TEM)

The figure 14 shows TEM images of SBA-15 and TPA$_3$/SBA-15 at various magnifications. The TEM images of SBA-15 Figure 96 (a) shows the morphology of 2-D hexagonal arrays of channels with uniform pore size. Figure 96 (c) clearly shows hexagonal mesopores. The TEM images of TPA$_3$/SBA-15 (figure 9 b, d) shows well ordered nanochannels and the nanochannels were arranged on 2D hexagonal structure over very large scales. The uniform structure of SBA-15 was well maintained throughout the structure even after TPA loading, which reveals that the TPA species were well dispersed inside the hexagonal channels.

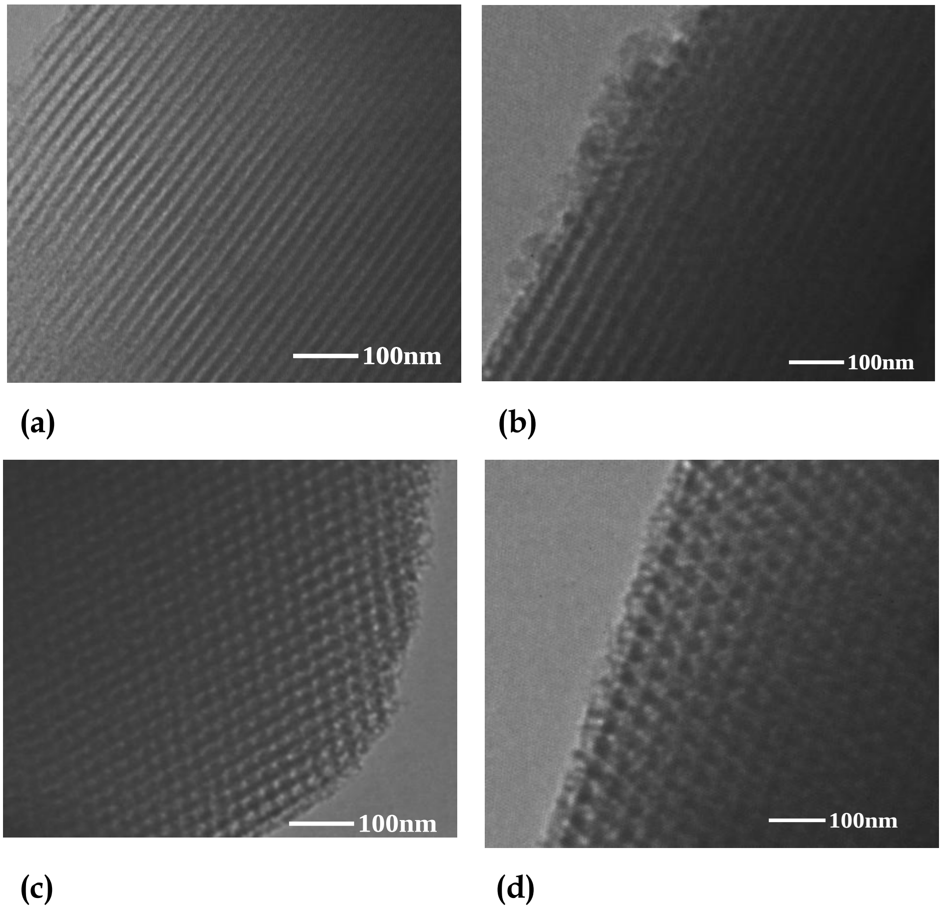


Figure 96. TEM images of SBA-15(a, c) and TPA$_3$/SBA-15(b, d)

Acidity measurements

(a) Total acidity

Total acidity values for all the catalysts are presented in Table 45. Total acidity values indicate that SBA-15 is fairly acidic. As the TPA loadings increases acidity values also increase and the results are as expected.

Table 45. Total acidity values

Catalyst	Total acidity (mmol/g)
SBA-15	1.11
TPA_1/SBA-15	1.62
TPA_2/SBA-15	1.74
TPA_3/SBA-15	1.82
TPA_4/SBA-15	1.88

(b) Determination of acidic strength

According to Vasquez et al [21], the potentiometric titrations with 0.05 N n-butyl amine enable the quantitative determination of Bronsted acid sites. As suggested by Vasquez et al, sites at potential > 100mV are very strong sites, sites at mV 0< E<100 are strong and those at -100<E<0 are weak.

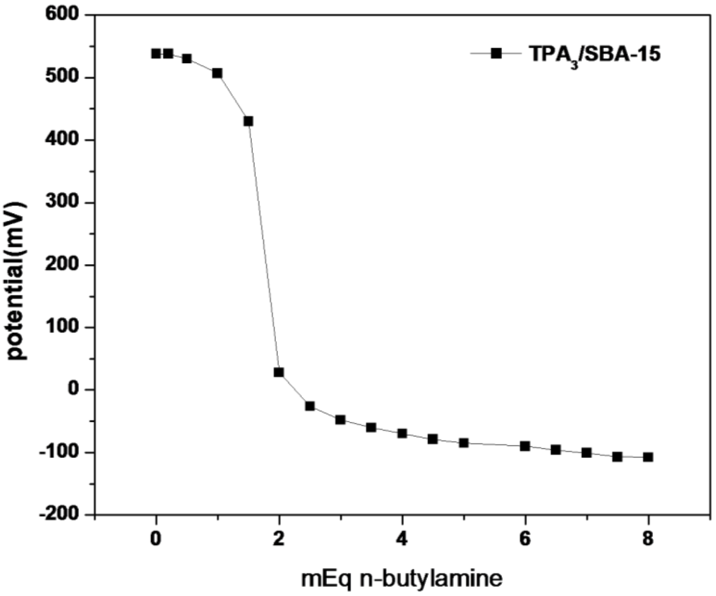


Figure 97. Potentiometric titration of TPA_3/SBA-15 with n-butylamine

From the plot shown in figure 97, an equivalent mass of 2.4 mg n-butyl amine was determined for TPA_3/SBA-15 at potential above 100 mV, corresponding to TPA acidic protons and indicating that all those sites were very strong. The silica support, SBA-15 was titrated at lower potentials (E < 0 mV) in the range of very weak acid sites.

Conclusion

- SBA-15 was synthesized by non-hydrothermal synthetic method, and that was used for anchoring TPA. XRD and TEM confirm the formation of SBA-15 with hexagonal long range order in the material.

- FT-IR, DRS and ^{31}P NMR spectra shows that Keggin ion structure of TPA remains intact even after anchoring to SBA-15.

- BET surface area and the ^{29}Si NMR data, shows that there is a strong hydrogen bonding between terminal oxygens of TPA with the surface silanol groups of SBA-15 (figure 98).

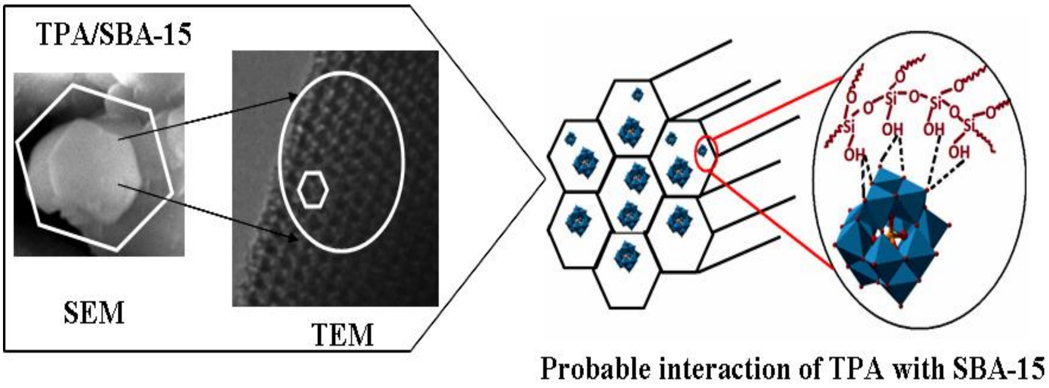


Figure 98. Interaction of TPA with SBA-15

- XRD, SEM and TEM show that TPA is uniformly dispersed inside the channels without disturbing the hexagonal array of SBA-15.

References

1. D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc*. 120, 6024 (1998).
2. D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science*. 279, 548 (1998).
3. L. Cao, T. Man, M. Kruk, *Chem. Mater*. 21, 1144 (2009).
4. L. Cao, M. Kruk, *Colloids Surf. Physicochem. Eng. Aspects*. 357, 91 (2010)
5. H. Zhang, J. Sun, D. Ma, X. Bao, A. Klein-Hoffman, G. Weinberg, D. Su, R. Schlogl, *J. Am. Chem. Soc.* 126, 7440 (2004).
6. J. Sun, H. Zhang, R. Tian, M. Ding, X. Bao, D.S. Su, H. Zou, *Chem. Comm*. 1322 (2006)
7. M. Impéror-Clerc, P. Davidson, A. Davidson, *J. Am. Chem. Soc*. 122, 11925 (2000)
8. R. Ryoo, C.H. Ko, M. Kruk, V. Antochshuk, M. Jaroniec, *J. Phys. Chem. B*. 104, 11465 (2000).
9. M. Kruk, M. Jaroniec, C.H. Ko, R. Ryoo, *Chem. Mater.* 12, 1961 (2000)
10. S. Ruthstein, V. Frydman, S. Kababya, M. Landau, D. Goldfarb*, J. Phys. Chem. B.* 107, 1739 (2003).
11. C. Göltner-Spickermann, *Curr. Opin. Colloid Interface Sci.* 7, 173 (2002).
12. L. Vradman, L. Titelman, M. Herskowitz, *Micropor.Mesopo.r Mater.* 93, 313 (2006).
13. G. D. Yadav, V. V. Bokade, *Appl. Catal. A* 147, 299 (1996).
14. C. Rocchiccioli-Deltcheff, *Inorg. Chem.* 22, 207 (1983).
15. M.T. Pope, Heteropolyacid and Isopolyoxometallates , Sringer-Verlag, Berlin (1983)
16. Y. Luo, Z. Hou, R. Li, X. Zheng, *Micropor. Mesopor. Mater.* 109, 585 (2008)
17. T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41, 113 (1994).
18. R.C. Schroden, C.F. Blanford, B.J. Melde, B.J.S. Johnson, A. Stein, *Chem. Mater.* 13, 1074 (2001).
19. W.H. Zhang, J. Lu, B. Han, M. Li, J. Xiu, P. Ying, C. Li, *Chem. Mater.* 14, 3413 (2002).

20. Q.Y. Liu, W.L. Wu, J. Wang, X.Q. Ren, Y.R. Wang, *Micropor.Mesopor.Mater.*76, 51 (2004).
21. P. Vasquez, L. Pizzio, C. Caceres, M. Blanco, H. Thomas, E. Alesso, L. Finkielsztein, L. Lantano, G. Moltrasio, J. Aguirre, *J. Mol. Catal. A: Chem*. 161,223 (2000).

Chapter 5B

Catalytic activity of TPA/SBA-15

I. Esterification

(a) Esterification of Dicarboxylic acids (Succinic & Malonic acid)

(b) Esterification Fatty acid (Lauric acid)

II. Application in Biodiesel production by

(a) Esterification of free fatty acids (Palmitic acid & oleic acid)

(b) Transesterification of Jatropha oil & Waste cooking oil

Papers Published

Appl. Catal A: Gen, 403(2011) 161-172.

Applied Catalysis A: General 403 (2011) 161–172

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

12-Tungstophosphoric acid anchored to SBA-15: An efficient, environmentally benign reusable catalysts for biodiesel production by esterification of free fatty acids

Varsha Brahmkhatri, Anjali Patel*

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Vadodara 390002, India

ARTICLE INFO

Article history:
Received 30 March 2011
Received in revised form 20 June 2011
Accepted 29 June 2011
Available online 6 July 2011

Keywords:
12-Tungstophosphoric acid
SBA-15
Oleic acid
Waste cooking oil
Biodiesel

ABSTRACT

12-Tungstophosphoric acid anchored to SBA-15 was synthesized and characterized by various physico-chemical techniques such as TGA, FT-IR, DRS, XRD, N_2 adsorption–desorption, solid state NMR (^{31}P and ^{29}Si), SEM and TEM. The use of synthesized catalyst was explored for biodiesel production by esterification of free fatty acid, oleic acid with methanol. Influence of various reaction parameters (such as catalyst concentration, acid/alcohol molar ratio and reaction temperature) on catalytic performance was studied. The catalyst shows high activity in terms of conversion of oleic acid as well as high turnover frequency of 9.3 min^{-1}. It also shows potential of being used as recyclable catalyst material after simple regeneration. Kinetic investigation reveals that the esterification reaction of oleic acid with methanol follows a first order dependency on the concentration of the oleic acid and the catalyst. The influence of temperature on rate constant was also studied and the activation energy was found to be 44.6 kJ mol^{-1}. As an application, preliminary study was carried out for biodiesel production from waste cooking oil, as feedstock without any pre-treatment, with methanol. Studies show that the catalyst can be used for biodiesel production from waste cooking oil under mild conditions.

The present chapter deals with the catalytic activity of TPA/SBA-15 in various organic transformations. Esterification of dicarboxylic acids, succinic acid and malonic acid as well as fatty acid lauric acid with butanol was studied. Biodiesel production by esterification of free fatty acids, palmitic acid and oleic as well as trasesterification of triglycerides, jatropha oil and waste cooking oil was studied. The effect of various reaction parameters such as catalyst concentration, acid/ alcohol molar ratio and temperature were studied to optimize the conditions for maximum conversion. Also the catalyst was regenerated and reused. A detailed kinetic study was carried out for the same esterification of lauric acid, palmitic acid and oleic acid. The rate constants as well as the activation energy for the reaction were determined.

Finally, the effect of supports, MCM-41 and SBA-15 on catalytic activity of TPA in various organic transformations was studied. Based on the catalytic and kinetic data the best catalyst was also proposed.

I. Esterification

(a) Esterification of dicarboxylic acids (Succinic acid& Malonic acid)

Experimental

Materials

All chemicals used were of A.R. grade. Succinic acid, malonic acid n-butanol, hexanol and octanol were used as received from Merck.

Esterification of dicarboxylic acids.

The esterification reaction of malonic acid with alcohols was carried out in a 100 ml batch reactor provided with a double walled air condenser, Dean–Stark apparatus, magnetic stirrer and a guard tube. Dean–Stark apparatus was attached to a round bottom flask to separate the water formed during the reaction. The reaction mixture was refluxed at 80 °C for 4hrs. The obtained products were analyzed on a Gas Chromatograph (Nucon-5700) using BP1 capillary column. Products were identified by comparison with the authentic samples and finally by Gas Chromatography–Mass Spectroscopy (GC–MS).

Results and Discussion

Esterification of dicarboxylic acids to diesters requires strong Bronsted acidity as compared to simple esterification reactions. The esterification reaction is an equilibrium-limited reaction. In order to overcome the equilibrium limitation, it is necessary either to carry out esterification by taking one of the reactant in excess. The yields can be increased by increasing the concentration of either alcohol or acid. In a practical means, to obtain maximum yield for economic reasons, the reactant that is usually less expensive is taken in excess. In present study corresponding alcohol is taken in excess.

Esterification of succinic acid and malonic acid with butanol

The effect of various reaction parameters such as % loading of TPA, acid/ alcohol molar ratio, amount of catalyst and reaction time were studied to optimize the conditions for maximum yields for diesters.

Effect of % loading of TPA

To study the effect of % loading of TPA esterification reaction was carried out with 10, 20, 30 and 40 loadings of TPA. The obtained results are shown in Figure 99. It is observed from the figure that with increase in the % loading of TPA, % yield towards diester also increases. For TPA$_3$/SBA-15 and TPA$_4$/SBA-15 catalyst, the difference in % yield is not that much appreciable. Hence the catalyst containing 30% loading of TPA i.e. TPA$_3$/SBA-15 was selected for the detail study.

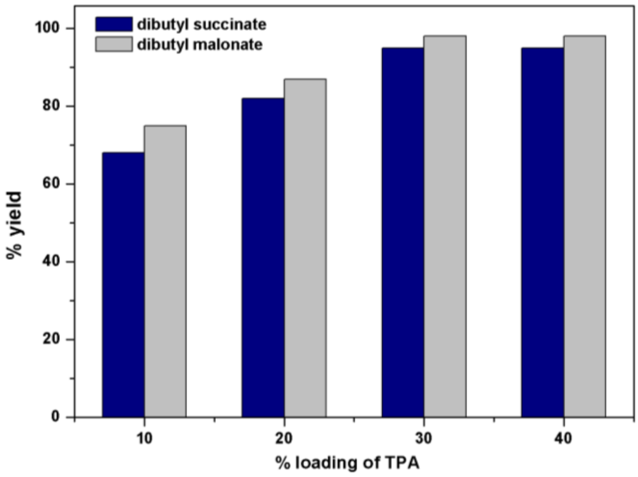


Figure 99. Effect of % loading of TPA; (Reaction conditions: mole ratio of acid/ alcohol: 1:3, Amount of catalyst: 0.1 g, Reaction temperature 80 °C, Reaction time: 8 h for succinate esters, 4 h for malonate esters)

Effect of mole ratio of acid /alcohol

It is seen from the figure 100 that, with change in mole ratio of acid to butanol, there is drastic change in the yields of products. Initially, the yield towards diester increases from 1:2 to 1:3 molar ratios. On further increasing the alcohol concentration equilibrium is attained and no further increase in % yield of diester was observed. Hence, 1:3 molar ratio of reactants i.e. acid/ alcohol was selected for the detail study.

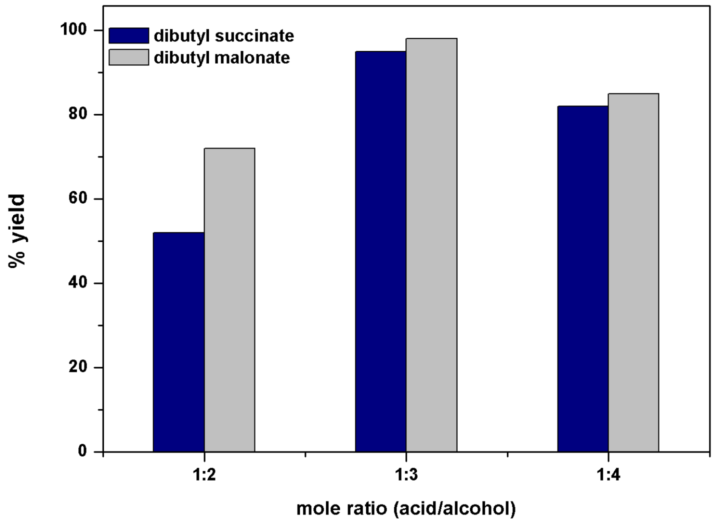


Figure 100. Effect of mole ratio of acid /alcohol; (Reaction conditions: Amount of catalyst: 0.1 g, Reaction temperature 80 °C, Reaction time: 8 h for succinate esters, 4 h for malonate esters)

Effect of amount of catalyst

To study the effect of the amount of the catalyst, the reaction was carried out with different amount of the catalyst keeping the mole ratio of acid to alcohol 1: 3 at 80 °C. As it is observed from Figure 101 that with increase in amount of catalyst % yield towards diester increases. With 0.1 g catalyst % yield towards diesters is maximum.

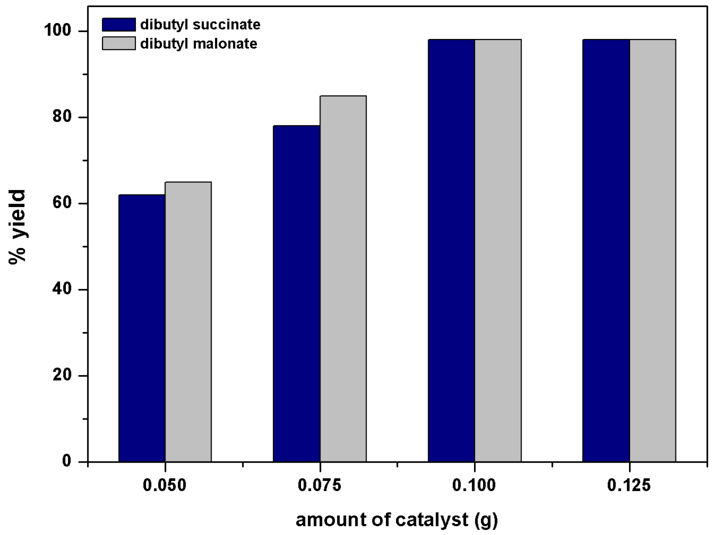


Figure 101. Effect of amount of catalyst; (Reaction conditions: Amount of catalyst: 0.1 g, Reaction temperature 80 °C, Reaction time: 8 h for succinate esters, 4 h for malonate esters)

Effect of reaction time

Effect of reaction time was studied. It was observed (Figure 102) that the % yields of diester's increases with increase in reaction time. After 4 h 80% yield of dibutyl malonate was achieved. After 14 h 90 % yield of dibutyl succinate was achieved.

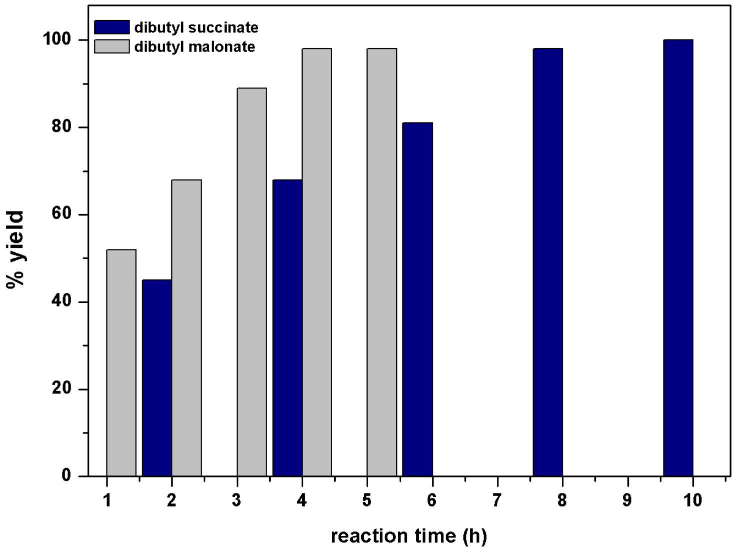


Figure 102. Effect of reaction time ;(Reaction conditions: mole ratio of acid/ alcohol: 1:3,Amount of catalyst: 0.1 g, Reaction temperature 80 °C, Reaction time: 8 h for succinate esters, 4 h for malonate estrers)

The optimized conditions for esterification of succinic acid and maolonic acid with n-butanol using TPA_3/SBA-15 are: Mole ratio of acid to alcohol 1:3; Amount of catalyst 0.1 g; Reaction Temperature 80 °C and Reaction Time 8 h and 4h for succinate esters and malonic acid respectively.

The control experiments with support, SBA-15 and TPA were also carried out under optimized conditions

Table 46. Control experiments for esterification of dicarbixylic acid (succinic acid and malonic acid) with butanol

^a^Material	%yield	
	dibutyl succinate	dibutyl malonate
SBA-15	<2	<5
[b]TPA	89	94
TPA_3/SBA-15	99	98

[a]Reaction conditions: mole ratio alcohol to acid 1:3, amount of catalyst 0.1 g, reaction temperature 80 °C, reaction time 8 and 4 h for succinate and malonate esters respectively
[b]amount of catalyst for TPA : 23 mg

It can be seen from Table 46 that support SBA-15 was not much active towards the esterification of succinic acid and malonic acid indicating the catalytic activity is mainly due to TPA. The same reaction was carried out by taking the active amount of TPA; 23 mg. It was found that the active catalyst TPA gives 89 and 94%yield for dibutyl succinate and dibutyl malonate respectively. Almost the same activity was obtained for the catalysts indicates that TPA is the real active species. Thus, we were successful in anchoring TPA to mesoporous support, SBA-15 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Esterification of dicarboxylic acids with different alcohols

The esterification of dicarboxylic acids (succinic acid/malonic acid) with different alcohols such as ethanol, hexanol and octanol was also carried out under optimized conditions and the % yields of corresponding esters are shown in the Figure 103.

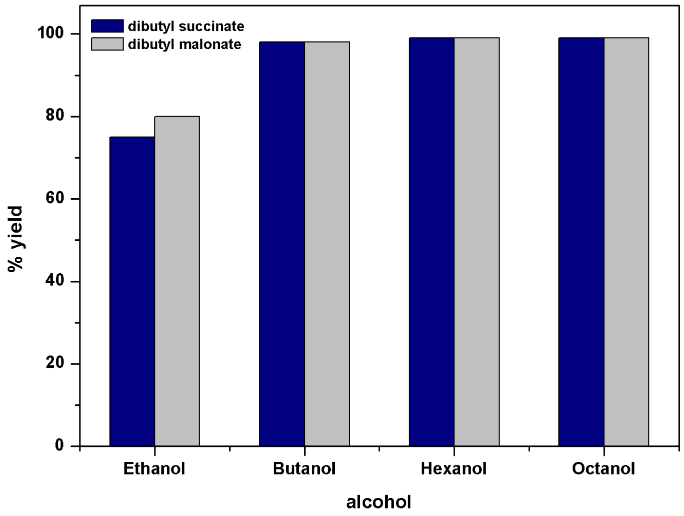


Figure 103. Esterification of dicarboxylic acid with different alcohols (Reaction conditions: Mole ratio of acid to alcohol; 1:3, Reaction temperature 80 °C, Reaction time: 8 and 4 h succinate esters and malonate esters respectively

It is very interesting observation that formation of malonate esters is easier than succinate esters over same catalyst. This may be due to the size of the reactants, malonic acid being C3 carbon molecule and succinic acid C4. Further malonic acid being smaller can easily reach inside the channels of the porous catalyst than Succinic acid being bigger facing considerable hindrance.

Regeneration and Recycling of the catalyst

Characterization of Regenerated Catalysts

In order to investigate the details of the deactivation, repeated use of the catalyst was examined. To see any change in the structure of catalyst after completion of reaction, the used catalysts were characterized for DRS, elemental analysis as well as acidity measurements.

Figure 104 illustrates the DRS of fresh catalyst as well as used catalysts. No difference in DRS indicates the stability of the used catalysts after the reaction. Further the filtrate of reaction mixture was also checked for the presence of any leached TPA by Uv-visible. The absence of blue colour indicates no leaching of TPA.

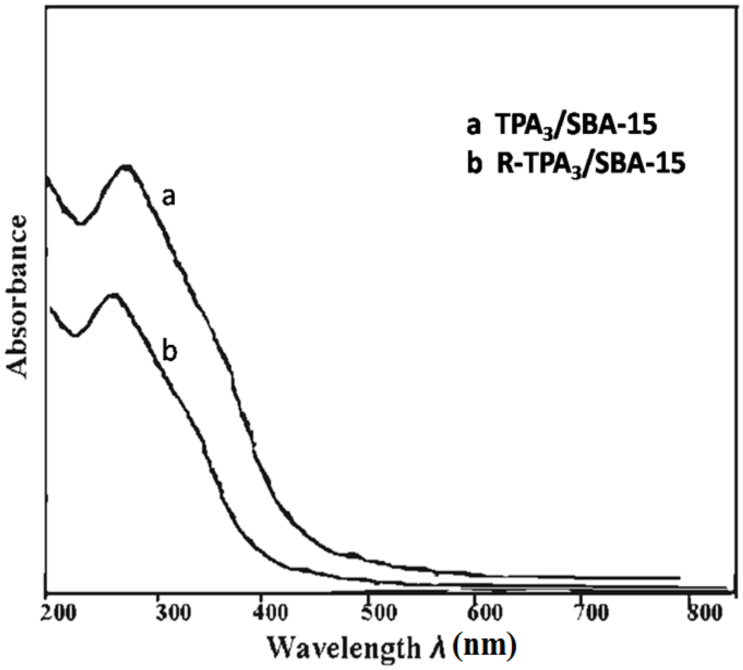


Figure 104. DRS spectra of fresh and recycled catalyst

Leaching as well as Heterogeneity Test

Any leaching of the active species from the support makes the catalyst unattractive and hence it is necessary to study the stability as well as leaching of TPA from the support. Rigorous proof of heterogeneity can be obtained only by filtering the catalysts at the reaction temperature before completion of the reaction and testing the filtrate for activity [1].

The leaching of W from catalyst was confirmed by carrying out an analysis of the used catalyst (EDX) as well as the product mixtures (AAS). Analysis of the product mixtures shows that if any W was present it was below the detection limit, which corresponds to less than 1 ppm. These observations strongly suggest no leaching of any active species, TPA, form the support, SBA-15.

For the rigorous proof of heterogeneity, a test was carried out by filtering the catalysts from the reaction mixture at 80 ◦C after 4 h and the filtrate was allowed to react up to 6 h. The reaction mixture of 4 h and the filtrates were analyzed by Gas Chromatogram. From the heterogeneity test it was found that there was no change in the % yield of esters, indicating the present catalyst fall into category C [1]. On the basis of these results, it can be concluded that there is no leaching of TPA species from the support, SBA-15 and the present catalyst is truly heterogeneous in nature.

The EDS analysis and the acidity of the fresh as well as the reused catalyst was carried out and the obtained results are shown in table 47.The elemental analysis values of the recycled catalysts were close to that for fresh catalysts. Further the total acidity values of reused catalysts were almost the same as compared to the fresh catalysts. Hence there is no deactivation of catalyst. This also confirms the truly heterogeneous mode of action.

Table 47. Elemental analysis (EDS) and acidity characterization of reused catalysts

Catalyst	Elemental analysis (weight %)						Total acidity (mmol/g)
	O	Si	W		P		
			By EDS	Theoretical	By EDS	Theoretical	
TPA_3/SBA-15	53.93	27.8	17.97	19	0.30	0.32	1.82
R-TPA_3/SBA-15	53.9	27.9	17.8	19	0.30	0.32	1.80

Catalytic activity of regenerated catalysts

The catalyst was recycled for four times in order to test its activity as well as stability. The catalyst was separated from the reaction mixture by simple filtration, washed with double distilled water till the filtrate was free from the unreacted succinic acid/malonic acid, if any, dried at 100 °C and the recovered catalysts were charged for the further run. The obtained results are as shown in figure 105. It is seen from the table that the catalysts can be used up to four cycles without any appreciable change in the percentage yield.

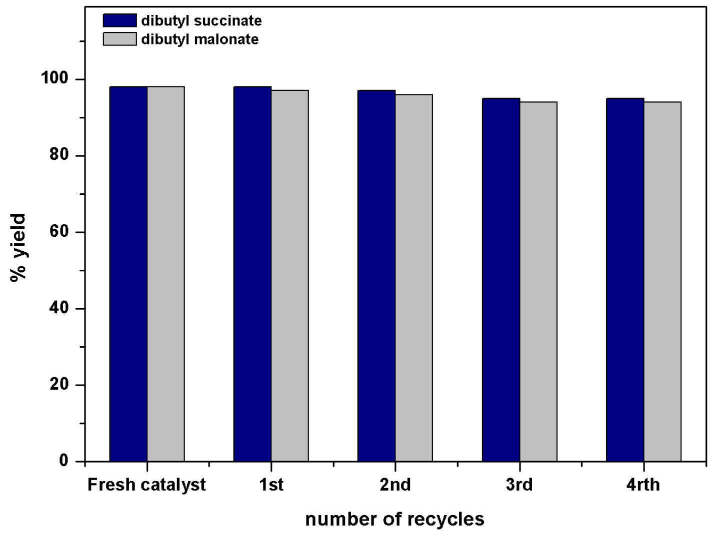


Figure 105. Recycling of the catalyst ;(Reaction conditions: mole ratio of acid/ alcohol: 1:3,Amount of catalyst: 0.1g, Reaction temperature 80 °C, Reaction time: 8 h for succinate esters, 4 h for malonate esters)

(b) Esterification of fatty acid (Lauric acid)

Experimental

Materials

All chemicals used were of A.R. grade. Lauric acid and n-butanol were used as received from Merck.

Catalytic reaction

The esterification of lauric acid with alcohols were carried out in a 50 mL batch reactor provided with a double walled air condenser, Dean–Stark apparatus, magnetic stirrer and a guard tube. Dean–Stark apparatus was attached to a round bottom flask to separate the water formed during the reaction. The reaction mixture was refluxed at 90°C for 4 h. The obtained products were analyzed on a Gas Chromatograph (Nucon-5700) using BP1 capillary column. Products were identified by comparison with the authentic samples and finally by Gas Chromatography–Mass Spectroscopy (GC–MS). TON and TOF were also calculated as mentioned earlier.

RESULTS AND DISCUSSION

The esterification of fatty acid is an equilibrium-limited reaction. In order to overcome the equilibrium limitation, generally esterification of fatty acids is carried out by taking alcohol in excess in order to favor the forward reaction. In the present case butanol was taken in excess for economic reasons. The esterification of lauric acid with alcohol is shown in figure 106.

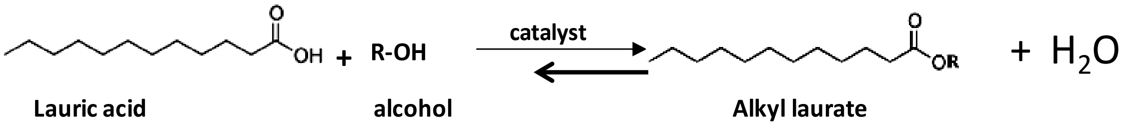


Figure 106. Esterification of lauric acid with alcohol

The effect of various reaction parameters such as % loading of TPA, acid/ alcohol molar ratio, amount of catalyst and reaction time were studied to optimize the conditions for maximum conversion of lauric acid.

Effect of % loading of TPA

The esterification reaction was carried out with 10, 20, 30 and 40% loadings of TPA. The obtained results are shown in Figure 107. It is observed from the figure 107 that with increase in the % loading of TPA onto SBA-15, conversion also increases. For 30 and 40 % loadings, the difference in yield is not that much appreciable. Hence $TPA_3/SBA\text{-}15$ was used for the detail study.

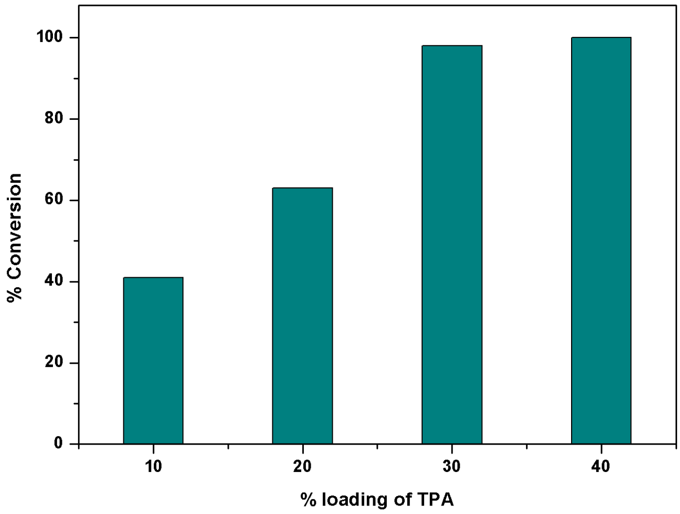


Figure 107. Effect of % loading of TPA; (reaction conditions: mole ratio of acid to alcohol 1:2, amount of catalyst 0.2 g, reaction temperature 90 °C, reaction time 2 h)

Effect of Mole ratio

The reaction was carried out by varying mole ratio of lauric acid to n-butanol , with 0.2 g of the catalyst for 4 h at 90 ^{0}C. It is observed that with increase in concentration of alcohol % conversion of lauric acid increases (figure 108). With 1:2 mole ratio of lauric acid to n-butanol maximum conversions up to 99 was achieved. With further increase in n-butanol concentration not much difference was observed. Hence, further reactions were carried out in 1:2 molar ratio of acid to alcohol.

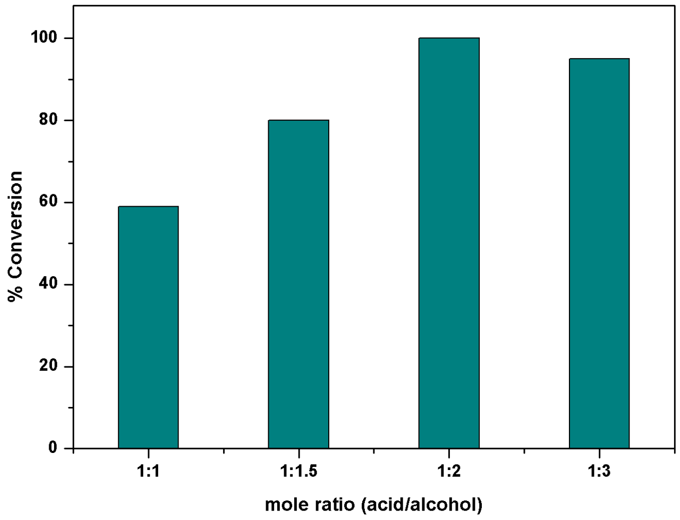


Figure 108. Effect of Mole ratio of acid/alcohol; (Reaction conditions; amount of catalyst 0.2 g, reaction temperature 90 °C, reaction time 2 h)

Effect of amount of catalyst

To study the effect of the amount of the catalyst, the reaction was carried out with different amount of the catalyst keeping the mole ratio of acid to alcohol 1:2 for 4 h at 90 °C. The observed conversions of lauric acid are reported in Figure 109. It is seen from the figure that initially the % conversion increases with an increase in the amount of the catalyst. On further increase with the amount from 0.25 to 0.25 g of the catalyst, maximum conversion of lauric acid was achieved. The effect of the amount of the catalyst was studied keeping all other parameters (temperature, reaction time, mole ratio of alcohol to acid) constant. Under these conditions, no increase in the % conversion with increase in amount of catalyst indicates the attainment of the maximum equilibrium. The obtained results are as expected. Hence, 0.2 g is the optimized amount of the catalyst.

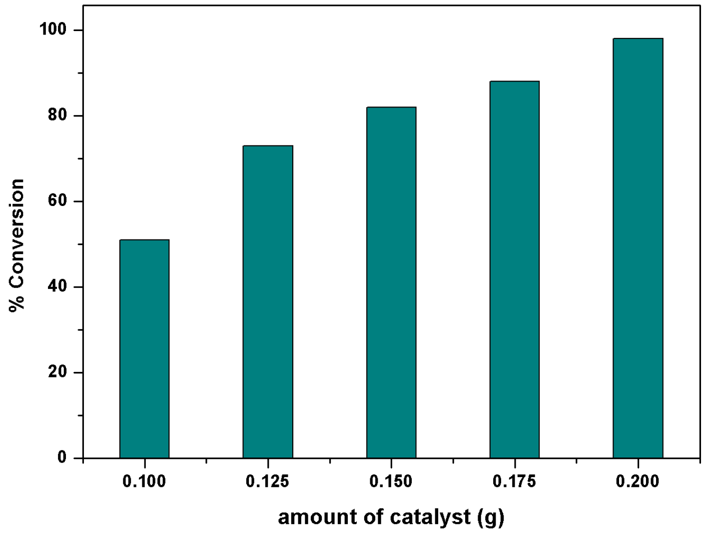


Figure 109. Effect of amount of catalyst; (Reaction conditions; acid to alcohol Mole ratio of acid /alcohol 1:2, reaction temperature 90 °C, reaction time 2 h)

Effect of reaction time

With increase in reaction time the % conversion of lauric acid increases (figure 110). Up to two hours maximum conversion was achieved. Further it does not increase with time.

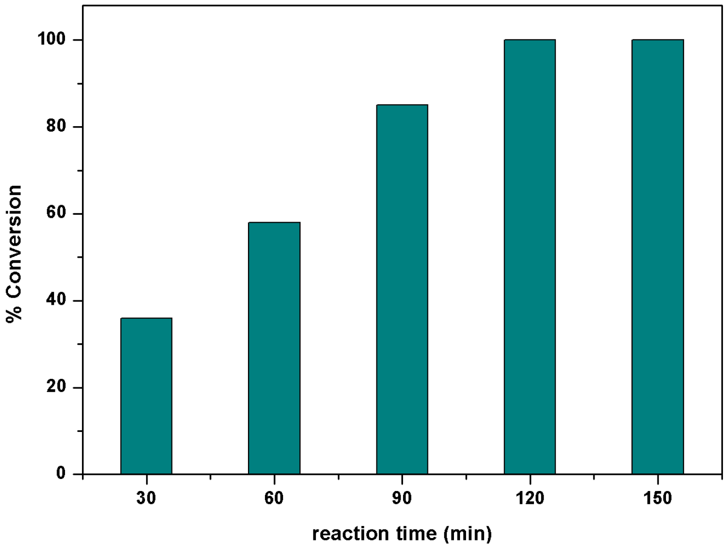


Figure 110. Effect of reaction time; (Reaction conditions; amount of catalyst 0.2 g, acid to alcohol mole ratio 1:2, reaction temperature 90 °C)

Effect of reaction temperature

With increase in reaction temperature % conversion of lauric acid increases (figure 111). At 90 ^{0}C maximum yield was obtained.

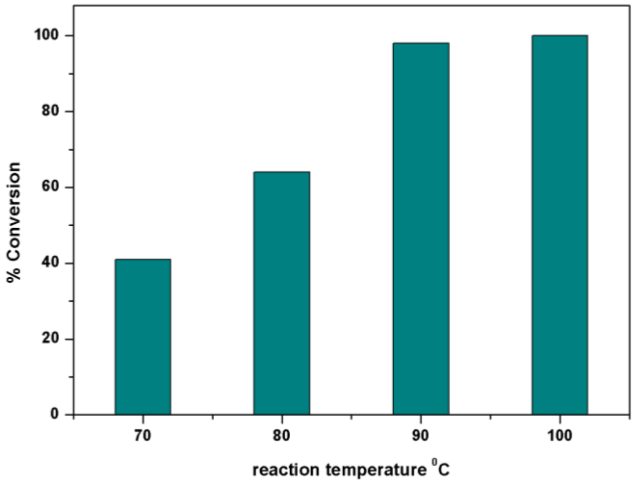


Figure 111. Effect of reaction temperature; (Reaction conditions; amount of catalyst 0.2 g, acid to alcohol mole ratio 1:2, reaction time 2 h)

The optimum conditions for esterification of lauric acid using TPA_3/SBA-15 are: Mole ratio of acid to alcohol 1:2; Amount of catalyst 0.2 g; Reaction Temperature 90 ^{0}C and Reaction Time 2 h.

The control experiments with support, SBA-15 and TPA were also carried out under optimized conditions

Table 48. Control Experiments for esterification of lauric acid

[a]Material	% Conversion
[b]TPA	92
SBA-15	<2
TPA_3/SBA-15	99

[a]Reaction conditions: acid to alcohol Mole ratio of acid /alcohol 1:2, reaction temperature 90 ^{o}C, reaction time 2 h; [b]amount of catalyst for TPA: 46 mg

It can be seen from Table 48 that support SBA-15 was not much active towards the esterification of lauric acid indicating the catalytic activity is mainly due to TPA. The same reaction was carried out by taking the active amount of TPA 46 mg. It was found that the active catalyst, TPA gives 92%conversion. Almost the same activity was obtained for the catalyst indicates that TPA is the real active species. Thus, we were successful in anchoring TPA to mesoporous support, SBA-15 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Regeneration and Recycling of the catalyst

Characterization of Regenerated catalysts

The regenerated catalysts were characterized for DRS, elemental analysis (EDS), acidity measurements, leaching as well as heterogeneity test, in order to confirm the retention of the catalyst structure, after the completion of the reaction as discussed earlier. The results are same and hence are not included.

Catalytic activity of regenerated catalysts

The catalysts were recycled in order to test its activity as well as stability. The catalyst was separated from the reaction mixture only by simple filtration, washed with conductivity water till the filtrate is free from the acid dried at 100 ^{0}C and the recovered catalyst was charged for the further run. There is no appreciable change in the %conversion using regenerated catalysts up to four cycles (Figure 112).

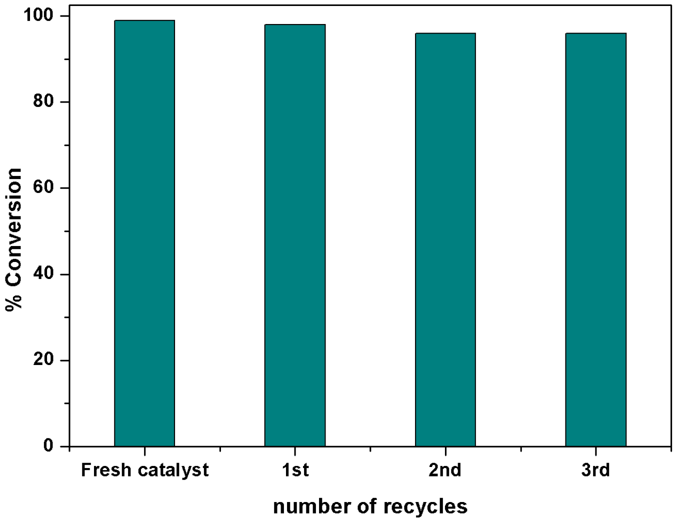


Figure 112. Recycling of the catalyst; (reaction conditions: mole ratio of acid to alcohol 1:2, amount of catalyst 0.2 g, reaction temperature 90 ^{o}C, reaction time 2 h)

Kinetics

A detail study on kinetic behavior for esterification of lauric acid with 1-butanol was carried out over $TPA_3/SBA-15$. In all the experiments, reaction mixtures were analyzed at fixed intervals at fixed intervals of time using gas chromatography.

The figure 113 shows second order plot for esterification of lauric acid. The linearity of the data indicates the validity of second order rate law.

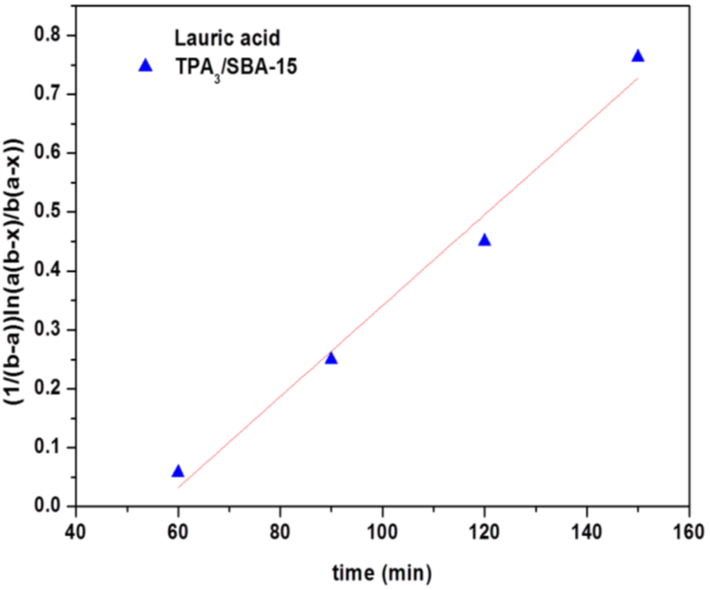


Figure 113. Second order plot for esterification of lauric acid with butanol

The increase in catalyst concentration shows noticeable effect on % conversion of lauric acid. This can be attributed to higher number of substrate molecules get activated in presence of catalyst. Thus the nucleophilic attack by 1-butanol becomes more favorable and consequently, an increase in the formation of ester was observed. The linearity of data obtained indicates second order dependence (figure 114) with respect to catalyst concentration

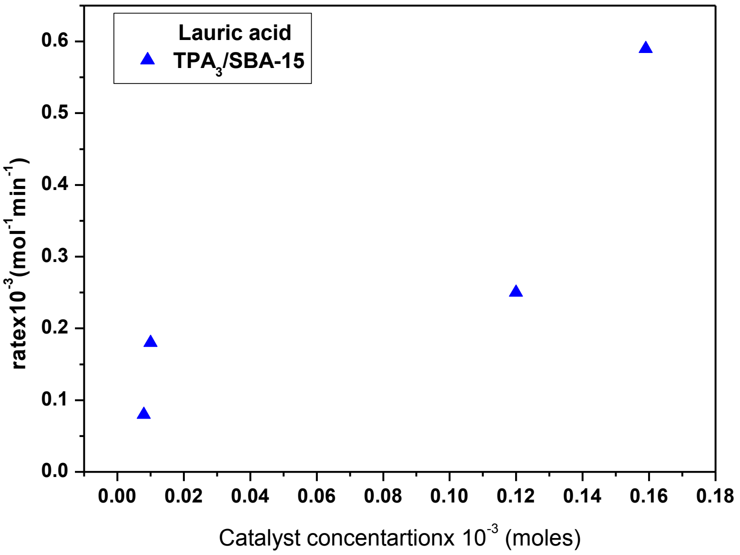


Figure 114. Plot of reaction rate vs catalyst concentration

Determination of Activation Energy

It was verified that temperature affects both reaction rate and yields. With increase in temperature higher yields were achieved. The increase in reaction temperature caused corresponding increase in the reaction rate, especially in the range of 343-373 K. From this data Arrhenius plot was constructed and from the obtained curve pre-exponential factor (A) and activation energy (Ea) for this reaction was calculated (figure 115).

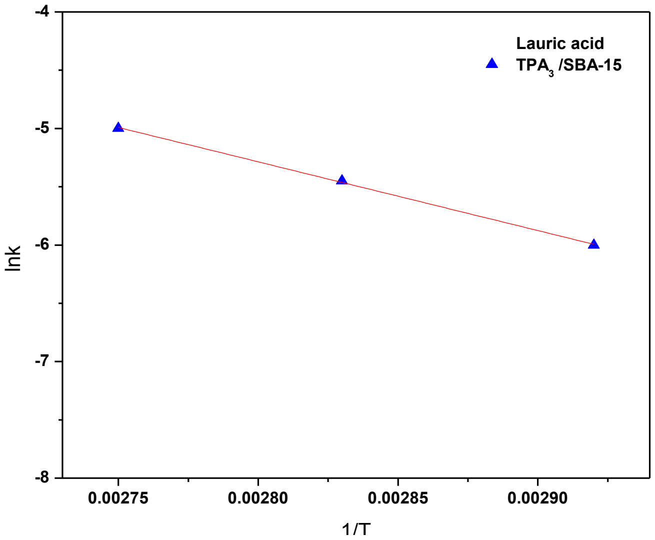


Figure 115. Arrhenius plot for esterification of lauric acid with n-butanol

The pre-exponential factor (A) and activation energy (Ea) was found to be 11.72 $mol^{-1}min^{-1}$ and 50.5 $kJmol^{-1}$ respectively. The rate constant (k′) for esterification reaction of lauric acid with butanol was found to be $6.75x10^{-3}$ $mol^{-1}min^{-1}$.

It is important to recognize that the whether the reaction rate is diffusion limited/mass transfer limited or it is truly governed by the chemical step where the catalyst is being used to its maximum capacity. It is reported that the activation energy for diffusion limited reactions is as low as 10-15 $KJmol^{-1}$ and for reactions whose rate is governed by a truly chemical step usually show activation energy excess of 25 $kJmol^{-1}$ [2]. In the present case the observed activation energy is 50.5 $kJmol^{-1}$ and hence the rate is truly governed by chemical step.

II. Applications in Biodiesel production

(a) Esterification of free fatty acids (Palmitic acid& oleic acid)

Experimental

Materials

All chemicals used were of A. R. grade. Palmitic acid, oleic acid methanol, , were obtained from Merck and used as received.

Catalytic reaction

The esterification of palmitic acid and oleic acid with methanol was carried out in a 100ml batch reactor provided with a double walled air condenser, Dean–Stark apparatus, magnetic stirrer and a guard tube. Dean–Stark apparatus was attached to a round bottom flask to separate the water formed during the reaction. The reaction mixture was refluxed at 60°C for 6hrs. The obtained products were analyzed on a Gas Chromatograph (Nucon-5700) using BP1 capillary column. Products were identified by comparison with the authentic samples and finally by Gas Chromatography–Mass Spectroscopy (GC–MS). TON and TOF were also calculated as mentioned earlier.

RESULTS AND DISCUSSION

The esterification of free fatty acids is an equilibrium-limited reaction. In order to overcome the equilibrium limitation, generally esterification of free fatty acids is carried out by taking alcohol in excess in order to favour the forward reaction. The esterification of palmitic cid with methanol is shown in figure 116.

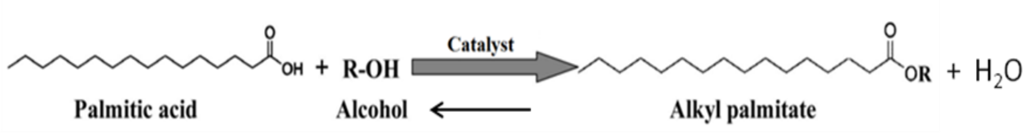


Figure 116. Esterification of palmitic acid acid with methanol

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

Effect of % loading of TPA

To study the effect of % loading of TPA esterification reaction was carried out with 10, 20, 30 and 40% loadings of TPA. The obtained results are shown in Figure 117. It is observed from the figure that with increase in the % loading of TPA, % conversion also increases. For 30 and 40% loadings, the difference in % conversion is not that much appreciable. Hence the catalyst containing 30% loading of TPA i.e. TPA_3/SBA-15 was selected to carry out detailed studies.s

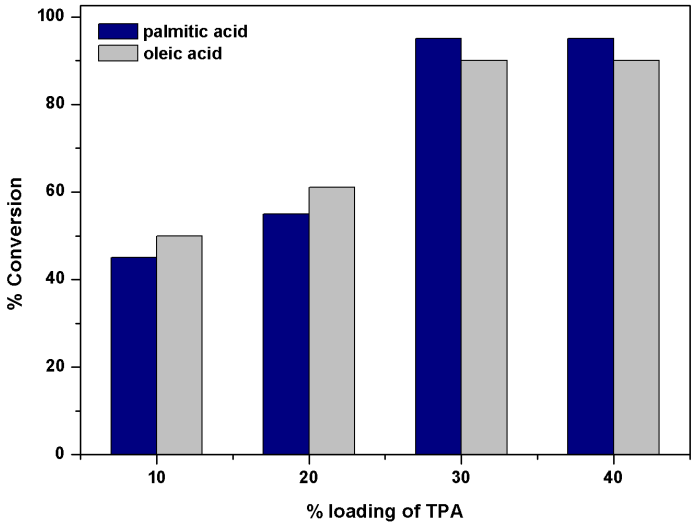


Figure 117. Effect of % loading of TPA; Reaction conditions: mole ratio of acid to alcohol; 1:40, amount of catalyst 0.1g, reaction temperature 60°C, reaction time 4h

The difference in the catalytic activity in terms of TOF could be explained by correlating with surface area and total acidity by taking oleic acid esterification as an illustration (table 49). As the TPA loading increases surface area decreases as expected. On the other hand acidity increases with increase in TPA loading which is also expected. The value of total acidity is directly related to the concentration of active species, TPA. Hence increase in total acidity with increase in % loading of TPA is obvious. Knowledge of the TOF allows a direct comparison of the catalytic activity of different catalysts. There was a direct correlation between TOF and total acidity of catalysts. As shown in table 3 as total acidity increases TOF also increases from TPA_1/SBA-15 to TPA_3/SBA-15. For TPA_3/SBA-15 and TPA_4/SBA-15 the % conversion is almost the same (figure 117) and as the number of moles of active species, TPA for later is greater than the former, the decrease in TOF is as expected for TPA_4/SBA-15 catalyst. TPA_3/SBA-15 shows maximum TOF, and hence the most efficient catalyst among the series. Therefore the catalyst containing 30% loading of TPA i.e. TPA_3/SBA-15 was selected for the detail study.

Table 49. Total acidity, surface area, TON and TOF

Catalyst	Surface area(m^2/g)	Total acidity (mmol/g)	TON	TOF(min^{-1})
SBA-15	834	1.11	-	-
TPA_1/SBA-15	784	1.62	1968	8.2
TPA_2/SBA-15	746	1.74	2040	8.5
TPA_3/SBA-15	714	1.82	2232	9.3
TPA_4/SBA-15	699	1.88	1848	7.7

Effect of molar ratio of acid to alcohol

To see the effect of mole ratio the reaction was carried out by varying mole ratio of palmitic and oleic acid to methanol, with 0.1 g of the catalyst for 4 h at 40 °C. It can be observed from figure 118 that the conversion increases with increase acid/ methanol ratio and reaches maximum 95 and 90% for palmitic acid and oleic acid respectively at oleic acid/methanol 1:40. With further increase in molar ratio, increase in conversion was not that much appreciable. Hence molar ratio of 1:40 was selected for obtaining high conversions.

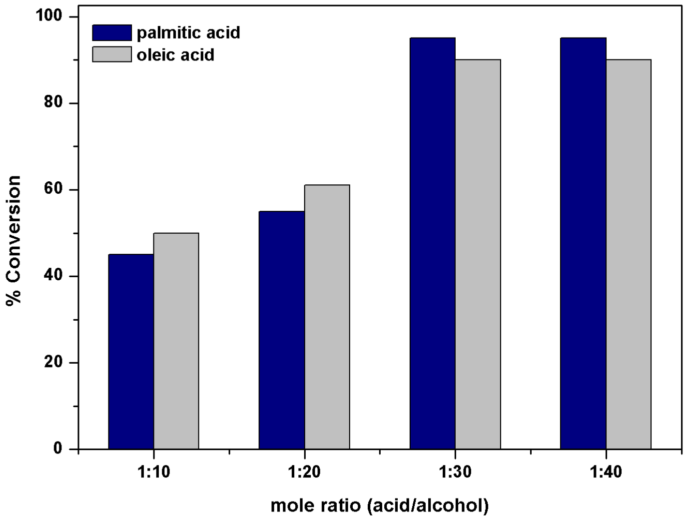


Figure 118. Effect of molar ratio; Reaction conditions: amount of catalyst 0.1 g, reaction temperature 60 °C, reaction time 4 h.

Effect of amount of catalyst

Effect of amount of catalyst on palmitic and oleic acid conversion was investigated. The catalyst amount was varied in the range of 25-150 mg. As shown in figure 119, with increase in amount of catalyst, conversion of oleic acid also increases. The maximum conversion obtained was 90% with 0.1 g of catalyst.

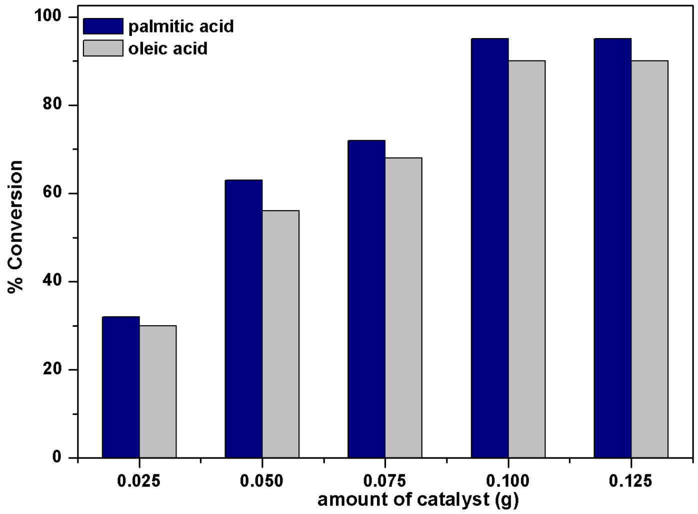


Figure 119. Effect of amount of catalyst; Reaction conditions: mole ratio of acid to alcohol; 1:40, reaction temperature 60 °C, reaction time 4 h

Effect of reaction time

Effect of reaction time on conversion of palmitic and oleic acid was studied. It was observed (Figure 120) that the conversion increases with increase in reaction time. After 4 h, 95 and 90% palmitic acid and oleic acid conversion was achieved respectively.

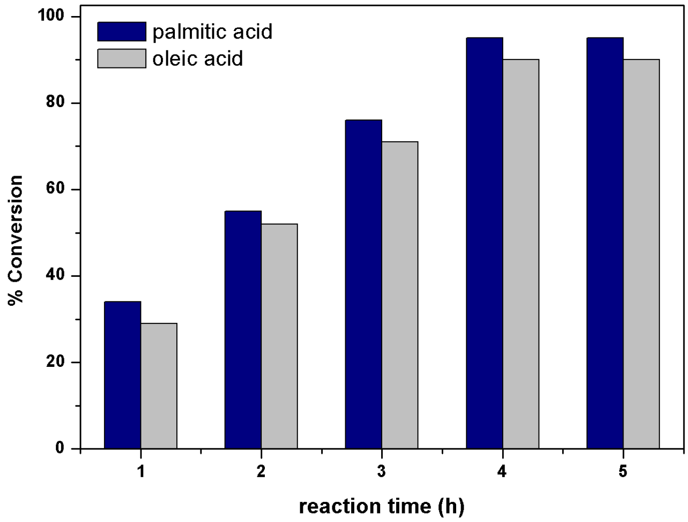


Figure 120. Effect of reaction time, Reaction conditions: mole ratio of acid to alcohol; 1:40, amount of catalyst 0.1 g, reaction temperature 60 °C

Effect of reaction temperature

Effect of reaction temperature on palmitic and oleic acid conversion was studied and it was found that with as the reaction temperature increases conversion of also increases (figure 121). At high temperature high conversion was achieved. However the lower temperature i.e. 40 ^{0}C was selected for esterification of palmitic and oleic acid.

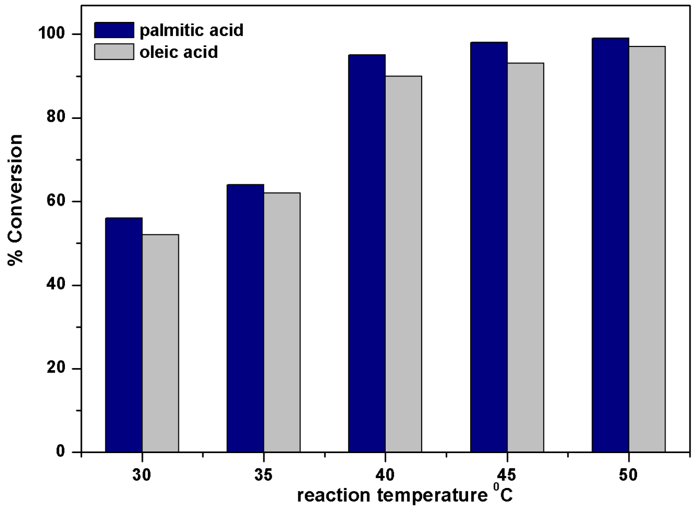


Figure 121. Effect of reaction temperature; Reaction conditions: mole ratio of acid to alcohol; 1:40, amount of catalyst 0.1 g, , reaction time 4 h

The optimized conditions for esterification of palmitic acid and oleic acid over $TPA_3/SBA-15$ are: Mole ratio of acid to alcohol 1: 40; Amount of catalyst 0.1 g; Reaction Temperature 40 °C and Reaction Time 4 h.

The control experiments with SBA-15 and TPA were also carried out under optimized conditions.

Table 50. Control Experiments for esterification of palmitic and oleic acid

[a]Catalysts	%conversion	
	Palmitic acid	Oleic acid
SBA-15	<2	<2
TPA	94	92
$TPA_3/SBA-15$	95	90

[a]Reaction conditions: amount of catalyst for SBA-15:0.1g,TPA :23mg, and $TPA_3/SBA-15$:0.1g; mole ration oleic acid to alcohol 1:40; reaction temperature40 °C; reaction time 4h

It can be seen from Table 50 that SBA-15 is not much active towards the esterification of oleic acid indicating the catalytic activity is mainly due to TPA. The same reaction was carried out by taking the active amount of TPA (23 mg). It was found that the active catalyst gives 92% conversion. Almost the same activity was obtained for $TPA_3/SBA-15$ catalyst indicates that TPA is the real active species. Thus, we were successful in anchoring TPA on SBA-15 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Regeneration and Recycling of the catalyst

Characterization of Regenerated catalysts

The regenerated catalysts were characterized for DRS, elemental analysis (EDS) and leaching as well as heterogeneity test in order to confirm the retention of the catalyst structure, after the completion of the reaction as discussed earlier. The results are same and hence are not included.

Catalytic activity of regenerated catalysts

The catalyst was recycled in order to test its activity as well as stability. The catalyst, TPA_3/SBA-15, was separated from the reaction mixture only by simple filtration, first washed with methanol till the filtrate is free from the acid (unreacted palmitic or oleic acid if any), followed by distilled water and then dried at 100 ^{0}C and the recovered catalyst was charged for the further run. There is no appreciable change in the % conversion of oleic acid using regenerated catalyst up to four cycles (Figure 122).

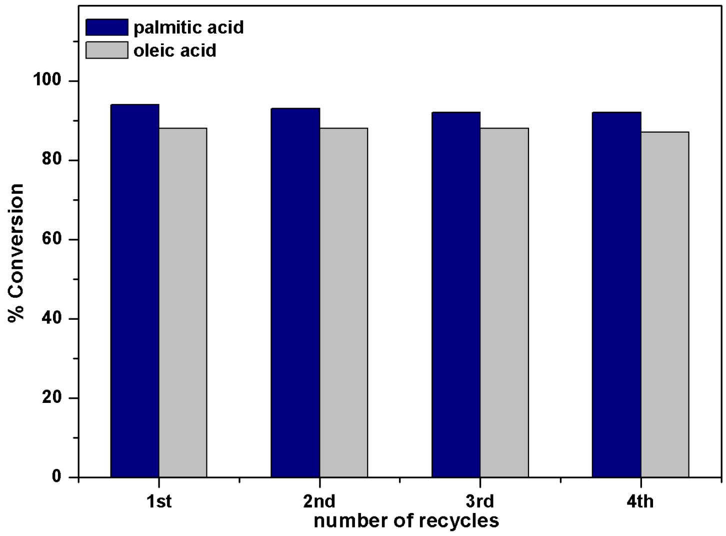


Figure 122. Recycling of the catalyst; Reaction conditions: mole ratio of acid to alcohol ; 1:40, amount of catalyst 0.1g, reaction temperature 60^{o}C, reaction time 4h

Kinetics

A detailed study on the kinetic behaviour was carried out for esterification of Oleic acid over $TPA_3/SBA-15$. In all the experiments, reaction mixtures were analyzed at fixed interval of time using gas chromatography.

Determination of Order as well as Rate of Reaction

It is well known that if one of the reactant in taken in large excess, that is concentration of any one reactant is very high, then rate of reaction depends on concentration of the reactant which is taken in lower concentration, in the present case oleic acid**.** The esterification of oleic acid with methanol was carried in 1:40 molar ratio, since methanol was taken in large excess, the rate law it is expected to follow first order dependence.

The plot of ln C/C_o *vs.* time (Figure 123) shows a linear relationship of substrate consumption with respect to time. With increase in reaction time there is a gradual and linear decrease in the substrate concentration over $TPA_3/SBA-15$ catalyst. These observations indicate the esterification of palmitic and oleic acid follows first order dependence with respect to the concentration of oleic acid.

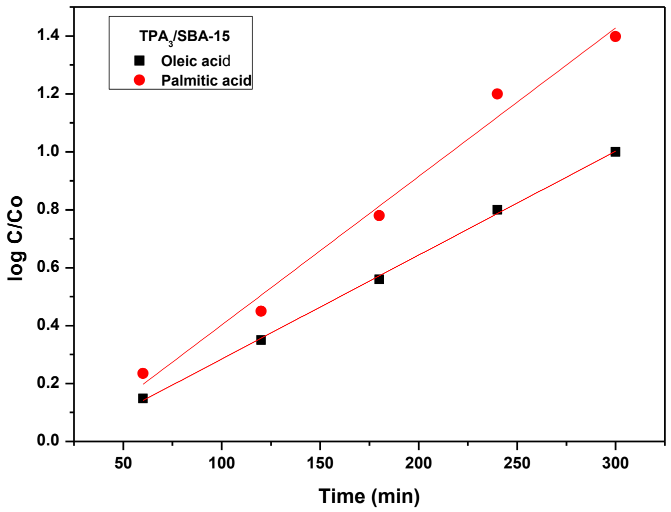


Figure 123. First order plot for esterification of palmitic acid and oleic acid

The effect of catalyst concentration on reaction rate was also studied. The catalyst concentration was varied form 2 x 10^{-3} to 10 x 10^{-3} mmol at fixed substrate concentration of 10 mmol and at temperature 40°C. It can be observed from the figure 9 that rate of reaction increases with increase in the catalyst concentration. The plot of rate constant vs. catalyst concentration (Figure 124) also shows a linear relationship for TPA_3/SBA-15 catalyst.

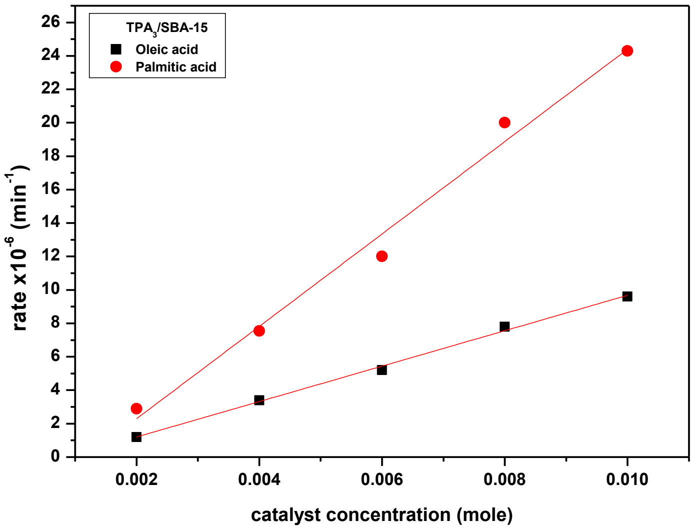


Figure 124. Plot of reaction rate vs catalyst concentrations

Estimation of activation energy

The graph of ln *k* vs. 1/T was plotted (Figure 125) and the value of activation energy (E_a) was determined from the plot. The value of activation energy (E_a), the pre-exponential factor (A) was determined using Arrhenius Equation.

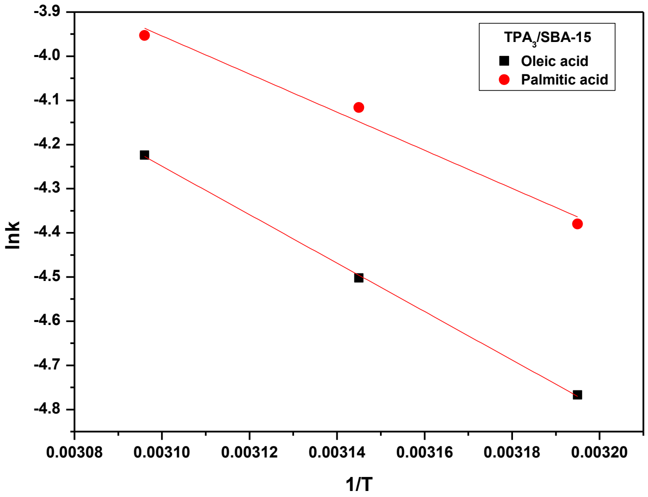


Figure 125. Arrhenius Plots for determination of activation energy

The kinetic parameters such as rate constant (k) , pre- exponential factor (A) and activation energy (Ea) for esterification reaction of palmitic and oleic acid are presented in Table 51.

Table 51. Kinetic parameters Esterification of free fatty acids

Catalyst	Free fatty acid	Kinetic parameters		
		Rate constant (min^{-1})	Arrhenius constant (A) (min^{-1})	Activation energy (k $Jmol^{-1}$)
TPA_3/SBA-15	Palmitic acid	11.9×10^{-3}	9.4	35.11
	Oleic acid	8.7×10^{-3}	12.75	44.6

It is important to recognize that whether the reaction rate is diffusion limited/mass transfer limited or it is truly governed by the chemical step where the catalyst is being used to its maximum capacity. It is reported that the activation energy for diffusion limited reactions is as low as 10-15 $kJmol^{-1}$ and for reactions whose rate is governed by a truly chemical step usually show activation energy excess of 25 $kJmol^{-1}$ [2]. In the present case the observed values activation energy are higher than 25 $kJmol^{-1}$ and hence the rate is truly governed by chemical step.

(b)Transesterification of triglycerides: Waste cooking oil and Jatropha oil

Experimental

Materials

All chemicals used were of A. R. grade. Methanol and KOH were obtained from Merck and used as received.

Transesterification reaction

The properties of waste cooking oil and jatropha oil are as follows: acid value of waste cooking oil and jatropha oil was 49 and 37 mg KOH/g respectively. Free fatty acid content of waste cooking oil and jatropha oil was 24.5 and 18.5 respectively. The typical reaction of transesterification was carried out in a 100 ml batch reactor, provided with thermometer, mechanical stirring and condenser. Waste cooking oil and methanol were added in 1:8 wt/wt ratios and followed by catalyst addition, and then reaction mixture was held at 65^0C for 8h with stirring in order to keep system uniform in temperature and suspension. After the reaction is completed, the mixture was rotary evaporated at 50 ^{0}C to separate the methyl esters. The conversion of FFA in the WCO to biodiesel was calculated by means of the acid value (AV) of the oil layer with the following equation [3]

$$\text{Conversion (\%)} = \left(1 - \frac{AV_{OL}}{AV_{WCO}}\right)$$

Where OL and WCO refer to oil layer and waste cooking oil respectively.

RESULTS AND DISCUSSION

Transesterification of triglycerides (TGs) with low molecular weight alcohols (figure 126) produces biodiesel. Jatropha oil (JO) is non-edible and does not compromise the edible oil, which are mainly used for food consumption. Non-edible oils are not suitable for human consumption because of the presence of toxic components. Further, *Jatropha* seed has a high content of oil and the biodiesel produced has similar properties to that of petroleum-based diesel. An interesting alternative for low cost biodiesel production is the utilization of low quality raw materials as feedstocks such as waste cooking oil (WCO) obtained from canteens restaurants and from houses which are rich in free fatty acids. Waste cooking oil used was a vegetable oil, obtained as waste from household activities.

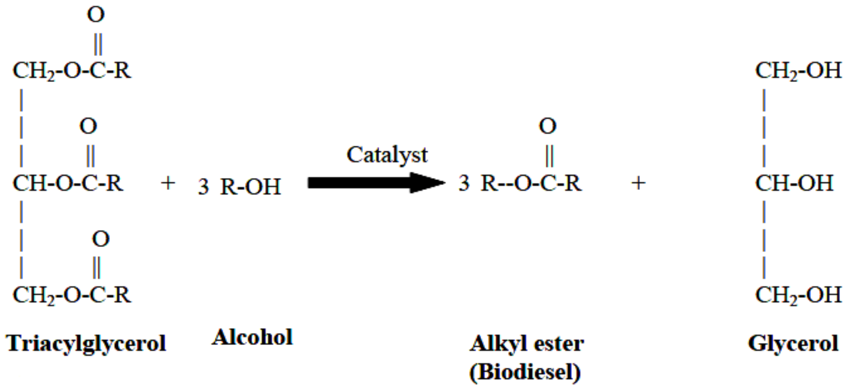


Figure 126. Transesterification of triglycerides with methanol

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

Effect of % loading of TPA

To study the effect of % loading of TPA esterification reaction was carried out with 10, 20, 30 and 40 % loadings of TPA. The obtained results are shown in Figure 127. It is observed from the figure that with increase in the % loading of TPA, % conversion also increases. For 30 and 40 % loadings, the difference in % conversion is not that much appreciable. Hence TPA_3/SBA-15 was selected for carrying out detailed study.

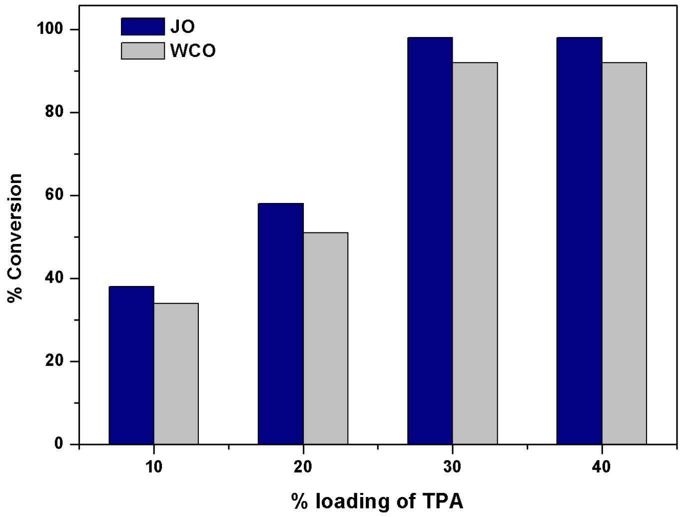


Figure 127. Effect of % loading of TPA; Reaction condition: mole ratio oil to alcohol 1:8, amount of catalyst 0.3 g, reaction temperature 65 °C, reaction time 6 h

Effect of mole ratio

An important variable which can effect on the yields of methyl ester is the molar ratio of oil to alcohol. The reaction stoichiometry requires three moles of alcohol per mole of triglyceride to yield three moles of fatty esters and one mole of glycerin. But in practice a higher alcohol/oil ratio is employed in order to obtain a higher yield of ester production. We selected molars ratio of oil to methanol (wt/wt) between 1:2 and 1:8 (Figure 128). The molar ratio 1:8 is suitable for obtaining high yields of products as summarized in Figure 128. It was observed that oil conversion increased with the increases of the oil/methanol ratio and reached a maximum at 1: 8; with a ratio of less than 1:8 the reaction was incomplete. When the oil/methanol ratio was higher than 1:8, the conversion decreased. So the molar ratio 1:8 is suitable for obtaining higher conversions.

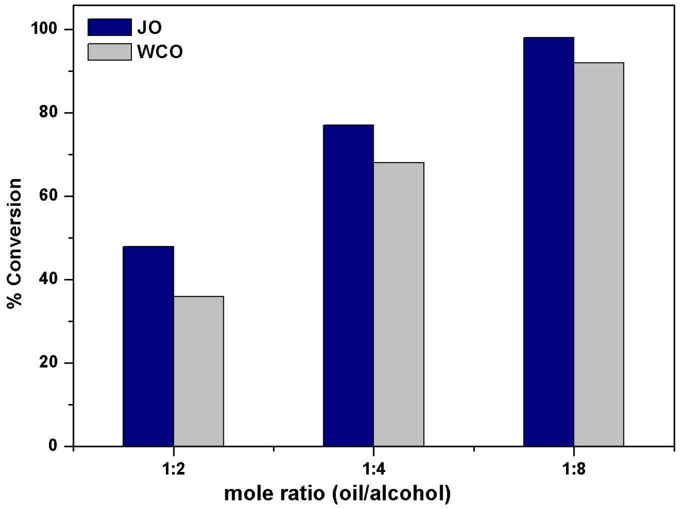


Figure 128. **Effect of mole ratio of oil/alcohol; Reaction condition: amount of catalyst 0.3 g, reaction temperature 65 ^{o}C, reaction time 6 h**

Effect of amount of catalyst

The effect of the catalyst amount on the oil conversion is shown in Figure 129. Experiments were carried out by varying the amount of the catalyst between 0.1 to 0.5 g keeping the oil to methanol ratio at 1:8 at 65 ^{o}C. It was observed that an increase in the conversion of oil was noticed when the amount of the TPA_3/SBA-15 increased from 0.1g to 0.3 g and acid-catalyzed process attains a maximum conversion at 0.3 g 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 from 0.3 to 0.5 g, decrease in the oil conversion was observed which may be due to the blocking of active sites.

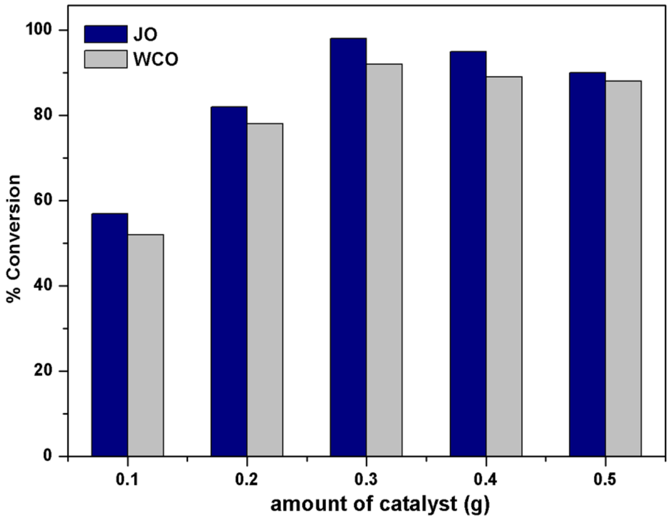


Figure 129. Effect of amount catalyst; Reaction condition: mole ratio oil to alcohol 1:8, reaction temperature 65 °C, reaction time 6 h

Effect of reaction time

Effect of reaction time on conversion of triglycerides was studied. It was observed (Figure 130) that the conversion increases with increase in reaction time. After 6 hours maximum 92% and 88% conversion was achieved for jatropha oil and waste cooking oil respectively.

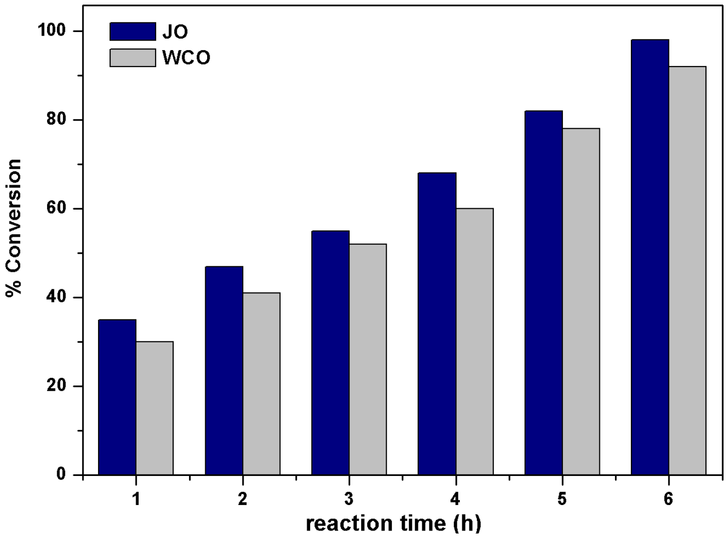


Figure 130. Effect of reaction time; Reaction condition: mole ratio oil to alcohol 1:8, amount of catalyst 0.3 g, reaction temperature 65 °C

Effect of reaction temperature

Methanolysis of oils is normally performed near the boiling point of the alcohol. Effect of reaction temperature on conversion was studied and it was found that with as the reaction temperature increases conversion also increases (figure 131). At 65 ^{0}C maximum 92% and 88% conversion was achieved for jatropha oil and waster cooking oil respectively. But with further increasing the temperature up to 70 ^{0}C, % conversion decreases. Usually the increase in reaction temperature, should lead to usual increase of reaction extent but also it could cause acceleration of secondary reactions which reduce the conversion towards desired product.

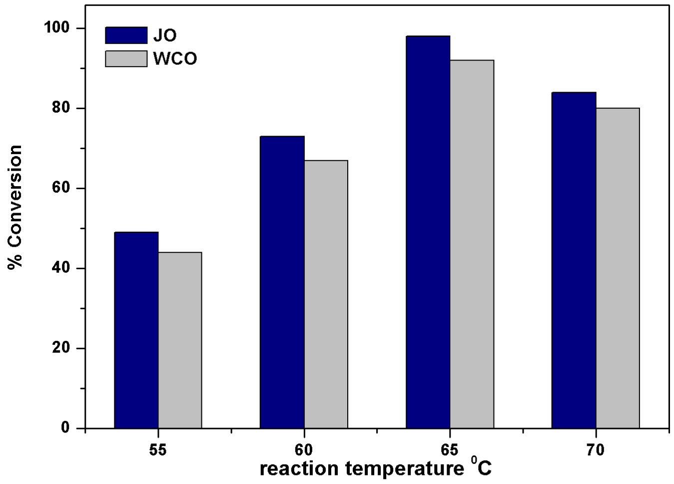


Figure 131. Effect of reaction temperature; Reaction condition: mole ratio oil to alcohol 1:8, amount of catalyst 0.3 g, reaction time 6 h

The optimized conditions for transesterification of WCO and JO over TPA_3/SBA-15 are: Mole ratio of acid to alcohol 1:8; Amount of catalyst 0.3 g; Reaction Temperature 65 ^oC and Reaction time 6 h.

The control experiments with SBA-15 and TPA were also carried out under optimized conditions.

Table 52. Contrl experiments for tranesterification of triglycerides

[a]Catalyst	%Conversion	
	Jatropha oil	Waste cooking oil
SBA-15	<5	<2
[b]TPA	95	90
$TPA_3/SBA-15$	98	92

[a]Reaction condition: mole ratio oil to alcohol 1:8, amount of catalyst 0.3 g, reaction temperature 65 °C, reaction time 6 h;[b] amount of active species TPA :69 mg.

It can be seen from Table 52 that SBA-15 is not much active towards the transesterification of triglycerides indicating the catalytic activity is mainly due to TPA. The same reaction was carried out by taking the active amount of TPA (69 mg). It was found that the active catalyst gives 95% conversion of jatropha oil and 90% conversion of waste cooking oil. Almost the same activity was obtained for $TPA_3/SBA-15$ catalyst indicates that TPA is the real active species. Thus, we were successful in anchoring TPA on SBA-15 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Regeneration and Recycling of the catalyst

Characterization of Regenerated catalysts

The regenerated catalysts were characterized for DRS, elemental analysis (EDS) and leaching as well as heterogeneity test, in order to confirm the retention of the catalyst structure, after the completion of the reaction as discussed earlier. The results are same and hence are not included.

Catalytic activity of regenerated catalysts

The catalyst was easily separated from the reaction mixture, because at the end of the reaction, the catalyst settled at the bottom of the reactor, and was used without any treatment. As the catalyst was able to settle from the mixture of fatty acid methyl ester and glycerin into the bottom of the reactor, the upper phase consists of fatty acid methyl ester did not contain any solid and did not need any washing treatment by base water, i.e., this process did not generate any waste water and is environmentally benign. The experiments were repeated four times by the same transesterification procedure and the conversions are given in Figure 132. This shows that there is no significant loss in activity of the catalysts even after four cycles.

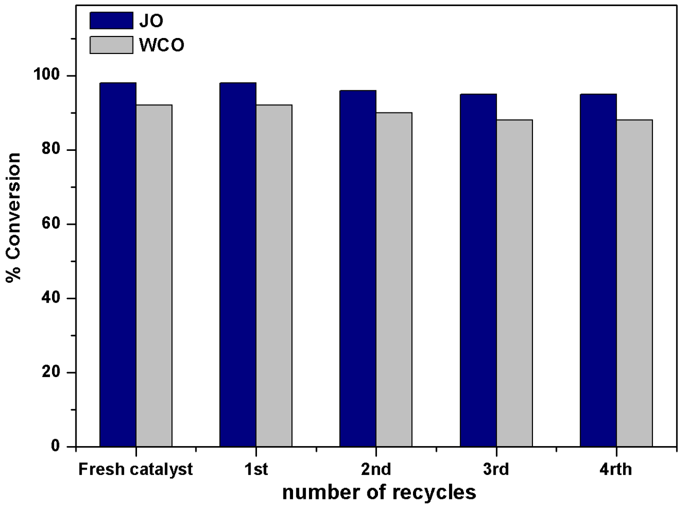


Figure 132. Recycling of the catalyst; Reaction condition: mole ratio oil to alcohol 1:8, amount of catalyst 0.3 g, reaction temperature 65 °C, reaction time 6 h

Characterization of biodiesel

The biodiesel obtained from transesterification of jatropha oil and waste cooking oil was characterized by FT-IR and ^{1}H NMR spectra. The biodiesel i. e. fatty acid esters obtained by transesterification of jatropha oil and waste cooking oil were designated as BD5 and BD6 respectively using TPA$_3$/SBA-15 catalyst. As the results obtained were the as mentioned earlier in chapter 4 and hence are not included.

Properties of biodiesel samples

The physical and chemical properties of biodiesel from jatropha oil and waste cooking oil were studied [4, 5]. The biodiesel was prepared in the laboratory scale. The biodiesel samples BD5 and BD6 were analyzed for various properties. The properties measured were compared with the ASTM specifications and the results are presented in Table 53.

Table 53. Properties of biodiesel

Property	Testing procedure	ASTM D6751 Standard for Biodiesel	ASTM D 975 Standard for diesel fuel	BD4	BD6
Viscosity at 40°C	ASTM D446	1.9-6	1.3-4.1	4.6	4.9
Flash point(°C)	-	100-170	60-80	115	129
Pour point(°C)	ASTM D97	-15 to 10	(-35) -15	-4	-6
Cetane number	ASTM D613-95	48-65	40-55	54	56
Copper strip corrosion	ASTM D130	No. 3	-	No.1	No.1

The kinematic viscosity indicates that the flow capability of any fuel and it was found that for all the samples it was within the limits of ASTM standards.

The flash point of biodiesel samples was within the limits of ASTM standard, biodiesel was safer than petro-diesel to handle and store because it has a little bit higher flash point than petro-diesel.

The pour point of biodiesel samples BD1 and BD3 was -2 and -1, which may be due to the higher content of unsaturated fatty acid in raw jatropha oil. The result was found to be within the specified limit and biodiesel samples were suitable not only for the tropical region but also for moderate temperate region.

The cetane index of biodiesel from jatropha oil with methanol was found to be within the ASTM specified limit. The higher cetane index of biodiesel compared to petrodiesel was indicated that it will be the high potential for engine performance. The copper strip corrosion test were also carried out and the results were within the ASTM specified limit for all the samples.

The biodiesel samples were stored for about 11 months without any significant change. But further research and development on additional fuel properties and the effects of biodiesel on the engine are necessary.

Effect of supports (MCM-41/SBA-15) on activity of TPA in various organic transformations

It is known that, 'Support' does not play always merely a mechanical role but it can also modify the catalytic properties of the HPAs. The nature of the support as well as its textural properties are the important factors for a successful reaction towards the better catalytic activity.

Textural properties of supports and catalyst are summarised in table 54 in order to correlate the catalytic activity.

Table 54. Textural properties of supports and catalyst

Catalyst	Surface area (m^2/g)	Pore diameter (nm)	Mesopore volume cm^3/g	total acidity (mmol/g)
MCM-41	659	4.70	0.79	0.822
$TPA_3/MCM-41$	360	3.01	0.50	1.41
SBA-15	834	6.80	1.26	1.11
$TPA_3/SBA-15$	714	6.20	1.12	1.82

The catalytic activity of TPA_3/MCM-41 and TPA_3/SBA-15 was compared in various reactions to see the effect of support (table 55, 56, 57 and 58).

Table 55. Esterification of dicarboxylic acids

[a]Catalyst	Alcohol	% Yield	
		dialkylsuccinate	*dialkylmalonate
$TPA_3/MCM-41$	Butanol	85	90
$TPA_3/MCM-41$	Ethanol	71	79
$TPA_3/SBA-15$	Butanol	98	98
$TPA_3/SBA-15$	Ethanol	75	80

[a]Reaction conditions: amount of catalyst 0.1 g; mole ratio alcohol to acid 3:1; reaction temperature 80 °C; reaction time 8 and 4 h for dibutylsuccinate and dibutylmalonate

Table 56. Esterification of fatty acid, lauric acid

Catalysts	Surface area (m^2/g)	Pore diameter (nm)	Total acidity (mmol/g)	Keggin ion density TPA nm^{-2}	Activation energy (kJ mol^{-1})	TOF (min^{-1})
TPA_3/MCM-41	360	3.0	1.41	0 .1741	78	25.93
TPA_3/SBA-15	714	6.2	1.82	0.0878	50.5	38.90

Table 57. Esterification of free fatty acids, palmitic and oleic acid

Catalysts	Fatty acid	Activation energy (kJ mol^{-1})	TOF (min^{-1})
TPA_3/MCM-41	Palmitic acid	38	8.3
TPA_3/SBA-15		35	9.8
TPA_3/MCM-41	Oleic acid	52.4	3.4
TPA_3/SBA-15		44.6	9.3

Table 58. Transesterification of triglycerides

[a]Catalysts	feedstock	% Conversion
TPA_3/MCM-41	Jatropha oil	48
TPA_3/SBA-15		98
TPA_3/MCM-41	Waste cooking oil	40
TPA_3/SBA-15		92

[a]Reaction conditions: amount of catalyst 0.3 g; mole ratio of oil to alcohol 1:8; reaction temperature 65 °C; reaction time 6 h.

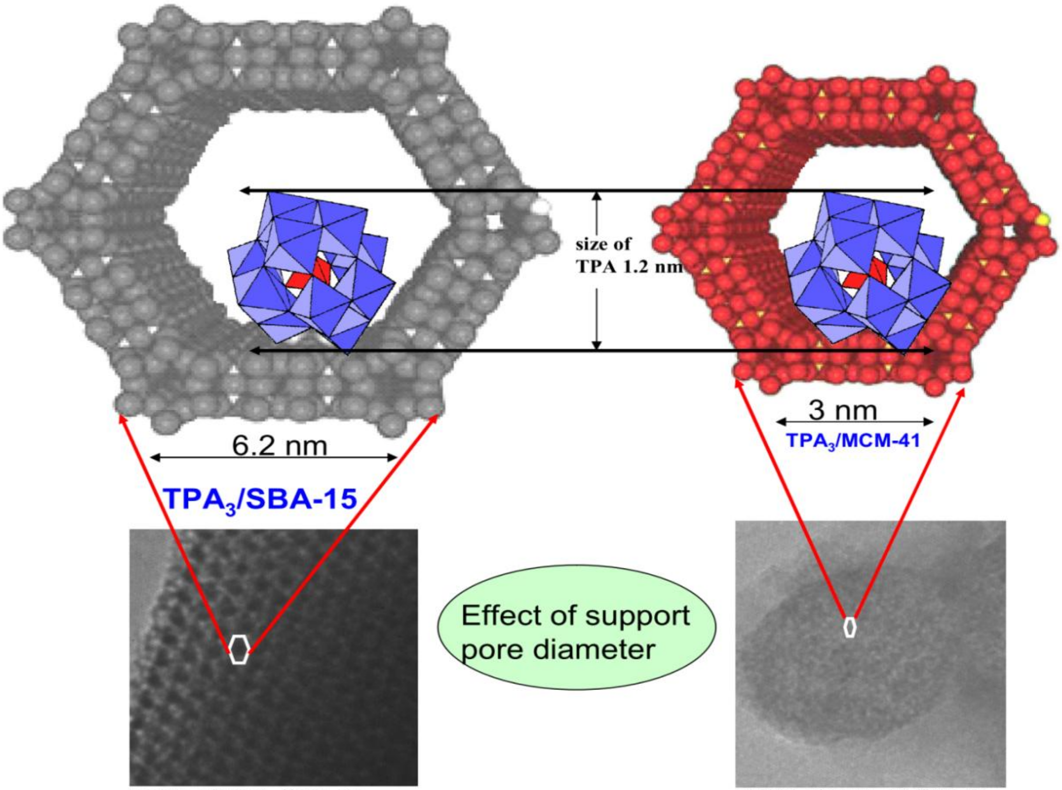
In all the reactions TPA_3/SBA-15 exhibited excellent activity as compared to that of TPA_3/MCM-41. The obtained difference in catalytic activity may be due to the nature of supports and this can be explained as follows.

First of all surface area of SBA-15 is higher than that of MCM-41 and the same trend was observed for the catalysts. Increase in surface area may be due to the nature of support. The higher value of surface area for TPA_3/SBA-15 as compared to that of TPA_3/MCM-41 is responsible for higher catalytic activity.

The total acidity of TPA_3/SBA-15 is higher than TPA_3/MCM-41 catalyst, even though the % loading of TPA is same for both the supports. It is well known that the SBA-15 is more acidic support as compared to MCM-41. Therefore the higher value of total acidity for TPA_3/SBA-15 was observed collectively from TPA as well as support SBA-15. As the total acidity of TPA_3/SBA-15 is higher as compared to TPA_3/MCM-41, superior catalytic activity from TPA_3/SBA-15 is as expected.

The density of Keggin ion (TPA nm^{-2}) is expressed as number of Keggin anion per square nanometre, was calculated according to actual TPA loading and catalyst surface area. As seen from table 56 the Keggin ion density of TPA_3/MCM-41 is higher as compared to TPA_3/SBA-15, suggesting multilayer formation of TPA when anchored to MCM-41. In other word fewer Bronsted acid sites are available. Whereas Keggin ion density of TPA_3/SBA-15 is low suggesting monolayer formation of TPA and hence more number of Bronsted acid sites are available for catalytic reaction.

. In the present case, for SBA-15 support, pore diameter is 6.8 nm and after anchoring TPA it decreases to 6.2 nm, still there is enough space available for reactants to enter. Whereas for MCM-41 support, pore diameter is 4.7nm which decreases to 3.0 nm after anchoring TPA, hence the available space is much more suitable for small molecules rather than bigger molecules as reactants as shown in figure 133.



TEM of TPA_3/SBA-15 TEM of TPA_3/MCM-41

Figure 133. Effect of support pore diameter

This effect was more prominent in case of esterification of fatty acids such as lauric acid, palmitic acid and oleic acid as well as in transesterification of triglyceride feedstocks such as waste cooking oil and jatropha oil. This can be explained well by taking example of oleic acid esterification. As oleic acid is long chain fatty acid with carbon chain length of C18, a large molecule easily diffuse into hexagonal channels of TPA_3/SBA-15 catalyst as compare to TPA_3/MCM-41 because of the nature of support, that's clearly demonstrated in catalytic activity. Hence, TPA_3/SBA-15 exhibits higher activity as compared to TPA_3/MCM-41.

Conclusion

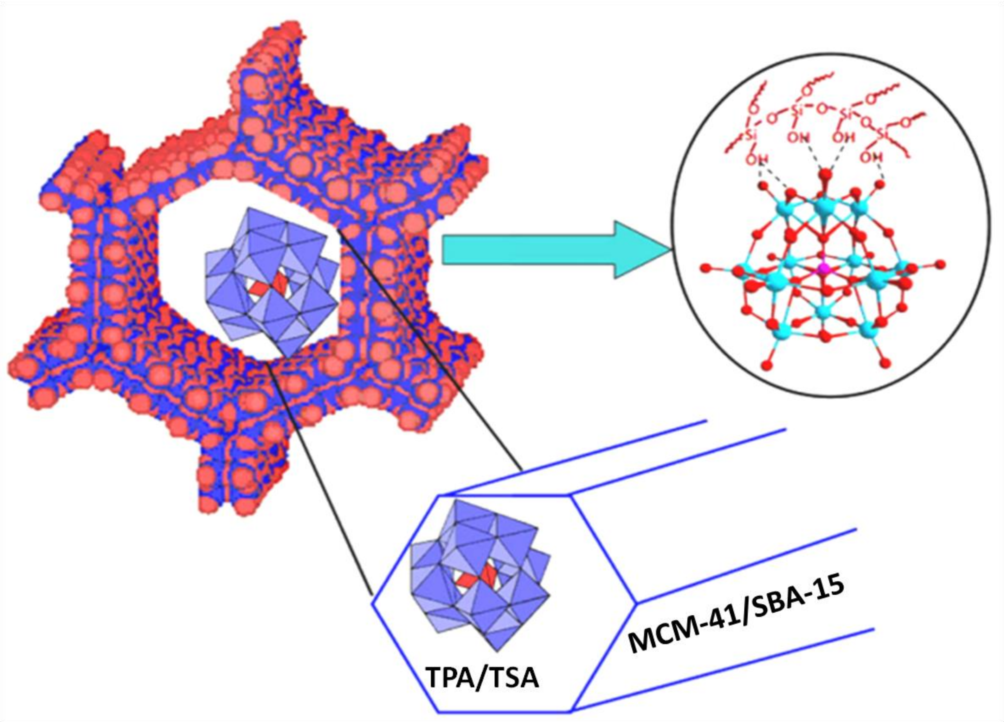
- The catalytic activity of TPA_3/SBA-15 was explored for esterification of dicarboxylic acids, succinic acid, and malonic acid.
- The catalyst shows high activity in terms of higher yields toward diesters, especialy for dioctyl malonate; 99% yield was obtained.
- Esterification of fatty acid, lauric acid with 1-butanol was successfully carried out over TPA_3/SBA-15
- 99% conversion was obtained for lauric acid esterification.
- The kinetic studies reveal that the reaction follows the second order kinetic law with respect to reactants as well as the catalyst.
- The influence of temperature on rate constant was also studied and the activation energy was found to be 50.5 $kJmol^{-1}$
- The present catalyst exhibits excellent activity toward biodiesel production via esterification of free fatty acid, palmitic acid and oleic acid under relatively mild conditions.
- Kinetic studies show that esterification of palmitic acid follows first order rate law.
- The influence of temperature on rate constant was also studied and the activation energy was found to be 35 and 44.6 $kJmol^{-1}$ for palmitic acid and oleic acid esterification respectively.
- The present catalyst also exhibits excellent activity for the transesterification of triglyceride feedstocks, waste cooking oil and Jatropha oil with methanol under mild conditions.
- Catalyst was regenerated and reused upto four cycles.
- TPA_3/SBA-15 exhibits excellent catalytic activity compared to TPA_3/MCM-41 due higher pore diameter of former than the later.
- Also the catalytic results demonstrated that the size of the support channels plays a crucial role in catalyst performance

References

1. M. Sheldon, M. Walau, I.W.C.E. Arends, U. Schuchurdt, *Acc. Chem. Res*. 31, 485 (1998)
2. G. C. Bond Heterogeneous Catalysis: principles and applications. Oxford Chemistry series, Ch 3, p 49 (1974)
3. Y. Wang, S. Ou, P. Liu, Z. Zhang, *Energy Convers. Manage.* 48, 184 (2007).
4. F. Chai, F. Cao, F. Zhai, Y. Chen, X. Wang, Z. Su, *Adv. Synth. Catal.* 349, 1057 (2007)
5. A. S. Ramadhas, S. Jayaraj, C. Muraleedharan, *Fuel*. 84, 335 (2005)

Main Conclusion

- DRS, Raman studies and ^{31}P MAS-NMR all confirms the retainment of Keggin structure of HPAs even after anchoring to mesoporous silica MCM-41 and SBA-15.
- BET surface area, Raman studies and ^{29}Si NMR data shows that there is a strong interaction, hydrogen bonding, between terminal oxygens of HPAs with the surface silanol groups of mesoporous silica MCM-41 and SBA-15.



Interaction of HPA with mesoporous silica.

- The catalysts were found to be successful in esterification of succinic and malonic acid with butanol. Especially TPA_3/SBA-15 gives 100% and 98% yield for dibutyl succinate and dibutyl malonate.
- The catalysts were successfully used in esterification of fatty acids, lauric acid with butanol. The kinetic study reveals that the reaction follows the second order kinetic law with respect to reactants.

- The catalysts were successfully used in biodiesel production by esterification and transesterification.
- Kinetic studies show that esterification of palmitic acid and oleic acid follows first order rate law. Also the activity of the present catalysts is much higher than the traditional sulphuric acid catalyst and the other solid acid catalysts.
- Studies also reveal that the catalysts were successfully used for biodiesel production from waste cooking oil and jatropha oil without any pretreatment. Especially TPA_3/SBA-15 gives 92 and 98% conversion was achieved for waste cooking oil and jatropha oil respectively over
- Hence the present catalyst can be employed for the feedstocks that are rich in free fatty acids where simultaneous esterification and transesterification over heterogeneous acid catalysts provides an alternative single step process for biodiesel production.
- This excellent catalytic performance is mainly attributed to the large surface area and pore diameter of the mesoporous supports, MCM-41 and SBA-15 as well as the Bronsted acid strength of HPAs, as active sites.
- Also the catalysts shows potential of being used as recyclable catalytic material for all studied reactions (esterification and transesterification) after a simple regeneration without any significant loss in conversion.

Novelty of the work

- A non-hydrothermal synthetic route for synthesis of mesoporous silica MCM-41, SBA-15 was developed.
- We have overcome the key issues with “Supported Heteropolyacids” such as retention of polyanion structure of Keggin HPAs, their firm fixation and uniform dispersion.
- We could successfully develop, a green process for synthesis of diesters over present catalysts.
- Biodiesel production by using waste cooking oil as feedstock’s over synthesized catalysts.
- We have successfully developed environmentally benign catalysts and established its use for biodiesel production as a contribution towards Green Chemistry for Sustainability.