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Biodiesel Production by Esterification of Free Fatty Acids over 12-Tungstophosphoric Acid Anchored to MCM-41

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ABSTRACT: Heterogeneous acid catalyst comprising 12-tungstophosphoric acid (30%) and MCM-41 was synthesized and characterized by X-ray diffraction (XRD), surface area measurement (BET method), and solid state ^{29}Si NMR. The use of synthesized catalyst was explored for biodiesel production by esterification of free fatty acid, palmitic acid with methanol. 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. The catalyst shows high activity in terms of 100% conversion toward palmitic acid and a high turnover number, 1992. The kinetic studies as well as the Koros Nowak test were also carried out, and it was found that esterification of palmitic acid follows first order kinetics and the rates are not mass transfer limited. The excellent catalytic performance is attributed to the large surface area and pore diameter of the mesoporous support, MCM-41 as well as the Bronsted acid strength of TPA, as active sites. The catalyst shows the potential of being used as a recyclable catalytic material after simple regeneration without significant loss in conversion. As an application, preliminary studies were carried out for biodiesel production from waste cooking oil, as feedstock without any pretreatment, and with methanol over the present catalyst. Studies also reveal that the catalyst can be used for biodiesel production from waste cooking oil.

1. INTRODUCTION

Biodiesel is gaining much attention in recent years as a renewable fuel. It is a nonpetroleum based fuel that consists of alkyl esters derived from either the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with low molecular weight alcohols.[1−4]

The conventional biodiesel production technology involves the use of alkaline homogeneous catalysts such as NaOH and KOH, but sometimes $NaOCH_3$ or $KOCH_3$ are also employed mainly in large-scale production plants. These are not compatible for feedstocks with large amounts of free fatty acids (FFAs) and moisture due to the formation of soaps that strongly affect the feasibility of glycerol separation which is an important coproduct of transesterification reaction.

The traditional liquid acids such as HCl and H_2SO_4 were found to be more efficient, but they need a very long reaction time and a very high molar ratio of methanol to oil. Also corrosion of reaction vessels and problem of recycling are the key issues with traditional liquid acids. Therefore commercialization of biodiesel production is difficult due to the technological drawbacks such as separation and purification steps that increase the cost factor to maximum.

An interesting alternative for low cost biodiesel production is the utilization of low quality raw materials as feedstocks such as waste cooking oil obtained from canteens restaurants and from houses which are rich in free fatty acids. A literature survey shows that biodiesel production becomes a two step process where high free fatty acid-containing feedstocks are used as raw materials.[5] Simultaneous FFA esterification and TGs transesterification using acid catalysts provides an alternative single step process for poor quality oils containing high FFA levels.[6−10] This is only possible with heterogeneous acid catalysts.

Table 1. Elemental Analysis (EDS)

catalyst	elemental analysis (weight %)					
			W		P	
	O	Si	by EDS	theoretical	by EDS	theoretical
TPA$_3$/MCM-41	53.9	27.8	18.0	19	0.30	0.32
R-TPA$_3$/MCM-41	53.9	27.9	17.8	19	0.30	0.32

Considering heterogeneous solid acid catalysts, a literature survey shows that there are fewer reports than those on solid bases. Compared with solid base catalysts, solid acid catalysts have lower activity but higher stability, thus they can be applied for feedstock with large amounts of free fatty acids without catalyst deactivation.

Catalysis by supported HPAs has been greatly expanded during the past few years from the viewpoint of their variety of structures and compositions. They provide the opportunities for tuning their chemical properties, such as acidities, and reactivities by choice of appropriate support. Considering acidic properties, they have found enormous applications in various industrially important classes of reactions such as alkylations, acylations, and esterifications.[11−16] Recently, they have gained tremendous interest, in the synthesis of biodiesel.

In the present contribution esterification of free fatty acid, palmitic acid was taken as a model reaction for biodiesel production, as it is present in most of the fatty acids derived

Table 2. Textural Properties and ^{29}Si MAS-NMR Data of MCM-41 and TPA$_3$/MCM-41

				^{29}Si MAS NMR data			
catalyst	surface area (m^2/g)	d^a (Å)	mesopore volume/porosity (Å) cm^3/g	Q^4%	Q^3%	Q^2%	(Q^3+Q^2)/Q^4
MCM-41	659	47.90	0.79	73	23	36	0.37
TPA$_1$/MCM-41	400	30.69	0.55	-	-	-	-
TPA$_2$/MCM-41	372	30.53	0.50	-	-	-	-
TPA$_3$/MCM-41	360	30.13	0.50	69.5	26.2	4.3	0.44

^{a} d: pore diameter.

Table 3. Acidity Characterization

catalyst	n-butyl amine acidity (mmol/g)
MCM-41	0.82
TPA$_1$/MCM-41	1.28
TPA$_2$/MCM-41	1.32
TPA$_3$/MCM-41	1.41
TPA$_4$/MCM-41	1.48

from vegetable oils and animal fat. The esterification of palmitic acid with methanol has been carried out over heteropolyacids supported onto different supports such as alumina, silica, zirconia, and activated carbon.[17−20] However very few reports are available for the same using heteropolyacids anchored to mesoporous materials.[21] Therefore it was thought of interest to carry out biodiesel production by esterification of free fatty acid over a heterogeneous acid catalyst comprising 12-tungstophosphoric acid and MCM-41.

In the present paper, esterification of palmitic acid with methanol was studied for 30% 12-tungstophosphoric acid (TPA) anchored to MCM-41. The effect of various reaction parameters such as catalyst concentration, acid/alcohol molar ratio, and temperature was studied to optimize the conditions for maximum conversion. Also the catalyst was regenerated and reused up to four cycles. A detailed kinetic study was carried out for the same. The rate constants as well as the activation energy for the reaction were determined. The Koros Nowak test for heat and mass transfer limitations was also carried out. As an application of the above studies, preliminary studies were carried out for biodiesel production from waste cooking oil, as feedstock without any pretreatment, with methanol over the present catalyst.

2. EXPERIMENTAL SECTION

2.1. Materials. All chemicals used were of A.R. grade. H$_3$PW$_{12}$O$_{40}$.nH$_2$O (Loba chemie, Mumbai), CTAB, tetraethyl orthosilicate, palmitic acid, and methanol were used as received from Merck.

2.2. Synthesis of Support (MCM-41). MCM-41 was synthesized using a reported procedure[22] with a slight modification. Surfactant (CTAB) was added to the very dilute solution of NaOH with stirring at 60 °C. When the solution became homogeneous, TEOS was added dropwise, and the obtained gel was aged for 2 h. The resulting product was filtered, washed with distilled water, and then dried at room temperature. The obtained material was calcined at 555 °C in air for 5 h and designated as MCM-41.

2.3. Synthesis of the Catalyst (TPA Anchored to MCM-41). A series of catalysts containing 10−30% of TPA anchored to MCM-41 were synthesized by impregnation. One g of MCM-41 was impregnated with an aqueous solution of TPA (0.1/10−0.4/40 g/mL of double distilled water) and dried at 100 °C for 10 h. The obtained materials were designated as TPA$_1$/MCM-41, TPA$_2$/MCM-41, TPA$_3$/MCM-41, and TPA$_4$/MCM-41, respectively.

3. CHARACTERIZATION

SEM and elemental analysis were carried out using JSM 5910 LV combined with an INCA instrument for EDX-SEM. Adsorption−desorption isotherms of samples were recorded on a Micromatries ASAp 2010 surface area analyzer at −196 °C. From adsorption−desorption isotherms surface area was calculated using the BET method. The XRD pattern was obtained by using PHILIPS PW-1830. The conditions used were as follows: CuKα radiation (1.5417 A°), scanning angle from 0° to 60°. The magic-angle spinning (MAS) solid state NMR study was carried out on a BRUKER NMR spectrometer under ambient conditions. The ^{29}Si NMR spectra were recorded at 121.49 MHz using a 7 mm rotor probe with TMS as an external standard. The spinning rate was 5−7 kHz. The total acidity for all the materials has been determined by n-butylamine titration. A 0.025 M solution of n-butylamine in toluene was used for estimation. The catalyst weighing 0.5 g was suspended in this solution for 24 h, and excess base was titrated against trichloroacetic acid using neutral red as an indicator. This gives the total acidity of the material.

3.1. Catalytic Reaction. The esterification of palmitic acid (0.01 mol, 2.5 g) with methanol (0.4 mol, 16.2 mL) 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. A 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 4 h. The obtained products were analyzed on a gas chromatograph (Nucon-5700) using a BP1 capillary column. Products were identified by comparison with the authentic samples and finally by gas chromatography−mass spectroscopy (GC−MS).

4. RESULTS AND DISCUSSION

EDS analysis for TPA$_3$/MCM-41 catalyst is shown in Table 1. The EDS results are close to the theoretical value. The textural properties of the support MCM-41 and all the catalysts, such as surface area measurement and average pore diameter, are presented in Table 2. The acidity characterization data comprising n-butyl amine acidity value are presented in Table 3. Specific surface area, porosity, and pore diameter all strongly decreased for TPA-containing MCM-41 samples relative to the starting support, MCM-41. The decrease in surface area is the first
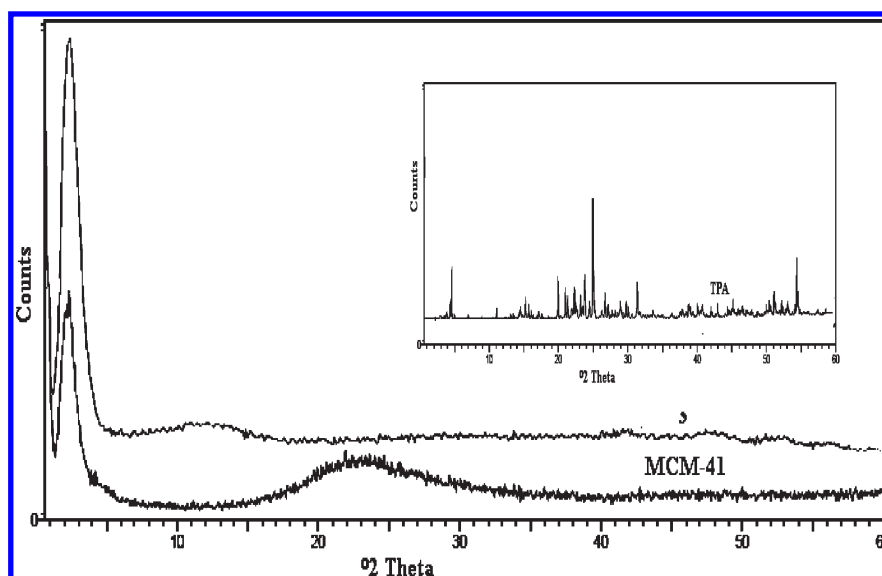
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dx.doi.org/10.1021/ie102066q |Ind. Eng. Chem. Res. 2011, 50, 6620–6628

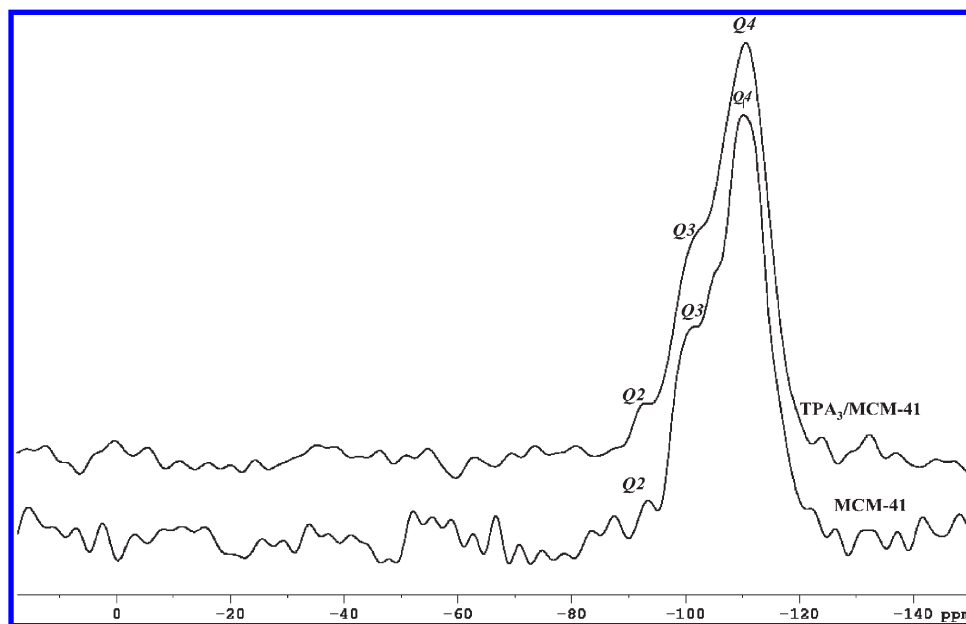**Figure 1.** XRD of MCM 41 and TPA$_3$/MCM-41.

Figure 2. Solid state ^{29}Si MAS NMR of MCM-41 and TPA$_3$/MCM-41.

indication of chemical interaction between TPA and MCM-41. N-Butyl amine acidity values indicate that MCM-41 is fairly acidic, and after TPA loading acidity increases and the results are as expected.

The XRD patterns of pure MCM-41 TPA$_3$/MCM-41 are shown in Figure 1. The XRD pattern of the calcined MCM-41 showed a sharp peak around $2\theta = 2°$ and a few weak peaks in $2\theta = 3-5°$, which indicated a well-ordered hexagonal structure of MCM-41. No separate HPA crystal phase of TPA was observed in the TPA$_3$/MCM-41. Further the absence of characteristic peaks of crystalline phase of TPA indicates that TPA is finely dispersed inside the hexagonal channels of MCM-41. Hence, there must be some chemical interaction between the host MCM-41 and the guest TPA.

^{29}Si MAS NMR is the most important method to study chemical environment around the silicon nuclei in mesoporous silica materials. Figure 2 shows the ^{29}Si MAS NMR spectra of the MCM-41 and TPA$_3$/MCM-41. A broad peak between -90 and -125 ppm was observed which can be attributed to three main components with chemical shifts at -93, -103, and -110 ppm. These signals resulted from Q^2 (-93 ppm), Q^3 (-103 ppm), and Q^4 (-110 ppm) silicon nuclei, where Q^x corresponds to a silicon nuclei with x siloxane linkages, i.e., Q^2 to disilanol Si-(O—Si)$_2$(-O-X)$_2$, where X is H or TPA, Q^3 to silanol (X-O)-Si-(O—Si)$_3$, and Q^4 to Si-(O—Si)$_4$ in the framework.[23−25]

The spectra of TPA$_3$/MCM-41 were relatively broad as compared to MCM-41 which may be due to the presence of TPA. Also the intensity of the Q^2 and Q^3 peaks decreases when the support, MCM-41, is loaded with TPA, i.e., in catalysts TPA$_3$/MCM-41. This reveals that the MCM-41 mesoporous structure may be perturbed due to the presence of TPA inside the

hexagonal channels. The fractions of Q^2, Q^3, and Q^4 units and their relative values derived from Figure 3 are given in Table 1. If the values of $(Q^3+Q^2)/Q^4$ for MCM-41 and TPA$_3$/MCM-41 were compared, the greater value obtained for the TPA$_3$/MCM-41 catalyst indicates a strong interaction between MCM-41 frameworks with TPA.

Thus from surface area analysis and ^{29}Si MAS NMR data, it is concluded that there is a strong interaction, hydrogen bonding between terminal oxygens of TPA and the surface silanol hydroxyls of MCM-41 (Scheme 1).

4.1. Esterification of Palmitic Acid. 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 favor the forward reaction. The esterification of palmitic acid with alcohol over the present catalyst is shown in Scheme 2.

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.

To study the effect of % loading esterification reaction was carried out with TPA$_1$/MCM-41, TPA$_2$/MCM-41, TPA$_3$/MCM-41, and TPA$_4$/MCM-41. The obtained results are shown in Figure 3. It was observed that with an increase in the % loading of TPA, % conversion also increases. For 10% and 20% loading, conversions for palmitic acid are considerably low even though the surface area is higher, this may be due to their less acidity as shown in Table 2. For 30 and 40% loading, the difference in % conversion is not that much appreciable. Hence the catalyst containing 30% loading of TPA, i.e. TPA$_3$/MCM-41, was used for the detail study.

To see the effect of the mole ratio, the esterification reaction was carried out by varying the mole ratio of palmitic acid to methanol, with 0.1 g of the catalyst for 4 h at 60 °C. It can be observed from Figure 4. The palmitic acid conversion increases with an increase in the palmitic acid/methanol ratio and reaches a maximum of 80% at the palmitic acid/methanol mole ratio of 1:40. With a further increase in the molar ratio there is only a small increase in conversion. Hence the molar ratio of 1:40 is optimum for obtaining high conversion products.

The effect of the amount of catalyst on palmitic acid conversion was investigated. The catalyst amount was varied in the range of 25–125 mg. As shown in Figure 5, the palmitic acid conversion increased with the increase in a catalytic amount of TPA$_3$/MCM-41 and reaches a maximum of 80% conversion. But with a further increase in the amount of catalyst the palmitic acid conversion remains constant. The maximum conversion reaches 80% with 100 mg of catalyst.

The effect of reaction time on conversion of palmitic acid was investigated. It was observed (Figure 6) that the palmitic acid conversion increases with an increase in reaction time. The palmitic acid conversion was 80% in 4 h. After 6 h 100% palmitic acid conversion was achieved.

The effect of reaction temperature on palmitic acid conversion was studied, and it was found that with an increase in reaction temperature % conversion of palmitic acid increases (Figure 7). At 80 °C 100% conversion of palmitic acid was achieved at 4 h. At 60 °C 100% palmitic acid conversion was achieved at 6 h of reaction time. Therefore all the reactions
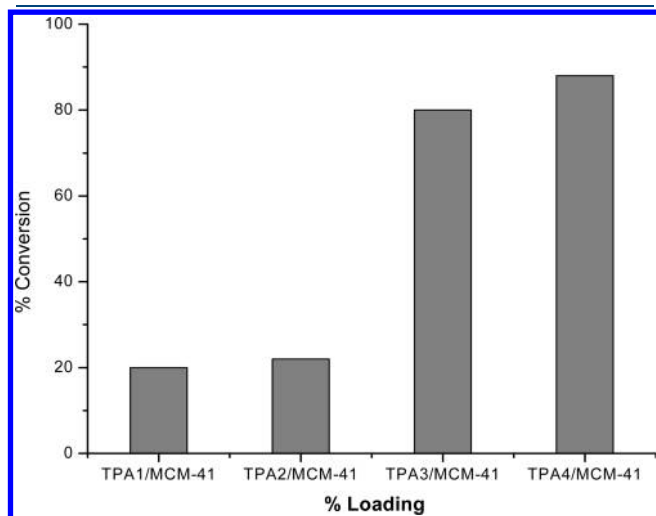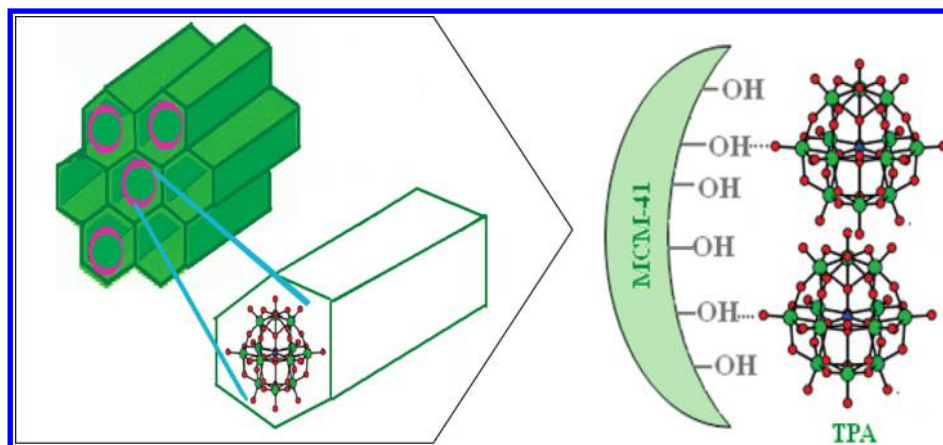

Figure 3. Effect of % loading of TPA onto MCM-41, Reaction conditions; mole ratio of palmitic acid (0.01 mol)/methanol (0.4 mols) 1:40, amount of catalyst 0.1 g, reaction temperature 60 °C, reaction time 4 h.

Scheme 2. Esterification of Palmitic Acid with Alcohol over TPA$_3$/MCM-41

Scheme 1. Probable Interaction of TPA with MCM-41

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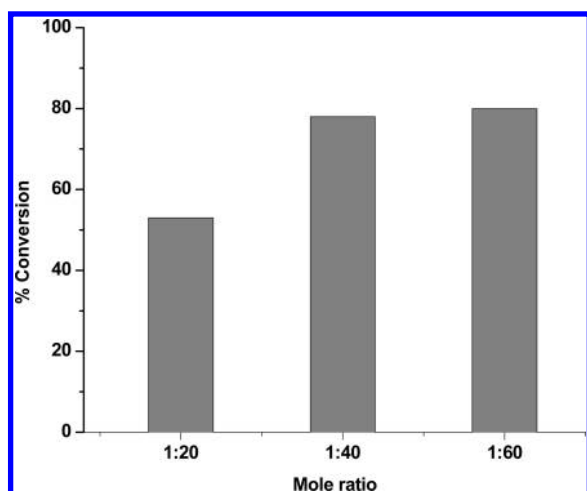dx.doi.org/10.1021/ie102066q |*Ind. Eng. Chem. Res.* 2011, 50, 6620–6628

Figure 4. Effect of mole ratio, reaction conditions; amount of catalyst 0.1 g of TPA$_3$/MCM-41, reaction temperature 60 °C, reaction time 4 h.
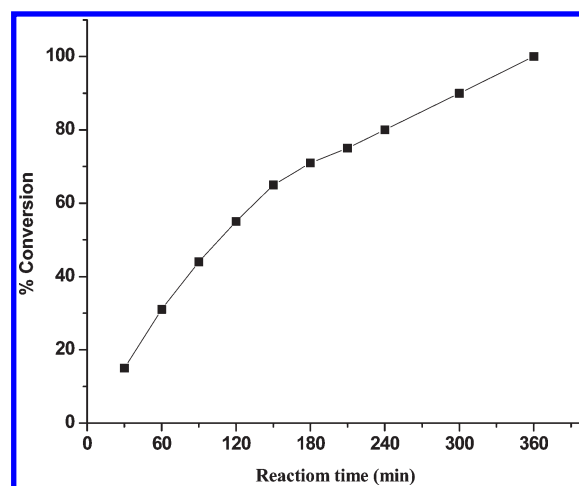

Figure 6. Effect of reaction time, reaction conditions; mole ratio 1:40, amount of catalyst 0.1 g, reaction temperature 60 °C.
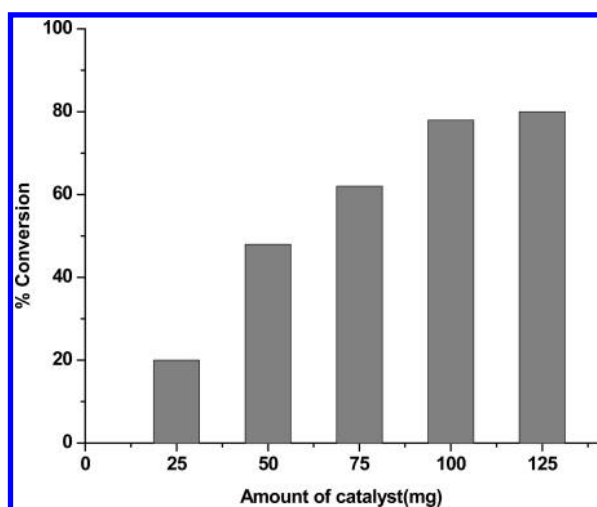

Figure 5. Effect of amount of catalyst, reaction conditions; mole ratio 1:40, reaction temperature 60 °C, reaction time 4 h.
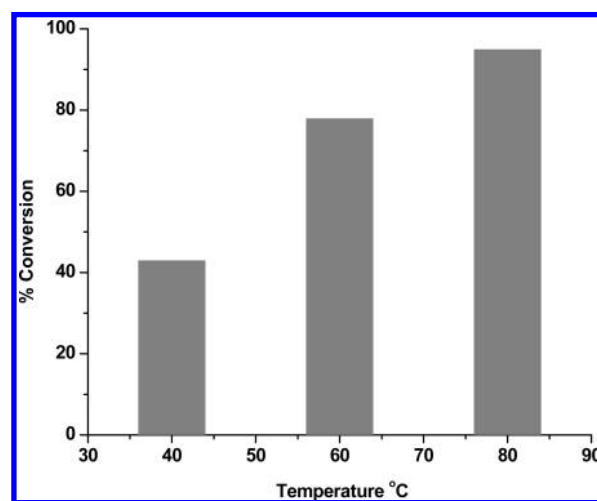

Figure 7. Effect of reaction temperature, reaction conditions; amount of catalyst 0.1 g, mole ratio 1:40, reaction time 4 h.

for palmitic acid esterification were studied at lower temperature, i.e. 60 °C.

The optimized conditions for esterification of palmitic acid over TPA$_3$/MCM-41 are as follows: mole ratio of acid to alcohol 1:40; amount of catalyst 0.1 g; reaction temperature 60 °C, and reaction time 6 h.

The esterification of palmitic acid with different alcohols was also carried out under optimized conditions, and the conversions of palmitic acid for corresponding esters are shown in Table 4. The order of catalytic activity is methyl palmitate < ethyl palmitate < propyl palmitate < butyl palmitate < isobutyl palmitate < isopropyl palmitate. The activities of alcohols were decreased as the carbon chain of the alcohols grew longer. This could be explained due to the alcohol reactivity that was strongly affected by bulky hindrance on the hydroxyl group. Probably with the increase of hindrance on secondary hydroxyl, the attack onto fatty acid, palmitic acid carbonyl became more difficult, lowering the formation of esters.

4.2. 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.[26]

The leaching of W from TPA$_3$/MCM-41 was confirmed by carrying out an analysis of the used catalyst (EDX) as well as the product mixtures (AAS). Analysis of used catalyst did not show any appreciable loss in W content as compared to the fresh catalyst. 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 form the support.

For the rigorous proof of heterogeneity, a test was carried out by filtering the catalysts from the reaction mixture at 60 °C after 4 h, and the filtrate was allowed to react up to 6 h. The reaction mixture of 6 h and the filtrates were analyzed by gas chromatogram. There was no change in the % conversion, indicating the present catalyst falls into category C.[26] On the basis of these results, it can be concluded that there is no leaching of TPA

species from the support MCM-41, and the present catalyst is truly heterogeneous in nature.

The EDS analysis of the reused catalyst R1-TPA₃/MCM-41 is shown in Table 1. The elemental analysis values are close to the fresh catalyst. The n-butyl amine acidity value of reused catalyst was i.e. 1.40 that was almost the same as compared to the fresh catalyst. This also confirms the heterogeneous mode of action of the catalyst.

Table 4. Effect of Alcohol Chain Length on Palmitic Acid Conversion[a]

alcohol	% conversion	TOF (min^{-1})
methanol	80	8.3
ethanol	58	6.0
n-propanol	42	4.3
isopropanol	19	1.9
butanol	32	3.32
isobutanol	30	3.29

[a] Reaction conditions; mole ratio 1:40, amount of catalyst 0.1 g, reaction temperature 60 °C, reaction time 4 h.
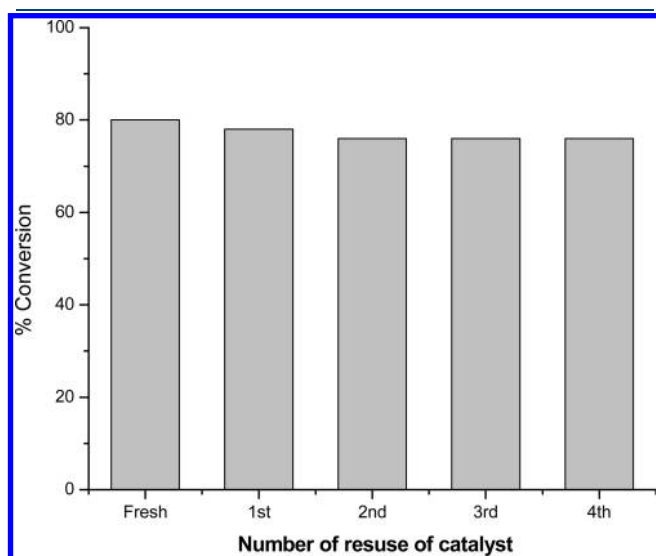

Figure 8. % conversion of methyl palmitate with recycled catalyst, reaction conditions; amount of catalyst 0.1 g, acid to alcohol mole ratio 1:40, reaction temperature 60 °C, reaction time 4 h.

4.3. Recycling of the Catalyst. The catalyst was recycled in order to test its activity as well as stability. The catalyst was separated from the reaction mixture only by simple filtration; the first washing was given with methanol to remove unreacted palmitic acid, then the subsequent washings were done by conductivity water and then drying at 100 °C, and the recovered catalyst was charged for the further run. There is no appreciable change in the % conversion of palmitic acid using a regenerated catalyst up to four cycles (Figure 8).

5. COMPARISON WITH REPORTED CATALYSTS

The superiority of the present catalyst lies in obtaining higher conversion of palmitic acid under mild reaction conditions. It is observed from Table 5 that 100% conversion was obtained with PW-Silica catalyst,[17] but the reaction time is very long, 30 h, as well as the high molar ratio of reactants which ultimately requires an excess of methanol. With the TPA supported onto niobia catalysts,[27] a very high mole ratio of reactants was used, and also there were no data about catalyst regeneration. The alumina incorporated MCM-41 catalyst[28] shows considerable activity at high reaction temperature. In the case of methanesulfonic acid sulfuric acid,[29] 95% conversion was achieved at the cost of very high temperatures and a corrosive nature of catalyst. Further, all the reported sulfated zirconia catalysts[30,31] exhibit sulfur leaching. For sulfonic acid modified SBA-15[32] and sulfated zirconia on SBA-15[33] catalysts systems, there are no data about catalyst deactivation behavior and regeneration of catalysts.

The present catalyst exhibits high palmitic acid conversions under mild reaction conditions. Further it is also interesting to note that the present catalyst gives very high TOF.

6. KINETICS

A detailed study on the kinetic behavior was carried out for esterification of palmitic acid over TPA₃/MCM-41. In all the experiments, reaction mixtures were analyzed at a fixed interval of time using gas chromatography. In the esterification of palmitic acid methanol was carried with a 1:40 molar ratio; since methanol was taken in large excess, the rate law is expected to follow first order dependence.

The plot of ln C/C_o vs time (Figure 9) shows a linear relationship of palmitic acid consumption with respect to time. With an increase in reaction time there is a gradual and linear

Table 5. Comparison of Conversion of Palmitic Acid with Reported Catalyst

reference	catalyst	reaction conditions[a]	% conversion	comments
present work	TPA₃/MCM-41	0.1 g:40:60:6	100	mild reaction condition, no deacticvation and easy regeneration
17	PW-silica	0.2 g:4:60:30	100	long reaction time
27	TPA/Nb2O5	10:300:65:4	97.5	very high mole ratio, no data about catalyst regeneration
28	Al-MCM-41	0.6:60:130:2	79	high temp
29	methanesulfonic acid sulfuric acid	0.01:3:130:1	95	high temp, homogeneous catalyst
30	tungstated zirconia 1.0 meq H+ g-1	75:200:60:6	>95	tetragonal ZrO2 and amorphous WO3 is required
31	sulfated zirconia 0.6 meq H+ g-1	40:30:60: 0.42	90	sulfur leaching—deactivation
32	sulfonic acid modified SBA15	0.05 g:30:60:6	55	low PA conversion
33	sulfated zirconia on SBA-15 1.3 meq H+ g-1	2:80:68:6	89.2	no data about deactivation behavior

[a] Reaction conditions: amount of catalyst (%w/w, in some cases unit is g):mole ratio of methanol/palmitic acid: reaction temperature: reaction time (h).
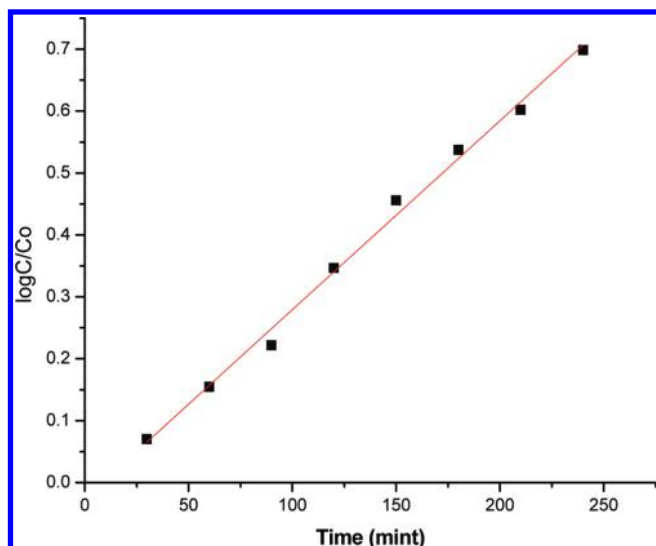
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Figure 9. First order plot for esterification of palmitic acid over TPA$_3$/MCM-41.
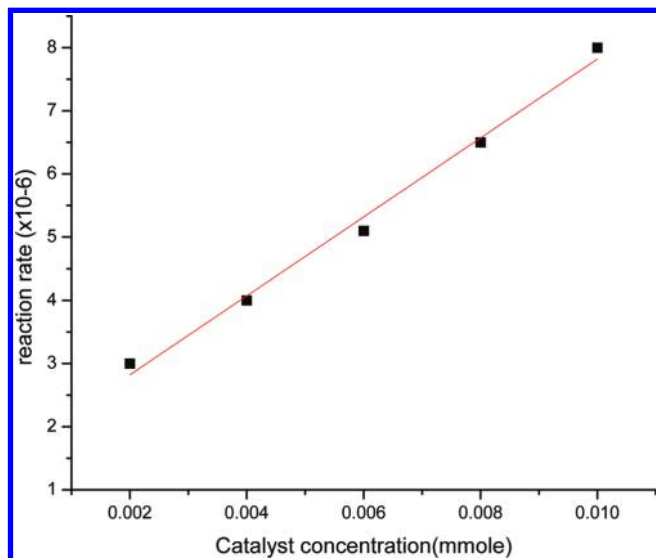

Figure 10. Plot of reaction rate vs catalyst concentrations.

decrease in the palmitic acid concentration over TPA$_3$/MCM-41 catalyst. These observations indicate the esterification of palmitic acid follows first order dependence with respect to time.

This was further supported by the study of the effect of catalyst concentration on the rate of esterification of palmitic acid. The catalyst concentration was varied from 2×10^{-3} to 10×10^{-3} mmol 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 with an increase in the catalyst concentration. The plot of reaction rate vs catalyst concentration (Figure 10) also shows a linear relationship for the TPA$_3$/MCM-41 catalyst.

6.1. Estimation of Activation Energy. The graph of ln k vs 1/T was plotted (Figure 11), and the value of activation energy (E$_a$) was determined from the plot. The value of activation energy (E$_a$) and the pre-exponential factor (A) were determined using the Arrhenius equation.
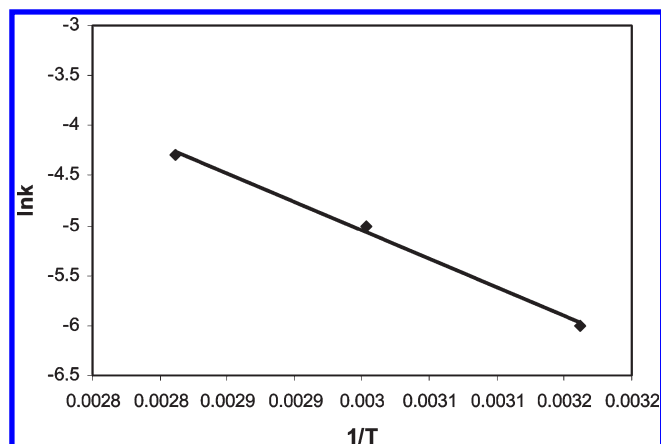

Figure 11. Arrhenius plot for determination of activation energy.

Table 6. Kinetic Parameters at Different Temperatures (Reaction Time 4 h)

temperature (°C)	rate constant (k) min^{-1}	pre-exponential factor (A) min^{-1}	activation energy (E$_a$) KJ mol^{-1}
40	2.3×10^{-3}	9.0	38
60	6.4×10^{-3}		
80	12.2×10^{-3}		

The kintetic parameters such as rate constant (k) for esterification reaction of palmitic acid at different temperatures, pre-exponential factor (A), and activation energy (E$_a$) are presented in Table 6. As the esterification reactions are temperature sensitive, the effect of temperature on the esterification of palmitic acid was also studied by varying the temperature between 313 and 353 K, keeping the palmitic acid:methanol ratio of 1:40 and catalyst concentration of 8×10^{-3} mmol. As the temperature increases from 313 to 353 K, the rate constant increases. This may be due to the activation of the catalytic species with an increase in temperature.

It is important to recognize 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 $10-15$ KJ mol^{-1}, and for reactions whose rate is governed by a truly chemical step usually show activation energy excess of 25 KJ mol^{-1}.[34] In the present case the observed activation energy is 38 KJ mol^{-1}, and hence the rate is truly governed by chemical step.

6.2. Koros Nowak Test. Koros and Nowak proposed an elegant experimental test to identify heat or mass transfer limitations in measurements of catalytic rates.[35,36] If the observed TOFs are the same, it can be concluded that, under tested conditions, rates are not subjected to heat or mass transfer limitations. In the present case, rate measurements were carried on the catalyst with similar dispersion but different active species loading (in the present case TPA). The comparison was done at the same conversion of palmitic acid. As shown in Table 7 the observed TOFs are the same at different TPA loadings, and hence the rates are not heat and mass transfer limited.

6.3. Comparison of Activation Energy with the Reported Catalysts. Comparison of activation energies obtained for esterification of palmitic acid for the reported catalysts with the present catalyst is shown in Table 8.

Table 7. Koros Nowak Test for Heat and Mass Transfer Limitations[a]

catalyst (%TPA anchored to MCM-41)	concentration of active species TPA (mg)	rate ($\times 10^{-6}$ min^{-1})	TOF (min^{-1})
TPA$_1$/MCM-41	9.1	1.7	11.1
TPA$_2$/MCM-41	16.7	4.0	11.1
TPA$_3$/MCM-41	23.1	5.1	11.1
TPA$_4$/MCM-41	28.6	6.7	11.1

[a] Reaction conditions: mole ratio palmitic acid (0.01 mol)/alcohol (0.4 mol): 1/40, amount of catalyst; 0.1 g, reaction temperature; 60 °C, reaction time; time at which the same palmitic acid conversion was observed.

Table 8. Comparison of Activation Energy with the Reported Catalysts

reference	catalyst	free fatty acid	activation energy
present work	TPA$_3$/MCM-41	palmitic acid	9.2 kcal mol^{-1}
37	sulfuric acid	palmitic acid	13.34 kcal mol^{-1}
29	sulfuric acid	palmitic acid	15.046 kcal mol^{-1}
	methanesulfonic acid		10.122 kcal mol^{-1}
27	TPA/Nb$_2$O$_5$	palmitic acid	13.68 kcal mol^{-1}

Scheme 3. Biodiesel Production from Waste Cooking Oil over TPA$_3$/MCM-41
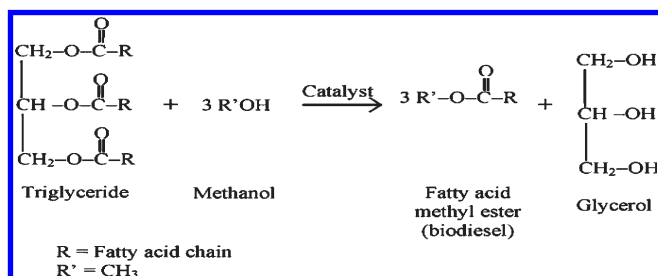
The observed activation energy value (9.2 kcal mol^{-1}) for esterification of palmitic acid with methanol over TPA$_3$/MCM-41 is much less than the activation energy obtained by using traditional homogeneous sulfuric acid catalysts.[37,29] Further, comparing with other reported solid acid catalysts[27] the present catalyst exhibits much lower activation energy for the esterification of palmitic acid.

6.4. Transesterification of Waste Cooking Oil. Transesterification of triglycerides (TGs) with low molecular weight alcohols (Scheme 3) produces biodiesel. Waste cooking oil is an attractive low cost feedstock which can help in improving the economical feasibility of biodiesel production.

The typical reaction of transesterification was carried out in a 100 mL round reactor, provided with thermometer, mechanical stirring, and condenser. Waste cooking oil and methanol were added in a 1:2 V/V ratio and followed by catalyst addition, and then the reaction mixture was held at 65 °C for 12 h with stirring at 600 rpm order to keep the system uniform in temperature and suspension.

After the reaction is completed, the mixture was rotary evaporated at 50 °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[38]

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

where OL and WCO refer to oil layer and waste cooking oil, respectively. The conversion of FFAs is 65%. The superiority lies in getting 65% conversions of FFAs for biodiesel production under mild conditions from waste cooking oil over the present catalyst.

7. CONCLUSION

The present work shows that 12-tungstophosphoric acid anchored to MCM-41 exhibits significant activity toward biodiesel production via esterification of free fatty acid, palmitic acid, under relatively mild conditions. This excellent catalytic performance is mainly attributed to the large surface area and pore diameter of the mesoporous support, MCM-41 as well as the Bronsted acid strength of TPA, as active sites. Also the catalyst shows the potential of being used as a recyclable catalytic material after a simple regeneration without any significant loss in conversion. Kinetic studies show that the esterification of palmitic acid follows the first order rate law. Also the activity of the present catalyst is much higher than the traditional sulfuric acid catalyst and the other solid acid catalysts.

Studies also reveal that the catalyst could be used for biodiesel production from waste cooking oil without any pretreatment. Hence the present catalyst can be employed for the feedstocks that are rich in free fatty acids where simultaneous FFA esterification and TGs transesterification using a heterogeneous acid catalysts provides an alternative single step process for biodiesel production.

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