



An efficient green catalyst comprising 12-tungstophosphoric acid and MCM-41: synthesis characterization and diesterification of succinic acid, a potential bio-platform molecule

Varsha Brahmkhatri & Anjali Patel

To cite this article: Varsha Brahmkhatri & Anjali Patel (2012) An efficient green catalyst comprising 12-tungstophosphoric acid and MCM-41: synthesis characterization and diesterification of succinic acid, a potential bio-platform molecule, Green Chemistry Letters and Reviews, 5:2, 161-171, DOI: [10.1080/17518253.2011.607471](https://doi.org/10.1080/17518253.2011.607471)

To link to this article: <https://doi.org/10.1080/17518253.2011.607471>



Copyright Taylor and Francis Group, LLC



Published online: 06 Dec 2011.



Submit your article to this journal [↗](#)



Article views: 796



View related articles [↗](#)



Citing articles: 3 View citing articles [↗](#)

RESEARCH LETTER

An efficient green catalyst comprising 12-tungstophosphoric acid and MCM-41: synthesis characterization and diesterification of succinic acid, a potential bio-platform molecule

Varsha Brahmkhatri and Anjali Patel*

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

(Received 13 October 2010; final version received 19 May 2011)

An efficient green catalyst comprising 12-tungstophosphoric acid (TPA) and MCM-41 was synthesized. The catalytic activity was evaluated for liquid phase solvent free diesterification of succinic acid. The support and the synthesized catalyst were characterized by various physico-chemical techniques. Fourier transform infrared, diffuse reflectance spectroscopy, and ^{31}P NMR spectra indicate that the Keggin structure of TPA was not destroyed after anchoring to MCM-41. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy show that TPA is uniformly dispersed inside the channels without disturbing the hexagonal array of MCM-41. The present contribution reports solvent free diesterification of succinic acid with alcohols under mild reaction conditions. The catalyst shows higher activity toward diester, especially for dioctyl succinate 99% yield was obtained with very high turnover number, 12.43×10^4 . Also the catalyst shows potential of being used as recyclable catalytic material after simple regeneration without loss of any catalytic activity.

Keywords: green catalyst; MCM-41; 12-tungstophosphoric acid; diesterification; bioplatfrom molecule

1. Introduction

The green chemical transformations of the bio-plat-form molecules can build up new environmentally compatible and sustainable chemical technologies. The biomass-derived platform molecules are potentially useful building blocks for chemical synthesis (1). Among the top bio-platfrom molecules, recently succinic acid is gaining much importance as it can be converted to variety of products.

Diesterification of succinic acid is very important as the obtained esters are known to be entirely biorenewable or green chemicals that can replace petroleum-based solvents. Succinate esters have exceptional solvent properties and thus find commercial application as solvents and in consumer products such as drug pharmaceuticals, perfumes, cosmetics, plasticizers, and paint strippers. Succinate esters are excellent fuel oxygenates. In addition, succinate esters are intermediates in the production of poly butylene succinate which is entirely bio-renewable material. A conventional process for succinate esters production involves a stirred batch or continuous reactor with H_2SO_4 as a homogeneous catalyst. Due to the known disadvantages of traditional liquid acids, much attention has been paid to the development of ecologically and environmentally benign processes

and redesigning of commercially important processes using solid acid catalysts. A number of solid acid catalysts such as Clays (2), ion exchange resins (3), carbonaceous materials (4), and phosphotungstic acid anchored to Al-MCM-41 (5) have been reported for diesterification of succinic acid. Most of the reported diesterifications of succinic acid have been carried out using solvents and at longer reaction period.

From the viewpoint of environmental concern as well as importance of succinate esters, the designing of solvent free catalytic reaction would be of much interest in the area of green synthesis.

In the last decades, “Supported heteropolyacids” have attracted much attention as an economically and environmentally friendly catalyst. Among them, Keggin type, 12-tungstophosphoric acid (TPA) supported onto different supports (6–16) has been studied well because of its high thermal stability and acidity (17–19).

Keeping in mind the importance of green synthesis of succinate esters as well as supported heteropolyacids, in the present contribution we have made an attempt to develop a green catalyst and green process for the synthesis of diesters. In the present paper we are reporting the results for solvent free diesterification of succinic acid over a green catalyst

*Corresponding author. Email: aupatel_chem@yahoo.com

comprising TPA and MCM-41. Here, we are also reporting the use of non-hydro thermally synthesized MCM-41 as support for anchoring TPA, since the traditional hydrothermal procedures have some disadvantages, such as the obligatory crystallization time and high aging temperature (20).

A series of catalysts, containing 10–40% TPA anchored to MCM-41, were synthesized. The support and catalysts were characterized by various thermal and spectral techniques such as thermo gravimetric analysis (TGA), Fourier transform infrared (FT-IR), diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), surface area measurement (BET method), pore size and pore volume distribution, and ^{31}P NMR studies. Further, the surface morphology of support and catalyst was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The total surface acidity was determined by *n*-butylamine titration. The catalytic activity was evaluated for liquid phase diesterification of succinic acid by varying different parameters such as mole ratio, amount of the catalyst, and reaction time to optimize the conditions for obtaining maximum yields for diesters. Diesterification of succinic acid with different alcohols (*n*-butanol, hexanol, and octanol) was also carried out under optimized conditions. The catalyst was also regenerated and reused up to four cycles.

2. Results and discussion

The leaching test study indicates the presence of chemical interaction between TPA and the support, MCM-41.

Thermo gravimetric analysis (TGA) of MCM-41 (Figure 1) showed initial weight loss of 6.14% at 100°C. This may be due to the loss of adsorbed water

molecules. The final 7.92% 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. The TGA of $\text{TPA}_3/\text{MCM-41}$ (Figure 1) shows initial weight loss of 3.6% due to the loss of adsorbed water. Second weight loss of 1.2% between 150 and 250°C corresponds to the loss of water of crystallization of Keggin ion. After that another gradual weight loss was also observed from 250 to 500°C due to the difficulty in removal of water contained in TPA molecules inside the channels of MCM-41. The results are in good agreement with the reported one (27). This type of inclusion causes the stabilization of TPA molecules inside the channels of MCM-41, which can be further seen in FT-IR.

Fourier transform infrared (FT-IR) of MCM-41 (Figure 2) shows a broad band around 1300–1000 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 due to the absorption of Si–OH on surface, which provides opportunities for forming the hydrogen bond.

Fourier transform infrared (FT-IR) spectra of $\text{TPA}_3/\text{MCM-41}$ (Figure 2) is almost same as that of MCM-41. The reported bands for TPA, at 1088, 987, and 800 cm^{-1} corresponding to W–O–W bending, W–O and P–O symmetric stretching, respectively, are absent in $\text{TPA}_3/\text{MCM-41}$. If TPA is dispersed onto the surface of support, the mentioned bands for TPA should be seen in the FT-IR spectra. The lack of FT-IR band of TPA may be either because of very low amount of TPA or due to the superimposition of TPA bands with those of support, MCM-41.

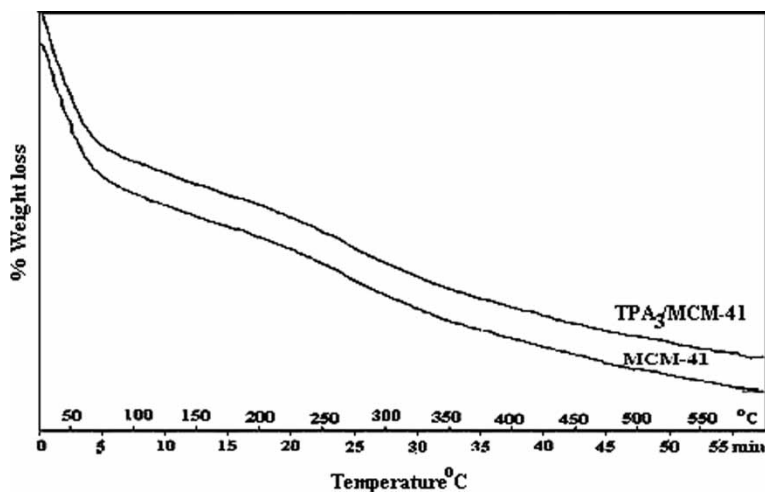


Figure 1. TGA of MCM-41 and $\text{TPA}_3/\text{MCM-41}$.

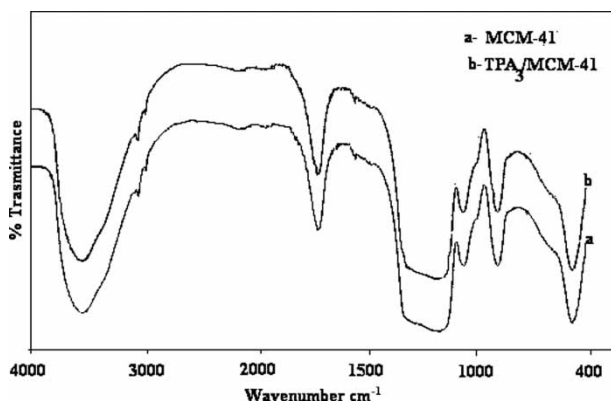


Figure 2. FT-IR spectra of MCM-41 and TPA₃/MCM-41.

The DRS spectra of MCM-41, TPA, and TPA₃/MCM-41 are shown in Figure 3. 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 $\text{PW}_{12}\text{O}_{40}^{3-}$ which is in agreement with a previous report (22). The DRS spectra of TPA₃/MCM-41 shows λ_{max} at 260 nm which is in good agreement with the earlier reported data (15) giving evidence for the presence of the undegraded $\text{H}_3\text{PW}_{12}\text{O}_{40}$ species in MCM-41.

The XRD patterns of pure MCM-41 and TPA₃/MCM-41 are shown in Figure 4. The XRD pattern of the calcined MCM-41 showed a sharp peak around $2\theta = 2^\circ$ and few weak peaks in $2\theta = 3 \sim 5^\circ$, which indicated well-ordered hexagonal structure of MCM-41. No separate HPA crystal phase of TPA was observed in the TPA₃/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.

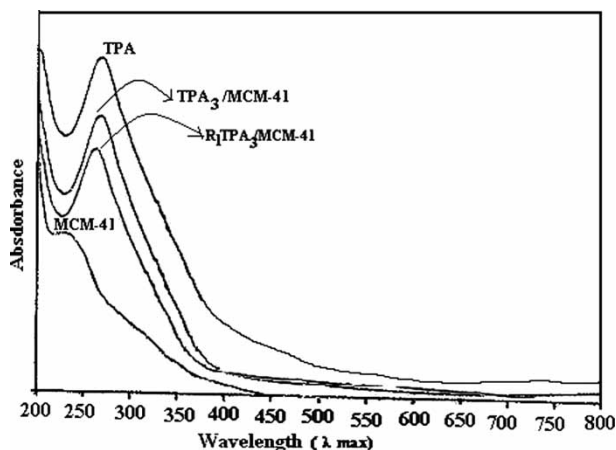


Figure 3. DRS spectra of MCM-41 and TPA₃/MCM-41 and recycled catalyst R₁TPA₃/MCM-41.

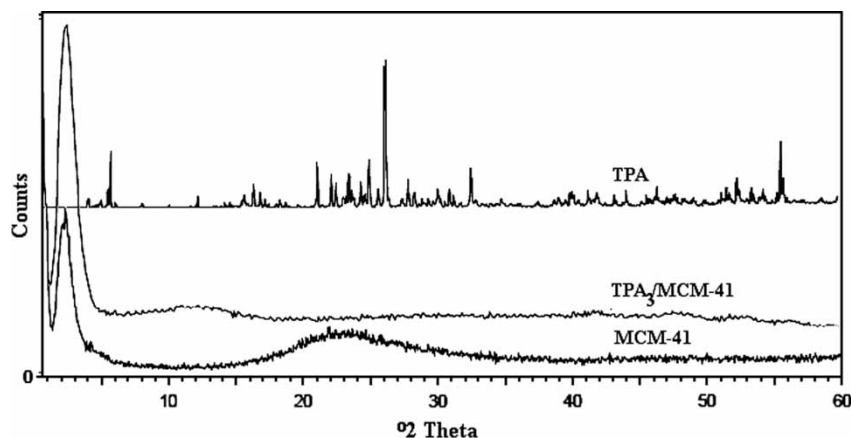
The N₂ adsorption–desorption isotherms of pure MCM-41 and TPA₃/MCM-41 are shown in Figure 5 (a, b). All the N₂ adsorption–desorption isotherms are of type IV in nature according to the IUPAC classification and exhibited an H1 hysteresis loop which is a characteristic of mesoporous solids (23). The adsorption branch of each isotherm showed a sharp inflection, which means a typical capillary condensation within uniform pores. 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. The inset in Figure 5 shows that all the samples have narrow pore size distribution within the mesopore range.

The results for surface area, pore size, and pore volumes are presented in Table 1. It was observed from Table 1 that specific surface area, porosity, and pore diameter, all strongly decreased for TPA-containing MCM-41 samples relative to the starting support. Even though the 20% loading of TPA containing catalyst, TPA₂/MCM-41, shows high surface area, pore volume, and pore diameter than TPA₃/MCM-41, it was not selected for carrying out detailed catalytic studies. TPA₃/MCM-41 was selected for the same. This can be explained on the basis of ³¹P NMR.

The total acidity values for all the materials determined by *n*-butylamine titration method are shown in Table 1. The obtained results indicate that MCM-41 was found to be fairly acidic. Also as percentage loading of TPA increases in anchored catalysts the total acidity also increases and the results are as expected.

The ³¹P NMR is the most important method to study chemical environment around the phosphorous in heteropoly compounds. The ³¹P NMR spectra of TPA, TPA₂/MCM-41, and TPA₃/MCM-41 are shown in Figure 6. The pure TPA shows single peak at -15.626 ppm and is in good agreement with the reported one (17).

The ³¹P NMR spectra of TPA₂/MCM-41 show two peaks: one at -15.44 ppm and another peak of lower intensity at -13.3 ppm. The peak at -15.44 ppm is as expected and is in good agreement with the reported one (17). Another peak at -13.3 ppm might indicate that the part of Keggin structure was deformed or distorted due to strong interactions with the support, but the fundamental Keggin structure was preserved. The results are in good agreement with the earlier reported one (24). As there was presence of two different structures of heteropolyacid inside the mesopores of MCM-41, TPA₂/MCM-41 was not selected for carrying out detailed catalytic studies.

Figure 4. XRD of MCM 41 and TPA₃/MCM-41.

The ^{31}P NMR spectra of TPA₃/MCM-41 show single peak at -15.523 ppm. No appreciable change in chemical shift value reveals that the surrounding environment around phosphorous does not change in TPA when anchored to MCM-41. In other words the Keggin ion structure is retained after anchoring to MCM-41. Hence TPA₃/MCM-41 was selected for detailed catalytic studies.

Figure 7 (a) and (b) shows the SEM image of MCM 41 and TPA₃/MCM41. The surface morphology of supported catalyst is almost identical to that of pure MCM-41. 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 TPA₃/MCM41. This can be clearly observed by XRD diffraction pattern.

Figure 8 (a, b) and (c, d) shows the TEM image of MCM 41 and TPA₃/MCM41, respectively. Figure 8 (a, b) clearly shows hexagonal mesopores in MCM-41. The TEM images of TPA₃/MCM41 (Figure 8 (c, d)) show that most of the hexagonal pores are covered with dark colored fine particles. This indicates uniform dispersion of TPA inside the hexagonal pores of MCM-41.

3. Experimental

3.1. Materials

All chemicals used were of A.R. grade. $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ and Cetyl triethyl ammonium bromide (CTAB) (Loba Chemie, Mumbai). Tetraethylorthosilicate (TEOS), succinic acid *n*-butanol,

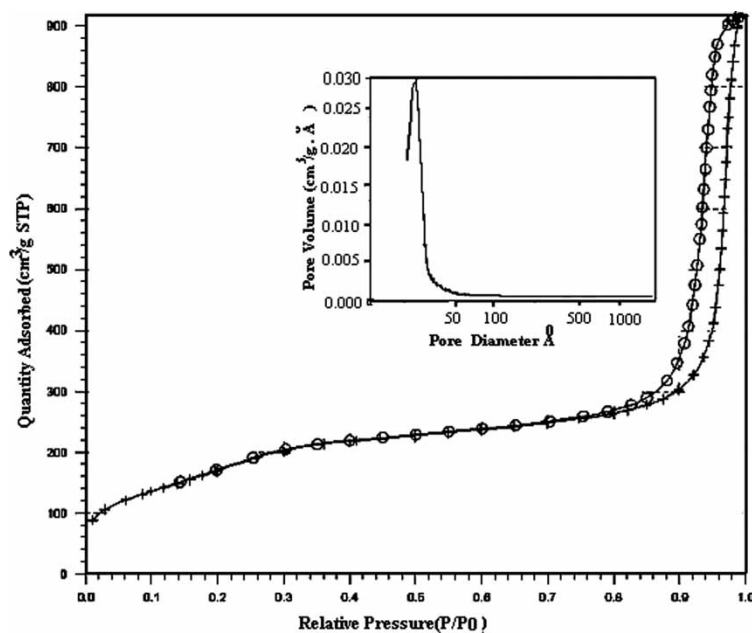


Figure 5a. Nitrogen sorption isotherms and pore size distribution of MCM-41.

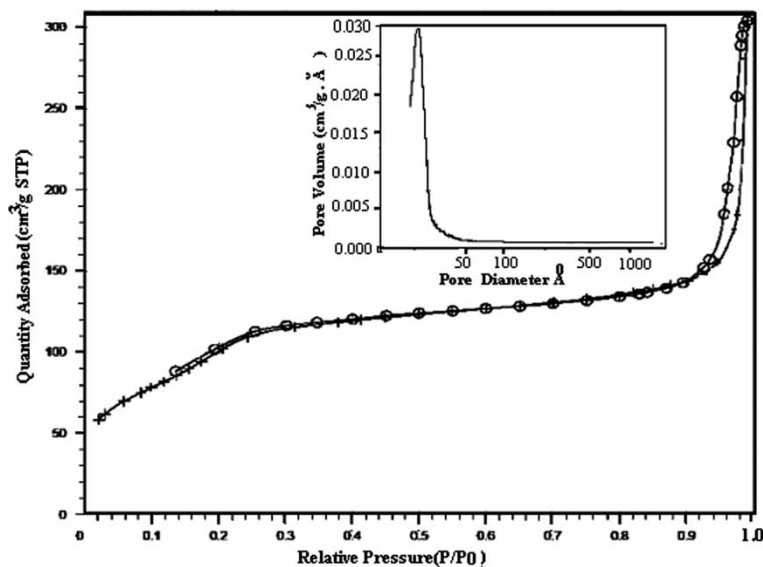


Figure 5b. Nitrogen sorption isotherms and pore size distribution of TPA₃/MCM-41.

hexanol, and octanol were used as received from Merck.

3.2. Synthesis of support (MCM-41)

MCM-41 was synthesized using reported procedure (25) with 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 drop wise and the obtained gel was aged for 2 hours. The resulting product was filtered, washed with distilled water, and dried at room temperature. The obtained material was calcined at 555°C in air for 5 hours and designated as MCM-41.

3.3. Synthesis of catalyst (TPA anchored to MCM-41)

A series of catalysts containing 10–40% of TPA anchored to MCM-41 were synthesized by impregnation. One gram of MCM-41 was impregnated with an aqueous solution of TPA (0.1/10 to 0.4/40 g/ml of double distilled water) and dried at 100°C for 10 h. The obtained materials were designated as TPA₁/

MCM-41, TPA₂/MCM-41, TPA₃/MCM-41, and TPA₄/MCM-41, respectively.

3.4. 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 color, which is observed when reacted with a mild reducing agent such as ascorbic acid (26). 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 λ_{max} of 785 cm⁻¹ for its absorbance values. A standard calibration curve was obtained by plotting values of absorbance against percent concentration. One gram of catalyst with 10 ml conductivity water was refluxed for 24 hours. Then 1 ml of the supernatant solution was treated with 10% ascorbic acid. Development of blue color was not observed indicating that there was no leaching. The same

Table 1. Textural properties.

Catalyst	Surface area (m ² /g)	<i>d</i> (Å) pore diameter	Mesopore volume (cm ³ /g)	<i>n</i> -butylamine surface acidity (mmol/g)
MCM-41	659	47.90	0.79	0.822
TPA ₁ /MCM-41	400	30.69	0.55	1.28
TPA ₂ /MCM-41	372	30.53	0.50	1.32
TPA ₃ /MCM-41	360	30.13	0.50	1.41

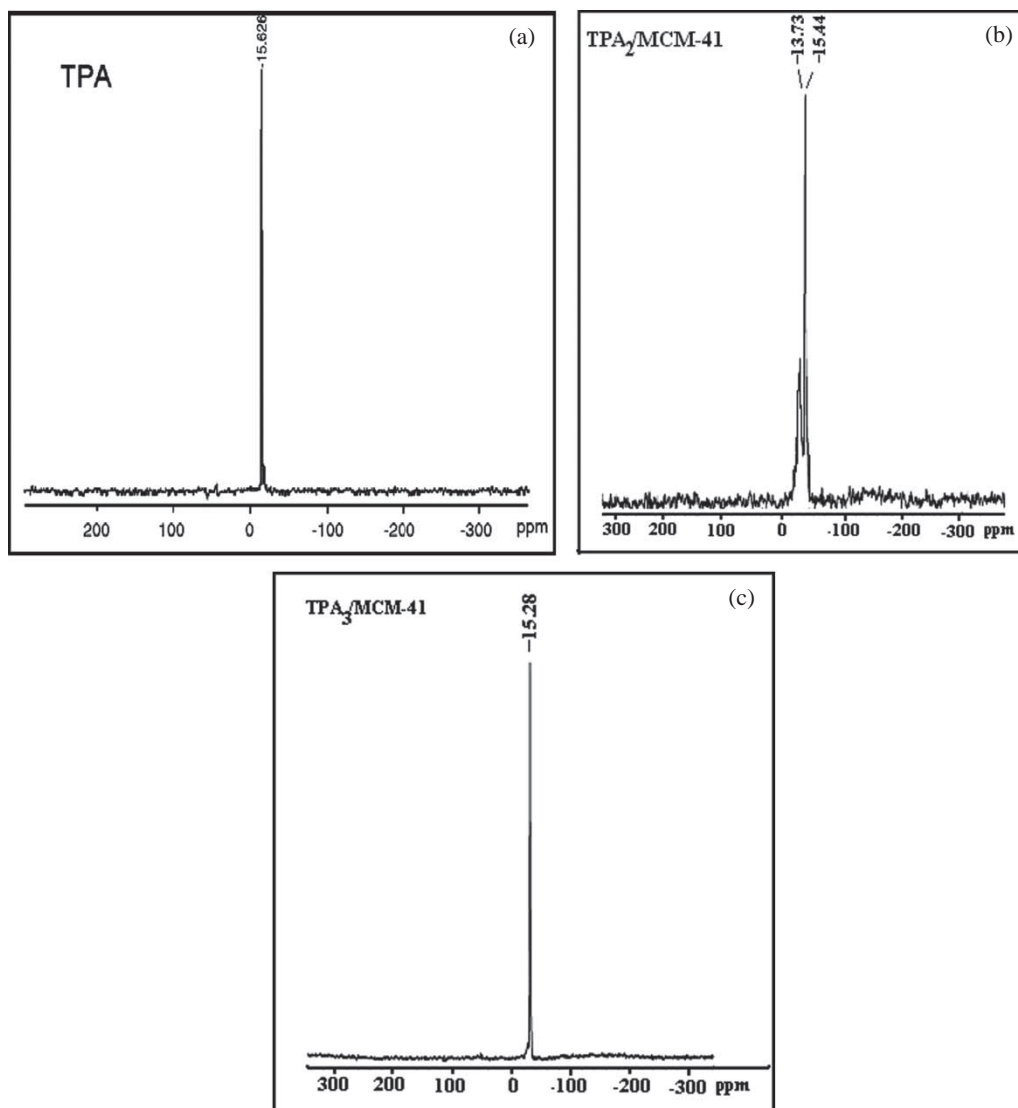


Figure 6. Solid state ^{31}P NMR of (a) TPA, (b) $\text{TPA}_2/\text{MCM-41}$, and (c) $\text{TPA}_3/\text{MCM-41}$.

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 color indicates no leaching of TPA.

3.5. Characterization

Thermo gravimetric analysis (TGA) was carried out on METTLER TOLEDO STAR SW 7.01 instrument. The FT-IR spectra of the samples were obtained by using KBr pellet on Perkin-Elmer. The DRS of sample were recorded at room temperature on Perkin Elmer 35 LAMDA instrument using barium sulfate as a reference. The XRD pattern was obtained by using PHILIPS PW-1830. The conditions used were CuK α radiation (1.5417 Å), scanning

angle from 0° to 60° . Adsorption–desorption isotherms of samples were recorded on a Micromatrics ASAp 2010 surface area analyzer at -196°C . From adsorption–desorption isotherms, surface area was calculated using BET method. The magic-angle spinning (MAS) solid state NMR study was carried out on a BRUKER NMR spectrometer under ambient conditions. The ^{31}P NMR spectra were recorded at 121.49 MHz using a 7 mm rotor probe with 85% phosphoric acid as an external standard. The spinning rate was 5–7 kHz. Catalyst samples after treatment were kept in a desiccator over P_2O_5 until the NMR measurement. The surface morphology of the support and supported catalyst was studied by SEM using a Jeol SEM instrument (model-JSM-5610LV) with scanning electron electrode at 15 kV. Scanning was done at 1 mm range and images

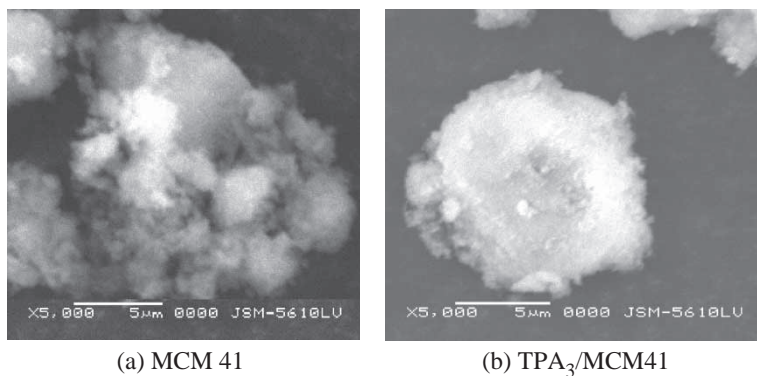


Figure 7. SEM of (a) support MCM 41 and (b) catalyst TPA₃/MCM-41.

taken at a magnification of $5000\times$ for MCM-41, TPA₃/MCM-41. TEM was done on JEOL (JAPAN) TEM instrument (model-JEM 100CX II) with accelerating voltage 100 kV. The samples were dispersed in ethanol and ultrasonicated for 5–10 minutes. A small drop of the sample was then taken in a carbon coated copper grid and dried before viewing.

3.6. Total acidity determination

The total surface acidity for all the materials has been determined by *n*-butylamine titration (27). A 0.025M solution of *n*-butylamine in toluene was used for estimation. The catalyst weighing 0.5 g was suspended in this solution for 24 hours and excess base was titrated against trichloroacetic acid using neutral

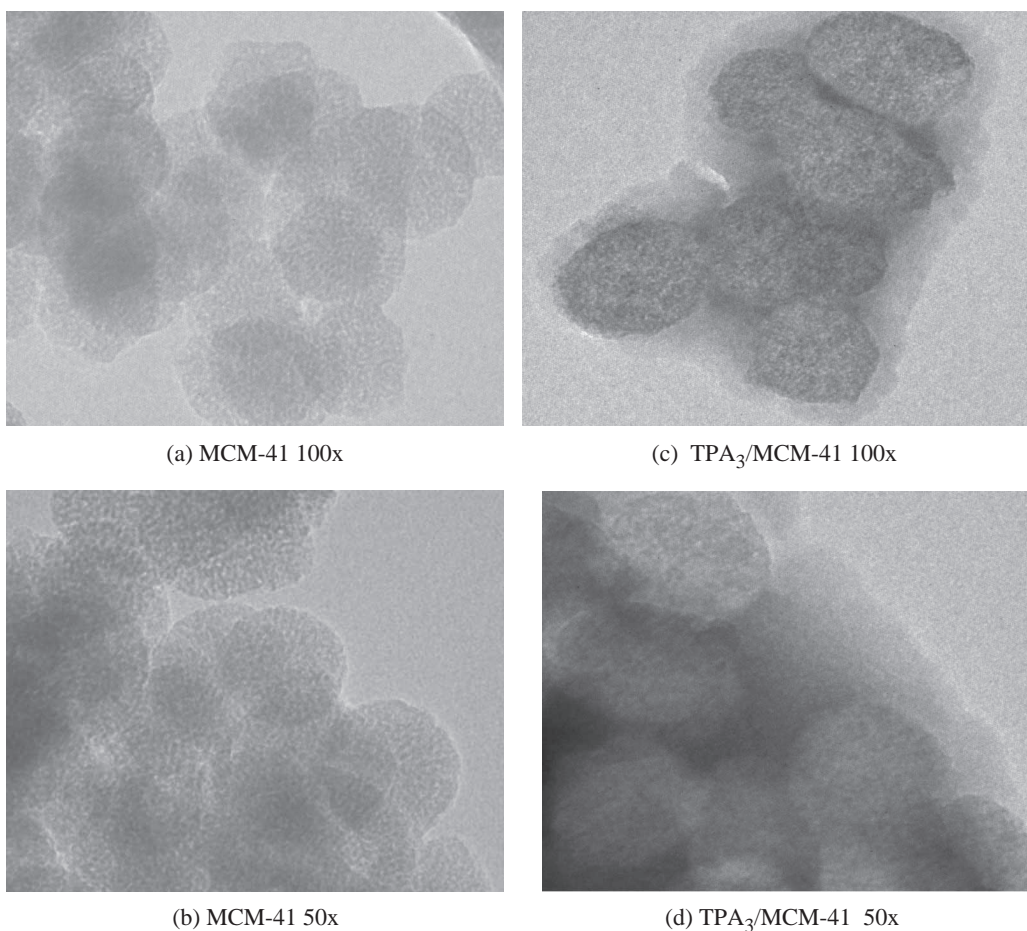


Figure 8. TEM of MCM41 (a, b) and TPA₃/MCM-14 (c, d).

red as an indicator. This gives the total surface acidity of the material.

3.7. Diesterification reaction

The diesterification reaction of succinic 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 8 hours. 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).

4. Diesterification of succinic acid to succinate diesters

Diesterification reaction of dicarboxylic acids to diesters requires strong Bronsted acidity as compared to simple esterification reactions. The diesterification of succinic acid 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 the present study corresponding alcohol is taken in excess. A diesterification reaction of succinic acid with an alcohol is shown in Scheme 1.

4.1. Effect of percentage loading of TPA onto MCM-41

The diesterification of succinic acid was carried out over TPA₁/MCM-41, TPA₂/MCM-41, TPA₃/MCM-41, and TPA₄/MCM-41. The conditions were: mole ratio of succinic acid to *n*-butanol is 1:3, reaction temperature 80°C and reaction time 8 hours, amount of the catalyst is 0.1 g. Results of the experiments are shown in Chart 1.

It is observed from Chart 1 that with increase in the percentage loading of TPA on to MCM-41, percentage yield of diester also increases. Even though the surface area of TPA₁/MCM-41 and

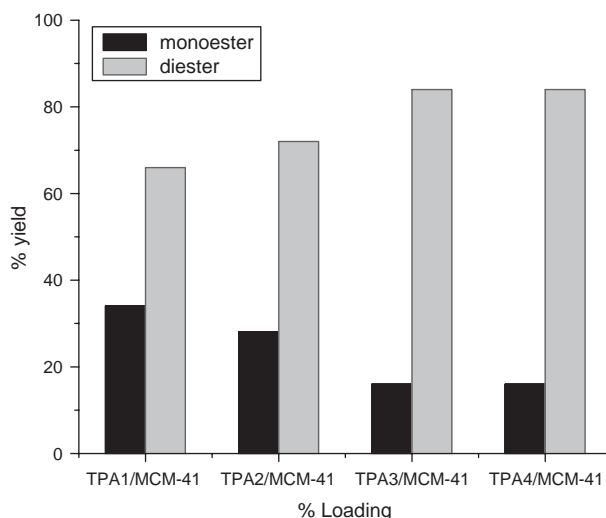


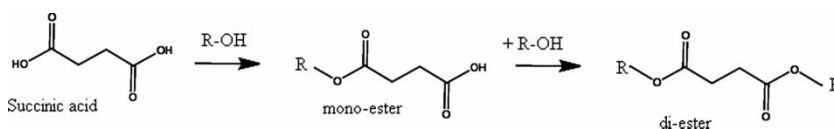
Chart 1. Percentage yields of esters with different percentage loading of TPA.

TPA₂/MCM-41 is greater than TPA₃/MCM-41, percentage yield for diester was less as compared to that of TPA₃/MCM-41. This may be explained from the acidity characterization, i.e. *n*-butyl amine acidity values of these catalysts. It can be observed from Table 1 that TPA₃/MCM-41 exhibits higher *n*-butyl amine acidity value as compared to TPA₁/MCM-41 and TPA₂/MCM-41.

As the 30% loading of TPA onto MCM-41 shows better activity, a detailed study was carried out over TPA₃/MCM-41.

4.2. Effect of mole ratio of succinic acid to *n*-butanol

It is seen from Chart 2 that with increase in the concentration of *n*-butanol, there is a drastic change in percentage yield of the products. Initially with increase in *n*-butanol concentration yield towards diester increases from 48 to 84% when the molar ratio changes from 1:2 to 1:3. On further increasing the alcohol concentration equilibrium is attained and no further increase in percentage yield of diester was observed. This can be explained by competitive adsorption of reactants on catalyst. On increasing *n*-butanol in the reaction mixture, a majority of the adsorption sites of the catalyst surface are occupied by *n*-butanol molecules. Hence fewer sites remain available for the reactant (succinic acid). Hence



Scheme 1. Reaction scheme for diesterification of succinic acid with an alcohol.

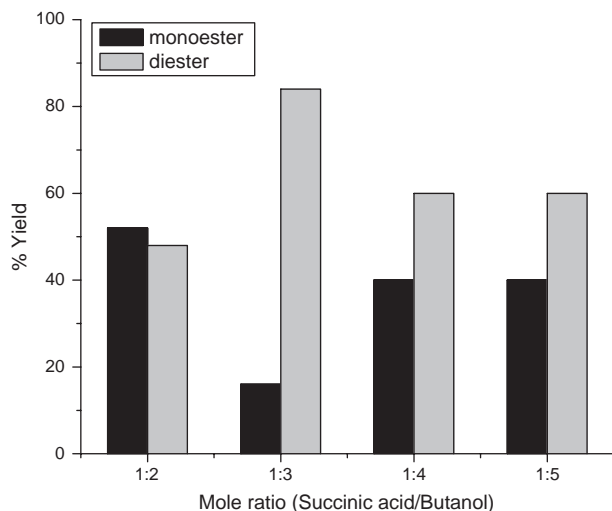


Chart 2. Percentage yields of esters with different molar ratio of succinic acid to *n*-butanol.

further reactions were carried out in 1:3 molar ratio of acid to alcohol.

4.3. Effect of amount of catalyst

To study the effect of the amount of the catalyst, the reaction was carried out with different amounts of the catalyst, keeping the mole ratio of acid to alcohol 1:3 for 8 hours at 80°C. As it is seen from Chart 3 that with increase in amount of catalyst percentage yield towards diester increases. With 0.1 g catalyst percentage yield towards diester is maximum.

4.4. Effect of reaction time

It is interesting to note down the change in distribution of products with increase in the reaction time.

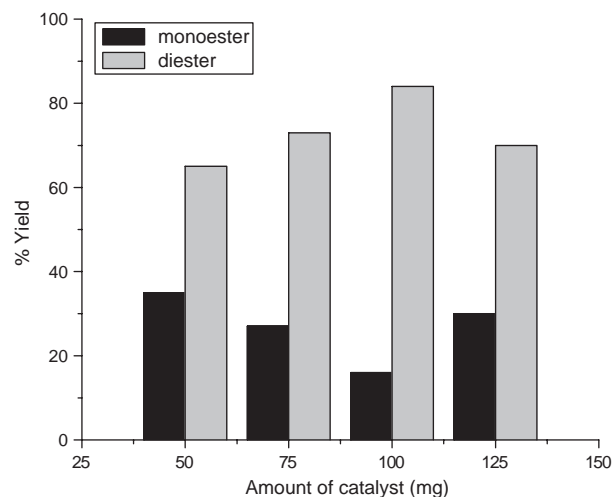


Chart 3. Percentage yields of esters with different amount of catalyst.

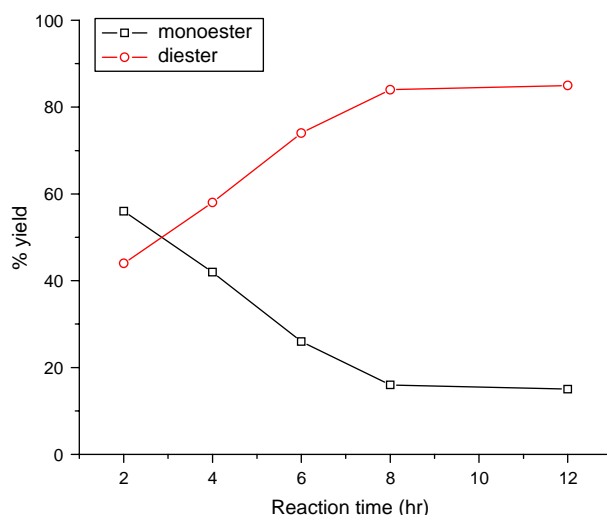


Chart 4. Percentage yields of esters by varying reaction time.

Initially the major product is mono-ester and minor product is diester. As the reaction time increases the product yield shifts towards diester. The mechanism of diesterification of succinic acid over TPA₃/MCM-41 is similar to that of conventional mechanism which involves the protonation of succinic acid, followed by nucleophilic attack of alcoholic group to yield respective mono-ester. The carboxylic group present in the mono-ester gets further esterified following the same mechanism which results in the formation of diester. The formation of diester from mono-ester is a slow reaction as compared to that of formation of mono-ester from succinic acid. As time increases more and more mono-ester is converted to diester. The obtained results are as expected (Chart 4).

The optimized conditions for diesterification of succinic acid with *n*-butanol using TPA₃/MCM-41 are: mole ratio of acid to alcohol 1:3, amount of catalyst 0.1 g, reaction temperature 80°C, and reaction time 8 hours.

4.5. Diesterification of succinic acid with various alcohols

The diesterification of succinic acid with different alcohols such as pentanol, hexanol, and octanol was also carried out under optimized conditions and the percentage yields of corresponding esters are shown in Table 2.

4.6. Recycling of the catalyst

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 DRS of used catalyst was recorded.

Table 2. Yield of esters with different alcohols in optimized condition.

Alcohol ^a	Percentage yield/TON ^b	
	Monoester	Diester
Butanol	16/2 × 10 ⁴	84/10.5 × 10 ⁴
Pentanol	25/3.1 × 10 ⁴	75/9.3 × 10 ⁴
Hexanol	23/2.8 × 10 ⁴	77/9.8 × 10 ⁴
Octanol	0.6/0.075 × 10 ⁴	99.4/12.43 × 10 ⁴

^aReaction conditions: Amount of catalyst: 0.1 g; mole ratio, 1:3; reaction temperature, 80°C; reaction time, 8 hours.

^bTON is defined as mole substrate reacted per mole catalyst.

Figure 3 illustrates the DRS of fresh catalyst as well as used catalyst. No difference in DRS indicates the stability of the used catalyst 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 color indicates no leaching of TPA.

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 un-reacted succinic acid, if any, dried at 100°C in an oven for 5 hours, and the recovered catalyst was charged for the further run. The obtained results are as shown in Table 3. It is seen from the table that the catalyst can be reused up to four cycles without any appreciable change in the percentage yield.

5. Conclusion

Thermo gravimetric analysis (TGA) confirms the stability of the catalyst up to 600°C. DRS spectra indicate that the Keggin structure of TPA was not destroyed after anchoring to MCM-41. The ³¹P NMR spectrum confirms that the Keggin ion structure of TPA

was retained even after anchoring to MCM-41. XRD shows that TPA is present in highly dispersed form inside the mesopores of MCM-41. TEM images clearly show the uniform dispersion of TPA throughout all the regions without disturbing the hexagonal array of MCM-41.

The present contribution reports solvent free diesterification of succinic acid, a potential bioplat-form molecule, with alcohols under mild reaction conditions over an efficient green catalyst comprising TPA and MCM-41. The catalyst shows high activity in terms of higher yields toward diesters, especially for dioctyl succinate 99% yield was obtained.

The present catalyst exhibits all excellent properties to consider its use for large-scale and/or commercial processes and is promising cleaner alternative to the traditional catalysts.

Acknowledgements

One of the authors, Ms. Varsha Brahmkhatri, is thankful to BRNS, Project. No. 2007/37/20/BRNS/917, BARC, Mumbai, for the financial assistance.

References

- (1) Werpy, T., Pedersen G., Eds. *Top Value Chemicals from Biomass*, 2004; <http://www1.eere.energy.gov/biomass/pdfs/35523.pdf>
- (2) Reddya, C.R.; Iyengara, P.; Nagendrappab, G.; Jai Prakash, B.S. Esterification of Dicarboxylic Acids to Diesters over Mn+ Montmorillonite Clay Catalysts. *Catal. Lett.* **2005**, *101*, 87–91.
- (3) Kolah, A.K.; Asthana, N.S.; Vu, D.T.; Lira, C.T.; Miller, D.J. Reaction Kinetics for the Heterogeneously Catalyzed Esterification of Succinic Acid with Ethanol. *Ind. Eng. Chem. Res.* **2008**, *47*, 5313–5317.
- (4) Clark, J.H.; Budarin, V.; Dugmore, T.; Luque, R.; Macquarrie, D.J.; Strelko, V. Catalytic Performance of Carbonaceous Materials in the Esterification of Succinic Acid. *Cat. Comm.* **2008**, *9*, 1709–1714.
- (5) Nandhini, K.U.; Arabindo, B.; Palanichamy, M.; Murugesan, V. Al-MCM-41 Supported Phosphotungstic Acid: Application To Symmetrical and Unsymmetrical Ring Opening of Succinic Anhydride. *J. Mol. Catal. A: Chem* **2009**, *243*, 183–193.
- (6) Kozhevnikov, I.V.; Sinnema, A.; Janse, R.J.; Pamin, K.; Bekkum, V.H. New Acid Catalyst Comprising Heteropoly Acid on a Mesoporous Molecular Sieve MCM-41. *Catal. Lett.* **1995**, *30*, 241–252.
- (7) Kozhevnikov, I.V. Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions. *Chem. Rev.* **1998**, *98*, 171–198.
- (8) Angelis, A.D.; Amarilli, S.; Berti, D.; Montunari, L.; Perego, C. Alkylation of Benzene Catalysed by Supported Heteropolyacids. *J. Mol. Catal. A* **1999**, *146*, 37–44.

Table 3. Percentage yield of esters with recycled catalysts.

Catalyst	Butanol	Pentanol	Hexanol	Octanol
	DBS	DPS	DHS	DOS
Fresh catalyst	84	75	77	99.4
1st	83	73	75	99.0
2nd	83	73	75	99.0
3rd	83	73	75	99.0
4th	83	73	75	99.0

Reaction conditions: amount of catalyst, 0.1 g; mole ratio, 1:3; reaction temperature, 80°C; reaction time, 8 hours.

Abbreviations: DBS, dibutylsuccinate; DPS, dipentylsuccinate; DHS, dihexylsuccinate; DOS, dioctylsuccinate.

- (9) Izumi, Y.; Hisano, K.; Hidu, T. Acid Catalysis of Silica-Included Heteropolyacid in Polar Reaction Media. *Appl. Catal. A* **1999**, *181*, 277–282.
- (10) Mao, J.; Kamiya, Y.; Okuhara, T. Alkylation of 1,3,5-Trimethylbenzene with γ -Butyrolactone over Heteropolyacid Catalysts. *Appl. Catal. A* **2003**, *255*, 337–344.
- (11) Devussy, B.M.; Shanbhag, G.V.; Lefebvre, F.; Halligudi, S.B. Alkylation of *p*-Cresol with Tert-Butanol Catalyzed by Heteropoly Acid Supported on Zirconia Catalyst. *J. Mol. Catal. A* **2004**, *210*, 125–130.
- (12) Patel, S.; Purohit, N.; Patel, A. Synthesis, Characterization and Catalytic Activity of New Solid Acid Catalyst, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ Supported onto Hydrous Zirconia. *J. Mol. Catal. A: Chem.* **2003**, *192*, 195–202.
- (13) Sharma, P.; Vyas, S.; Patel, A. Heteropolyacid Supported onto Neutral Alumina: Characterization and Esterification of 1° and 2° Alcohol. *J. Mol. Catal. A: Chem.* **2004**, *214*, 281–286.
- (14) Sharma, P.; Patel, A. Tungstophosphoric Acid Supported onto Hydrous Zirconia: Physicochemical Characterization and Esterification of 1° and 2° Alcohol. *Bull. Mater. Sci.* **2006**, *29*, 439–447.
- (15) Bhatt, N.; Shah, C.; Patel, A. 12-tungstophosphoric and 12-tungstosilicic acid Supported onto Hydrous Zirconia for Liquid Phase Tert-Butylation of *m*-Cresol. *Cat. Lett.* **2007**, *117*, 146–152.
- (16) Bhatt, N.; Sharma, P.; Patel, A.; Selvam, P. Supported 12-Tungstophosphoric acid: An Efficient and Selective Solid Acid Catalyst for Tert-Butylation of Phenol and Cresols. *Cat. Comm.* **2008**, *9*, 1545–1550.
- (17) Okuhara, T.; Mizuno, N.; Misono, M. Catalytic Chemistry of Heteropoly Compounds. *Adv. Catal.* **1994**, *41*, 113–252.
- (18) Mizuno, N.; Misono, M. Heterogeneous Catalysis. *Chem. Rev.* **1998**, *98*, 199–218.
- (19) Moffat J.B.; Twigg, M.V.; Spencer M.S., Eds. *Metal Oxygen Cluster, The Surface and Catalytic Properties of Heteropoly Oxometalate*; Kluwer Academic Publisher: New York, 2001, pp 42, 146.
- (20) Lim, M.H.; Branford, C.F.; Stein, A. Synthesis and Characterization of a Reactive Vinyl-Functionalized MCM-41: Probing the Internal Pore Structure by a Bromination Reaction. *J. Am. Chem. Soc.* **1997**, *119*, 4090–4091.
- (21) Kamalakar, G.; Komura, K.; Kubota, Y.; Sugi, Y. Friedel-Crafts Benzoylation of Aromatics with Benzyl Alcohols Catalyzed by Heteropoly Acids Supported on Mesoporous Silica. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 981–988.
- (22) Hu, J.C.; Wang, Y.D.; Chen, L.F.; Richards, R.; Yang, W.M.; Liu, Z.C.; Xu, W. Synthesis and Characterization of Tungsten-Substituted SBA-15: An Enhanced Catalyst for 1-Butene Metathesis. *Micropor. Mesopor. Mater.* **2006**, *93*, 158–263.
- (23) Yang, L.; Qi, Y.; Yuan, X.; Shen, J.; Kim, J. Direct Synthesis, Characterization and Catalytic Application of SBA-15 Containing Heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$. *J. Mol. Catal. A: Chem.* **2005**, *229*, 199–205.
- (24) Chena, L.F.; Wanga, J.A.; Noren, L.E.; Aguilarb, J.; Navarretec, J.; Salasc, P.; Montoyac, J.A.; Del Angel, P. Synthesis and Physicochemical Properties of Zr-MCM-41 Mesoporous Molecular Sieves and Pt/ $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /Zr-MCM-41 Catalysts. *J. Solid State Chem.* **2007**, *180*, 2958–2972.
- (25) Cai, Q.; Luo, Z.S.; Pang, W.Q.; Fan, Y.W.; Chen, X.H.; Cui, F.Z. Dilute Solution Routes to Various Controllable Morphologies of MCM-41 Silica with a Basic Medium. *Chem. Mater.* **2001**, *13*, 258–263.
- (26) Yadav, G.D.; Bokade, V.V. Novelty of Heteropoly Acid Supported on Clay: Etherification of Phenethyl Alcohol with Alkanols. *Appl. Catal. A: Gen.* **1996**, *147*, 299–323.
- (27) Sahu, H.R.; Rao, G.R. Characterization of Combustion Synthesized Zirconia Powder by UV-vis, IR and Other Techniques. *Bull. Mater. Sci.* **2000**, *23*, 349–354.