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Synthesis and Characterization of 12-Tungstosilicic Acid Anchored to MCM-41 as well as Its Use as Environmentally Benign Catalyst for Synthesis of Succinate and Malonate Diesters

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ABSTRACT: 12-Tungstosilisic acid anchored to MCM-41 was synthesized and characterized by various physicochemical techniques such as thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), laser-Raman spectroscopy, diffuse reflectance spectroscopy (DRS), N₂ adsorption—desorption, ²⁹Si-magic-angle spinning (MAS) NMR, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The total acidity was determined by *n*-butyl amine titration. The types of acidic sites (acidic strength) were determined by potentiometric titration. The use of synthesized material was explored for esterification of diacarboxylic acids with butanol. Influence of various reaction parameters (catalyst concentration, acid/alcohol molar ratio and reaction time) on catalytic performance was studied. The catalyst shows high activity in terms of higher yields toward diesters, especially for dioctyl succinate and dioctyl malonate. The catalyst was also regenerated and reused for four cycles. All these characteristics imply the high potential of an environmentally benign catalyst for synthesis of succinate and malonate diesters.

1. INTRODUCTION

In the last decades, "supported hetropolyacids" have attracted much attention as economically and environmentally benign catalyst. Because of the growing importance of their use for industrial chemistry, they are acquiring considerable importance in a variety of industrially important organic transformations such as hydrogenations, oxidations, aklylation, acylation, and esterifications. ^{1–5}

Among the variety of acid catalyzed reactions, especially esterification reactions have been carried out over 12-tungsto-phosphoric acid supported onto different supports. At the same time, even though 12-tungstosilicic acid is the next acidic and stable 10-13 heteropoly acid in the Keggin series, not much work has been carried out for this acid. T. Dogu et al. have reported silicotungstic acid impregnated MCM-41-like meso-porous solid acid catalysts for dehydration of ethanol. Halligudi et al. reported silicotungstic acid/zirconia immobilized on SBA-15 for esterification. Thus, a literature survey shows that there are no reports for the use 12-tungstosilicicacid anchored to MCM-41 for esterification of dicarboxylic acids.

Esterification of diacarboxylic acids is very important as the obtained diesters are known to be entirely biorenewable or green chemicals that can replace petroleum-based solvents. Due to their high oxygen content, many diesters are used as additives in fuels. They are important intermediates in the synthesis of fine chemicals, drugs, plasticizers, food preservatives, pharmaceuticals, and cosmetics. Among all, esters of succinic acid and malonic acid are most important as they find applications in synthesis of plasticizers, perfumes, fragrance in food and cosmetics, diluents in paints and coatings, and intermediates in drugs and dye stuffs. ¹⁶

The conventional procedures for production of diesters involve a stirred batch or continuous reactor with sulphuric acid 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, by use of solid acid catalysts. A number of solid acid catalysts such as clays,¹⁷ ion exchange resins,¹⁸ carbonaceous materials,¹⁹ and phosphotungstic acid anchored to Al-MCM-41²⁰ have been reported for esterification of succinic acid. Most of the reported esterifications of succinic acid have been carried out using solvents and at a longer reaction period. A literature survey also shows that malonate esters have been generally synthesized by transesterification.^{21–23} Transesterification of malonate esters requires high reaction temperature and time.

Hence, keeping in mind the importance of succinate and malonate esters as well as supported heteropolyacids, in the present contribution, it was thought of interest to explore the potential of 12-tungstosilicicacid (TSA) anchored to MCM-41 as an environmentally benign catalyst for esterification of dicarboxylic acids, succinic acid, and malonic acid. A series of catalysts, containing 10-40% TSA anchored to MCM-41, were synthesized. The support and catalysts were characterized by various thermal and spectral techniques such as thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), laser Raman spectroscopy, diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), surface area measurement (BET method), pore size and pore volume distribution, and ²⁹Si 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-butyl amine titration. The types of acidic sites were determined by potentiometric titration. The catalytic activity was

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evaluated for liquid phase esterification of succinic acid and malonic acid with *n*-butanol 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. Esterification of succinic acid and malonic with different alcohols (ethanol, hexanol, octanol) was also carried out under optimized conditions. The catalyst was regenerated and reused up to four cycles.

2. EXPERIMENTAL SECTION

- **2.1. Materials.** All chemicals used were of A.R. grade. $H_4SiW_{12}O_{40}$, nH_2O , and cetyl triethyl ammonium bromide (CTAB) were from Loba chemie (Mumbai). Tetraethylorthosilicate (TEOS), malonic acid, n-butanol, hexanol, and octanol were used as received from Merck.
- **2.2.** Synthesis of Support (MCM-41). MCM-41 was synthesized using a reported procedure²⁴ 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 dropwise and the obtained gel was aged for 2 h. 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 h and designated as MCM-41.
- **2.3.** Synthesis of the Catalyst (TSA Anchored to MCM-41). A series of catalyst containing 10-40% of TSA anchored to MCM-41 were synthesized by impregnation. One gram of MCM-41 was impregnated with an aqueous solution of TPA (0.1 g/10 mL-0.4 g/40 mL of double distilled water) and dried at 100 °C for 10 h. The obtained materials were designated as TSA₁/MCM-41, TSA₂/MCM-41, TSA₃/MCM-41, and TSA₄/MCM-41, respectively.
- **2.4. 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 TSA from the support. HPA can be quantitatively characterized by the heteropoly blue color, which is observed when it reacted with a mild reducing agent such as ascorbic acid. In the present study, this method was used for determining the leaching of TSA from the support. Standard samples containing 1-5% of TSA 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 % concentration. One gram of catalyst with 10 mL of conductivity water was refluxed for 24 h. 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 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 TSA. The absence of blue color indicates no leaching of TSA.
- **2.5. Characterization.** TGA was carried out on METTLER TOLEDO STAR SW 7.01 instrument. The FT-IR spectra of the samples were obtained using KBr pellet on Perkin-Elmer. The Raman spectra were recorded on a FT-Raman Spectrophotometer Model Bruker FRA 106. The DRS of samples was recorded at room temperature on Perkin-Elmer 35 LAMDA instrument using barium sulfate as a reference. The XRD pattern was obtained using PHILIPS PW-1830. The conditions used were as follows: Cu K α radiation (1.5417 A°) and scanning angle from 0° to 60°. Adsorption—desorption isotherms of samples

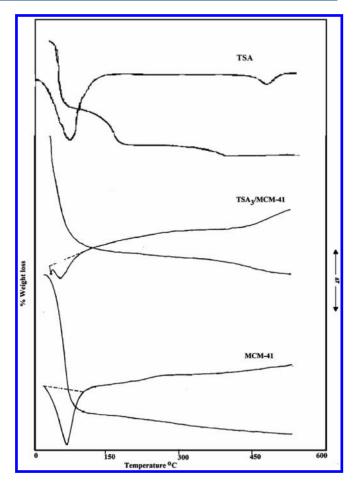


Figure 1. TGA of MCM-41 and TSA₃/MCM-41.

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 magicangle spinning (MAS) solid state NMR study was carried out on a BRUKER NMR spectrometer under ambient conditions. The ²⁹Si NMR spectra were recorded at 121.49 MHz using a 7 mm rotor probe, number of acquisitions AQ: 0.0048888 s, with TMS as an external standard. The surface morphology of the support and supported catalyst was studied by scanning electron microscopy. SEM and elemental analysis were carried out using a Jeol SEM instrument (model-JSM-5610LV) combined with an INCA instrument for energy dispersive X-ray spectroscopyscanning electron microscopy (EDS-SEM), with scanning electron electrode at 15 kV. Scanning was done at 1 mm range, and images were taken at a magnification of 5000× for MCM-41 and TPA₃/MCM-41. TEM was done on JEOL (JAPAN) TEM instrument (model-JEM 100CX II) with accelerating voltage of 100 kV. The samples were dispersed in ethanol and ultrasonicated for 5–10 min. A small drop of the sample was then taken in a carbon coated copper grid and dried before viewing.

2.6. Total Acidity Determination. The total surface acidity for all the materials has been determined by *n*-butylamine titration. ²⁵ 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 surface acidity of the material.

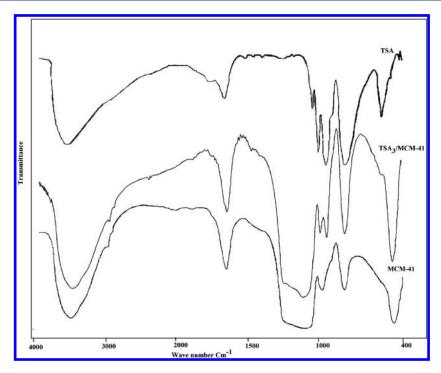


Figure 2. FT-IR spectra of MCM-41, TSA, and TSA₃/MCM-41.

2.7. Determination of Acidic Strength. The determination of the types of acidic sites and their quantification was made by potentiometric titration with 0.05 N *n*-butyl amine in acetonotrile. A sample of 0.5 g of the catalyst was added to 50 mL of acetonitrile, and the system was magnetically stirred at 25 °C. The initial potential was measured after electrode signal stabilization. Small aliquots (0.5 mL) of 0.05 N *n*-butyl amine in acetonotrile were added, and the potential was measured after stabilization of readings.²⁶

2.8. Esterification Reaction. 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. The 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 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).

3. RESULTS AND DISCUSSION

For TSA_3/MCM -41, the analytically calculated percentage of elements was as follows (%): W, 19; Si, 27.0; O, 54.0. Results obtained by EDS were as follows (%): W, 17.97; Si, 27.0; O, 55.3. The results obtained from EDS were in good agreement with the theoretical values.

TGA of pure TSA, MCM-41, and TSA₃/MCM-41 is shown in Figure 1. The TGA of 12-tungstosilicicacid (TSA) shows 4-6% weight loss within a temperature range of 100-180 °C which is due to the loss of adsorbed water molecules. Further, it shows 1-3% weight loss at 250-280 °C due to the loss of water of crystallization and 1-3% weight loss at 470-500 °C, which is due to the decomposition of heteropolyacid, and this is in good agreement with the reported one. 12

TGA of MCM-41 shows initial weight loss of 6.14% at $100\,^{\circ}\mathrm{C}$. 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, the absence of any weight loss indicates that support is stable up to $600\,^{\circ}\mathrm{C}$.

The TGA of TSA_3/MCM -41 shows initial weight loss of 10.5% due to the loss of adsorbed water. Second weight loss of 2.8% 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 TSA molecules inside the channels of MCM-41. This type of inclusion causes the stabilization of TSA molecules inside the channels of MCM-41.

FT-IR spectra of MCM-41, TSA, and TSA₃/MCM-41 are shown in Figure 2. The FTIR of TSA has five characteristic bands at 1020, 980, 926, 878, and 779 cm⁻¹ which corresponds to W=O symmetrical and asymmetrical, Si-O asymmetrical, W-Ob-W asymmetrical, and W-Oc-W asymmetrical, respectively.¹²

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 bands at 460 and 808 cm⁻¹ might be attributed to the bending vibration of the Si–O–Si bonds and free silica. 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.

The FT-IR spectrum of TSA₃/MCM-41 (Figure 2) is almost the same as that of the support, MCM-41. The typical bands for TSA, at 979 cm⁻¹ and 923 cm⁻¹, corresponding to W—O and Si—O symmetric stretching, respectively, are clearly observed in TSA₃/MCM-41. The presence of these bands strongly reveals that the primary structure of TSA Keggin anion is preserved even after anchoring to MCM-41 support. The absence of vibration

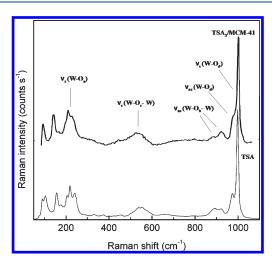


Figure 3. Raman spectra of TSA and TSA₃/MCM-41.

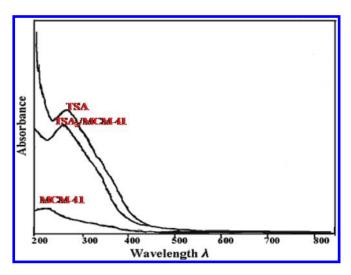


Figure 4. DRS spectra of MCM-41, TSA and TSA₃/MCM-41.

band at 799 cm⁻¹ of TSA may be because of very low concentration of TSA, or the TSA bands may be superimposed with those of support.

In addition to the characteristic band for TSA, FT-IR spectra of TSA₃/MCM-41 also shows the infrared absorption peaks at 1637 and 3450 cm⁻¹ with a shoulder at 3250 cm⁻¹, probably corresponding to the bending and stretching vibrations of bridging hydroxyl, respectively, because of the interaction of TSA anions and surface silanol groups of MCM-41. Raman spectra of TSA and TSA₃/MCM-41 are shown in Figure 3. The Raman spectrum of TSA shows bands at 1019, 981, 927, 881, and 785, which corresponds to ν_s (W-O_d), ν_{as} (W-O_d), ν_{as} (W-O_d), ν_{as} (W-O_b-W), ν_s (W-O_c-W), and ν_s (W-O_a), respectively (Figure 4) where O_a, O_b, O_c, and O_d correspond to the oxygen atoms linked to silicon, 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.²⁷ The Raman spectrum of TSA₃/MCM-41 remains almost the same, confirming the retainment of the Keggin structure. Furthermore, the absence of a significant band shift in the spectra indicates that the environment of the Keggin unit is similar in the TSA and anchored catalysts, TSA₃/MCM-4.

Table 1. Textural Properties of Support and Catalysts

material	BET surface area (m^2/g)	pore diameter d(Å)	mesopore volume/ porosity cm ³ /g
MCM-41	659	47.9	0.79
TSA ₁ /MCM-41	539.29	29.62	0.39
TSA ₂ /MCM-41	464.16	29.45	0.30
TSA ₃ /MCM-41	349.26	29.23	0.26

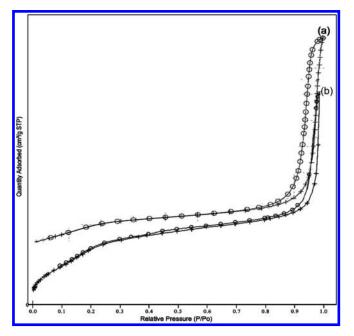


Figure 5. N_2 adsorption—desorption isotherms of pure (a) MCM-41 and (b) TSA₃/MCM-41.

The DRS spectra of MCM-41, TSA, and TSA₃/MCM-41 are shown in Figure 4. A broad band from 260 to 275 was observed for TPA. This characteristic band can be assigned to the oxygen—metal charge transfer of tungstophosphate anion ${\rm SiW_{12}O_{40}}^{-4}$ which is in agreement with a previous report. 28 The DRS spectra of TSA₃/MCM-41 show $\lambda_{\rm max}$ at 260 nm, giving evidence of presence of the stable Keggin ion species in MCM-41.

The values of surface area, pore size, and pore volumes are presented in Table 1. Specific surface area, porosity, and pore diameter all strongly decreased for TSA₃/MCM-41 relative to MCM-41. As the TSA loading increases surface area, pore diameter and pore volume both strongly decrease. The reason is, as the TSA species will enter the mesopores, it decreases the pore diameter and, also, probably some TSA species will appear in the mesoporous channels that decrease the average pore volume as well as the surface area.

The $\rm N_2$ adsorption—desorption isotherms of pure MCM-41 and TSA₃/MCM-41 are shown in Figure 5. All the $\rm N_2$ adsorption—desorption isotherms are the type IV in nature according to the IUPAC classification and exhibited an H1 hysteresis loop which is a characteristic of mesoporous solids. ²⁹ 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 TSA. The position of the inflection point is clearly related to the diameter of the

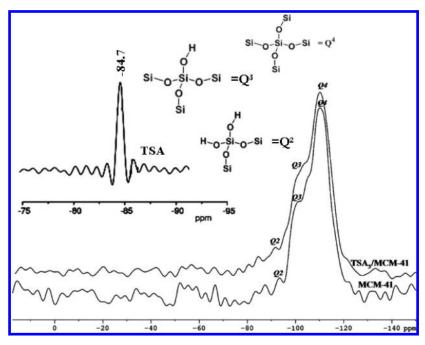


Figure 6. ²⁹Si MAS NMR spectra of the MCM-41 and TSA₃/MCM-41.

Table 2. ²⁹Si MAS-NMR Data of MCM-41 and TSA₃/MCM-41

		²⁹ Si MAS NMR data					
catalyst	Q4%	Q3%	Q2%	(Q3 + Q2)/Q4			
MCM-41	73	23	36	0.37			
TSA ₃ /MCM-41	67.5	28	4.5	0.48			

mesopore, and the sharpness of this step indicates the uniformity of the mesopore size distribution. In addition, narrow pore size distribution was observed for both MCM-41and TSA₃/MCM-41, indicating long-range order over large scales. The decrease in pore diameter in the catalyst TSA₃/MCM-41 is due to the presence of TSA.

 $^{29}\mathrm{Si}$ MAS NMR is the most important method to study chemical environment around the silicon nuclei in mesoporous silica materials. Figure 6 shows the $^{29}\mathrm{Si}$ MAS NMR spectra of the pure TSA, MCM-41, and TSA₃/MCM-41. $^{29}\mathrm{Si}$ NMR of pure TSA shows a single peak at 84.7 ppm. $^{29}\mathrm{Si}$ MAS NMR spectra of MCM-41 and TSA₃/MCM-41show three peaks which can be attributed to signals with chemical shifts at -93, -103, and -110 ppm. These signals result from Q²(-93 ppm), Q³ (-103 ppm), and Q⁴ (-110 ppm) 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 TSA, Q³ to silanol (X-O)-Si-(O-Si)₃, and Q⁴ to Si-(O-Si)₄ in the framework. 30,31

The spectra of TSA₃/MCM-41 were relatively broad as compared to MCM-41 which may be due the presence of TSA. Also, the intensity of the Q^2 and Q^3 peaks decreases when the support, MCM-41, is loaded with TSA, i.e., in catalysts TSA₃/MCM-41. This reveals that MCM-41 mesoporous structure may be perturbed due to the presence of TSA inside the hexagonal channels. The fractions of Q^2 , Q^3 , and Q^4 units and their relative values derived from the Figure 6 are given in Table 2. If the values of $(Q^3 + Q^2)/Q^4$ for MCM-41 and TSA₃/MCM-41 were

compared, the greater value obtained for TSA₃/MCM-41 catalyst would indicate strong interaction between MCM-41 frameworks and TSA.

FT-IR and DRS spectra show that Keggin ion structure of TSA remains intact even after anchoring to MCM-41. ²⁹Si NMR data and Raman studies show that there is a strong interaction, hydrogen bonding, between terminal oxygens of TSA with the surface silanol groups of MCM-41.

To study the dispersion of TPA species into SBA-15, materials were further characterized for XRD, SEM, and TEM. The XRD patterns of support MCM-41 and TSA₃/MCM-41 are shown in Figure 7. The XRD pattern of the calcined MCM-41 showed a sharp peak around 2θ =2° and few weak peaks in 2θ =3-5°, which indicated well-ordered hexagonal structure of MCM-41. No separate HPA crystal phase of TSA was observed in the TSA₃/MCM-41. Further, the absence of characteristic peaks of crystalline phase of TSA indicates that TSA is finely dispersed inside the hexagonal channels of MCM-41.

Figure 8a,b shows the SEM image of MCM 41 and TSA₃/MCM41. The surface morphology of supported catalyst is almost identical to that of pure MCM-41. No change in surface morphology of the catalyst indicates TSA species are well dispersed inside the hexagonal pores. Further, no separate crystallites of bulk phase of TSA were found in TSA₃/MCM41.

Panels (a, b, c) and (d, e, f) of Figure 9 show the TEM image of MCM 41 and $TSA_3/MCM41$, respectively. Figure 9a,b,c clearly shows hexagonal mesopores in MCM-41. The TEM images of $TSA_3/MCM41$ (Figure 9d,e,f) shows that most of the hexagonal pores are covered with dark colored fine particles. This indicates uniform dispersion of TSA inside the hexagonal pores of MCM-41. Another possibility is that TSA has formed very small (nm) crystals in these channels.

Thus, XRD, SEM, and TEM confirm the uniform distribution of TSA inside the hexagonal channels of MCM-1. Total acidity values for all the catalysts are presented in Table 3. Total acidity

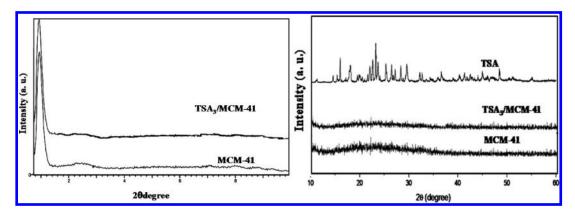


Figure 7. XRD of MCM-41 and TSA₃/MCM-41.

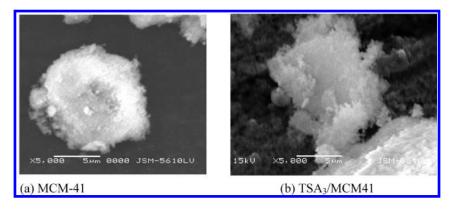


Figure 8. SEM images of MCM 41 and TSA₃/MCM41.

values indicate that MCM-41 is fairly acidic. As the TSA loadings increase, acidity values also increase and the results are as expected.

According to Vasquez et al, 32 the potentiometric titration with 0.05 N n-butyl amine enables the quantitative determination of Bronsted acid sites. As suggested by Vasquez et al, sites at potential >100 mV are very strong sites, sites at 0 mV < E < 100 mV are strong, and those at -100 mV < E < 0 mV are weak. From the plot shown in Figure 10, an equivalent mass of 1.2 mg of n-butyl amine was determined for TSA $_3$ /MCM-41 at potential above 100 mV, corresponding to TSA acidic protons and indicating that all those sites were very strong. The silica support, MCM-41, was titrated at lower potentials (E < 0 mV) in the range of very weak acid sites.

4. ESTERIFICATION OF DICARBOXYLIC ACIDS

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 to carry out esterification by taking one of the reactants 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, the corresponding alcohol is taken in excess.

4.1. Esterification of Succinic Acid and Malonic Acid with Butanol. The effect of various reaction parameters such as % loading of TSA, acid/alcohol molar ratio, and amount of catalyst and reaction time were studied to optimize the conditions for maximum yields for diesters.

- **4.2. Effect of % Loading of TSA.** To study the effect of % loading of TPA, the esterification reaction was carried out with TSA₁/MCM-41, TSA₂/MCM-41, TSA₃/MCM-41, and TSA₄/MCM-41. The obtained results are shown in Figure 11. It is observed from the figure that, with increase in the % loading of TSA, % yield toward diester also increases. For 30% and 40% loading, the difference in % yield is not that appreciable. Hence, the catalyst containing 30% loading of TSA, i.e., TSA₃/MCM-41 was selected for the detail study.
- **4.3.** Effect of Mole Ratio of Acid/Alcohol. It is seen from Figure 12 that, with change in mole ratio of acid to butanol, there is drastic change in the yields of products. Initially, the yield toward 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 detailed study.
- **4.4. 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 at 80 $^{\circ}$ C. It is observed from Figure 13 that, with an increase in the amount of catalyst, % yield toward diester increased. With 0.1 g of catalyst, % yield toward diesters was at the maximum.
- **4.5. Effect of Reaction Time.** Effect of reaction time was studied. It was observed (Figure 14) that the % yields of diester's increases with an increase in reaction time. After 4 h, 80% yield of dibutyl malonate was achieved. After 14 h, 90% yield of dibutyl succinate was achieved.

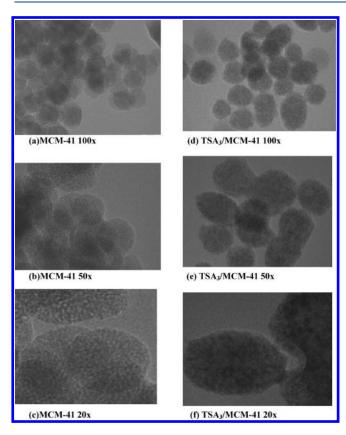


Figure 9. TEM images of MCM 41 and TSA₃/MCM41.

Table 3. Total Acidity Values

material	total acidity (mmol/g)
MCM-41 TSA $_1$ /MCM-41 TSA $_2$ /MCM-41	0.82 1.14 1.21
TSA ₃ /MCM-41	1.33

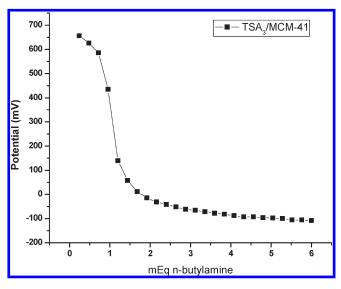


Figure 10. Potentiometric titration of TSA₃/MCM-41 with *n*-butylamine.

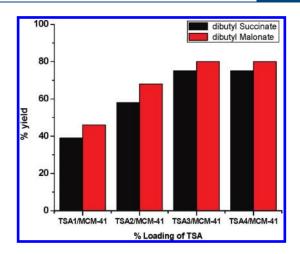


Figure 11. Effect of % loading of TSA. Reaction conditions: amount of catalyst, 0.1 g; mole ratio of acid/alcohol, 1:3; reaction time, 8 h for succinate esters and 4 h for malonate esters; reaction temperature, 80 °C.

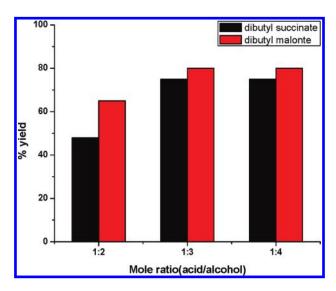


Figure 12. Effect of mole ratio. Reaction conditions: amount of catalyst, 0.1 g; reaction time, 8 h for succinate esters and 4 h for malonate esters; reaction temperature, $80\,^{\circ}$ C.

The optimized conditions for esterification of succinic acid and maolonic acid with n-butanol using TSA3/MCM-41 are as follows: mole ratio of acid to alcohol, 1:3; amount of catalyst, 0.1 g; reaction temperature, 80 °C; and reaction time, 14 h; while for malonic acid, reaction time was 4 h.

4.6. 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 Figure 15.

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

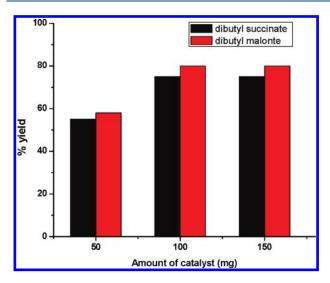


Figure 13. Effect of amount of catalyst. Reaction conditions: mole ratio of acid to alcohol, 1:3; reaction time, 8 h for succinate esters and 4 h for malonate esters; reaction temperature, 80 °C.

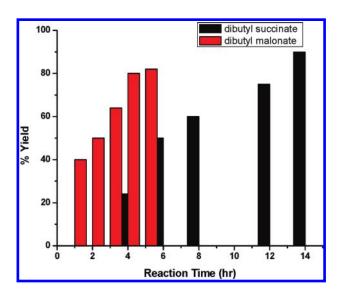


Figure 14. Effect of reaction time. Reaction conditions: mole ratio of acid to alcohol, 1:3; amount of catalyst, 0.1 g; reaction temperature, 80 $^{\circ}$ C.

4.7. 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 TSA 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. ³³

The leaching of W from TSA₃/MCM-41 was confirmed by carrying out an analysis of the used catalyst (energy dispersive X-ray, EDX) as well as the product mixtures (atomic absorption spectroscopy, 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, TSA, form the support, MCM-41.

For the rigorous proof of heterogeneity, a test was carried out by filtering the catalysts from the reaction mixture at 80°C

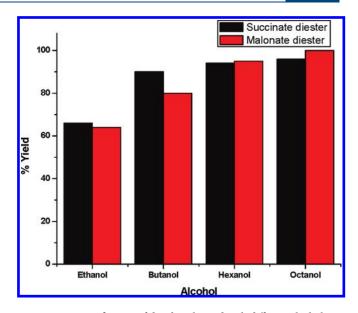


Figure 15. Esterification of dicarboxylic acid with different alcohols.

Table 4. Elemental Analysis (EDS) and Acidity Characterization of Reused Catalyst

	e	lemental			
catalyst	0	Si	by EDS	theoretical	total acidity (mmol/g)
TSA ₃ /MCM-41 R-TSA ₃ /MCM-41	53.92 54.2	28.12 27.9	17.97 17.8	19 19	1.33 1.30

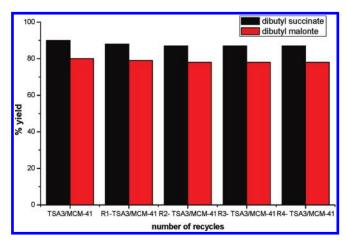


Figure 16. Recycling of the catalysts. Reaction conditions: amount of catalyst, 0.1 g; mole ratio of acid/alcohol; 1:3; reaction time, 8 h for succinate esters and 4 h for malonate esters; reaction temperature, 80 °C.

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 a gas chromatogram. From the heterogeneity test, it was found that there was no change in the % yield of esters, indicating the present catalyst fell into category C. ³³ On the basis of these results, it can be concluded that there is no leaching of TSA

Table 5. Comparison with Reported Catalyst

reference	catalyst	alcohol	reaction conditions ^a	% yield dialkylsuccinate	% yield dialkylmalonate
present work	TSA ₃ /MCM-41	butanol	0.1:3:80:14	90	80^a
present work	TSA ₃ /MCM-41	ethanol	0.1:3:80:14	66	64 ^a
17	Al ³⁺ -mon	butanol	0.5:3:80:8	94	77
34	IB	butanol	0.2:5:80:8	94	
35	Al ³⁺ -mon	iso-butanol	0.5:3:80:8	96	24
19	Starbon-400-HSO ₃	ethanol	0.1:30:80:8	95	
19	DARCO-HSO ₃	ethanol	0.1:30:80:8	27	
20	PW/Al-MCM-41	ethanol	0.1:3:120:12	11.3	
36	ZTPA(zirconium titanium phosphate)	ethanol	0.2:2.5:145:10		79.2

^a Reaction conditions: amount of catalyst (% w/w, in some cases unit is g):mole ratio of alcohol/acid:reaction temperature:reaction time (h); reaction time for malonic acid esterification, 4 h.

species from the support MCM-41 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 4.The elemental analysis values of R-TSA₃/MCM-41 were close to that for fresh catalyst. Further, the total acidity value of reused catalyst was almost the same as compared to the fresh catalyst. Hence, there is no deactivation of catalyst. This also confirms the truly heterogeneous mode of action.

- **4.8. Recycling of the Catalyst.** 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 until the filtrate was free from the unreacted malonic acid, if any, and dried at $100\,^{\circ}\text{C}$ in an oven for 5 h, and the recovered catalyst was charged for the further run. The obtained results are as shown in Figure 16. It is seen from the table that the catalyst can be used up to four cycles without any appreciable change in the percentage yield.
- **4.9. Comparison with the Reported Catalysts.** It is observed from Table 5 that much higher yields were obtained for dibutyl succinate with the reported catalyst, ^{17,34,35} but the amount of catalyst required is very high, i.e., 0.5 g, whereas in the present case only 0.1 g is required. For diethyl succinate, also, considerably high yields were obtained as compared to the other reported catalysts. ^{19,20,36}

Further, the % yield for dibutyl malonate is comparatively low in the case of reported catalysts, ^{35,36} whereas in the present case it is 80%. The present catalyst is advantageous in three ways: low amount of catalyst, short reaction time, 4 h, and higher yields of dibutyl malonate. Thus, the superiority of the present catalyst lies in obtaining higher yields of diesters under mild reaction conditions.

5. CONCLUSION

The present contribution reports synthesis and characterization of 12-tungstosilisic acid anchored to MCM-41. Thermal stability of TSA increases after anchoring to MCM-41, and the catalyst is stable up to 600 °C. FT-IR and DRS spectra show that Keggin ion structure of TSA remains intact even after anchoring to MCM-41. ²⁹Si NMR data and Raman studies show that there is a strong interaction, hydrogen bonding, between terminal oxygens of TSA with the surface silanol groups of MCM-41. XRD, SEM, and TEM studies reveal that TSA is uniformly dispersed inside the channels without disturbing the hexagonal array of MCM-41.

The catalytic activity was explored for esterification of dicarboxylic acids, succinic acid, and malonic acid. The catalyst shows high activity in terms of higher yields toward diesters, especially for dioctyl malonate; 99% yield was obtained. The catalyst was also regenerated and reused up to four cycles. All these characteristics show the high potential of an environmentally benign catalyst for synthesis diesters under mild conditions.

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