

Esterification of acetic acid with propanol isomers under autogeneous pressure: A catalytic activity study of Al-MCM-41 molecular sieves

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Abstract

Catalytic activity of mesoporous Al-MCM-41 (Si/Al = 30, 51, 72 and 97) molecular sieves, which were synthesised and characterised by XRD, BET (surface area) and FT-IR was tested towards esterification of acetic acid with propanol isomers such as isopropanol and *n*-propanol under autogeneous pressure condition. The effect of Si/Al ratios of Al-MCM-41, reaction temperature, time, mole ratio (alcohol:acid) and catalyst loading on propanol conversion was studied. Al-MCM-41 (Si/Al = 30) was found to be more active than other Si/Al ratios owing to its high density of Brönsted acid sites and the reaction was also influenced by hydrophobic properties of the catalyst. The reaction was also studied over HY zeolite and H mordenite under same condition as Al-MCM-41 and their results are compared. The requirement of Brönsted acid sites for the reaction was clearly established by running the reaction in the absence of catalyst. Occurrence of the reaction mainly within the pores was confirmed by running the reaction over the uncalcined catalyst that provides less conversion than the calcined material.

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1. Introduction

Esterification reactions are used in synthetic organic chemistry [1]. Sulphuric acid or tin octoate, which are corrosive and virulent [2] which need to be neutralized after the completion of the reaction are used as typical catalysts for this reaction. But in case of metal containing Lewis acid catalysts, the metal needs to be removed carefully after the reaction which can be done, for instance, by adsorption on bleaching earth, which however leads to the formation of large of amounts wastes [3]. These problems can be overcome by using heterogeneous catalyst. Many heterogeneous catalysts reported in the literature for esterification reaction includes ion-exchange resin [4], H-ZSM-5 [5], zeolite-Y [6], niobic acid [7], sulphated oxides [8] and heteropoly acids. Supported heteropoly acid (HPA) [9], which have been proved to be nearly comparable in their efficiency for a series acid-catalysed reactions to sulphuric acid in liquid phase [10], their high solubility in the polar media, often made them difficult to

separate from the reaction products, that problematic in industrial processes [11]. So the challenge was to replace them by solid acid catalysts such as zeolite or resins. But in case of zeolite, in spite of its high activity, its reaction always gives a variety of undesired by-products due to higher reaction temperature [12]. To overcome these zeolites, Al-MCM-41 (Si/Al = 30, 51, 72 and 97), which was discovered by Mobil Oil Corporation (one of the member in the family of M41S) in 1992 [13,14] were synthesised and tested for the esterification of acetic acid with isopropanol and *n*-propanol under autogeneous pressure conditions.

2. Experimental

2.1. Materials and methods

The hydrothermal crystallization procedure reported by Beck et al. [13] was adopted for the synthesis of Al-MCM-41 molecular sieves with various Si/Al ratios (30, 51, 72 and 97). In a typical synthesis, 10.6 g of sodium silicate nanohydrate (Merck) in demineralized water was combined with the appropriate amount of aluminum sulphate (Merck). The mixture was then acidified with 1 M H₂SO₄ to bring down the pH to 10.5

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under vigorous stirring. After 30 min of stirring, an aqueous solution of cetyltrimethylammonium bromide (CTAB) (Merck) was added and the surfactant silicate mixture was stirred for a further 30 min at room temperature. The molar composition of the resultant mixture was $\text{SiO}_2:0.2 \text{ CTAB}:X \text{ Al}_2\text{O}_3:0.89 \text{ H}_2\text{SO}_4:120 \text{ H}_2\text{O}$ (X varies with the Si/Al ratio). The resultant gel was autoclaved and heated for 48 h at 145 °C. The solid obtained was filtered and dried at 100 °C in air. The sample was then calcined at 525 °C in air for 5 h in a muffle furnace to expel the template. The samples that calcined by this procedure were ion exchanged repeatedly with one molar solution ammonium nitrate and then filtered, dried and calcined at 550 °C for 12 h.

2.2. Characterization

The XRD powder diffraction pattern of the calcined mesoporous Al-MCM-41 (Si/Al ratio 30, 51, 72 and 97) molecular sieves was obtained with a Stereoscan diffractometer using nickel-filtered Cu K α radiation ($\lambda = 0.154 \text{ nm}$) and a liquid nitrogen cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range of 0–10° in the steps of 0.02° with a count time of 15 s at each point for MCM-41 molecular sieves.

Surface area, pore volume and pore size distribution of Al-MCM-41 were measured by nitrogen adsorption at 77 K using an ASAP-2010 porosimeter from Micromeritics Corporation, GA. The samples were degassed at 623 K and 10^{-5} Torr overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.9 by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distribution was estimated using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) available as built-in software from Micromeritics.

Mid-infrared spectra of Al-MCM-41 molecular sieves were recorded on a Nicolet (Avatar 360) instrument by KBr pellet technique. About 4 mg of the sample was ground with 200 mg of spectral grade KBr to form a mixture, which was then made into a pellet using a hydraulic press. This pellet was used to record the infrared spectra in the range 4000–400 cm^{-1} .

Aluminium content in Al-MCM-41 for various ratios was estimated by ICP-AES with Allied Analytical ICAP 9000.

2.3. Acidity measurements

The acidity of Al-MCM-41 was analysed by pyridine adsorption followed by FT-IR spectroscopy. A finely ground catalyst sample (10–15) was pressed for 2 min at 10 tonnes/ cm^2 pressure under vacuum into a self-supporting wafer. The wafers were calcined under vacuum ($133.322 \times 10^{-3} \text{ N/m}^2$) at 500 °C for 2 h, followed by exposure to pyridine vapour at ambient temperature for 1 h to allow the pyridine to permeate the samples. The thin wafer was placed in the FT-IR cell and the spectrum recording was carried out under vacuum in absorbance mode on a Nicolet 800 (AVATAR) FT-IR spectrometer, fully controlled by the OMNIC software, and an all-glass high-vacuum system. The difference between the spectra of pyridine adsorbed on the samples and that of the reference was obtained by subtraction.

2.4. Catalytic runs

Esterification reactions were carried out under batch process conditions using an autoclave in the temperature range of 100–200 °C using 15 ml stainless steel batch reactors (teflon coated) under autogeneous pressure conditions. A typical reaction mixture in the reactor contained acetic acid (0.1 mol), propanol (0.1 mol) and a freshly activated catalyst (0.1 g). The catalyst was activated by heating it at 500 °C in furnace for 3 h. The autoclave temperature was then slowly raised to 100, 125, 150, 175 and 200 °C as required and maintained at the desired temperature, using oven during the reaction period of 8 h. The effect of Si/Al ratios of Al-MCM-41, reaction period, mole ratio of reactants and catalyst loading were studied to get more conversion.

2.5. Analysis

The reaction mixture was collected from the autoclave after cooled to room temperature and the catalyst was removed from the reaction mixture by filtration. Then the reaction mixture was analyzed by an Shimadzu gas chromatograph GC-17A using a DB-5 capillary column with FID detector. Comparing the retention values of the known standards with those of the products the latter were confirmed. The products analyzed by GC revealed the formation of isopropyl acetate and *n*-propyl acetate with 100% selectivity. The percentage of propanol conversion is based on the GC analysis.

$$\text{conversion} = \frac{\text{initial wt.\%} - \text{final wt.\%}}{\text{initial wt.\%}} \times 100\%$$

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD powder diffraction patterns of the calcined mesoporous catalysts are shown in Fig. 1, which show that samples exhibit an intense diffraction peak at about (2θ) due to [1 0 0] plane confirming the hexagonal mesophase of the material [15–17]. The d_{100} spacing and the lattice parameter (a_0) calculated as per the literature procedure are presented in Table 1. The calcined materials possess well-defined pore structure due to the condensation of Si–OH groups. These XRD patterns coincide well with the data already reported in the literature for mesoporous aluminosilicate molecular sieves [18].

In order to know the structure damage of Al-MCM-41 (Si/Al = 30) after NH_4^+ exchange, XRD analysis was performed. The XRD diffraction pattern of Al-MCM-41 (after NH_4^+ exchanged) is same as Al-MCM-41 (Si/Al = 30) (Fig. 2), which confirmed the absence of structural damage of Al-MCM-41.

3.1.2. Nitrogen adsorption isotherms

BET surface area, pore size and pore volume for calcined materials are presented in Table 1. Adsorption isotherms and

Table 1
Textural properties of the catalysts

| Catalyst | Si/Al | ICP | d_{100} (Å) | Unit cell- a_0 (nm) | Surface area (m ² /g) | Pore size, BJH (nm) | Pore volume, BJH (cm ³ /g) |
|----------------------|-------|-----|---------------|-----------------------|----------------------------------|---------------------|---------------------------------------|
| Al-MCM-41 (Si/Al=30) | 25 | 30 | 37.45 | 4.32 | 1044 | 2.665 | 0.9596 |
| Al-MCM-41 (Si/Al=51) | 50 | 51 | 37.16 | 4.29 | 1039 | 2.652 | 0.9560 |
| Al-MCM-41 (Si/Al=72) | 75 | 72 | 37.81 | 4.37 | 979 | 2.559 | 0.9428 |
| Al-MCM-4 (Si/Al=97) | 100 | 97 | 37.81 | 4.37 | 953 | 2.502 | 0.9478 |
| HM (Si/Al=12) | – | – | – | – | 431 | – | – |
| HY (Si/Al=4) | – | – | – | – | 821 | – | – |

pore size distribution for calcined materials (BJH method) are shown in Figs. 3 and 4A and B, and they coincide with reported values [19,20]. Three well-defined stages may be identified: (i) a slow increase in nitrogen uptake at low relative pressures, corresponding to monolayer–multilayer adsorption on the pore walls, (ii) a sharp step at intermediate relative pressures indicative of capillary condensation within mesopores and (iii) a plateau with

a slight inclination at high relative pressures associated with multilayer adsorption on the external surface of the crystals [21].

The pore size decreases with increase in Al content of the Al-MCM-41. The possible hypothesis that we would propose for this case is as observed by Selvaraj et al. [22], is based on the ring strain release during the formation of non-framework Al species.

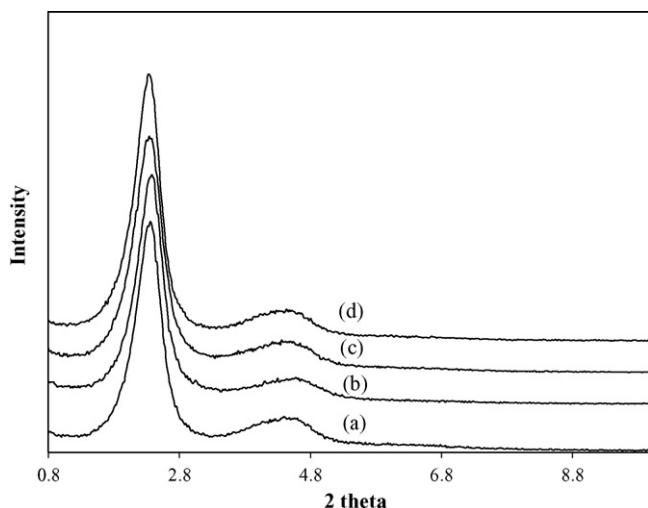


Fig. 1. X-ray diffraction patterns of calcined Al-MCM-41: (a) Al-MCM-41 (Si/Al=30); (b) Al-MCM-41 (Si/Al=51); (c) Al-MCM-41 (Si/Al=72); (d) Al-MCM-41 (Si/Al=97).

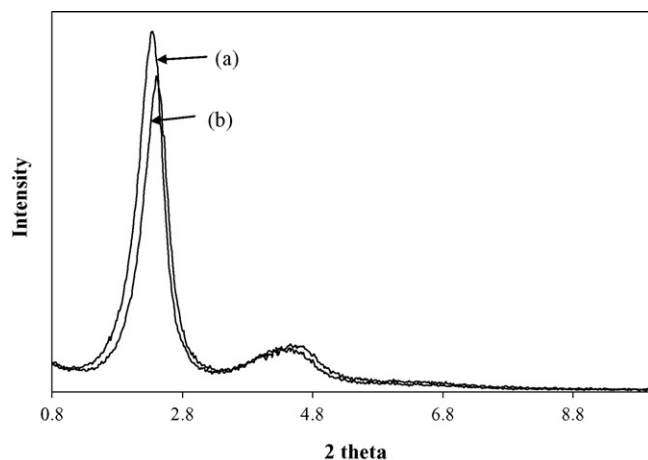


Fig. 2. X-ray diffraction patterns of Al-MCM-41: (a) Al-MCM-41 (Si/Al=30); (b) Al-MCM-41 (Si/Al=30) after NH₄⁺ exchanged.

3.1.3. FT-IR spectroscopy

The FT-IR spectra of the uncalcined and calcined samples are given in Figs. 5 and 6, respectively. The presence of absorption bands around 2921 and 2851 cm⁻¹ for the uncalcined materials corresponds to asymmetric and symmetric CH₂ vibrations of the surfactant molecules. The infrared spectrum of the calcined samples indicates that broad envelop around 3500 cm⁻¹ is due to O–H stretching of surface hydroxyl groups, bridged hydroxyl groups and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the adsorption bands at 1623–1645 [23]. The peaks between 500 and 1200 cm⁻¹ are assigned to framework vibrations. The peaks around 1230 and 1088 cm⁻¹ are attributed to the asymmetric stretching of T–O–T groups are observed around 800 and 544 cm⁻¹ and the peak at 460 cm⁻¹ is due to the bending mode of T–O–T. These special features resemble with those reported by previous workers [16,24].

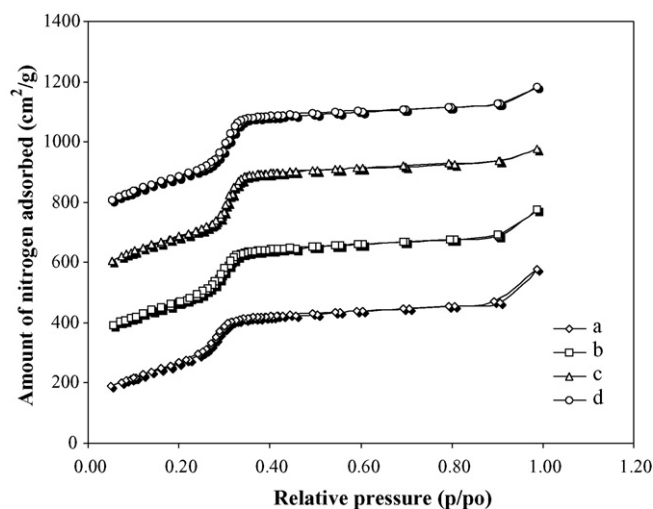
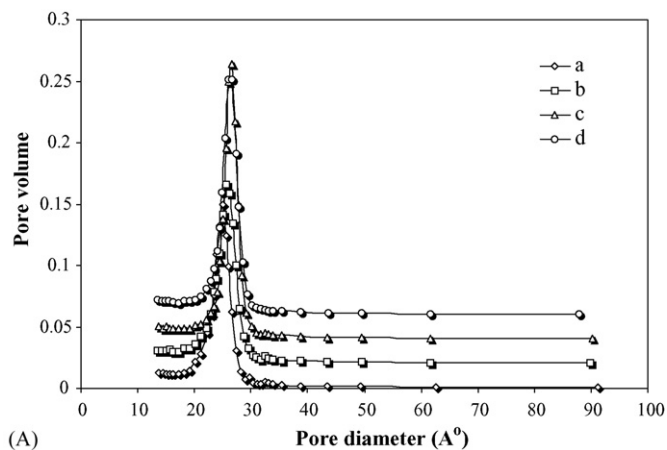
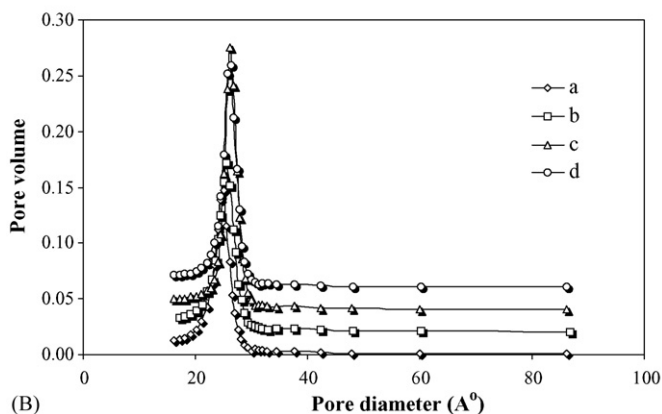


Fig. 3. Adsorption isotherms of Al-MCM-41 molecular sieves: (a) Al-MCM-41 (Si/Al=97); (b) Al-MCM-41 (Si/Al=72); (c) Al-MCM-41 (Si/Al=51); (d) Al-MCM-41 (Si/Al=30).



(A)



(B)

Fig. 4. (A) Pore size distribution (for adsorption method) in Al-MCM-41: (a) Al-MCM-41 (Si/Al=97); (b) Al-MCM-41 (Si/Al=72); (c) Al-MCM-41 (Si/Al=51); (d) Al-MCM-41 (Si/Al=30). (B) Pore size distribution (for desorption method) in Al-MCM-41: (a) Al-MCM-41 (Si/Al=97); (b) Al-MCM-41 (Si/Al=72); (c) Al-MCM-41 (Si/Al=51); (d) Al-MCM-41 (Si/Al=30).

3.1.4. Pyridine adsorbed FT-IR spectroscopy

The FT-IR spectra for Al-MCM-41 (Si/Al=30), Al-MCM-41 (Si/Al=51), Al-MCM-41 (Si/Al=72) and Al-MCM-41 (Si/Al=97), containing adsorbed pyridine are presented in Fig. 7. It is observed that all the catalysts have both Brønsted and

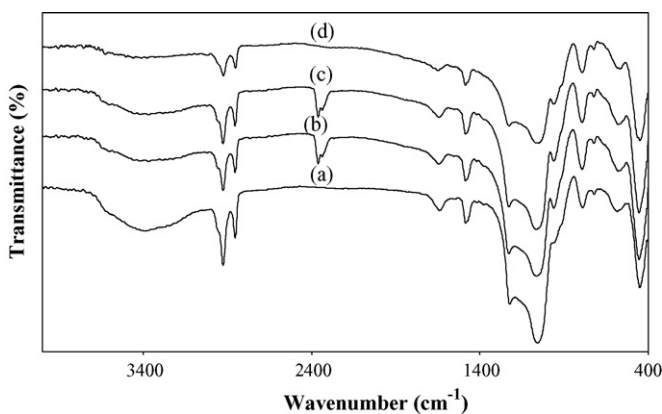


Fig. 5. FT-IR spectra of uncalcined mesoporous materials: (a) Al-MCM-41 (Si/Al=30); (b) Al-MCM-41 (Si/Al=51); (c) Al-MCM-41 (Si/Al=72); (d) Al-MCM-41 (Si/Al=97).

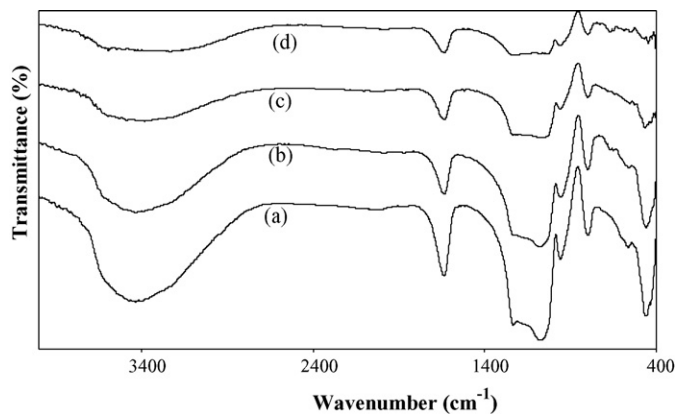


Fig. 6. FT-IR spectra of calcined mesoporous materials: (a) Al-MCM-41 (Si/Al=30); (b) Al-MCM-41 (Si/Al=51); (c) Al-MCM-41 (Si/Al=72); (d) Al-MCM-41 (Si/Al=97).

Lewis acid sites. A typical sharp peak appeared at 1545 cm^{-1} is the indication of pyridine adsorbed on Brønsted acid sites. A small peak at 1455 cm^{-1} and a high-intensity peak around 1620 cm^{-1} indicate the pyridine adsorbed on Lewis acid sites.

3.1.5. ICP-AES analysis

The aluminum content in Al-MCM-41 for various Si/Al ratios 30, 51, 72 and 97 was recorded using various ICP-AES with

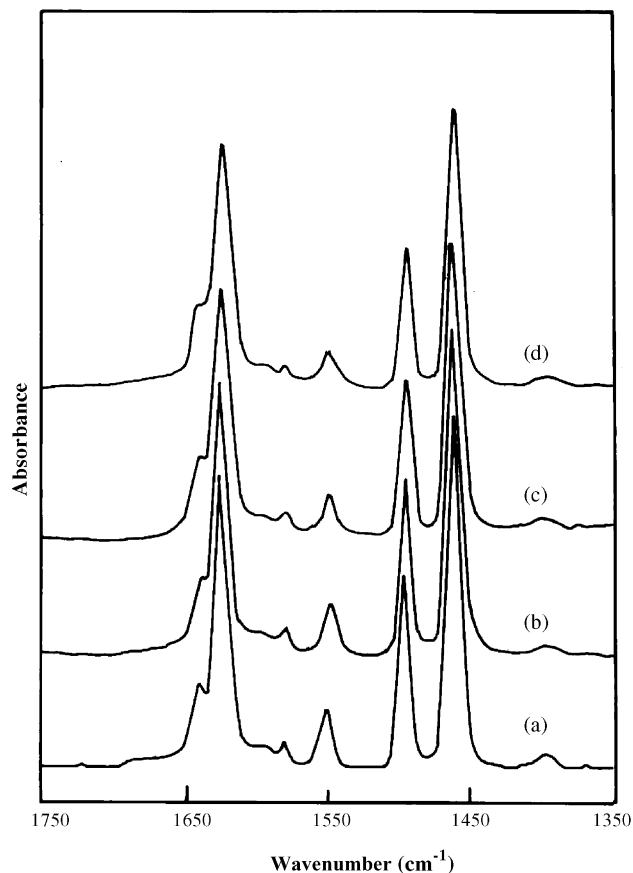


Fig. 7. FT-IR spectra of (a) Al-MCM-41 (Si/Al=30), (b) Al-MCM-41 (Si/Al=51), (c) Al-MCM-41 (Si/Al=72) and (d) Al-MCM-41 (Si/Al=97) catalysts containing adsorbed pyridine.

Table 2
Catalytic activity of Al-MCM-41 (Si/Al = 30, 51, 72 and 97) for esterification of acetic acid with propanol isomers at different temperature

| Catalyst | Temperature (°C) | Conversion of isopropanol (%) | Conversion of <i>n</i> -propanol (%) |
|------------------------|------------------|-------------------------------|--------------------------------------|
| Al-MCM-41 (Si/Al = 97) | 100 | 51.81 | 54.68 |
| | 125 | 73.13 | 69.63 |
| | 150 | 85.25 | 80.14 |
| | 175 | 85.42 | 82.99 |
| | 200 | 86.14 | 83.78 |
| Al-MCM-41 (Si/Al = 72) | 100 | 41.67 | 48.25 |
| | 125 | 72.17 | 64.97 |
| | 150 | 78.55 | 76.23 |
| | 175 | 83.69 | 79.27 |
| | 200 | 83.94 | 81.01 |
| Al-MCM-41 (Si/Al = 51) | 100 | 53.38 | 49.39 |
| | 125 | 76.57 | 65.81 |
| | 150 | 84.58 | 75.92 |
| | 175 | 84.69 | 81.05 |
| | 200 | 84.75 | 81.97 |
| Al-MCM-41 (Si/Al = 30) | 100 | 54.97 | 57.47 |
| | 125 | 77.29 | 70.92 |
| | 150 | 85.54 | 83.74 |
| | 175 | 86.21 | 84.12 |
| | 200 | 86.84 | 85.19 |

Conditions: time = 8 h; mole ratio = 1:2 (alcohol:acid); catalyst loading = 0.1 g.

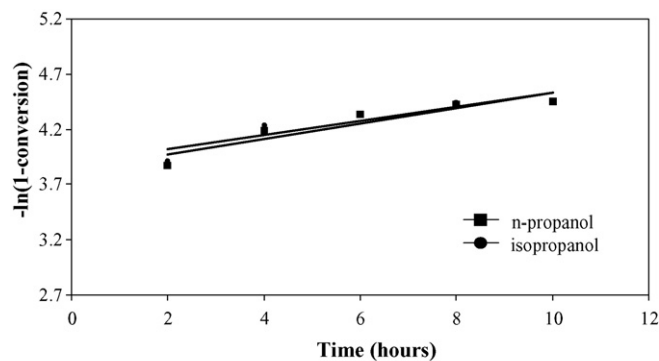
Allied Analytical ICAP 9000. The results of Si/Al ratios of the materials are given in Table 1.

3.2. Catalytic reaction

The esterification of acetic acid with propanol isomers is an electrophilic substitution. The reaction is relatively slow and needs activation either by high temperature or by a catalyst to achieve higher conversion to a reasonable amount. The effects of various parameters on the esterification reaction are discussed later. The zeolites such as HM (Si/Al = 12) and HY (Si/Al = 4) are tested in order to have a comparative understanding on the catalytic activity for the reaction.

3.2.1. Effect of temperature

Esterification of acetic acid with isopropanol and *n*-propanol was studied over Al-MCM-41 (Si/Al = 30, 51, 72 and 97) at 100, 125, 150, 175 and 200 °C with mole ratio = 1:2 (propanol:acetic acid), weight of the catalyst = 0.1 g and reaction time = 8 h. The results are presented in Table 2. A common trend in conversion over all the catalysts is increase of alcohol conversion with increase in temperature. Since esterification involves establishment of equilibrium, it is evident from these results that the shift in equilibrium towards ester side occurs with increase in temperature. High temperature may be required to reduce, intermolecular association of propanol for dispersed adsorption and to avoid the clustering of alcohols around the Brönsted acid sites by hydrogen bonding. And also, conversion increased with increased in temperature due to increase in the removal of by-product water formed in the reaction. Conversion of isopropanol and *n*-propanol is found to be more over Al-MCM-



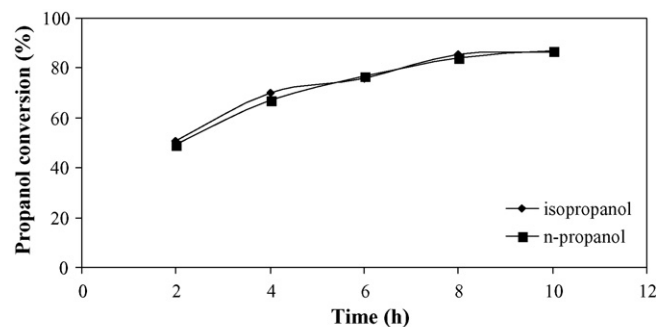
Conditions: Catalyst = Al-MCM-41 (Si/Al=30); mole ratio (1:2); T = 150°C; wt. of the catalyst = 0.1 g

Fig. 8. Relation between $-\ln(1 - \text{conversion})$ and time (hours).

41 (Si/Al = 30) than other ratios owing to its high density of Brönsted acid sites. The reaction could also be influenced by hydrophobic property of the catalyst [25–27], as water formed from the reaction could be repelled away from the pores. Hence, there might be avoidance of poisoning of the active sites by water. The conversion over Al-MCM-41 (Si/Al = 97) is nearly equal to Al-MCM-41 (Si/Al = 30). The kinetics data under pseudo-first-order conditions are also derived; the results are illustrated in Fig. 8. The rate constants derived by the first-order plot for *n*-propanol and isopropanol are 0.069 and 0.064, respectively. The rate constants also follow the order $k_1N > k_2I$ (N = *n*-propanol; I = isopropanol), which also matches the activity of the catalyst. Further, in order to know the presence of any dehydrated product, liquid product was treated with bromine water. Liquid product was not decolourised the bromine water that confirmed the absence of any dehydrated product.

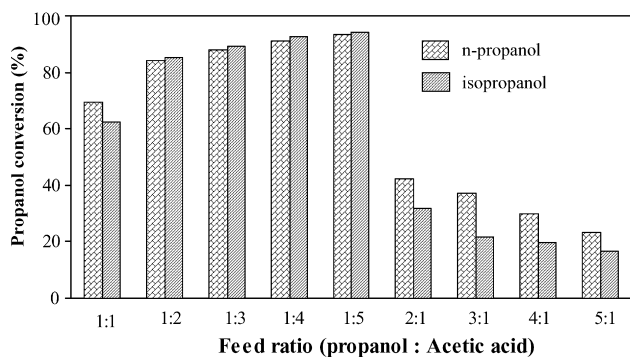
3.2.2. Effect of reaction time

The effect of reaction period on the esterification of acetic acid with isopropanol and *n*-propanol using Al-MCM-41 (Si/Al = 30) was studied at 150 °C with mole ratio 1:2 (propanol:acetic acid). The results are illustrated in the Fig. 9. Conversion with respect to isopropanol increases from 50.8% at 2 h to a maximum of 86.31% at 10 h. Similarly, the conversion with respect to *n*-propanol increases from 49.17% at 2 h to a



Conditions: Catalyst = Al-MCM-41 (Si/Al=30); mole ratio (1:2); T = 150°C; wt. of the catalyst = 0.1 g

Fig. 9. Effect of reaction time.



Conditions: catalyst = Al-MCM-41 (Si/Al=30); T = 150°C; wt. of the catalyst = 0.1 g; time = 8 h

Fig. 10. Effect of mole ratio.

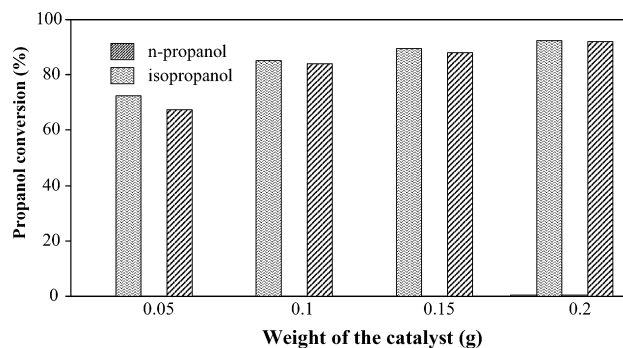
maximum of 86.75. A gradual increase in the conversion was seen with increase in the duration of the reaction period. This observation is a normal feature for reaction procedures of this kind.

3.2.3. Effect of mole ratio

The effect of mole ratio 1:1, 1:2, 1:3, 1:4, 1:5, 2:1, 3:1, 4:1 and 5:1 (propanol:acetic acid) on isopropanol and *n*-propanol conversion was studied over Al-MCM-41 (Si/Al = 30) at 150 °C for 8 h. The results are illustrated in the Fig. 10. The conversion of isopropanol increases from 1:1 to 1:5. Since, acetic acid is proposed to get chemisorbed on the Brönsted acid site, increase in acetic acid content increased conversion. The reaction was also studied by taking more alcohol content in the feed. The conversion was more altered for a change of feed ratio from 2:1 to 5:1 in the case of isopropanol. Although the increase in alcohol content might be expected to increase in conversion, there might be dilution of acetic acid; hence a decrease in conversion was observed. The same trend was also observed for the conversion of *n*-propanol. Hence in both these cases there might be dilution of acetic acid by increased alcohol contents, thereby preventing acetic acid adsorption on Bronsted acid sites. So far, this study can conclude that an increase in the acetic acid in the feed is better for esterification than a decrease in the acetic acid content in the feed.

3.2.4. Effect of catalyst loading

It is not practical interest to use such a large amount of catalyst and moreover the removal of high molecular weight adsorbed products from the catalyst is quite expensive too [28]. Hence, the effect of catalysts amount of Al-MCM-41 (Si/Al = 30) on the conversion of isopropanol and *n*-propanol were studied by varying the catalyst amount from 0.05, 0.1, 0.15 and 0.2 g at 150 °C for a period of 8 h and their result are illustrated in Fig. 11. As proposed in the literature before, establishment of equilibrium accelerates with increase in the concentration of the catalyst. Increase in conversion with increase in the catalyst amount is because of the availability of large surface area and regular pore dimension, which favours the dispersion of more active species. Therefore the accessibility of the large molecule of the reactant to the catalyst active site is favoured.



Conditions: catalyst = Al-MCM-41 (Si/Al=30); mole ratio (1:2); T = 150°C; time = 8 h

Fig. 11. Effect of catalyst loading.

3.2.5. Comparative study on zeolites

The esterification of acetic acid with isopropanol and *n*-propanol was also tested with 0.1 g of HY zeolite and H Mor-denite (United catalysts India Ltd.) at optimised temperature of 150 °C with the mole ratio of 1:2 (propanol:acetic acid) for 8 h. The results were presented in the Table 3. Except zeolites all other catalyst were found to be more active. The less activity for zeolites might be due to their micropores with which the diffusional constraint for the reaction and the product might be more. The zeolites offer resistance to diffusion for the reactant into the pores as well as for the product to out of the pores. So from this study, it can be concluded that Al-MCM-41 material can also be exploited as catalyst for this reaction. This observation clearly supported the molecular concession free esterification inside the pores of MCM-41. Further, in order to know whether the reaction occurs mainly inside the pore, outside the pore or on both, the study was carried out with uncalcined catalyst, which is incapable of permitting the reaction inside the pore due to template blocking. So, the reaction was performed with uncalcined Al-MCM-41 (Si/Al = 30) under the same condition at the temperature of 100 °C with the mole ratio of 1:2 (propanol:acetic acid) where it shows the conversion of 49.1 and 47.43% for isopropanol and *n*-propanol respectively. Whereas, the calcined materials conversion was 85.54 and 83.74%, respectively, which was 36.44 and 36.31% less conversion than the calcined sample. So the reaction is more prone to occur within the pores of the catalyst rather than on the outer surface. In order to verify the active influence of the catalysts, the reaction was also studied

Table 3
Effect of catalysts on esterification of acetic acid with propanol isomers

| Catalyst | Conversion of isopropanol (%) | Conversion of <i>n</i> -propanol (%) |
|-----------------------------------|-------------------------------|--------------------------------------|
| Al-MCM-41 (Si/Al = 30) | 85.54 | 83.74 |
| Al-MCM-41 (Si/Al = 51) | 84.58 | 75.92 |
| Al-MCM-41 (Si/Al = 72) | 78.55 | 76.23 |
| Al-MCM-41 (Si/Al = 97) | 85.25 | 80.14 |
| HM (Si/Al = 12) | 72.41 | 62.29 |
| HY (Si/Al = 4) | 76.85 | 66.76 |
| Without catalyst | 15.02 | 9.90 |
| Uncalcined Al-MCM-41 (Si/Al = 30) | 49.10 | 47.43 |

Conditions: T = 150 °C; time = 8 h; mole ratio = 1:2 (alcohol:acid); catalyst loading = 0.1 g.

in the absence of the catalyst under the conditions, mole ratio of 1:2 (propanol:acetic acid) 150 °C for 8 h. After completion of the reactions, the reaction mixtures were analysed and the isopropanol and *n*-propanol conversion was found to be 15.01 and 9.9%, respectively. This observation therefore clearly establishes the active role of the catalyst for this reaction.

In order to know the reusability of the catalyst, esterification reaction of acetic acid with propanol isomers was carried out for five cycles by regenerating the Al-MCM-41 (Si/Al = 30) at 500 °C for 6 h in furnace with air for each cycle. It has been observed that Al-MCM-41 (Si/Al = 30) has retained its activity up to three cycles, after that slight decreasing trend in the activity of the Al-MCM-41 is observed due to dealumination, which has been proved by ICP-AES. Loss of aluminium content in Al-MCM-41 (Si/Al = 30) is not observed up to three cycles. But at the end of fourth and fifth cycle, some loss of aluminium content i.e from Si/Al = 30 to Si/Al = 34 and Si/Al = 40 are observed, respectively, which proves the dealumination.

4. Conclusion

From this study, it can be concluded that esterification of acetic acid with isopropanol and *n*-propanol over Al-MCM-41 has proved its catalytic efficiency by increase in conversion with 100% selectivity. The effects of Si/Al ratios of Al-MCM-41, reaction temperature, time, mole ratio (propanol:acetic acid) and catalyst loading on isopropanol and *n*-propanol conversion was studied and optimised to get more conversion. Al-MCM-41 (Si/Al = 30) is found to be very active compare to other commercial catalysts such as HY zeolite and H mordenite. This study confirms that reaction was occurred mainly within the pore of Al-MCM-41. This observation indirectly proves planting of Brönsted acid sites insides the pores of the catalyst.

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