

A highly efficient catalyst for the esterification of acetic acid using *n*-butyl alcohol

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Abstract

Mesoporous Al-MCM-41 molecular sieves in the Si/Al ratios 33, 52, 72 and 114 were synthesized under hydrothermal condition. They were characterized using powder X-ray diffraction (XRD), FT-IR, BET and thermogravimetric-differential thermal analyser (TGA-DTA). The XRD spectra showed that the materials were of hexagonal mesoporous structure. The FT-IR spectra revealed the order of hydrophobic character of the catalyst materials by comparing the broad envelope due to the O–H stretching of water in the higher energy region. The acidity of the catalyst was measured by FT-IR using pyridine as the diagnostic base. The BET surface area measurements indicated the surface areas between 900 and 1000 m²/g and pore diameter around 26 Å units. The catalytic activity of the materials was tested for the vapour phase esterification of acetic acid and *n*-butanol under autogenous condition. The effect of reaction temperature, mole ratio of the reactant, time and catalyst loading on *n*-butanol conversion and selectivity of *n*-butyl acetate was studied and the results are discussed. Al-MCM-41 (33) was found to be more active than the other catalysts owing to its high density of Brønsted acid sites. The reaction was also influenced by the hydrophobic property of the catalyst, as the conversion over Al-MCM-41 (114) is nearly equal to Al-MCM-41 (33). The requirement of Brønsted 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 as-prepared catalyst that provides 60% less conversion than the calcined material. The reaction was also studied over H-Mordenite, H-beta, H-ZSM-5 and HY zeolites, and the results are compared.

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1. Introduction

Esterification of acetic acid with *n*-butyl alcohol is commercially important as the product *n*-butyl acetate whose applications is vital in the manufacture of lacquer, artificial perfume, flavouring extract, leather, photographic films, plastics and safety glass. It is also used as a natural gas and a dehydrating agent. The demand for *n*-butyl acetate has been grown from 340 million pounds in 1998 to 358 million pounds in 2003. The reaction was thoroughly studied by Essex and Clark [1]. Although the percentage of esterification at equilibrium was high, the reaction velocity was low and the space required to handle a ton of vapours was

large. For these reasons the vapour phase esterification has not been attracted by industries. Liquid phase esterification is an important method for producing this ester. Conventional method of the esterification reaction involves use of either mineral acids such as sulphuric acid or tin octoate. Mineral acids are corrosive and virulent which need to be neutralised after the completion of the reaction. In the 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 amounts of waste [2]. Many other heterogeneous catalysts reported in the literature for esterification reaction include ion exchange resin [3], H-ZSM-5 [4], zeolites-Y [5], niobic acid [6], sulphated oxides [7], and supported heteropolyacids (HPA) [8]. Though HPA has many advantages as a solid acid catalyst, its low thermal stability,

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low surface area and difficulty in separation from reaction mixture make usage of HPA a cumbersome catalyst. Even though zeolites showed higher activity, their reactions were accompanied with side products at higher reaction temperature [9]. Further, in the esterification reaction using alcohol, water is formed as a by-product, thereby requiring azeotropic distillation to remove water during the reaction, which otherwise leading to the deactivation of the catalyst [10]. These hectic procedures have been thwarted with the use of mesoporous catalyst, Al-MCM-41, which was discovered in Mobil central research laboratory in 1992 [11,12]. They can easily separated from the product and reactants by filtration and also regenerated with ease [13].

The activity presented here are far better than reported, Michel et al. [8] who reported a very low activity for MCM-41 (Si/Al = 16) and ascribed it to its low acid strength. They showed both PW_{12} and SiW_{12} supported on MCM-41 as the active catalyst in the vapour phase esterification of acetic acid with 1-butanol. But though conversion was found to be 95% the ester was accompanied with side products like 1- and 2-butene and di-butyl ether. Further, clustering of HPA was found on the external surface of MCM-41 in the liquid phase esterification. In the present study we have found excellent catalytic activity for the protonated form of Al-MCM-41 under autogenous pressure in the batch process.

2. Experimental

2.1. Materials

The syntheses of Al-MCM-41 materials were carried out by hydrothermal method using sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), aluminum sulfate ($\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$), cetyltrimethylammonium bromide ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_2\text{N}^+\text{Br}^-$), sulfuric acid (H_2SO_4). The chemicals used were of AR grade purchased from M/s Aldrich & Co., USA.

2.2. Commercial catalytic materials

H-M (Si/Al = 12, PQ), H- β (Si/Al = 8, PQ), H-Y (Si/Al = 4, PQ), H-ZSM (Si/Al = 15, PQ) were obtained from commercial sources.

2.3. Synthesis of Al-MCM-41

The Al-MCM-41 with various Si/Al ratios 33, 52, 72 and 114 was synthesised according to the previous report [11,14] using a hydrothermal method with the gel composition of $\text{SiO}_2 : X\text{Al}_2\text{O}_3 : 0.2\text{CTAB} : 0.89\text{H}_2\text{SO}_4 : 120\text{H}_2\text{O}$ using sodium meta silicate as the silicon source, H_2SO_4 , cetyltrimethylammonium bromide as the structure directing agent and aluminium sulphate as the aluminium source. 21.21 g of sodium meta silicate was dissolved in 80 ml of water and allowed to stir for half an hour. Then required quantity of aluminium sulphate, which was dissolved in 15 ml of water, was added and allowed to stir for 1 h. Then 40 ml of 4N sulphuric acid

was added drop by drop until the gel formed. The Stirring was continued for 2 h. Exactly 7.28 g of cetyltrimethylammonium bromide (CTAB), dissolved in 25 ml of water, was added and stirring was continued for further 2 h. After that, the gel was transferred to an autoclave and it was kept in a hot air oven at 145 °C for 36 h. Then the product obtained was filtered, washed several times with double distilled water and dried at 80 °C in an air oven for 2 h. Then it was calcined in a muffle furnace at 550 °C for 6 h to remove the template.

2.4. Catalytic runs

Esterification reactions were carried out under batch reaction conditions using a 15 ml stainless steel batch reactors fitted with a reflux condenser and a thermometer. The outlet of the reflux condenser was connected to a constant pressure gas collector. The 1-butene formed, which was insignificant in the reaction was analysed by collecting it in the gas collector at the atmospheric pressure [15,23]. Autoclave was slowly raised to the temperature ranging from 398 to 473 K, at autogenous pressure conditions. A typical reaction mixture in the reactor contained acetic acid (2.86 ml), *n*-butyl alcohol (2.28 ml) and a freshly activated catalyst (0.1 g). Activation of the catalyst was done by calcinations at 773 K in air for 3 h. The autoclave temperature was then slowly raised to 398, 423, 448 and 473 K as required and maintained at the desired temperature during the specified reaction periods. The effect of the reaction period, the molar ratios of the reactants, and the amount of catalyst required on *n*-butanol conversion and product selectivity was studied.

2.5. Analysis

The reaction mixture was collected from the autoclave after cooled to room temperature. This solution was removed from the catalyst by filtration. The reaction mixture was analysed 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 product analysed by GC revealed the formation of *n*-butyl acetate with very high selectivity. Some small peaks corresponding to the dehydrated products of *n*-butanol were also observed. The percentage conversion and selectivity calculation are based on the GC analysis. The selectivity to a product is expressed as the percentage weight of the product *n*-Butyl acetate divided by sum of the weight percentage of the entire product.

$$\% \text{Conversion} = \frac{\text{Initial wt.\%} - \text{final wt.\%}}{\text{Initial wt.\%}} \times 100$$

% of the product

$$= \frac{\text{Mole percentage of the product}}{\text{Mole percentage of alcohol converted}} \times 100$$

2.6. Characterization

Mesoporous materials, in general are characterized by a variety of techniques including XRD (Rigaku, D-Max/111-VC model) using nickel filtered Cu K α radiation $\lambda = 1.5406 \text{ \AA}$. Surface area measurements were carried out using Quantachrome instrument (NOVA 1200, USA) by nitrogen adsorption at 77 K in an ASAP-2010 volumetric adsorption analyser manufactured by Micromeritics Corporation (Norcross, Ga). Before the nitrogen adsorption–desorption measurements, each sample was degassed at 623 K at $1.333 \times 10^{-3} \text{ N/m}^2$ overnight. The specific areas of the samples were determined from the linear part of the BET plots. The pore size distribution was calculated using the BJH algorithm (ASAP201 built in software from Micromeritics). Mid-infrared spectra of 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 $4000\text{--}400 \text{ cm}^{-1}$. Thermal analysis was carried out in Mettler TA 3001 analyser. Zeolites used in this study were of commercial origin.

2.7. Acidity measurements

The acidity of Al-MCM-41 was analysed by pyridine adsorption followed by FT-IR spectroscopy. Finely ground catalyst sample (10–15) was pressed for 2 min at 10 t/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 $500 \text{ }^\circ\text{C}$ for 2 h, followed by exposure to pyridine vapour at ambient temperature for 1 h to allow the pyridine to permeate the samples. After adsorption of the pyridine vapours on the wafer, the physisorbed pyridine molecules have been expelled using high vacuum for 30 min. After expelled physisorbed vapours on the catalyst wafer it was placed in the FT-IR cell and the spectrum was recorded 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.

3. Results and discussion

3.1. Characterization of Al-MCM-41

3.1.1. XRD

The diffraction patterns shown in Fig. 1 and the data are presented in the Table 1 illustrate the characteristics of a typical mesoporous MCM-41 structure. As can be seen from the diffraction patterns that the d_{100} reflections of calcined Al-MCM-41 have been shifted to higher values compared to its as synthesized analogue. This is in agreement with Borade and Clearfield [16] suggesting the framework substitution of

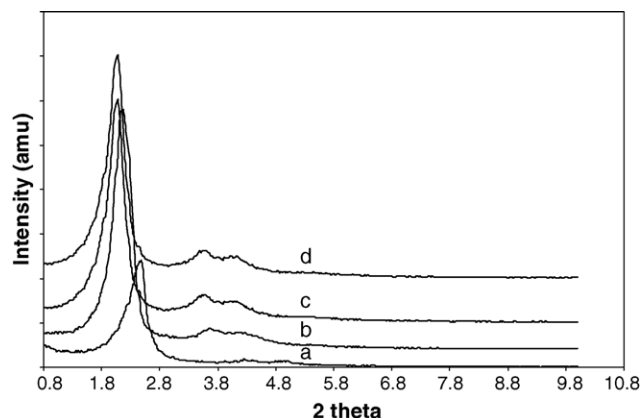


Fig. 1. X-ray diffraction pattern of calcined Al-MCM-41 (a) Al-MCM-41 (33), (b) Al-MCM-41 (52), (c) Al-MCM-41 (72) and (d) Al-MCM-41 (114).

Table 1
Textural properties of the catalysts

Catalysts	Si/Al	Calcined	
		d_{100}	Unit cell- a_0 (nm)
Al-MCM-41 (33)	25	35.38	4.09
Al-MCM-41 (52)	50	40.60	4.69
Al-MCM-41 (72)	75	42.50	4.90
Al-MCM-41 (114)	100	42.50	4.90

alumina in MCM-41 structure. During calcinations at 823 K the d values are generally shifted towards the lower values or higher 2θ values though to a smaller extent, implying shrinkage in the unit cell as a result of the removal of the surfactant molecules used as templates [17].

3.1.2. Nitrogen adsorption isotherms

BET surface area, pore size and pore volume of calcined materials are presented in Table 2. Adsorption and desorption isotherms and pore size distribution for calcined materials (BJH method) are shown in Figs. 2 and 3, which coincide with the reported values [18,19]. It can be seen that MCM-41 presents the highest surface area and pore volume, with all pore being in the mesopore range. The pore size distribution of calcined MCM-41 shows a unique peak centered at about 25 \AA diameter (Fig. 3) as given in literature [20].

Table 2
Surface area, pore size and pore volume of the microporous and mesoporous catalysts

Catalysts	Surface area (m^2/g)	Pore size BJH _{Ads} (nm)	Pore volume BJH _{Ads} (cc/g)
Al-MCM-41 (114)	1023	2.644	0.9575
Al-MCM-41 (72)	1018	2.631	0.9540
Al-MCM-41 (52)	976.6	2.538	0.9407
Al-MCM-41 (33)	950.8	2.501	0.9457
HM (12)	431	–	–
H8 (8)	694	–	–
HY (4)	821	–	–
HZSM-5 (15)	393	–	–

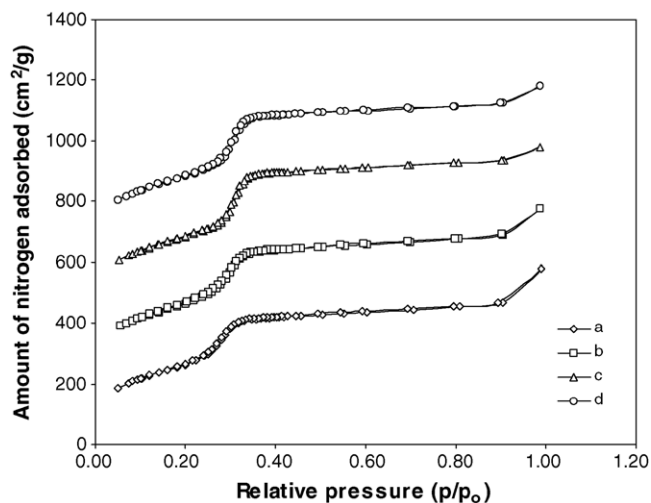


Fig. 2. Adsorption isotherm of nitrogen on MCM-41 at 77 K: (a) Al-MCM-41 (114), (b) Al-MCM-41 (72), (c) Al-MCM-41 (52) and (d) Al-MCM-41 (33).

All samples exhibited type IV isotherm with capillary condensation steps occurring at a partial pressure corresponding to Horvath–Kawazoe pore size distributions centered around 25 Å. The BET surface areas were calculated by fitting the straight part of the $p/x(p - p_0)$ versus p/p_0 curve (where p is the presence of nitrogen, and x is the number of grams of adsorbed nitrogen per gram of solid). The resulting surface area ranged from 950.8 to 1023 m²g⁻¹.

3.1.3. FT-IR spectroscopy

The FT-IR spectra of the as-synthesised and calcined samples are given in Figs. 4 and 5, respectively. The presence of absorption bands around 2921 and 2851 cm⁻¹ for the as-synthesised materials corresponds to asymmetric and symmetric CH₂ vibrations of the surfactant molecules. In the FT-IR spectrum of calcined samples, comparison of the broad envelope due to OH stretch of

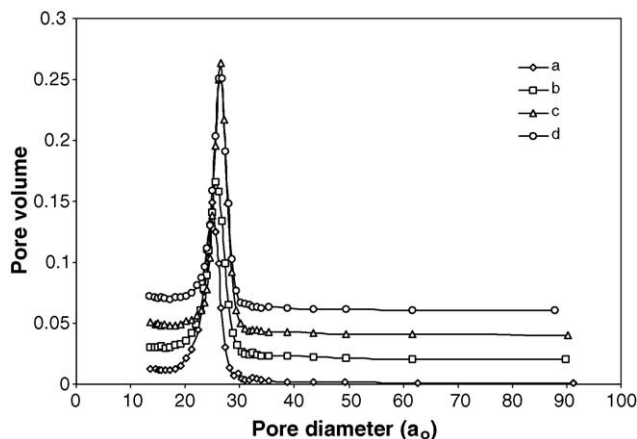


Fig. 3. Pore size distribution in Al-MCM-41 (adsorption isotherms): (a) Al-MCM-41 (114), (b) Al-MCM-41 (72), (c) Al-MCM-41 (52) and (d) Al-MCM-41 (33).

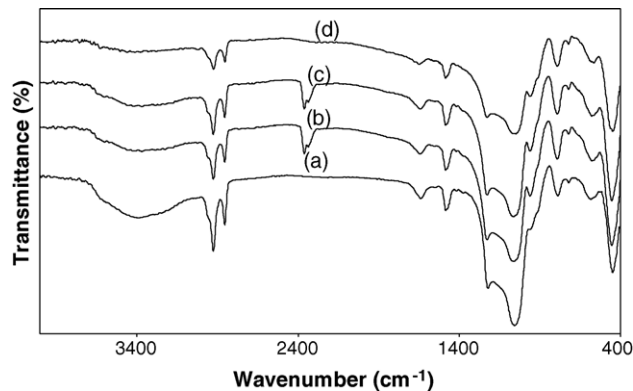


Fig. 4. FT-IR spectra of as-synthesised mesoporous materials: (a) Al-MCM-41 (33), (b) Al-MCM-41 (52), (c) Al-MCM-41 (72) and (d) Al-MCM-41 (114).

water in the higher energy region and the corresponding OH₂ bending mode around 1637 cm⁻¹ very well correlate with the water adsorption property (Hydrophilic property) of the catalysts. The intensity of the bands due to water for the catalyst decreases in the order MCM-41 (33) > MCM-41 (52) > MCM-41 (72) > MCM-41 (114), which is also the order of the hydrophilic property of the catalysts.

3.1.4. Pyridine adsorbed FT-IR spectroscopy

The FT-IR spectra for Al-MCM-41 (33), Al-MCM-41 (52), Al-MCM-41 (72), Al-MCM-41 (114), containing adsorbed pyridine are presented in Fig. 6. It is observed that all the catalysts have both Brönsted and Lewis acid sites. A typical sharp peak appeared at 1545 cm⁻¹ is the indication of pyridine adsorbed on Brönsted 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. Thermal analysis

The thermal properties of the samples were investigated by TGA. Their thermograms presented in Fig. 7. The initial weight loss up to 120 °C is due to desorption of physically

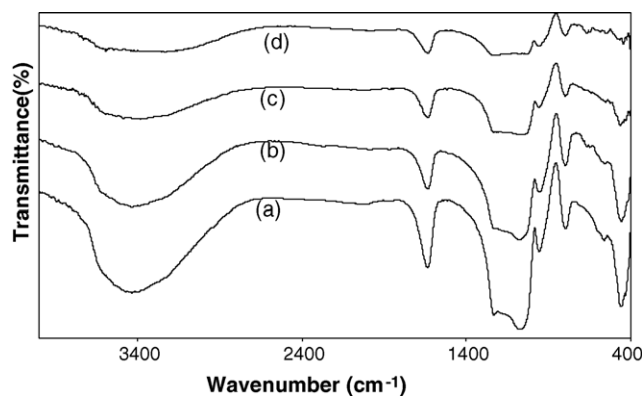


Fig. 5. FT-IR spectra of calcined mesoporous materials: (a) Al-MCM-41 (33), (b) Al-MCM-41 (52), (c) Al-MCM-41 (72) and (d) Al-MCM-41 (114).

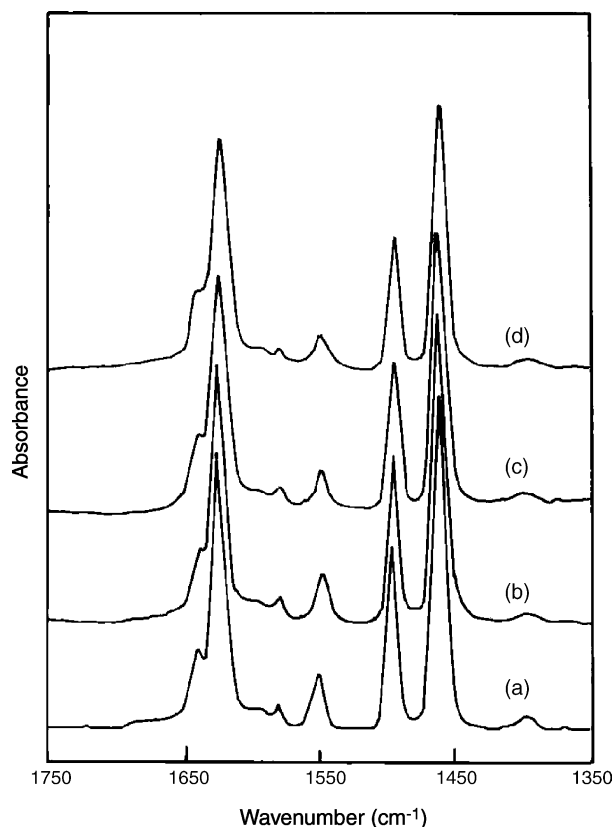


Fig. 6. Pyridine adsorbed FT-IR spectrum of MCM-41 has been recorded at the room temperature: (a) Al-MCM-41 (33), (b) Al-MCM-41 (52), (c) Al-MCM-41 (72) and (d) Al-MCM-41 (114).

adsorbed water. Weight loss from 120 to 350 °C due to organic template. The oxidative desorption of the organic template takes place at 180 °C and the minute quantity of weight loss above 350–550 °C is related to water loss from the condensation of adjacent Si–OH groups to form siloxane bond [21]. It is seen that as the Al content in MCM-41 framework increases the amount of water desorbed increases and the organic species decreased which confirms the decrease in the hydrophobic character of the catalyst with increasing Al content [22].

3.2. Application of Al-MCM-41 (33), Al-MCM-41 (52), Al-MCM-41 (72) and Al-MCM-41 (114) catalysts to the esterification of acetic acid

3.2.1. Esterification

The esterification of acetic acid with *n*-butanol is an electrophilic substitution. The reaction is relatively slow and need activation either by high temperature or by a catalyst to achieve equilibrium conversion to a reasonable amount. The effect of various parameters on the esterification reaction is discussed later. This study was also extended to other zeolites like H-Mordenite, H- β , H-ZSM-5 and H-Y in order to have a comparative understanding of the catalytic activity and selectivity of the products for the reaction.

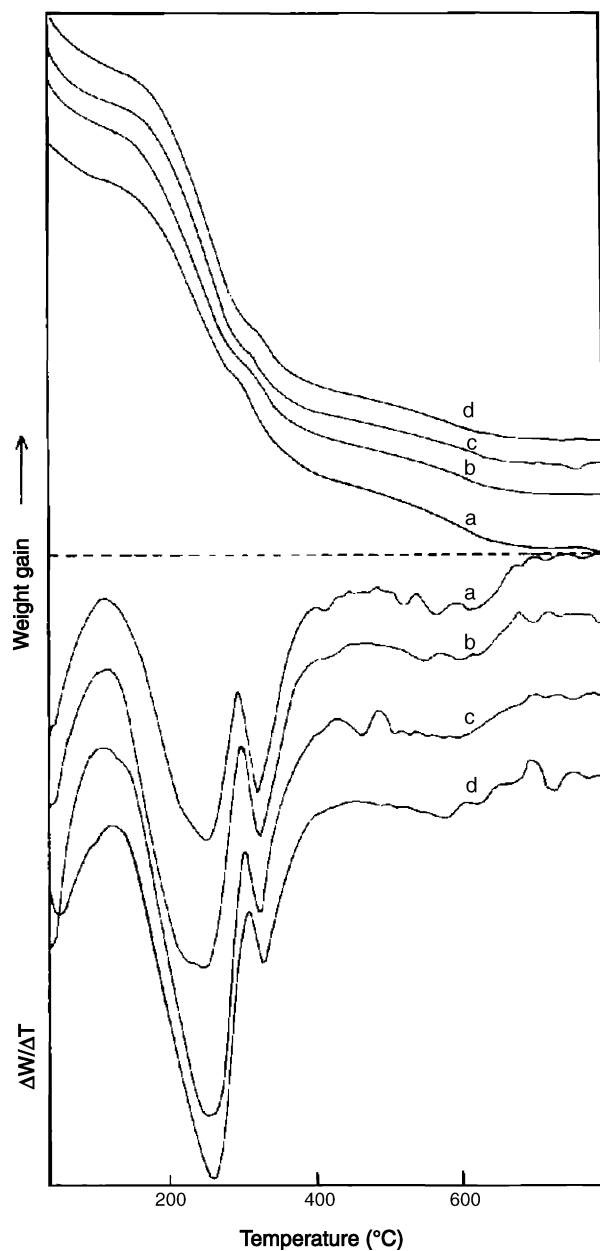


Fig. 7. TGA and DTA spectra of uncalcined mesoporous: Al-MCM-41: (a) Al-MCM-41 (114), (b) Al-MCM-41 (72), (c) Al-MCM-41 (52) and (d) Al-MCM-41 (33).

3.2.2. Variation with reaction temperature

The reaction was carried out at various reaction temperatures, ranging from 398 to 473 K at a given *n*-butanol to acetic acid ratio of 1:2 for 9 h. The reaction conditions and the conversion with respect to *n*-butanol over Al-MCM-41 with different Si/Al ratios and the selectivity of the product are given in Table 3, and selectivity of *n*-butyl acetate versus reaction temperature in Fig. 8. For each temperature, the activity of the catalysts follows the order: Al-MCM-41 (33) > Al-MCM-41 (52) > Al-MCM-41 (72) > Al-MCM-41 (114), and it is also the order of the density of acid sites of the catalysts. Since the reaction yields water as one of the by-products,

Table 3
Catalytic activity of Al-MCM-41 (33, 52, 72 and 114) for esterification of acetic acid

Catalyst	Temperature	%Conversion of <i>n</i> -butanol	%Selectivity to products	
			<i>n</i> -Butyl acetate	Others
Al-MCM-41 (114)	125	58.5	99.7	0.3
	150	78.2	99.6	0.4
	175	79.0	99.5	0.5
	200	81.0	99.1	0.9
Al-MCM-41 (72)	125	60.9	99.5	0.5
	150	70.3	99.3	0.7
	175	80.0	98.6	1.4
	200	85.2	98.0	2.0
Al-MCM-41 (52)	125	58.2	99.6	0.4
	150	79.0	99.1	0.9
	175	80.0	97.5	2.5
	200	87.2	97.0	3.0
Al-MCM-41 (33)	125	61.6	99.6	0.4
	150	87.3	99.6	0.4
	175	88.5	98.5	1.5
	200	88.7	97.0	3.0

Time = 9 h; feed ratio = 1:2.

Al-MCM-41 (114) might be expected to have high activity, as it is more hydrophobic with which it can expel water out of the pores as and when it is formed in the reaction. But the conversion results are not in line with our view. *n*-Butyl acetate is formed with nearly 100% selectivity. As the liquid product decolourised bromine water, dehydrogenation of alcohol to olefin is proposed to be a side reaction in this study. Based on the yield of the olefinic product, it can be suggested that protonation of *n*-butyl alcohol to give carbonium ion may be a necessity for the present esterification of acetic acid. Nearly similar conversion level (less than 10%) at each temperature over all the catalysts also suggests that it is to be the case. High hydrophobicity of Al-MCM-41 (114) can easily permit

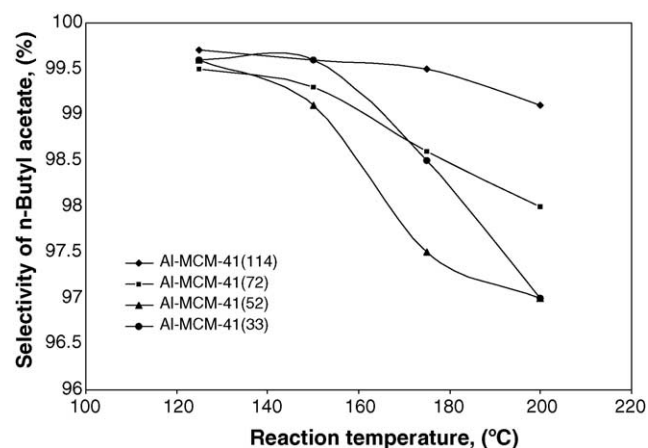


Fig. 8. Variation of Selectivity of *n*-butyl acetate (%) with reaction temperature. Reaction conditions: catalyst weight 0.1 g; molar ratio = 1:2 (acetic acid/*n*-butanol); temperature = 398–473 K; time = 9 h; pressure = autogenous.

n-butyl alcohol to enter the pores, but the density of acid sites is not much. But the opposite force might be acting on acetic acid, and as the result the conversion over Al-MCM-41 (114) is lowered, and nearly equalised to Al-MCM-41 (33) which is more hydrophilic and with which alcohol would be repelled.

3.2.3. Influence of reaction time

The effect of reaction period on the esterification was studied on Al-MCM-41 (33) at 423 K. *n*-Butanol conversion is presented in Table 4 and selectivity to *n*-butyl acetate is depicted in Fig. 9. A gradual arise in the conversion was seen with increase in the duration of the reaction period. The selectivity to *n*-butyl acetate on the other hand remains same from 99.7 to 99.5% at 12 h. Though this observation is a normal feature for reaction procedures of this kind, the low time of reaction is a matter of consideration. As seen from the Table 4, 3 h of reaction time completes 82.3% of the reaction, whereas at the end of 12 h only 88.0% of the reaction is complete. This shows that between 3 and 12 h only a meagre increase of 8.0% is seen. This observation illustrates the lower time requisite for the reaction to attain equilibrium.

Table 4
Effect of reaction time on esterification of acetic acid over Al-MCM-41 (33)

Time	%Conversion of <i>n</i> -butyl alcohol	%Selectivity to products	
		<i>n</i> -Butyl acetate	Others
3	82.3	99.7	0.3
6	85.1	99.6	0.4
9	87.3	99.6	0.4
12	88.0	99.6	0.4

Temperature = 423 K; feed ratio = 1:2.

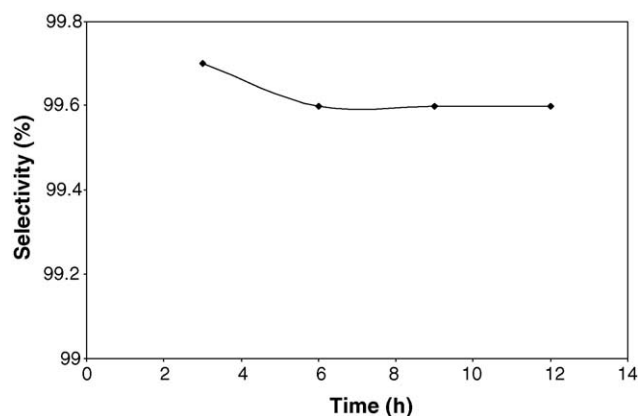


Fig. 9. The effect of reaction time on the esterification of acetic acid over Al-MCM-41 (33). Reaction conditions: catalyst weight = 0.1 g; molar ratio = 1:2 (*n*-butanol/acetic acid); temperature = 423 K; pressure = autogenous.

3.2.4. Influence of mole ratio of the reactants

The influence of mole ratio of the reactants on conversion and selectivity to *n*-butyl acetate was studied over Al-MCM-41 (33). Various mole ratios of *n*-butanol and acetic acid were studied at 423 K for a period of 6 h. The mole ratio of *n*-butanol: acetic acid was varied as 1:1, 1:2, 1:3, 1:4 and 1:5; the conversion and selectivity obtained are shown in Table 5. Further, the selectivity to *n*-butyl acetate with increasing mole ratio is depicted in Fig. 10. *n*-Butyl acetate was observed as the most selective product over all mole ratios of *n*-butanol and acetic acid. Initially, the conversion increased with increase in the mole ratios of the reactants. The conversion increased from 50.4% for a mole ratio of *n*-butanol:acetic acid 1:1 to 91.8% for 1:3, with further increase in the mole ratio a decrease in conversion was observed. The conversion observed was 70.7 and 68.0% for the feed ratios 1:4 and 1:5, respectively.

A marginal influence of mole ratio on *n*-butyl acetate selectivity was observed from 99.6 to 99.2% for the change of feed ratio 1:1 to 1:5. The selectivity to *n*-butyl acetate remains almost same for all the feed ratios. This illustrates absence of any side reactions to reduce the selectivity of *n*-butyl acetate. Although the mechanism is suggested to involve formation

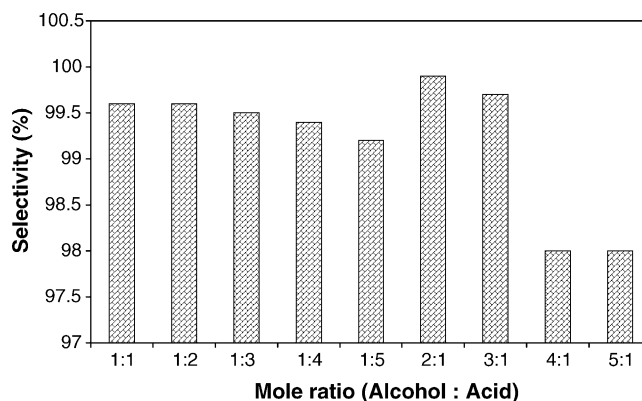


Fig. 10. The effect of molar ratio on the esterification reaction of acetic acid with *n*-butanol over Al-MCM-41 (33). Reaction conditions: weight of the catalyst = 0.1 g; temperature = 423 K; time = 6 h; pressure = autogenous.

of *n*-butyl cation to react with acetic acid to produce *n*-butyl acetate, the rearrangement of *n*-butyl cation to secondary or tertiary butyl cation is not observed. Hence the *n*-butyl cation once formed would react immediately with acetic acid to yield the ester. In addition the reaction conditions may not be adequate enough for the rearrangement of *n*-butyl cation to isobutyl or tertiary butyl cation. In order to verify this the reaction was also studied with feed ratio 2:1. Even at this feed ratio the tertiary butyl cation formation is not observed. Hence it can be said that both the catalyst surface and the reaction condition may not be adequate for isomerization. The effect of mole ratio over the conversion can be attributed with the occupancy of alcohols over the active sites and the availability of acid molecules for further esterification. At a mole ratio 1:1, following the Eley–Rideal mechanism, the alcohol is chemisorbed on the active sites to form carbonium ions. The attack of these stable carbo cations by the acid to form esters is least effective in the equimolar ratio stage. Further, when the concentration of acetic acid is doubled, the approach of acetic acid molecules to the carbocation is to be enhanced showing an increase in conversion. At a tripled concentration of acetic acid the ease of formation of ester is further enhanced. Increasing the mole ratio to 1:4 shows a decrease in conversion due to the flooding of active sites with acetic acid molecules rather than the alcohol. Further, decrease in conversion with increase in mole ratio confirms the dilution of alcohol, and hindrance in being protonated at the active site. In addition, the alcohol content of the feed is also increased in order to shed more light on the mechanism. The results are presented in the Table 5. Ester was the only product obtained in this reaction. Conversion remains the same for the feed ratios 1:1 and 1:2. This illustrates saturation of adsorption of alcohols at the feed ratio 1:1. In order to verify this the feed ratios 3:1, 4:1 and 5:1 were also used and tested. A decrease in concentration of about 7% is observed due to increase in the prevention of nucleophilic attack by shielding protonated alcohol by its own excess. This once again confirms Eley–Rideal mechanism with chemisorption of alcohol on the Brönsted acid sites.

Table 5
Effect of feed ratio on esterification of acetic acid over Al-MCM-41 (33)

Molar ratio (alcohol:acid)	%Conversion of <i>n</i> -Butanol	%Selectivity to products	
		<i>n</i> -Butyl acetate	Others
1:1	50.4	99.6	0.4
1:2	87.3	99.6	0.4
1:3	91.8	99.5	0.5
1:4	70.7	99.4	0.6
1:5	68.0	99.2	0.8
2:1	50.1	99.9	0.1
3:1	42.8	99.7	0.3
4:1	56.6	98.0	2.0
5:1	57.1	98.0	2.0

Temperature = 423 K; time = 6 h.

Table 6
Effect of amount of catalyst on esterification of acetic acid over Al-MCM-41 (33)

Catalyst amount	%Conversion of <i>n</i> -Butanol	% Selectivity to products	
		<i>n</i> -Butyl acetate	Others
0.05	83.6	99.6	0.4
0.10	87.3	99.6	0.4
0.15	87.6	99.3	0.7
0.20	89.1	98.0	1.2

Temperature = 423 K; feed ratio = 1:2; time = 6 h.

3.2.5. Influence of the catalyst loading

It is not of practical interest to use large amount of catalyst, and more over the removal of adsorbed high molecular weight products from the catalyst is quite expensive too [23]. Hence the optimisation of catalyst loading relative to the reactant was aimed. Table 6 and Fig. 11 show the effect of catalyst loading on the conversion and selectivity of *n*-butanol and *n*-butyl acetate respectively. Catalyst loading was varied as 0.05, 0.1, 0.15 and 0.2 at 423 K for a period of 6 h. As proposed in the literature, the establishment of equilibrium gets accelerated with increase in the catalyst loading. Increase of conversion from 83.6 to 89.1% with increase in catalyst loading was observed, due to the availability of large surface area and regular pore dimension, which favour the dispersion of more active species. Therefore, the accessibility of the large number of molecules of the reactants to the catalyst active site is favoured. With the increase in amount of catalyst a decisive marginal decrease in the selectivity is observed. The values in the Table 7 camouflage the increase in selectivity. Further, at the highest amount of catalyst (0.20 g), the Table reads the conversion of *n*-butanol to be 89.1% and the selectivity to *n*-butyl acetate to be 98%, the remaining 1.2% considered to be olefinic products. The amount of *n*-butanol being converted

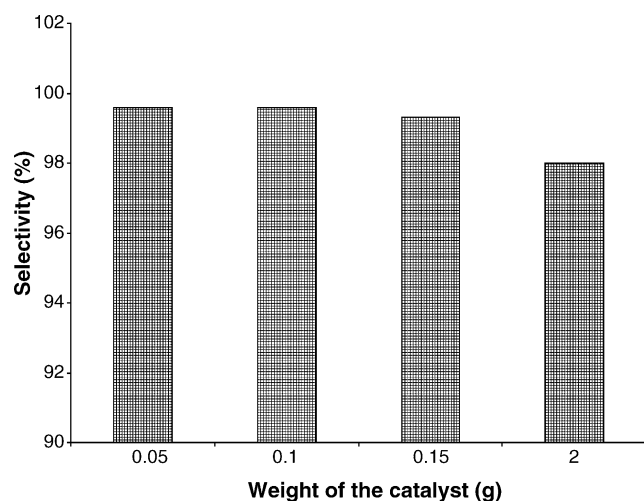


Fig. 11. The effect of amount of catalyst on the esterification of acetic acid over Al-MCM-41 (33). Reaction conditions: mole ratio = 1:2 (acetic acid/*n*-butanol); temperature = 423 K; time = 6 h; pressure = autogenous.

Table 7
A comparison of esterification of acetic acid over Al-MCM-41 with different Si/Al and other zeolites

Catalyst	Si/Al	Conversion (%)	%Selectivity to product
H-MCM-41	114	78.2	99
H-MCM-41	72	70.3	99
H-MCM-41	52	79.0	99
H-MCM-41	33	87.3	99
HM	12	40.4	99
Hβ	8	51.0	99
HY	4	50.0	99
HZSM-5	15	53.5	99
Without catalyst	–	22.0	99
As synthesized Al-MCM-41	100	28.0	99
Si-MCM-41	–	28.0	99

Temperature = 423 K; feed ratio = 1:2; time = 6 h.

to *n*-butyl acetate is 87.3%. Here is a 4.1% increase in the selectivity when increasing the amount of catalyst from 0.05 to 0.20 g. This observation and interpretation of the result suffices the need for lower amount of catalyst to carry out the reaction.

3.2.6. Comparative study on various zeolites

The influence of hydrophilic/hydrophobic property on conversion was again verified by studying the reaction with zeolites like H-Mordenite (Si/Al = 12), H-Beta (Si/Al = 8), H-ZSM-5 (Si/Al = 15) and H-Y (Si/Al = 4) at the optimised condition 423 K for the period of 6 h (Table 7). The conversions over these catalysts were 40.4, 51, 50 and 53.5%, respectively. Although these catalysts have more acid strength than Al-MCM-41, their less conversion than MCM-41 molecular sieves clearly establishes the influence of their hydrophobic properties. The alcohol, which is hydrophobic, cannot make its entry easy into the pores of the zeolites. Since the reaction was run under autogenous pressure, diffusion of the reactants into the pores may not be much hindered to the progress of the reaction. In order to verify the active influence of the catalysts, the reaction was also studied in the absence of the catalyst under the optimum conditions, feed ratio of 1:2 at 130 °C. After 9 h of the reaction the mixture was analysed and the acetic acid conversion was found to be 28%. It is 65% less than in the presence of catalyst. This observation therefore clearly establishes the active role of the catalyst for this reaction. 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 as-synthesised catalyst. As this catalyst is incapable of permitting the reaction inside the pore due to template blocking, the outer surface sites alone can catalyse the reaction. 28% acetic acid conversion was obtained which is 60% less than that of calcined sample. So the reaction is more prone to occur within the pores of the catalyst rather than on the outer surface. The reaction was also carried out in the presence of siliceous MCM-41. The conversion was 60% less than in the presence of Al-MCM-41 (33), which indirectly proves the occurrence of the

reaction due to Brönsted acid sites inside the pores of the catalyst.

4. Conclusions

From the studies on the esterification of acetic acid over various protonated Al-MCM-41 with different Si/Al ratios, the following conclusions were drawn. *n*-Butyl acetate was the major product obtained which is facilitated by weak and moderate Brönsted acid sites. The low reaction period and low amount of catalyst were required for converting a major amount of the reactants to product with high selectivity. The earlier work reporting the failure of this reaction even with very low Si/Al ratio, i.e., Si/Al = 16, has now been achieved with higher Si/Al ratio. This work has provided an alternative to the usage of Al-MCM-41 catalysts with very low Si/Al ratios. The application of autogenous pressure over the catalyst and the mild increased temperature bettered the previous results. The hydrophobic character also tends to have greater influence in spite of autogenous pressure, which was proved by carrying out the reaction with hydrophilic zeolites where the conversion decreased due to the lack of hydrophobic character. The reaction over as-prepared catalyst showed conversion 68% less than that of calcined sample. Hence the reaction is proposed to occur mainly within the pores of the catalyst. This observation indirectly proves planting of Brönsted acid sites inside the pores of the catalyst.

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