Vapour phase reaction of ethylbenzene with isopropyl acetate over mesoporous Al-MCM-41 molecular sieves

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Abstract

Al-MCM-41 mesoporous materials (Si/Al = 27, 52, 72 and 104) were synthesised hydrothermally and characterised by XRD, FTIR, BET (surface area) and ^{29}Si, ^{27}Al MAS–NMR techniques. The catalytic activity of these molecular sieves was tested in the reaction of ethylbenzene with isopropyl acetate in the vapour phase at 200, 250, 300 and 350 °C. Conversion of ethylbenzene decreased with increase in the temperature. The activity of these catalysts followed the order: Al-MCM-41 (27) > Al-MCM-41 (52) > Al-MCM-41 (72) > Al-MCM-41 (104). The reaction yielded alkylated and acetylated products namely 4-isopropylethylbenzene (4-IEB), 2-acetyl-4-isopropylethylbenzene (2-A-4-IEB), 2,6-diacetyl-4-isopropylethylbenzene (2,6-DA-4-IEB) and 2,4-diacetylethylbenzene (2,4-DAEB). The nature of acid sites in the catalyst was proposed to account for both alkylation and acylation. The selectivity to 4-IEB increased with increase in temperature whereas the selectivity to other products decreased. Increase in the feed ratio increased the conversion indicating the preferential adsorption of isopropyl acetate on the catalyst surface. The time on stream studies with Al-MCM-41 (27) showed nearly similar activity and selectivity for the products for 5 h.
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1. Introduction

Alkylated and acylated products of alkylaromatics are of high commercial significance. Among the alkylated products, ethylbenzene, isopropylbenzene, isopropyltoluene and C_{10}–C_{14} linear alkylbenzenes are a few of the many industrially important chemical intermediates obtained by acid-catalysed alkylation of the appropriate aromatics [1]. In case of the acylated products 2-acetyl-6-methoxynaphthalene, 4-isobutyl acetophenone, etc. are a few intermediates [2], which are highly viewed for its pharmaceutical activity. Acylated products are also commercially important for its use as drugs, fragrances, dyes and pesticides [3,4]. Acid catalysed alkylation and acylation over various solid supports have been reported [5,6]. The advantages and disadvantages of the various solid catalysts are viewed equally.

Friedel–Crafts alkylation and Friedel–Crafts acylation carried out through other catalysts have given rise to various types of drawbacks like regeneration [7–9], handling, corrosion and disposing [10,11]. In addition, alkylation and acylation carried out over micropores have lead to fast catalyst deactivation produced by coke deposition within the microporous material [12]. This has restricted their use. Enlargement of the pore size (>20 Å) and reduction in acid strength could solve these problems. Hence, preparation of the commercially significant alkylated and acylated aromatics through MCM-41 has come to focus in the recent past.

MCM-41 molecular sieves, apart from buffering all the above said problems, also have an important advantage of possessing various types of acid sites. In addition, with additional isomorphic substitution or ion exchange of metal ions, MCM-41 can be tailored to our desired property. A modified MCM-41 through isomorphic substitution will be enriched in Bronsted acid sites. Whereas, the active sites

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of an ion exchange MCM-41, mainly contains Lewis acid sites. Badamali et al. [13] have investigated the presence of variety in acid sites in MCM-41. They have explained the acid sites of the Fe-MCM-41 with the NH$_3$/TPD analysis, clarifying the nature of acid sites. This variety in acid sites can be attributed to three different types of Bronsted acid sites. Desorption peaks at 473, 465 and 524 K were attributed to weak acid sites due to surface/terminal hydroxyl groups, moderate structural acid sites and strong structural acid sites, respectively [14].

Hence, in our present investigation, Al-MCM-41 was used as the solid acid catalyst for a vapour phase reaction of ethylbenzene with isopropyl acetate. As the more reactive acetyl chloride is hazardous due to its production of hydrochloric acid vapours and as the less active acetic anhydride is a banned material in India, aliphatic ester has been chosen as acetylating and alkylating agent.

2. Experimental

2.1. Materials and methods

The hydrothermal crystallisation procedure reported by Beck et al. [15] was adopted for the preparation of Al-MCM-41 molecular sieves with Si/Al ratios (27, 52, 72 and 104). In a typical synthesis, 21.21 g of sodium meta silicate nanohydrate (Merck) in demineralised water was mixed with the appropriate amount of aluminium sulphate (Merck). It was then acidified with 1 M H$_2$SO$_4$ to bring down the pH to 10.5 under vigorous stirring. After 30 min, an aqueous solution of cetyltrimethylammonium bromide (7.286 g in 23 ml) (Merck) was added and the surfactant silicate mixture was stirred for further 30 min at room temperature. The molar composition of the resultant mixture was SiO$_2$:0.2CTAB:XAl$_2$O$_3$:0.89H$_2$SO$_4$:120H$_2$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.

2.2. Characterisation

The XRD powder diffraction patterns of the calcined mesoporous Al-MCM-41 (Si/Al ratio 27, 52, 72 and 104) molecular sieves were obtained from Stereoscan diffractometer using nickel-filtered Cu Kα radiation and a liquid nitrogen cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range of 0–10° in 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 were measured by nitrogen adsorption at 77 K with an ASAP-2010 porosimeter from Micromeritics Corporation, Noreross, GA, USA. The samples were degassed at 623 K at 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 0.5 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) built-in software from Micromeritics.

Mid-IR spectra of the mesoporous Al-MCM-41 molecular sieves were collected on Nicolote (Avatar 360) instrument using KBr pellet technique. About 10 mg of the sample was ground with 200 mg of spectral grade KBr to form a pellet under hydraulic pressure to record the IR spectrum in the range 4000–400 cm^{-1}.

^{29}Si MAS–NMR spectra were recorded in a DRX-500 FT–NMR Spectrometer at a frequency of 59.64 MHz, spinning speed of 8 KHz, pulse length of 2.50 μs (45° pulse), delay time of 10 s and spectral width of 335 ppm. Two thousand scans were acquired with reference to trimethylsilylpropane sulphonic acid (TSP). Solid-state ^{27}Al MAS–NMR spectra were recorded at a frequency of 104.22 MHz, spinning rate of 8 KHz, a pulse length of 1.0 μs, delay time of 0.2 s and a spectral width of 330 ppm. The total scans were 150 and the line broadening was 50 Hz. The ^{27}Al chemical shifts were reported in relation to the solution of aluminium nitrate.

2.3. Analysis of the product

The isopropylation and acetylation of ethylbenzene with isopropyl acetate were carried out in a fixed bed continuous down flow glass reactor of 40 cm length and 1 cm internal diameter. About 0.5 g of the catalyst was taken in the reactor and a motor driven syringe pump at predetermined flow rate fed the reaction mixture into the reactor. Analysis of the products collected for 1 h was carried out in a Hewlett Packard gas chromatograph 5890A equipped with a flame ionisation detector (FID) using an OV17 column and nitrogen as the carrier gas. After completion of each run, the reactor system was flushed with nitrogen to remove the physisorbed impurities. The catalyst was regenerated at 525 °C in a current of moisture-free air for 6 h.

3. Results and discussion

3.1. Characterisation

3.1.1. XRD

The XRD pattern of the calcined mesoporous catalysts (Fig. 1) shows intense diffraction peak at about 2θ due to [1 0 0] plane confirming the hexagonal mesophase of the material. The d_{100} spacing and lattice parameter (a_0) calculated as per the literature procedure [16–18] 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 [19].
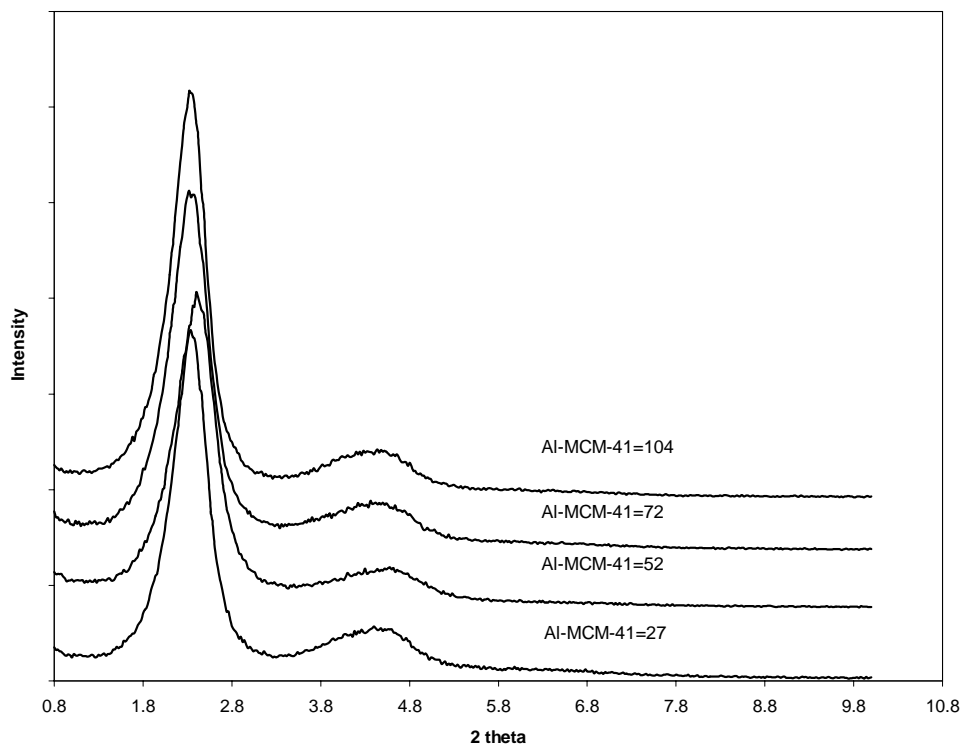
Fig. 1. X-ray diffraction pattern of Al-MCM-41 (27, 52, 72 and 104) obtained after calcination.

Table 1
Textural properties of the catalysts

Catalysts	Si/Al	ICP	Calcined		Un-calcined	
			d_{100}	Unit cell (a_0) (nm)	d_{100}	Unit cell (a_0) (nm)
Al-MCM-41 (27)	25	27	37.45	4.32	37.81	4.37
Al-MCM-41 (52)	50	52	37.18	4.29	38.19	4.41
Al-MCM-41 (72)	75	72	36.82	4.25	38.47	4.44
Al-MCM-41 (104)	100	104	37.45	4.32	38.19	4.41

3.1.2. Nitrogen adsorption isotherms

BET surface areas, pore size and pore volume for calcined materials are presented in Table 2. Desorption and adsorption isotherms and pore size distribution for calcined materials (BJH method) are shown in (Figs. 2 and 3) which coincide with reported values [20,21].

3.1.3. Thermal analysis

The thermal properties of the samples were investigated by TGA. The initial weight loss up to 100 °C is due to desorption of physically adsorbed water. The oxidative des-

orption of the organic template takes place at 180 °C and the minute quantity of weight loss above 300 °C is due to condensation of defective Si–OH groups. The obtained thermogram was similar to the one obtained elsewhere [16].

3.1.4. FT-IR spectroscopy

The FT-IR spectral analysis of the uncalcined and calcined Al-MCM-41 (Si/Al = 27, 52, 72 and 104) molecular sieves was carried out. FT-IR spectral features resemble those reported by previous workers [16,22].

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

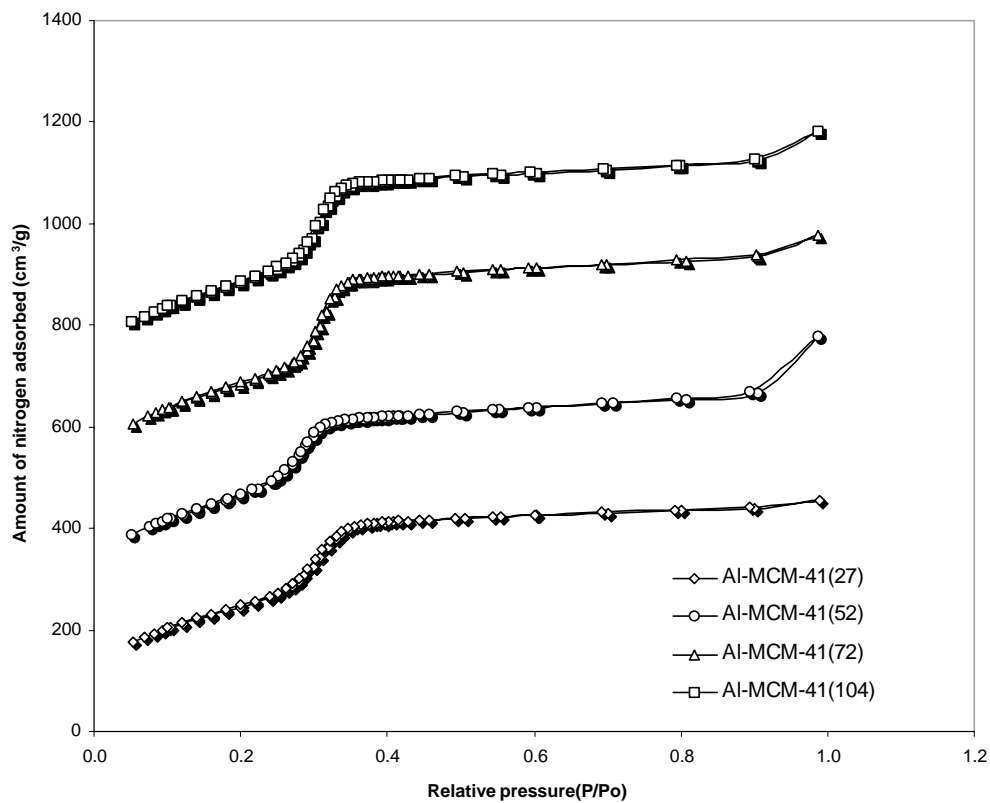| Catalysts	Surface area (m²/g)	Surface area BJH$_{Ads}$ (m²/g)	Surface area BJH$_{Des}$ (m²/g)	Pore size BJH$_{Ads}$ (nm)	Pore size BJH$_{Des}$ (nm)	Pore volume BJH$_{Ads}$ (cm³/g)	Pore volume BJH$_{Des}$ (cm³/g)
Al-MCM-41 (27)	898.3	1149	1084	2.607	2.626	0.752	0.724
Al-MCM-41 (52)	952.9	1231	1158	2.502	2.506	0.947	0.917
Al-MCM-41 (72)	1039	1354	1295	2.66	2.625	0.956	0.933
Al-MCM-41 (104)	1046	1332	1284	2.681	2.692	0.961	0.933

Fig. 2. Adsorption isotherms of Al-MCM-41 (27, 52, 72 and 104).
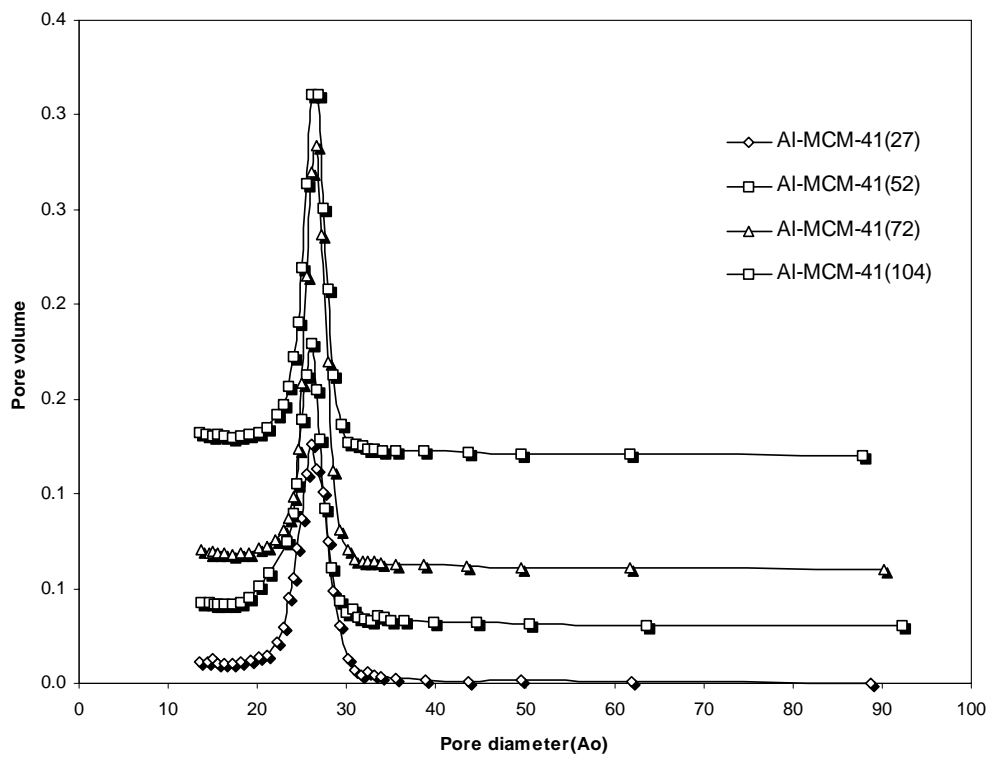

Fig. 3. Pore size distribution in Al-MCM-41 (adsorption isotherms).

3.1.5. ^{29}Si, ^{27}Al MAS–NMR

The ^{29}Si MAS–NMR spectra of the calcined Al-MCM-41 materials showed, broad signals at -111 ppm and the shoulders in the range between -103 and -108 ppm in the spectra coincide well with those reported by the previous workers [22,24,25]. The ^{27}Al MAS–NMR spectra of the samples showed the characteristic peak around 54.3 ppm, confirming the presence of aluminium in tetrahedral coordination [22,23]. ^{27}Al MAS–NMR of the calcined Al-MCM-41 (27, 52, 72) showed a less intense peak at 0 ppm due to the non-framework aluminium species in octahedral coordination [25].

3.1.6. ICP–AES analysis

The aluminium content in Al-MCM-41 of various ratios was recorded using ICP–AES with allied analytical ICAP 9000. The results of Si/Al ratios of the materials are given in Table 1.

3.2. Application of Al-MCM-41 (27), Al-MCM-41 (52), Al-MCM-41 (72) and Al-MCM-41 (104) catalysts to alkylation and acylation of ethylbenzene

3.2.1. Influence of temperature

The reaction of ethylbenzene with isopropyl acetate was studied at 200, 250, 300 and 350 °C over Al-MCM-41 (Si/Al = 27, 52, 72 and 104) in the ratio, ethylbenzene: isopropyl acetate 1:3, and WHSV 1.742 h^{-1}. The results of ethylbenzene conversion (EB-conversion), isopropyl acetate conversion (IPA-conversion) and products selectivity over Al-MCM-41 (27) are given in the Table 3. The products were found to be 4-isopropylethylbenzene (4-IEB), 2-acetyl-4-isopropylethylbenzene (2-A-4-IEB), 2,6-diacetyl-4-isopropylethylbenzene (2,6-DA-4-IEB), and 2,4-diacetylethylbenzene (2,4-DAEB). All the catalyst showed increase in isopropyl acetate conversion with increase in temperature and a decrease in ethylbenzene conversion with increase in temperature due to blocking of active sites by coke. Experiment was carried out on Al-MCM-41 (27) at a temperature 300 °C with a feed ratio of 1:3. A similar decrease in conversion was also noticed in the isopropylation of toluene with isopropanol in the vapour phase [26]. The observations from the mass balance calculations showed that a reactant quantity of 1.0447 g by weight gave a weight loss of 0.3196 g, i.e. 30.6%. After completion of the reaction, the catalyst was calcined for 5 h at 525 °C. There was a weight loss of 0.0522 g (5.1%) after calcination. This clearly proves the formation of coke. The remaining weight difference of about 0.2674 g (25.5%) may be due to propene formation. The decrease in EB-conversion is gradual between 200 and 300 °C and almost levelled between 300 and 350 °C. The results confirm that at low temperatures the rapid diffusion of the products out of the molecular sieves curb the formation of coke. But with the increase in temperature, multi-alkylation would become predominant and ultimately a reduction in the EB-conversion.

With increase in temperature there is increase in the selectivity of 4-IEB. The selectivity to 2,4-DAEB is about 20% at 200 and 250 °C and it decreases to less than 10% at 300 and 350 °C. The selectivity of 2-A-4-IEB, 2,6-DA-4-IEB are less than 10% at all temperatures. Thus, results confirm alkylation is a more favourable reaction than acylation. The formation of the acetyl cation or the acetylated surface is energetically less favoured than formation of the isopropyl cation or the isopropylated surface. When isopropyl acetate approaches the catalyst surface it can get chemisorbed through the C=O group of the ester or by the isopropoxide

Table 3

Catalytic activity of Al-MCM-41 (27, 52, 72 and 104) for isopropylation of ethylbenzene

| Catalysts	Temperature	Isopropylacetate conversion (%)	Ethylbenzene conversion (%)	Selectivity to products with respect to ethylbenzene conversion (%)				
				4-IEB	2,4-DAEB	2-A-4-IEB	2,6-DA-4-IEB	Others
Si/Al = 27	200	56.7	53.7	46.5	23.0	7.6	7.6	15.3
	250	62.2	33.1	61.1	18.6	2.8	2.4	15.1
	300	75.4	20.1	65.2	9.2	4.9	3.5	17.2
	350	82.5	17.5	71.6	6.3	3.1	2.0	17.0
Si/Al = 52	200	41.1	49.7	51.6	25.6	5.2	2.7	14.9
	250	54.7	31.0	62.5	15.6	3.6	1.9	16.4
	300	68.9	17.3	68.8	14.2	1.2	–	15.8
	350	71.3	12.1	72.8	9.9	–	–	17.3
Si/Al = 72	200	38.7	17.6	54.4	28.5	3.2	0.7	13.2
	250	47.2	12.1	63.5	19.6	1.7	–	15.2
	300	55.4	9.0	67.2	17.9	–	–	14.9
	350	62.5	5.1	72.5	10.3	–	–	17.2
Si/Al = 104	200	33.1	15.4	49.8	31.3	0.9	–	18.0
	250	41.9	10.4	66.2	20.9	–	–	12.9
	300	51.7	3.0	66.6	16.7	–	–	16.7
	350	58.2	2.1	76.4	10.4	–	–	13.2

WHSV: 1.741 h^{-1}.

oxygen. The isopropoxide oxygen is not electron rich due to delocalisation of the oxygen lone pair over the carbonyl group. This delocalisation is enhanced by protonation at the carbonyl oxygen. Hence the alkoxy C–O bond could be easily cleaved to give isopropyl cation and acetic acid. The effect of temperature on selectivity of the products also illustrate that, low temperature range is more favourable for acylation than alkylation.

From these results, it could be proposed that chemisorption on more acidic bridged hydroxyl groups (Scheme 1a) yield free isopropyl cation and on the less acidic hydroxyl sites (Scheme 1b) it yields a partly protonated ester as shown below. Formation of free acetyl cation could not be easily conceived by the proposed schemes. The difference in the

acidity of the Bronsted acid sites on the surface of the catalyst is due to different nature of coordination around aluminium tetrahedra. When aluminium is linked to four SiO_4 tetrahedra then Bronsted acid sites will be more acidic than other possible environments.

The gradual increase in the selectivity to 4-IEB with increase in temperature is due to the reduced availability of partly protonated ester, for subsequent acetylation of this product to yield 2-A-4-IEB and 2,6-DA-4-IEB. At 300 and 350 °C, the EB-conversion remains almost the same. Hence in 2-A-4-IEB and 2,6-DA-4-IEB density of active sites must be the same, but most of them must be more acidic Bronsted acid sites as the selectivity to 4-IEB shows higher values. Among the acetylated
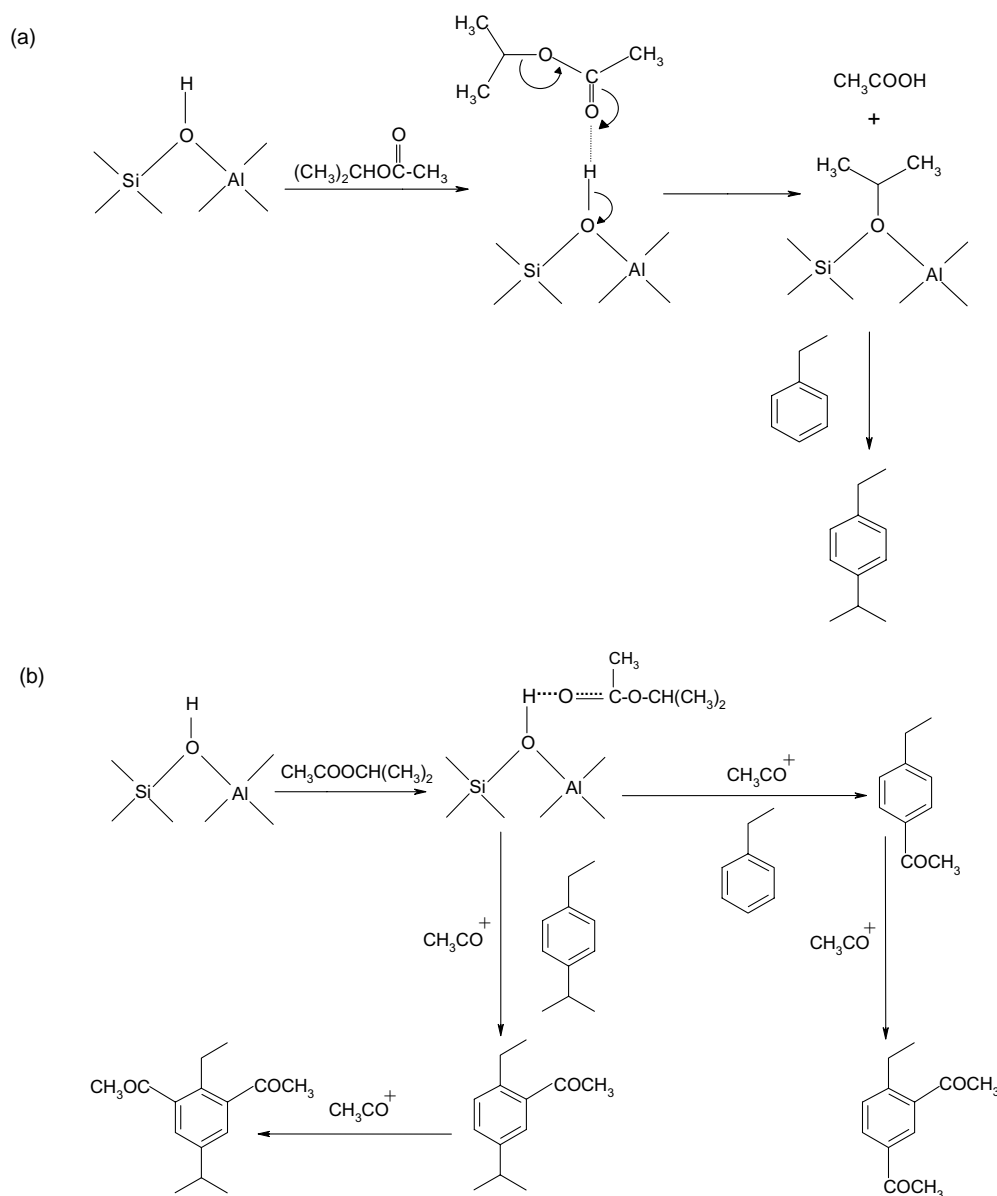
Scheme 1. (a) Effect of strong acid sites on the alkylation reaction of ethylbenzene with isopropyl acetate; (b) effect of weak acid sites on the acetylation reaction of ethylbenzene with isopropyl acetate.

products, the selectivity to 2,4-DAEB is higher than other products.

2-IEB is not observed in this study. This might be due to steric hindrance. Acetylation, ortho to the ethyl group is observed and is less subjected to steric hindrance. The selectivity to 2,4-DAEB is higher than to 2-A-4-IEB and 2,6-DA-4-IEB. As most of the ethylbenzene is chemisorbed on the Bronsted acid sites of the catalyst [27] due to high density of the acid sites of the catalyst [13,14], there would be acetyl cation and isopropyl cation close to chemisorbed ethylbenzene. Since isopropyl cation itself could demand more space on the catalyst surface, like the chemisorbed ethylbenzene, there might be less probability for the formation of partly protonated ester for acetylation. As a consequence of this, there might be less selectivity for 2-A-4-IEB and 2,6-DA-4-IEB.

Among the Bronsted acid sites, all the acid sites are not equally strong. Strong acid sites are required for the formation of isopropyl cation and slightly less acidic sites are required for the formation of acetyl cation. The heterogenity in the nature of acid sites must exist on the catalyst surface, as the products are not entirely isopropylated or acetylated. The presence of these various acid sites could be based on the fact that the nature of tetrahedral units surrounding any single T-atom need not be same throughout the framework.

Table 3 illustrates % EB-conversion and products selectivity at various temperatures over Al-MCM-41 (52). The data showed nearly similar trend in EB-conversion and products selectivity at different temperatures. At lower temperatures, slight decrease in EB-conversion is observed, compared to

Al-MCM-41 (27) as this catalyst possesses less dense acid sites. It is also seen that the selectivity to 4-IEB increases with increase in the Si/Al ratio of the catalyst. This also confirms the fact that strong acid sites are required for isopropylation. Both, % EB-conversion and % IPA-conversion decreases with increase in Si/Al ratio. % EB-conversion decreases and % IPA-conversion increases with an increase in the temperature (Figs. 4 and 5). The % EB-conversion is higher over Al-MCM-41 (27) and Al-MCM-41 (52) than over Al-MCM-41 (72) and Al-MCM-41 (104), at all temperatures. But the decrease in EB-conversion is not uniform with increase in Si/Al ratio, indicating that a few Al^{3+} sites might be buried in the bulk portion of the wall.

3.2.2. Influence of feed ratio

The effect of feed ratio on IPA-conversion, EB-conversion and products selectivity (with respect to ethylbenzene) has been studied over Al-MCM-41 (27) at the optimum temperature of 200 °C. As the % EB-conversion is more over Al-MCM-41 (27), this catalyst has been taken to investigate the effect of feed ratio (Table 4). As expected, the EB-conversion increased with increase in the ester content in the feed. IPA-conversion decreased with increase in the feed ratio. Although ethylbenzene could be adsorbed on the Bronsted acid sites of the catalyst surface, the adsorption decreases at feed ratio 1:5. Though decrease in selectivity to 4-IEB is observed with increase in the ester content in the feed, same selectivity to 4-IEB is maintained for 1:3 and 1:5 feed ratios. With the feed ratio 1:1, the selectivity to 2-A-4-IEB and 2,6-DA-4-IEB is very less, but at 1:3
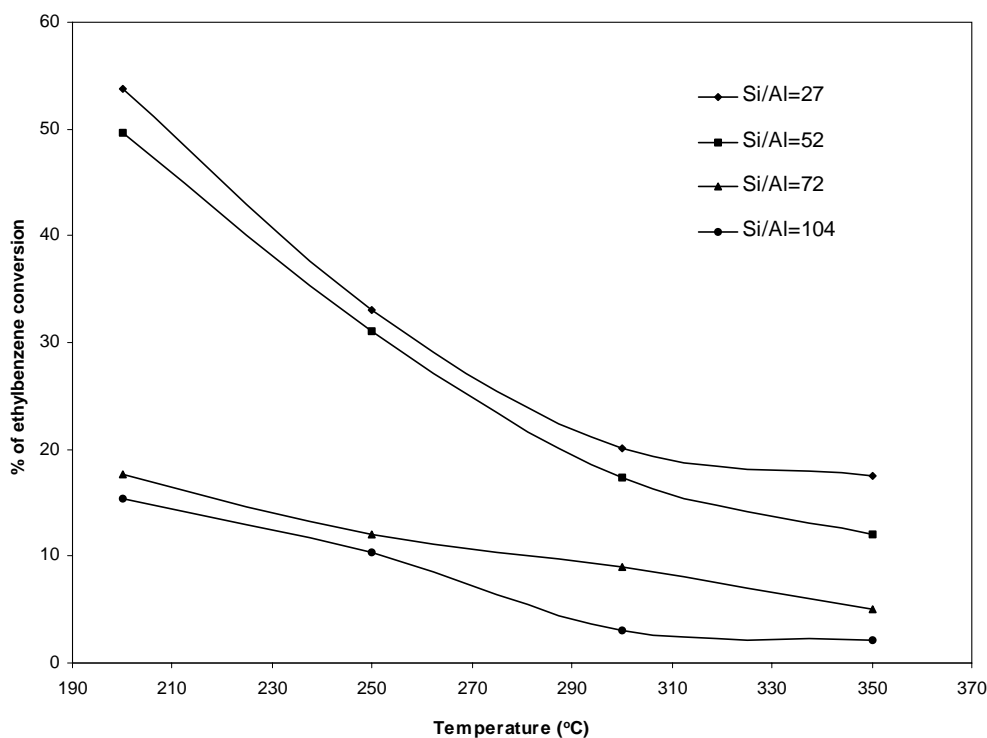

Fig. 4. Comparison of ethylbenzene conversion over different catalysts (Si/Al = 27, 52, 72 and 104); feed ratio: 1:3; WHSV: 1.742 h^{-1}.
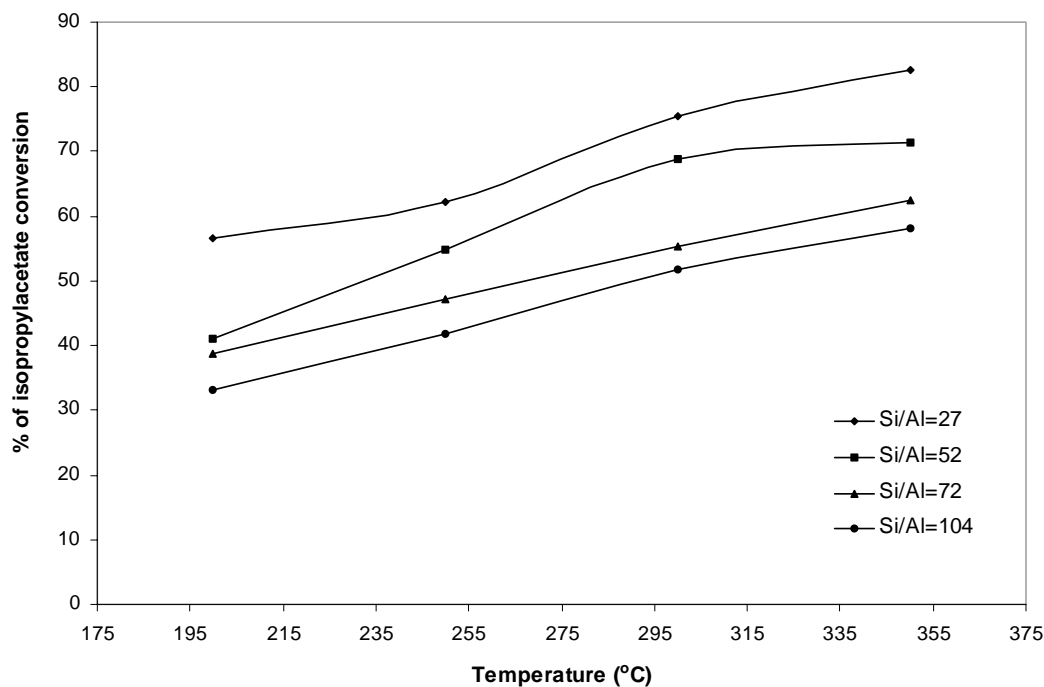
Fig. 5. Comparison of isopropyl acetate conversion over different catalysts (Si/Al = 27, 52, 72 and 104); feed ratio: 1:3; WHSV: $1.742\,h^{-1}$.

Table 4
Effect of feed ratio on isopropylation of ethylbenzene over Al-MCM-41 (27)

WHSV (h^{-1})	Feed ratio	Isopropylacetate conversion (%)	Ethylbenzene conversion (%)	Selectivity to products with respect to ethylbenzene conversion (%)				
				4-IEB	2,4-DAEB	2-A-4-IEB	2,6-DA-4-IEB	Others
1.738	1:1	84.2	24.7	57.7	23.4	2.1	1.6	15.2
1.741	1:3	68.4	53.7	48.6	23.0	7.6	7.6	13.2
1.742	1:5	52.7	62.6	48.0	24.7	9.2	8.5	9.6

Temperature: 200 °C.

and 1:5 feed ratios, it is increased, as the acetyl cation increases. The selectivity to 2,4-DAEB is almost same in all the feed ratios. The increase in the formation of acetyl cation at the feed ratio 1:3 and 1:5 is responsible for the formation of 2-A-4-IEB and 2,6-DA-4-IEB. Hence, the selectivity to 2,4-DAEB is levelled in all the three feed ratios.

3.2.3. Influence of time on stream

The effect of time on stream was studied at 200 °C over Al-MCM-41 (27) with the feed ratio 1:5 and WHSV

$1.742\,h^{-1}$. The EB-conversion, IPA-conversion and products selectivity (with respect to ethylbenzene) is present in Table 5. EB-conversion was steady between 60 and 70% for 5 h on stream. Similarly, IPA-conversion was stable during the same duration. Hence, multi-alkylation leading to coke formation to reduce the activity of the catalysts is not evidenced. Hence, existence of similar mechanism for the formation of products is expected in the entire stream. The selectivity of the products is also maintained. The selectivity to 2,6-DA-4-IEB is low at first hour, raised to about

Table 5
Effect of time on stream on isopropylation of ethylbenzene over Al-MCM-41 (27)

S. no.	Time (h)	Isopropylacetate conversion (%)	Ethylbenzene conversion (%)	Selectivity to products with respect to ethylbenzene conversion (%)				
				4-IEB	2,4-DAEB	2-A-4-IEB	2,6-DA-4IEB	Others
1	1	52.2	62.6	45.9	23.7	9.1	11.1	10.2
2	2	51.7	61.1	47.4	24.8	10.2	7.8	9.8
3	3	52.8	56.9	46.0	26.2	6.9	8.7	12.2
4	4	53.5	61.8	44.2	26.0	6.7	8.9	14.2
5	5	50.3	60.6	48.5	27.9	6.9	6.6	10.1

Feed ratio: 1:5, WHSV: $1.742\,h^{-1}$, temperature: 200 °C.

Table 6
Effect of time on stream on isopropylation of ethylbenzene over Al-MCM-41 (27)

S. no.	Time (h)	Isopropylacetate conversion (%)	Ethylbenzene conversion (%)	Selectivity to products with respect to ethylbenzene conversion (%)				
				4-IEB	2,4-DAEB	2-A-4-IEB	2,6-DA-4IEB	Others
1	1	75.4	20.4	65.2	9.2	4.9	3.5	17.2
2	2	71.6	18.2	61.4	10.5	2.7	5.1	20.3
3	3	68.7	16.7	58.3	12.8	1.1	6.4	21.4
4	4	65.2	13.5	57.2	14.2	–	8.1	20.5
5	5	61.9	11.6	54.7	16.8	–	10.2	18.3

Feed ratio: 1:3, WHSV: $1.741\,h^{-1}$, temperature: $300\,^\circ C$.

Table 7
Influence of WHSV on ethylbenzene conversion and product selectivity

S. no.	WHSV (h^{-1})	Isopropylacetate conversion (%)	Ethylbenzene conversion (%)	Selectivity to products with respect to ethylbenzene conversion (%)				
				4-IEB	2,4-DAEB	2-A-4-IEB	2,6-DA-4-IEB	Others
1	1.742	54.2	61.1	44.0	23.4	13.7	6.7	12.2
2	2.612	50.2	34.0	50.5	24.9	7.3	3.1	14.2
3	3.485	45.7	12.4	55.3	29.1	–	–	15.6

Feed ratio: 1:5, temperature: $200\,^\circ C$, catalyst: Al-MCM-41 (27).

10% at the second hour and maintained afterwards. Hence, diacetylation requires enough built-up of acetyl cation on the catalyst surface to attain steady state of formation of 2,4-DAEB.

The effect of time on stream was also studied at $300\,^\circ C$ over Al-MCM-41 (27) with the feed ratio 1:3 and WHSV $1.741\,h^{-1}$. The study was conducted for 5 h, and the results are presented in Table 6. EB-conversion as well as IPA-conversion decreased gradually with increase in stream. The decrease in EB-conversion with increase in stream might be attributed to gradual increase in the blocking of active sites by polypropene oligomers and coke formation [13]. Selectivity to 2,4-DAEB increases with increased stream. Therefore, there might be a consequent increase in the partly protonated ester for acetylation with stream, as the more active sites (strong active sites) might be more rapidly blocked than others. It is also reflected in the selectivity of 4-IEB, which has also decreased with increase in stream. Selectivity to 2A-4IEB decrease with stream, where as the selectivity to 2,6-DA-4IEB increases with increase in stream. This might be due to the consequent increase in the partly protonated ester for acetylation with stream.

3.2.4. Influence of WHSV

Table 7 shows the effect of flow rate on EB-conversion, IPA-conversion and products selectivity (with respect to ethylbenzene). The feed ratio was maintained at 1:5, and the study was performed at $200\,^\circ C$ over Al-MCM-41 (27). EB-conversion and IPA-conversion decrease with increase in the flow rate, while selectivity to 4-IEB increases with increase in the flow rate. Since the feed ratio is high, the previously suggested route of reaction between ethylbenzene and alkyl cation or protonated ester adsorbed on Bronsted acid sites could be ruled out. Ethylbenzene can react with either alkyl cation or protonated ester only in

the vapour phase. Again with increase in the flow rate, the probability of reacting 4-IEB with partly protonated ester would be less probable. It also accounts for decrease in the selectivity to isopropylated acetyl products with this feed ratio. The selectivity to 2-A-4-IEB and 2,6-DA-4-IEB reaches zero, at the WHSV $3.485\,h^{-1}$. The selectivity to 2,4-DAEB increases with increase in the flow rate. Hence, this suggests the formation of the products by successive acylation in the region, where the partly protonated ester would remain closer. As said above, this is quite probable, as the density of acid sites is more on this catalyst and also the availability of partly protonated ester plays a vital role. At the feed ratio 1:5, nearly the entire ethylbenzene is in the vapour state and at high flow rate there would be fast diffusion without reaction.

4. Conclusion

The study shows that isopropyl acetate can be an alkylating as well as an acetylating agent in the vapour phase. Formation of acetyl cation is favoured over slightly less acidic-bridged hydroxyl groups and isopropyl cation over strong acid sites. Increase in the ester content in the feed increased the EB-conversion. While increase in the flow rate decreased the EB-conversion. The time on stream indicates nearly levelling of EB-conversion and products selectivity for 5 h at $200\,^\circ C$ and 1:5 feed ratio. But at $300\,^\circ C$ and 1:3 feed ratio EB-conversion is found to decrease with increase in time on stream for 5 h. The selectivity to 4-IEB is more than the selectivity to other products, at different experimental conditions of the study over all the catalysts. It is also observed that selectivity to 4-IEB increases with increase in the Si/Al ratio, thus confirming the strong acid site dependence for the formation of isopropyl cation than acetyl

cation. With decrease in aluminium content, the probability for a [Si–OH–Al] unit, to have four SiO$_4$ units surrounding aluminium, will increase and hence, the acidity of the bridged hydroxyl increases.

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