

The vapour phase reaction of *tert*-butylbenzene and *tert*-butyl acetate over Al-MCM-41 molecular sieves

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Abstract

Hydrothermal synthesized Al-MCM-41 with different Si/Al ratios (30, 54, 78 and 107) were characterized by XRD, ICP-AES, BET, acidity measurement by pyridine adsorbed FT-IR spectroscopy, ²⁹Si and ²⁷Al MAS NMR techniques. The catalytic activity of these materials was tested in the vapour phase alkylation of *tert*-butylbenzene (TBB) with *tert*-butyl acetate (TBA) in the temperature range 200–400 °C. The products were found to be 1,4-di-*tert*-butylbenzene (1,4-DTBB), 1,3-di-*tert*-butylbenzene (1,3-DTBB), 4-acetyl-*tert*-butylbenzene (4A-TBB), 3-acetyl-*tert*-butylbenzene (3A-TBB), 2-acetyl-*tert*-butylbenzene (2A-TBB) and 2-acetyl-1,4-di-*tert*-butylbenzene (2A-1,4-DTBB). The selectivity towards 1,3-DTBB increased with increase in temperature, conversely the selectivity of 1,4-DTBB decreased. The selectivity to 4A-TBB, which is higher than that of other compounds, also increased with increase in temperature. The effect of temperature, flow rate and feed ratio was also studied over all the catalysts to arrive optimum conditions for higher conversion with product selectivity. The effect of time-on-stream was studied over all the catalysts and the results are discussed.

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1. Introduction

Alkylation and acylation of aromatic hydrocarbons are of high commercial significance. The industrially important chemical intermediates like ethylbenzene, isopropylbenzene and linear alkylated benzenes have been produced by acid catalyzed alkylation with appropriate aromatics [1,2]. Similarly acylation reactions are widely employed for large-scale production of important fine chemicals, synthetic fragrance and pharmaceuticals [3–9]. These reactions are catalyzed by mineral acids like HF, H₂SO₄, etc., but they are all hazardous. These acids can be replaced by eco-friendly solid acid catalysts such as zeolites and mesoporous molecular sieves. The major drawback in the use of zeolites for alkylation of aromatics is the low turn over number. As zeolites are microporous material, it would be difficult to use entire Brønsted acid sites into activity at any instant

[10]. Apart from diffusion problem, the density of acid sites in zeolites is high and hence they could also encourage coking [11,12]. These problems can be overcome by using mesoporous molecular sieves. These mesoporous molecular sieves possess large internal surface area, large pore volume, unidimensional pore geometry and hydrophobic surface property [13]. These properties have attracted much research attention owing to their potential applications as catalysts, ion-exchangers and adsorbents [14,15]. Al-MCM-41, a member of mesoporous molecular sieves has already proved to be an effective catalyst for hydrogenation, cracking, hydrocracking, isomerization and alkylation reactions [16]. *tert*-Butyl alcohol has been used as alkylating agent in conventional methods for most of the reactions. But it possesses certain demerits, as it could get aggregated near Brønsted acid sites through hydrogen bonding and suppress the dissociation. *tert*-Butyl acetate (TBA) as alkylating and/or acylating agent has some advantages, as it could better adsorb on the Brønsted acid sites [17]. This is due to easy availability of active sites for adsorption, namely, the carbonyl group compared to the sterically crowded alcoholic –OH group in *tert*-butyl alco-

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hol. Isopropyl acetate and *tert*-butyl acetate have already been reported as alkylating agents [18,19]. Considering the problems encountered with zeolites, and the advantage in the use of ester for both alkylation and acylation, it has been planned to study the vapour phase reaction of *tert*-butylbenzene and *tert*-butyl acetate over Al-MCM-41 (Si/Al = 30, 54, 78 and 107) molecular sieves. This particular reaction is important as both alkylated and acylated *tert*-butylbenzenes have commercial importance. The effect of important variables affecting the activity and selectivity of the catalysts such as reaction temperature, space velocity and mole ratios of the reactants on conversion and product selectivity have been investigated, and the results are discussed below.

2. Experimental

2.1. Materials and methods

All reagents viz., sodium metasilicate, aluminum sulphate, cetyltrimethyl ammonium bromide (CTAB), sulfuric acid, TBB and TBA were purchased from Merck and used as such. Samples of Al-MCM-41 (Si/Al = 30, 54, 78, 107) were synthesized hydrothermally using a gel of composition $\text{SiO}_2:x\text{Al}_2\text{O}_3:0.2\text{CTAB}:0.89\text{H}_2\text{SO}_4:120\text{H}_2\text{O}$ (x varies with Si/Al ratio). Sodium metasilicate in water was mixed with an appropriate amount of aluminum sulphate in distilled water, and pH of the solution was adjusted to 10.5 using 1 M sulfuric acid and stirred to form a gel. This gel was further homogenized by stirring the mixture for 1 h at room temperature. An aqueous solution of CTAB, prepared by dissolving 6.78 g of CTAB in appropriate amount of distilled water, was added slowly to the gel for a period of about 30 min. The resulting mixture was then stirred for about 12 h. After crystallization, Al-MCM-41 material was recovered by filtration, washed with distilled water and dried at 80 °C for 8 h. The occluded surfactant was removed by calcining the samples at 550 °C in air for 6 h.

2.2. Physico-chemical characterization

The powder X-ray diffraction patterns were recorded by using a Siemens D5005 Stereo scan diffractometer with nickel filtered $\text{Cu K}\alpha$ radiation (operating at 40 kV and 30 mA) source and a liquid nitrogen-cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range 0.8–10° in steps of 0.02° with a count time of 10 s at each point for Al-MCM-41 catalysts. Aluminum content in Al-MCM-41 catalysts was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with the Labtum Plasm 8440 instrument.

The specific surface area and pore properties of Al-MCM-41 were measured by nitrogen physisorption at –196 °C with an ASAP-2010 volumetric adsorption analyzer manufactured by Micrometrics Corporation (Norcross, USA). Before nitrogen adsorption–desorption measurements, Al-MCM-41 samples were degassed at 350 °C at a pressure of 10^{-5} torr overnight. The specific surface area of the samples was determined from the linear portion of BET plots. The pore size distribution was calculated from the desorption branch of N_2 adsorption–desorption

isotherms using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP 2010 built-in software from Micromeritics).

The acidity of samples was analyzed by infrared spectroscopy using pyridine as a probe. The infrared spectra of the samples were recorded using self-supported wafers of 10 mg/cm² at room temperature. The calcined samples were outgassed at 500 °C and 10^{-6} torr for 8 h. The temperature of the samples was brought down to 30 °C and pyridine was then admitted into the cell until complete saturation. After saturation the samples were degassed at 150, 247 and 348 °C under vacuum and cooled to room temperature. The infrared spectra of all the samples were then recorded. The acidity was calculated using the extinction coefficients of the bands of pyridine adsorbed Brønsted and Lewis acid sites [20].

²⁹Si MAS-NMR spectra were recorded in a DRX-500FT-NMR spectrometer at a frequency of 59.64 MHz, with a spinning speed 8 KHz, pulse length 2.50 μs (45° pulse), delay time 10 s and spectral width 335 ppm. Two thousand scans were acquired and processed with a line broadening of 50 Hz. The chemical shifts were reported with reference to trimethylsilylpropanesulfonic acid (TSP). Solid-state ²⁷Al MAS NMR measurements were performed on a Bruker MSL 400 spectrometer equipped with a magic-angle spinning (MAS) unit. The ²⁷Al MAS-NMR spectra were recorded at a frequency of 104.22 MHz, with a spinning speed 8 KHz, pulse length 1.0 μs, delay time 0.2 s and spectral width 330 ppm. The total scans were 150 and the line broadening was 50 Hz. ²⁷Al MAS-NMR chemical shifts were reported using aluminum nitrate as standard.

2.3. Catalytic reactor set up and product analysis

The *tert*-butylation of TBB with TBA was carried out in a fixed bed continuous downward flow glass reactor. The reactor system was a fixed-bed, vertical, flow-type reactor made up of a borosil glass tube of 40 cm length and 2 cm internal diameter. About 0.5 g of the catalyst was placed in the middle of the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. The glass reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator with a thermocouple. The reactants were fed into the reactor by a syringe infusion pump (SAGE instruments) that could be operated at different flow rates. At the bottom of the reactor, a coiled condenser and a receiver were connected to collect the products. The reaction was carried out at atmospheric pressure. The liquid product collected during first 10 min was discarded and the product collected after 1 h was analyzed. After each catalytic run, the reactor was heated continuously for 6 h at about 500 °C by passing moisture and carbon dioxide free air through it in order to eliminate the deposited coke. The percentage conversion of TBB was analyzed by a gas chromatograph (Shimadzu GC-17A) with FID detector equipped with 25 m capillary column (cross-linked 5% phenylmethyl polysiloxane). The identification of products and conversion of TBB was performed on a Perkin Elmer Auto System XL gas chromatograph connected to Turbo Mass Spectrometer with helium as carrier gas (1 ml/h).

Table 1
Textural properties of the catalysts

Catalysts	Gel composition	Framework composition	Calcined	
			d_{100}	Unit cell (a_0) (Å)
Al-MCM-41 (30)	25	30	40.58	46.91
Al-MCM-41 (54)	50	54	39.84	46.06
Al-MCM-41 (78)	75	78	38.84	44.90
Al-MCM-41 (107)	100	107	35.69	41.26

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD patterns of as-synthesized and calcined Al-MCM-41 samples with Si/Al ratios (30, 54, 78 and 107) are shown in Fig. 1. The XRD patterns show intense peak at $2\theta = 1.8^\circ$ due to [100] plane and weak signals between 2 and 4° (2θ) due to [110], [200] and [210] planes indicating the existence of hexagonal phase with d_{100} spacing between 35.69, 38.84, 39.84 and 40.58 Å for all Si/Al ratios. These peaks can be indexed for a hexagonal mesophase, as these spectral features resemble those reported by Chen et al. [21]. The intensity of peaks at about $2\theta = 1.8^\circ$ for calcined samples is more than that of as-synthesized samples due to condensation of defective sites during calcination. The lattice parameter (a_0) and d_{100} spacing calculated as per the literature procedure are shown in Table 1. These patterns resemble with the data already reported in the literature for Al-MCM-41 molecular sieves [22,23].

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

Catalysts	BET surface area (m^2/g)	Pore diameter (Å)	Pore volume (cm^3/g)
Al-MCM-41 (107)	1051	34.82	0.997
Al-MCM-41 (78)	1015	26.23	0.938
Al-MCM-41 (54)	996	25.94	0.956
Al-MCM-41 (30)	902	24.89	0.757

3.1.2. Nitrogen adsorption isotherm

BET surface area, pore volume and pore diameter (BJH method) for the calcined materials are presented in Table 2. The isotherms of nitrogen adsorption for calcined materials are measured at liquid nitrogen temperature (-196°C). The isotherms show well-defined stages and they resemble with those reported in the literature [24]. The existence of good mesoporous structural ordering and narrow pore size distribution is clearly evident from these isotherms (Fig. 2a and b). The surface area decreases in the following order: Al-MCM-41 (107) > Al-MCM-41 (78) > Al-MCM-41 (54) > Al-MCM-41 (30). Similarly the pore volume also decreases in the same order due to the presence of textural mesoporosity. The decrease is attributed to framework leaching of Al^{3+} to form nano islands of Al_2O_3 in the mesopores.

3.1.3. Acidity measurement by pyridine adsorbed FT-IR spectroscopy

The FT-IR spectra of pyridine adsorbed Al-MCM-41 catalysts are shown in Fig. 3. The peaks at 1450 and 1550 cm^{-1} are due to pyridine adsorbed on Lewis and Brønsted acid sites, respectively. The peak due to pyridine adsorbed Brønsted acid sites is less intense than pyridine adsorbed Lewis acid sites. The

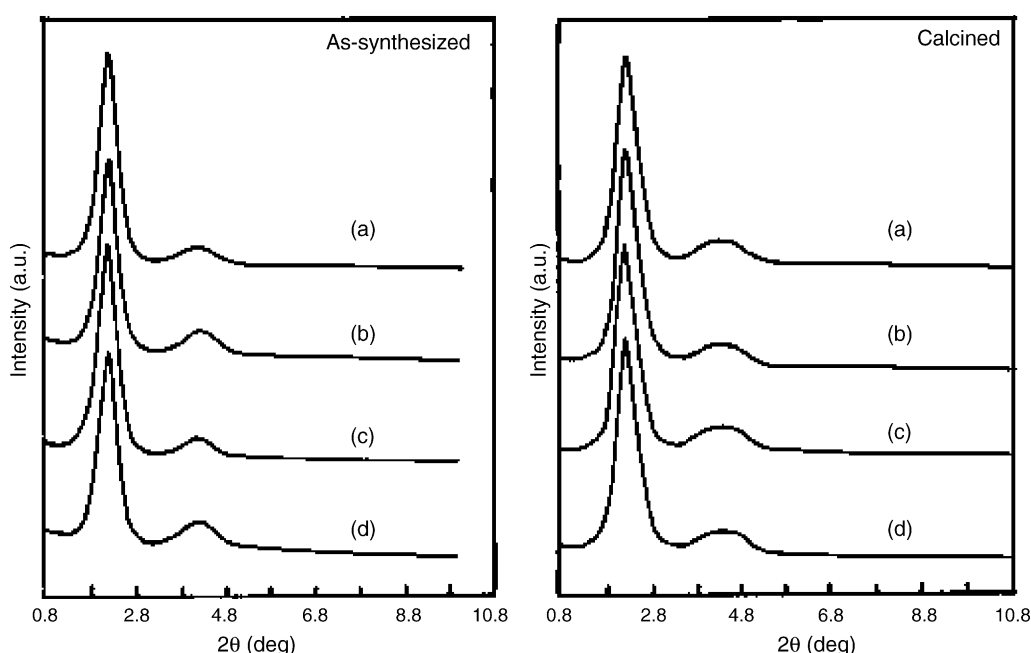


Fig. 1. XRD pattern of as-synthesized and calcined Al-MCM-41 molecular sieves: (a) Si/Al = 30; (b) Si/Al = 54; (c) Si/Al = 78 and (d) Si/Al = 107.

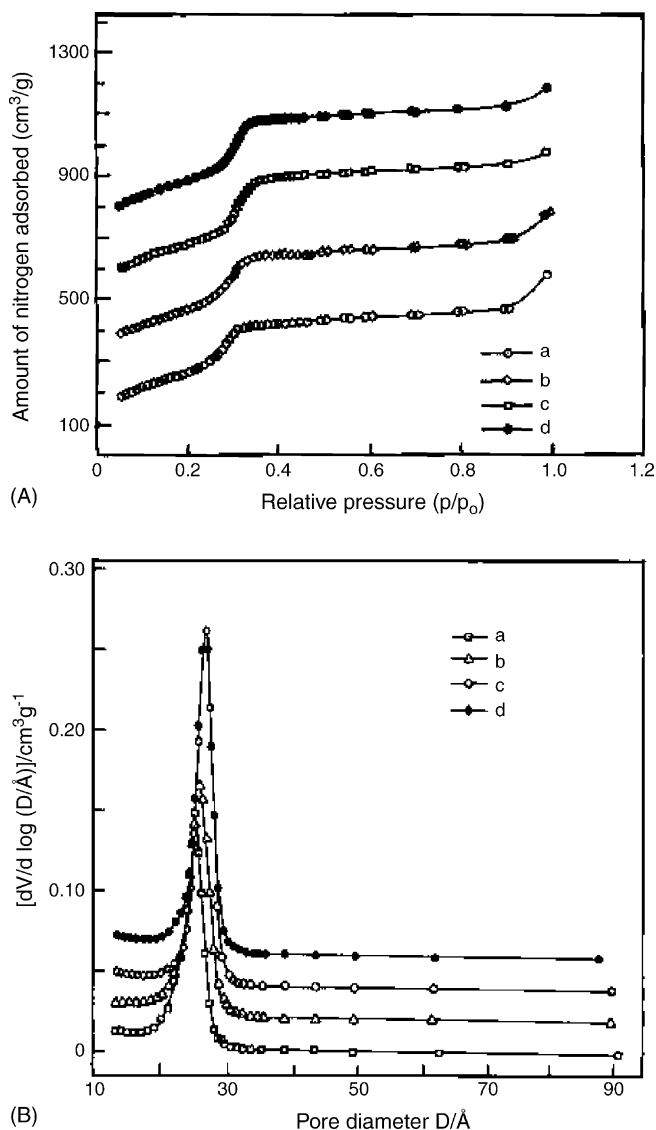


Fig. 2. (A) Adsorption isotherms of Al-MCM-41 molecular sieves: (a) Si/Al = 30; (b) Si/Al = 54; (c) Si/Al = 78 and (d) Si/Al = 107. (B) Pore size distribution (adsorption isotherms) in Al-MCM-41 molecular sieves: (a) Si/Al = 30; (b) Si/Al = 54; (c) Si/Al = 78 and (d) Si/Al = 107.

intensity of former decreases with increase in the Si/Al ratio, and such similar observations were reported by Climent et al. [25].

3.1.4. ^{27}Al and ^{29}Si MAS NMR

The incorporation of aluminum into the framework of Al-MCM-41 (30, 54, 78 and 107) molecular sieves was analyzed by ^{27}Al MAS NMR spectroscopy. The spectra of calcined materials are shown in Fig. 4. The spectrum of calcined sample shows a sharp resonance peak at about 54 ppm for tetrahedrally coordinated aluminum, indicating the incorporation of aluminum into the framework. The broad low intensity peak at 0 ppm indicates the presence of octahedral aluminum in the framework. The appearance of octahedral aluminum in calcined samples indicates that during the course of calcination some aluminum species are removed from the framework [26]. The ^{29}Si -MAS

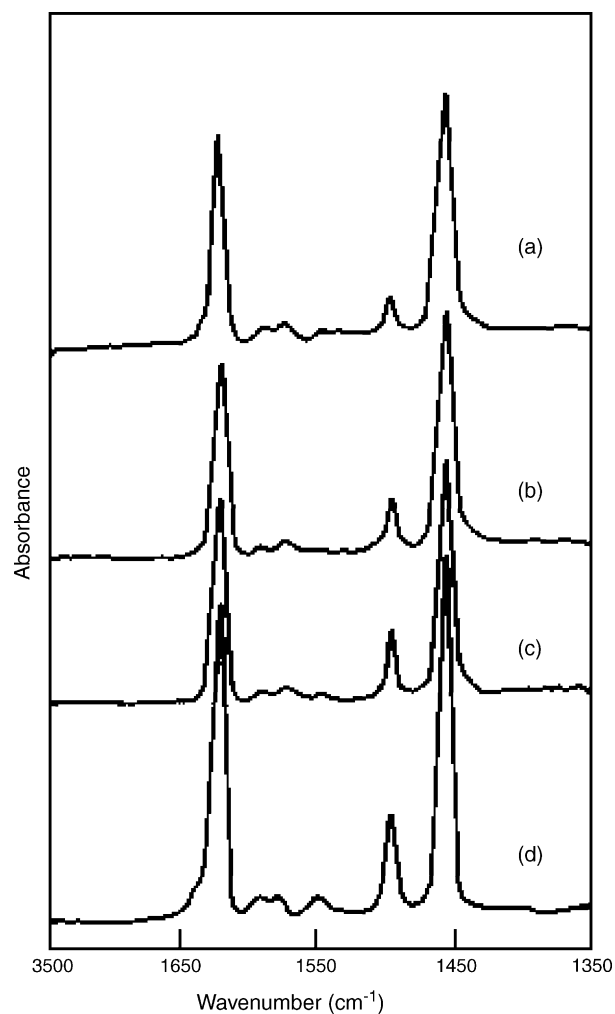


Fig. 3. Brønsted and Lewis acidity of Al-MCM-41: (a) Si/Al = 30; (b) Si/Al = 54; (c) Si/Al = 78 and (d) Si/Al = 107.

NMR spectra of calcined Al-MCM-41 materials are shown in Fig. 5. The broad signal at -111 ppm in the spectra can be assigned to $\text{Si}(\text{OSi})_4$. The shoulder in the range between -103 and -108 ppm is due to $\text{Si}(\text{OAl})$. These spectral features coincide well with those reported by previous workers [27,28,29].

3.1.5. ICP-AES analysis

The aluminum content in Al-MCM-41 for various Si/Al ratios (30, 54, 78 and 107) was recorded using ICP-AES. The results of Si/Al ratios of the materials are given in Table 1. Under the synthesis conditions used, the crystallization reaction was non-stoichiometric and a higher Si/Al ratio was noticed.

3.2. *tert*-Butylation of *tert*-butylbenzene over Al-MCM-41 molecular sieves

tert-Butylation of TBB with TBA was carried over mesoporous Al-MCM-41 (30, 54, 78 and 107) molecular sieves in the vapour phase. The influence of reaction temperature, feed ratio, WHSV and time-on-stream was studied and the results are discussed below.

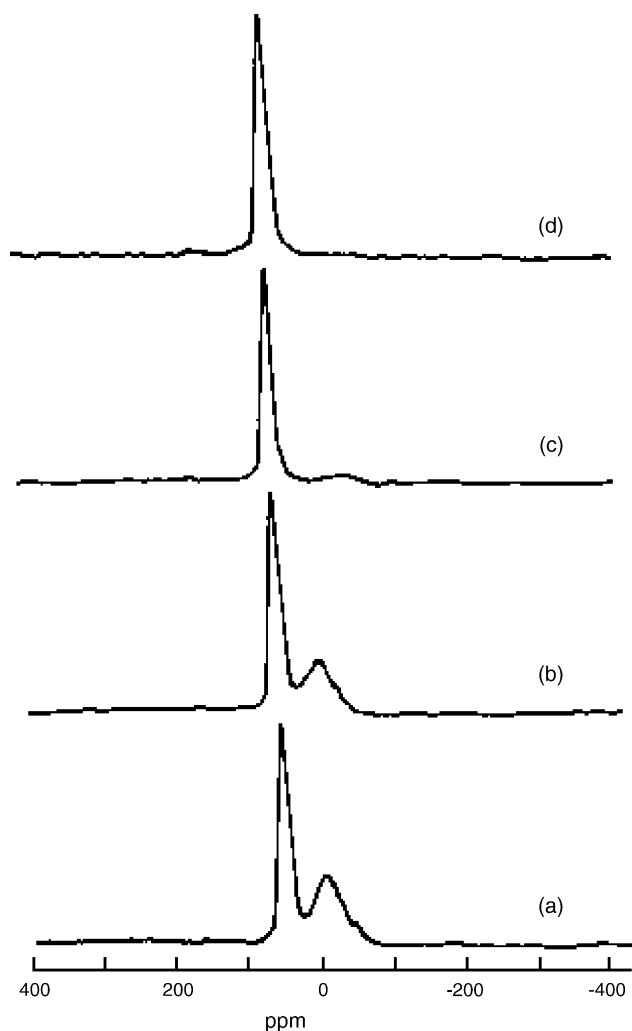


Fig. 4. ^{27}Al MAS-NMR spectra of Al-MCM-41: (a) Si/Al=30; (b) Si/Al=54; (c) Si/Al=78 and (d) Si/Al=107.

3.2.1. Effect of temperature

The vapour phase alkylation of TBB with TBA was carried out at 200, 250, 300, 350 and 400 °C over Al-MCM-41 (Si/Al = 30, 54, 78 and 107). The feed ratio was 1:3 (TBB:TBA) and WHSV 1.70 h⁻¹. The TBB conversion and products selectivity are presented in Table 3. Both ring alkylated and acylated products were obtained in this reaction. The conversion of TBB decreases with increase in temperature and this appears to be common for all the catalysts as shown in Fig. 6a. The decrease in conversion with increase in temperature over all the catalysts is due to coke formation [30]. The spent catalysts also appeared black after the reaction. The activity of the catalysts follows the order: Al-MCM-41 (30) > Al-MCM-41 (54) > Al-MCM-41 (78) > Al-MCM-41 (107), which is also the order of acidity of the catalysts. The difference in conversion for any two catalysts does not follow the difference in the level of their acidity. Hence, in addition to acid density, the strength of acid sites also plays an important role in the activity of the catalysts [31]. The hydrophobic property of catalysts is also an important factor, which increases with increase in Si/Al ratio. This also influences the activity of the catalyst, as high hydrophobicity is

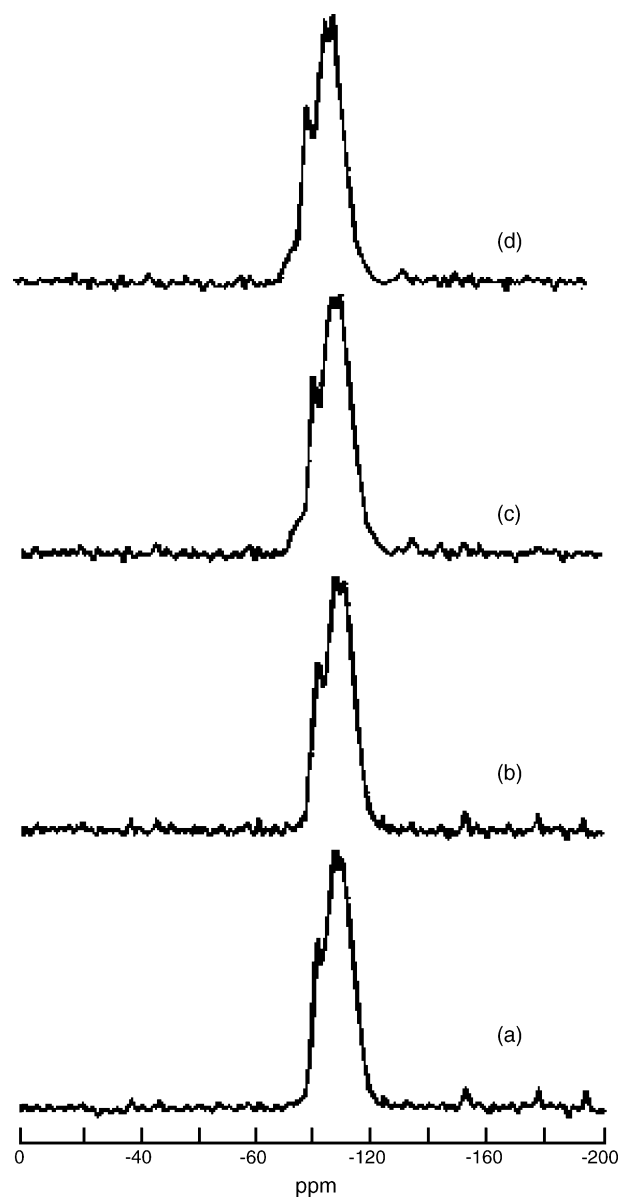


Fig. 5. ^{29}Si MAS-NMR spectra of Al-MCM-41: (a) Si/Al=30; (b) Si/Al=54; (c) Si/Al=78 and (d) Si/Al=107.

important for adsorption of hydrophobic TBA on the catalysts surface. It is also evident in this study that Al-MCM-41 (107), which is four times less acidic than Al-MCM-41 (30), exhibits conversion just 3.4% less than Al-MCM-41 (107) at 200 °C. The products obtained were 1,3-DTBB, 1,4-DTBB, 2A-1,4-DTBB, 4A-TBB, 2A-TBB and 3A-TBB. In addition, there were also other products in very small quantities and their selectivity is indicated in the last column of the table. The following reaction (Scheme 1) is suggested to account for the formation of alkylated products.

TBA is chemisorbed on the Brønsted acid sites of the catalyst through its carbonyl group and yields *tert*-butyl cation [32]. The electrophilic reaction of *tert*-butyl cation with *tert*-butylbenzene gives 1,4-DTBB as the major product. 1,2-DTBB is not observed due to steric crowding. The formation of 1,3-DTBB is ascribed to be the isomerisation of 1,4-DTBB on the

Table 3
tert-Butylbenzene conversion and products selectivity over Al-MCM-41 (30, 54, 78 and 107) molecular sieves

Catalysts	Temperature (°C)	TBB conversion (%)	Selectivity of products (%)						
			1,3-DTBB	1,4-DTBB	2A-1,4-DTBB	4A-TBB	2A-TBB	3A-TBB	Others
Al-MCM-41 (30)	200	42.5	11.9	31.5	12.4	19.2	10.9	9.6	4.5
	250	37.7	13.4	28.9	15.0	23.4	7.1	6.1	6.1
	300	33.2	16.2	25.4	16.9	27.2	5.3	4.2	4.8
	350	23.8	21.1	24.0	20.1	29.7	2.1	1.0	2
	400	19.6	23.0	21.0	23.2	31.5	–	–	1.3
Al-MCM-41 (54)	200	33.4	14.2	30.8	12.1	16.2	9.7	8.2	8.8
	250	30.1	17.6	26.3	13.5	21.8	6.5	5.4	8.9
	300	26.4	20.0	21.9	17.3	25.6	4.3	3.3	7.6
	350	20.7	23.0	19.0	19.9	27.6	2	–	8.5
	400	17.8	25.1	15.6	22.0	29.0	–	–	8.3
Al-MCM-41 (78)	200	30.6	18.9	29.0	11.7	14.9	9.0	7.5	9.0
	250	27.4	21.9	26.7	13.4	19.3	7.1	4.6	7.0
	300	24.5	23.0	24.1	14.9	23.2	4.3	2	8.5
	350	18.2	25.7	22.9	16.0	25.4	2	–	8
	400	15.8	28.6	13.0	20.8	27.6	–	–	10
Al-MCM-41 (107)	200	28.0	21.6	28.5	11.8	13.5	8.3	7.4	8.9
	250	25.8	22.7	26.5	13.8	18.7	4.5	4.8	9.0
	300	22.2	24.7	23.6	16.7	21.2	2.9	1.7	9.2
	350	16.1	27.6	19.6	19.8	23.5	–	–	9.5
	400	13.3	30.0	11.3	23.2	25.4	–	–	10.1

Reaction conditions: feed ratio = 1:3 (TBB:IPA); WHSV = 2.41 h⁻¹; time on stream = 1 h.

Brønsted acid sites of the catalysts. 1,4-DTBB undergoes acylation at the *ortho* position to form 2A-1,4-DTBB. Acylation can occur at 2, 3 and 4th positions to give 2A-, 3A- and 4A-TBB. The formation of acylated products is proceeding through partially protonated *tert*-butyl acetate on the defective Si–OH groups as shown below (Scheme 2).

Adsorption of ester group on the Si–OH groups has been suggested in the literature in the alkylation and acylation of aromatics with esters as the corresponding reagents [17–19]. The selectivity of 1,4-DTBB decreases with increase in temperature over all the catalysts. This is due to either isomerization to 1,3-DTBB or acylation to 2A-1,4-DTBB. The selectivity to 1,3-DTBB increases with increase in temperature over all the catalysts, as it is thermodynamically more stable than 1,4-DTBB. Although *tert*-butyl group offers steric hindrance for chemisorption of 1,4-DTBB on the Brønsted acid sites for isomerization, the acidity of the catalysts is sufficient enough for the fly of Brønsted acid sites from the catalyst surface to the carbon–carbon sigma bond of 1,4-DTBB to effect isomerisation. This process is kinetically more favourable with increase in temperature. The increase in the selectivity of 1,3-DTBB with increase in Si/Al ratio of the catalyst and temperature also supports the ease of proton transfer from the catalyst to 1,4-DTBB to effect isomerization as mentioned above. In other words increase in the acid strength of Brønsted acid sites increases the isomerization activity. Hence, the order of isomerization activity of the catalysts follows: Al-MCM-41 (107) > Al-MCM-41 (78) > Al-MCM-41 (54) > Al-MCM-41 (30) at all temperatures. Al-MCM-41 with low Si/Al ratio may be preferred in order to reduce isomerisation. The selectivity to 2A-1,4-DTBB increases

with increase in temperature. Hence acylation may be favoured at high temperatures and it may be possibly due to steric hindrance. The formation of 1,4-DTBB is favoured at high temperature as more quantity of 1,4-DTBB appears to be converted to 1,3-DTBB and 2A-1,4-DTBB. Acylation is more favoured at the fourth position than at the second or third position of TBB. Since acylation at the second position creates steric hindrance and the third position does not possess enough activation, the selectivity of these two products becomes much less. As the selectivity to 4A-TBB increases with increase in temperature, the reaction is high activation energy demanding process (Fig. 6b). 1,4-DTBB is not thermodynamically stable and hence it undergoes isomerization at higher temperatures, whereas 4A-TBB is thermodynamically stable at higher temperatures. 3A-TBB is not the isomerization product of 4A-TBB as its selectivity decreases with increase in temperature. Similarly 2A-1,4-DTBB is not the precursor of 2A-TBB or 3A-TBB, as the selectivity of the latter products decreases with increase in temperature. The selectivity of all products follows similar trend over all the catalysts with increase in temperature. Based on the selectivity of acylated products it can be visualized that Al-MCM-41 (30) has more number of defective Si–OH groups than other catalysts. In addition to alkylation and acylation, cracking of TBB to benzene is also observed. The selectivity of benzene is included in the last column of Table 3. Although cracking activity of the catalysts depends on the acidity, the strength of acid sites is observed to play a major role. This is confirmed by the higher cracking activity of Al-MCM-41 (54), Al-MCM-41 (78) and Al-MCM-41 (107) than Al-MCM41 (30). This concludes that Al-MCM-41 (30) is more active than other catalysts.

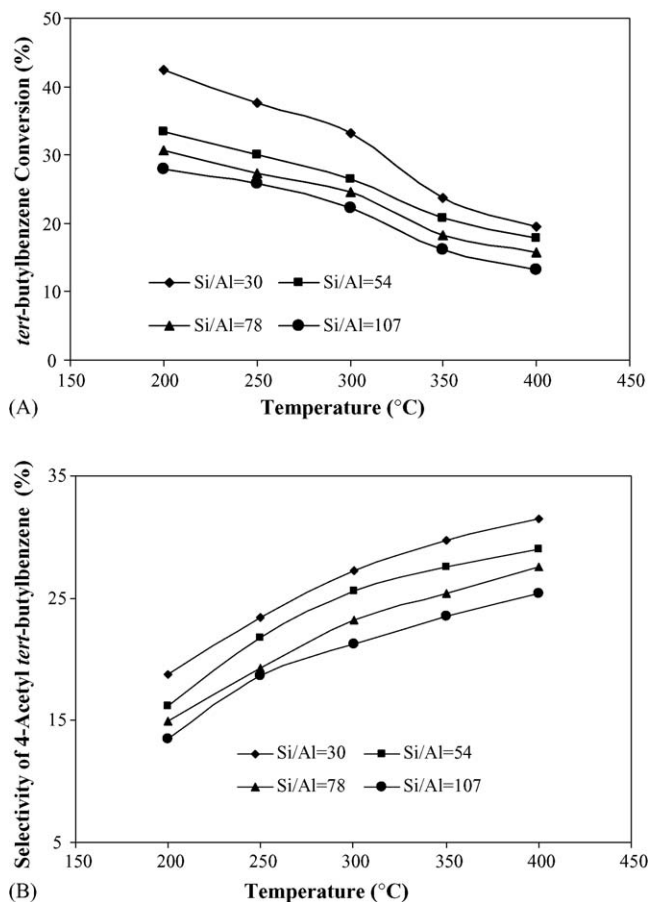


Fig. 6. (A) *tert*-Butylbenzene conversion over mesoporous Al-MCM-41 (Si/Al=30, 54, 78 and 107); feed ratio: 1:3; WHSV: 2.41 h⁻¹. (B) Selectivity of 4-acetyl-*tert*-butylbenzene over Al-MCM-41 (Si/Al=30, 54, 78 and 107); feed ratio = 1:3; WHSV = 2.41 h⁻¹.

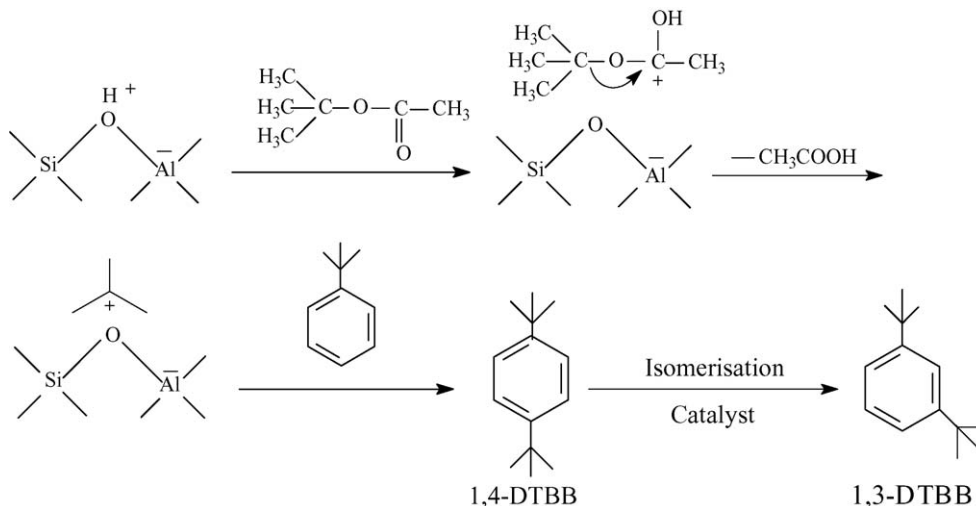
3.2.2. Effect of feed ratio

The effect of feed ratio on TBB conversion and products selectivity over Al-MCM-41 (30) at 200 °C was studied with the feed ratios 1:1, 1:2, 1:3 and 2:1 and WHSV 2.41 h⁻¹ and the results are presented in Table 4. As the reaction primar-

ily requires *tert*-butyl cations, the increase in TBA content in the feed increases the conversion of TBB. The selectivity to 1,4-DTBB decreases with increase in the TBA content but the decrease is not significant. Hence, the increase in the TBA content can significantly decrease the isomerization of 1,4-DTBB to 1,3-DTBB and acylation of 1,4-DTBB to 2A-1,4-DTBB. This is true as most of the acid sites are under the chemisorption TBA. The selectivity to 2A-TBB, 3A-TBB and 4A-TBB increases with increase in the TBA content as significant amount of TBA can be made available for adsorption on the defective Si–OH groups. In order to verify this, the reaction was also studied with the feed ratio 2:1 and the conversion of TBB is found to be higher than with feed ratio 1:1. The selectivity to 1,4-DTBB and 1,3-DTBB at 2:1 is slightly less than 1:1. But the cracking of TBB, which is indicated in the last column of the table, is high with high TBB content in the feed. The formation of benzene through cracking establishes unequivocally chemisorption of TBB on the Brønsted acid sites of the catalysts. This study establishes that a feed ratio of 1:3 is the optimum for high conversion of TBB and selectivity to 1,4-DTBB and 4A-TBB.

3.2.3. Effect of WHSV

Since isomerization and acylation of 1,4-DTBB are time dependent, the effect of WHSV on conversion and products selectivity was attempted to reduce such side reactions. The effect of WHSV was investigated over Al-MCM-41 (30) with a feed ratio 1:3 at 200 °C and the results are presented in Table 5. The conversion of TBB decreases with increase in WHSV but the decrease is high only at 3.012 h⁻¹. TBB may diffuse fast through the pores at higher WHSV without much reaction with *tert*-butyl cations on the catalyst surface. As expected, the selectivity to 1,4-DTBB at 3.012 h⁻¹ is higher than at low WHSV. Similarly the selectivity to 1,3-DTBB and 2A-1,4-DTBB is also lesser at 3.012 h⁻¹ than at low WHSV. This observation clearly establishes that 1,4-DTBB is the precursor for 1,3-DTBB and 2A-1,4-DTBB. The selectivity to acylated TBB isomers increases when the WHSV is increased from 1.808 to 2.41 h⁻¹. This increment is due to slight enhancement in the availabil-



Scheme 1. Alkylation reaction of *tert*-butylbenzene with *tert*-butyl acetate.

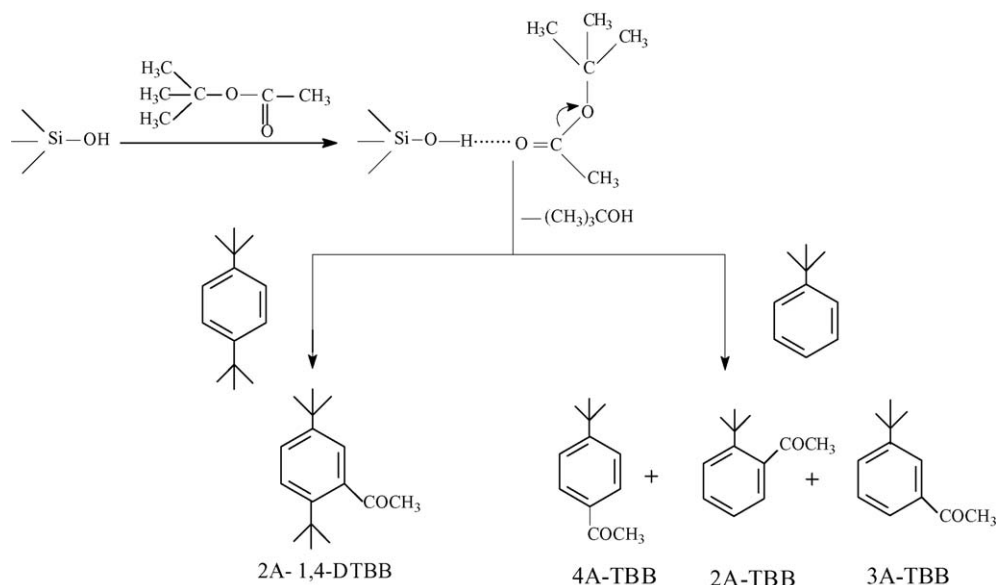


Table 4

Effect of feed ratio on *tert*-butylbenzene conversion and product selectivity over Al-MCM-41 (30)

WHSV (h^{-1})	Feed ratio (TBB:TBA)	TBB conversion (%)	Selectivity of products (%)						
			1,3-DTBB	1,4-DTBB	3A-1, 4-DTBB	4A-TBB	2A-TBB	3A-TBB	Others
2.41	2:1	15.5	20.1	23.2	17.3	21.0	3.1	–	15.3
2.41	1:1	11.2	24.4	33.5	14.1	18.4	4	–	5.6
2.41	1:2	30.8	21.1	32.7	14.0	18.0	3	5.2	6.0
2.41	1:3	42.5	11.9	31.5	12.4	19.2	10.9	9.6	4.5

Reaction conditions: temperature = 200 °C; catalyst = 0.5g; WHSV = 2.41 h^{-1} .

ity of TBB for electrophilic reaction with partially protonated TBA on the defective Si–OH groups. When the WHSV is further increased to 3.012 h^{-1} , the selectivity to 4A-TBB remains constant whereas 2A-TBB and 3A-TBB is drastically reduced. Hence, at high WHSV the electrophilic reaction between partially protonated ester and the *para* position of TBB is not much reduced, i.e., WHSV 3.012 h^{-1} is not sufficient enough to retard this reaction. The selectivity to benzene is rather high. This illustrates that chemisorption of TBB is not prevented even at high WHSV. This study revealed that the optimum WHSV is either 2.41 or 1.808 h^{-1} .

3.2.4. Effect of time-on-stream

The effect of time-on-stream on the conversion of TBB and products selectivity was studied over Al-MCM-41 (30) with

feed ratio 1:3 and WHSV 2.41 h^{-1} . The results are shown in Table 6. The conversion decreases with increase in time-on-stream as shown in Fig. 7, which is due to coke formation [33]. The selectivity of 1,3-DTBB decreases as the isomerization activity decreases. The selectivity of 1,4-DTBB increases as isomerization and acylation reactions decrease. The selectivity to 2A-TBB and 3A-TBB also decreases. This illustrates blocking of even defective Si–OH groups by coke. Generally coke may be formed mainly over strong acid sites but the observation concludes that oligomerization could occur even over defective Si–OH groups. Contrary to the above, the selectivity to 4A-TBB increases with increase in time-on-stream. Hence, there might be still enough number of defective Si–OH groups to activate TBB for acylation at the fourth position. Based on the observation, it can be visualized that acylation at *ortho* and *meta*

Table 5

Influence of WHSV on *tert*-butylbenzene conversion and products selectivity

WHSV (h^{-1})	TBB conversion (%)	Selectivity of products (%)						
		1,3-DTBB	1,4-DTBB	2A-1, 4-DTBB	4A-TBB	2A-TBB	3A-TBB	Others
1.808	43.5	17.1	35.4	12.2	15.6	5.4	4.2	10.1
2.410	42.5	11.9	31.5	12.4	19.2	10.9	9.6	4.5
3.012	13.1	15.1	38.6	10.1	18.9	3.1	2.0	12.2

Reaction conditions: feed ratio = 1:3 (TBB:TBA); temperature = 200 °C; catalyst = Al-MCM-41(30).

Table 6
Effect of time-on-stream on *tert*-butylbenzene conversion and product selectivity over Al-MCM-41 (30)

Time (h)	TBB conversion (%)	Selectivity of products (%)						
		1,3-DTBB	1,4-DTBB	2A-1, 4-DTBB	4A-TBB	2A-TBB	3A-TBB	Others
1	42.5	11.9	31.5	12.4	19.2	10.9	9.6	4.5
2	39.1	11.5	32.0	12.0	20.4	8.0	7.6	8.5
3	35.4	10.5	33.4	11.1	22.6	5.7	4.3	12.4
4	29.1	10.1	36.1	9.4	24.0	2.0	–	18.4
5	24.1	9.3	38.1	8.0	26.1	–	–	18.5

Reaction conditions: WHSV = 2.41 h⁻¹; temperature = 200 °C; feed ratio = 1:3 (TBB:TBA).

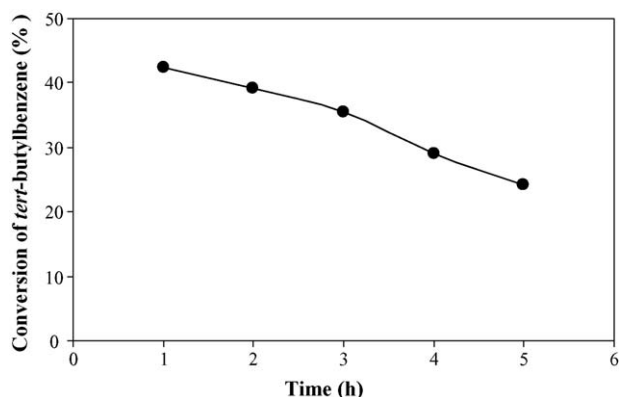


Fig. 7. Effect of time-on-stream over Al-MCM-41 (30). Feed ratio = 1:3; temperature = 200 °C; WHSV = 2.41 h⁻¹.

positions may require dense Si–OH groups whereas formation of 4A-TBB may require scattered distribution of active sites. The selectivity of others, including the cracked product benzene increase with increase in time-on-stream. This observation suggests that blocking of active sites by coke favours their selectivity. Since the selectivity of others increases with increase in time-on-stream, the catalysts still have active sites to crack TBB. Hence, it may be concluded that partially deactivated catalysts by coke may be suitable to give high selectivity of 1,4-DTBB and 4A-TBB. As blocking of strong active sites by coke gradually increases with increase in time-on-stream, the selectivity to 1,3-DTBB decreases. The selectivity to 2A-1,4-DTBB decreases with increase in time-on-stream similar to 2A-TBB and 3A-TBB due to gradual decrease in the density of defective Si–OH groups.

4. Conclusion

The investigation concludes that TBA can be used as alkylating and acylating agents. It can be used as a good alkylating agent by controlling the defective Si–OH groups. Al-MCM-41 (30) can be used as a convenient catalyst with optimum acidity for this reaction. 1,4-DTBB is more favoured than all other products at lower temperatures. It undergoes isomerization and electrophilic acylation at higher temperatures. The occurrence of these two reactions can be reduced by increase of TBA content in the feed. The increase of WHSV retards isomerization and acylation of 1,4-DTBB. The deactivation of the catalyst is observed when the reaction was carried out for 5 h. Partial block-

ing of active sites of Al-MCM-41 may be useful to enhance the selectivity of 1,4-DTBB and 4A-TBB.

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