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Vapor phase reaction of tert-butylbenzene with isopropyl acetate over mesoporous Al-MCM-41 molecular sieves

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Abstract

The vapor phase reaction of tert-butylbenzene (TBB) with isopropyl acetate (IPA) has been studied over mesoporous Al-MCM-41 (Si/Al = 30, 51, 72, and 97) from 200 to 350 °C. Catalysts were synthesized hydrothermally and characterized by XRD, FT-IR, BET (surface area), and ^{29}Si, ^{27}Al MAS-NMR techniques. Conversion of TBB decreases with the increase in temperature. The activity of these catalysts followed the order Al-MCM-41 (30) > Al-MCM-41 (51) > Al-MCM-41 (72) > Al-MCM-41 (97). The catalysts with less Si/Al ratios (Si/Al = 30 and 51) showed higher activity than the other catalysts. The reaction was observed to yield alkylated and acylated products namely 3-acetyl-4-isopropyl-tert-butylbenzene (3A-4ITBB), 4-acetyl-tert-butylbenzene (4-ATBB), 4-isopropyl-tert-butylbenzene (4-ITBB), Isopropylbenzene (IPB), and 2-acetyl-isopropyl benzene (2A-IPB). Both the alkylation and acylation reaction can be accounted by the nature of acid sites in the catalyst. The selectivity to 3A-4ITBB, 4-ATBB, and IPB 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 IPA on the catalyst surface. The time-on-stream studies with Al-MCM-41 (30) showed gradual decrease in conversion with the increase in stream was observed after 5 h.
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1. Introduction

Friedel–Crafts alkylation and acylation of aromatic hydrocarbons have high commercial significance. Ethylbenzene, isopropylbenzene, isopropyltoluene, and C_{10}–C_{14} linear alkylbenzenes are a few of the industrially important chemical intermediates obtained by acid catalyzed alkylation of the appropriate aromatics [1]. Likewise, 2-acetyl-6-methoxynaphthalene, 4-acetyl-phenol, 4-isobutyl-acetophenone etc., are a few of the acylated products. Acylation reactions at industrial scale are largely employed in fine chemical industry, synthetic fragrances, and pharmaceuticals [2–6].

Venuto et al. [8] observed β and Y zeolites to be better catalysts for benzene alkylation with olefins than amorphous silica–alumina gels [7]. The advantages and the uses of these solid acid catalysts, which make them applicable for alkylation, have been reported extensively [9–12]. Incorporation of aluminum [13] and other metals [14,15] into mesoporous structures have been investigated consequentially in order to introduce solid-state acidity and increase catalytic function.

Corma et al. [13] reported low catalytic activity at low Si/Al ratios of Al-MCM-41. Busio et al. attributed this lower activity to the collapse in structure of the mesoporous material due to the presence of octahedrally coordinated, non-framework aluminum [16]. The typical characteristic of Al-MCM-41 with a Si/Al ratio above 10 are the highly ordered mesoporosity, large surface area, high thermal stability, and acidity. Al-MCM-41 material also generally have large pore diameter with widely scattered distribution of mild Brönsted acid sites. They are expected to be more suitable for alkylation. In general, non-framework Lewis acid sites are preferred for acylation reactions.

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In the case of alkylating and acylating reagents, the more active acylating acylchlorides are hazardous as they produce HCl vapors; the usage of acetic acid is also not advantageous for acylation, as it would leach the framework aluminum. Similarly, acetic anhydride besides being less reactive produces acetic acid. Alcohols which are generally used as alkylating agent, generates carbonium ions at a very slow rate; hence, higher mole ratio of the alkylating agent is necessary. Aliphatic esters provide a better conversion rate as alkylating and acylating reagent due to faster rate of formation of carbocation on the catalyst surface. They are also least hazardous.

In the present study, an aliphatic ester viz., isopropyl acetate was employed over different Si/Al ratios of Al-MCM-41 as catalysts for the Friedel–Crafts reaction of tert-butylbenzene.

2. Experimental

2.1. Materials and methods

Hydrothermal crystallization procedure reported by Beck et al. [17] was adopted for the preparation of Al-MCM-41 molecular sieves with Si/Al ratios (30, 51, 72, and 97). In a typical synthesis 10.6 g of sodiummetasilicate nanohydrate (Merck) in demineralized water was combined with an appropriate amount of aluminum sulphate (Merck). It was then acidified with 1 M H_2SO_4 to bring down the pH to 10.5 under vigorous stirring. After 30 min of stirring, an aqueous solution of cetyltrimethylammonium bromide (CTAB) (Merck) was added and the surfactant silicate mixture was stirred for further 30 min at room temperature. The molar composition of the resultant mixture was SiO_2: 0.2 CTAB: X Al_2O_3: 0.89 H_2SO_4: 120, H_2O (X varies with the Si/Al ratio). The resultant gel was autoclaved and heated for 48 h at 145 °C. The solid thus 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. Characterization

The XRD powder diffraction patterns of the calcined mesoporous Al-MCM-41 (Si/Al ratio 30, 51, 72, and 97) 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 the steps of 0.02° with a count time of 15 s at each point for MCM-41 molecular sieves.

Surface area, pore volume, and pore size distribution were measured by nitrogen adsorption at 77 K with ASAP-2010 porosimeter from Micromeritics Corporation Noreross, GA, USA. The samples were degassed at 623 K and 10^{-5} Torr overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen ad-

sorbed 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 about 200 mg of spectral grade KBr to form a pellet under hydraulic pressure to record IR spectrum in the range of 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 sulfonic 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 aluminum nitrate.

2.3. Analysis of the product

The isopropylation and acetylation of TBB with IPA was 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 Hewlett-Packard gas chromatograph 5890Å equipped with a flame ionization detector (FID) using an OV17 column and nitrogen as the carrier gas. The identification of products was performed on Shimadzu GC-MS-QP1000EX with a PE-5 capillary column with scan mode 40–400 amu. After completion of each run, the reactor system was flushed with nitrogen to remove the physisorbed impurities. The catalyst was regenerated at 500 °C in a current of moisture-free air for 6 h.

2.4. Mass balance studies for coke formation

The formation of coke in the catalyst due to the effect of temperature and time-on-stream was studied by mass balance technique. The studies were carried out using 0.5 g of Al-MCM-41 (30) at feed ratio TBB:IPA of 1:3 at 200 °C. To study the effect of temperature, the reactant was left on-stream for 1 h, whereas, the reactant was on-stream for 5 h to determine the effect of time-on-stream. In both cases, the catalyst and the reactant were weighed before and after the experiment. The difference between the weight of the reactant and the mixture obtained at the product end gave the net weight loss.

The weighed catalyst was subjected to calcination at 500 °C for a period of 5 h. After attaining room temperature, the catalyst was weighed again. The difference in weight of the catalyst before and after calcination is the weight of the coke. Difference between the net weight loss and weight of the coke is probably the weight of propene.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The XRD powder diffraction patterns of the as-synthesized and calcined mesoporous catalysts show that calcined samples exhibit an intense diffraction peak at about 2θ due to [1 0 0] plane confirming the hexagonal mesophase of the material [18–20]. The d_{100} spacing and lattice parameter (a_0) calculated as per the literature procedure are presented in Table 1. The calcined materials possess well-defined pore structure due to the condensation of Si–OH groups. These XRD patterns coincided well with the data already reported in the literature for mesoporous aluminosilicate molecular sieves [21].

3.1.2. Nitrogen adsorption isotherms

BET surface areas, pore size, and pore volume for calcined materials are presented in Table 2. Adsorption isotherms and pore size distribution for the calcined materials (BJH method) observed are in good agreement with the reported values [22,23].

3.1.3. FT-IR spectroscopy

The FT-IR spectrum of the as-synthesized and calcined Al-MCM-41 (Si/Al = 30, 51, 72, and 97) molecular sieves was carried out. The broad envelope around 3500 cm^{-1} is due to O–H stretching of water, surface hydroxyl groups, and bridged hydroxyl groups. There are less intense peaks in the spectra of the as-synthesized samples just below 3000 cm^{-1} which are assigned to symmetric and asymmetric stretching modes of the –CH$_2$ group of the locked-in template. Their corresponding bending mode is observed at 1400 cm^{-1}. The peaks between 500 and 1200 cm^{-1} are assigned to framework vibrations. The intense peak at 1123 cm^{-1} is due to the asymmetric stretching of T–O–T groups. The symmetric stretching modes of T–O–T groups are observed around 800 cm^{-1} and the peak at 460 cm^{-1} is due to the bending mode of T–O–T. The peak at 963 cm^{-1} is assigned to the presence of defective Si–OH groups. The symmetric and asymmetric stretching modes of –CH$_2$ group of the template are not seen in the spectra of calcined samples. These spectral features resemble those reported by previous workers [18,24].

3.1.4. ^{29}Si, ^{27}Al MAS-NMR

The ^{29}Si MAS-NMR spectra of the calcined Al-MCM-41 materials showed that the broad signal at −111 ppm and the shoulders in the range between −103 and −108 ppm in the spectra coincided well with those reported by the previous workers [24,26,27]. The ^{27}Al MAS-NMR spectra of the samples showed the characteristic peak around 54.3 ppm, confirming the presence of aluminum in tetrahedral coordination [24,25]. ^{27}Al MAS-NMR of the calcined Al-MCM-41 (30, 51, 72) showed a less intense peak at 0 ppm due to the non-framework aluminum species in octahedral coordination [27].

3.1.5. ICP-AES analysis

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

Table 1
Textural properties of the catalysts

Catalysts	Si/Al	ICP	Calcined		Uncalcined	
			d_{100}	Unit cell-a_0 (nm)	d_{100}	Unit cell-a_0 (nm)
Al-MCM-41 (30)	25	30	37.81	4.37	38.47	4.44
Al-MCM-41 (51)	50	51	37.45	4.32	38.47	4.44
Al-MCM-41 (72)	75	72	37.45	4.32	38.19	4.41
Al-MCM-41 (97)	100	97	37.81	4.36	38.19	4.41

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

Catalysts	Surface area (m^2 g^{-1})	Surface area BJH$_{Ads}$ (m^2 g^{-1})	Surface area BJH$_{Des}$ (m^2 g^{-1})	Pore size BJH$_{Ads}$ (nm)	Pore size BJH$_{Des}$ (nm)	Pore volume BJH$_{Ads}$ (cc g^{-1})	Pore volume BJH$_{Des}$ (cc g^{-1})
Al-MCM-41 (97)	1044	1334	1274	2.671	2.630	0.959	0.933
Al-MCM-41 (72)	1037	1345	1295	2.660	2.625	0.956	0.934
Al-MCM-41 (51)	978	1205	1198	3.194	3.663	0.977	0.972
Al-MCM-41 (30)	955	1167	1163	3.482	3.352	0.969	0.962

3.2. Application of Al-MCM-41 (30), Al-MCM-41 (51), Al-MCM-41 (72), and Al-MCM-41 (97) catalysts to Friedel–Crafts reaction of tert-butylbenzene

3.2.1. Selectivity to p-acetyl-tert-butylbenzene (4-ATBB)

Friedel–Crafts reaction of TBB with IPA was carried out in the presence of Al-MCM-41 (Si/Al = 30, 51, 72, and 97). The temperature variation study indicates decrease in conversion with the increase in temperature. The activity of the catalysts follows the order Al-MCM-41 (30) > Al-MCM-41 (51) > Al-MCM-41 (72) > Al-MCM-41 (97), which is also the order of the acidity of the catalysts. The acetyl group in para position for 4-ATBB gives less steric hindrance as compared to other positions; this might be due to the higher selectivity to 4-ATBB. Al-MCM-41 (97) at 350 °C shows higher selectivity as compared to all other catalysts and temperature.

3.2.2. Variety in strength of acid sites

The catalysts should have acid sites of different strength [28,29]. Among the Brönsted acid sites, all 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. Heterogeneity 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 varieties in acid sites could be based on the fact that the nature of tetrahedral units surrounding any single tetrahedral atom (when aluminum is linked to 4 SiO_4 tetrahedra, then Brönsted acid sites become more acidic than the other possible environments) need not be same throughout the framework. Weak acid sites forming weak interaction with ester, coined as partly protonated esters, are responsible for the formation of acetyl cations.

3.2.3. Influence of temperature

The vapor phase reaction of TBB with IPA was studied over Al-MCM-41 (Si/Al = 30, 51, 72, and 97) at 200, 250, 300, and 350 °C at 1 atm. The feed ratio TBB:IPA was kept at 1:3 and WHSV at $1.740\,h^{-1}$. The products were 3A-4ITBB, 4-ATBB, 4-ITBB, IPB, and 2A-IPB. The formation of these products can be explained by the following reaction Scheme 1.

The amount of TBB conversion and products selectivity are presented in Table 3. Conversion of tert-butylbenzene (%) into products is shown in Fig. 1 and the selectivity to 4-ATBB is shown in Fig. 2. Conversion decreases gradually with the increase in temperature, for all the catalysts. The reaction is acid catalyzed, and since Al-MCM-41 (30) has more density of acidic sites, its activity is higher as compared to the other catalysts. Decrease in conversion with the increase in temperature might be attributed to gradual increase in the blocking of active sites by coke. The coke formation was visible even at 200 °C, which was confirmed by the mass balance technique. The observation from the mass balance calculations showed that a reactant quantity of 1.740 g (2 ml) by weight gave 1.423 g (81.75%) of products at the end of 1 h run. The catalyst showed 0.0946 g (5.45%) of coke, accounting to a weight loss of 0.223 g (12.79%), due to the formation of propene.

Al-MCM-41 (30) giving 43.7% conversion has acidity three times higher than that of Al-MCM-41 (97), having conversion of 32.3% at 200 °C. But the expected percentage of conversion for Al-MCM-41 (97) after three times decrease in the acidity, should have been approximately 16%. The drastic increased turnout in the observed percentage conversion indicates the role of hydrophobicity of Al-MCM-41 (97). Al-MCM-41 (97) is more hydrophobic than Al-MCM-41 (30). Hence, Al-MCM-41 (97) can preferentially bring
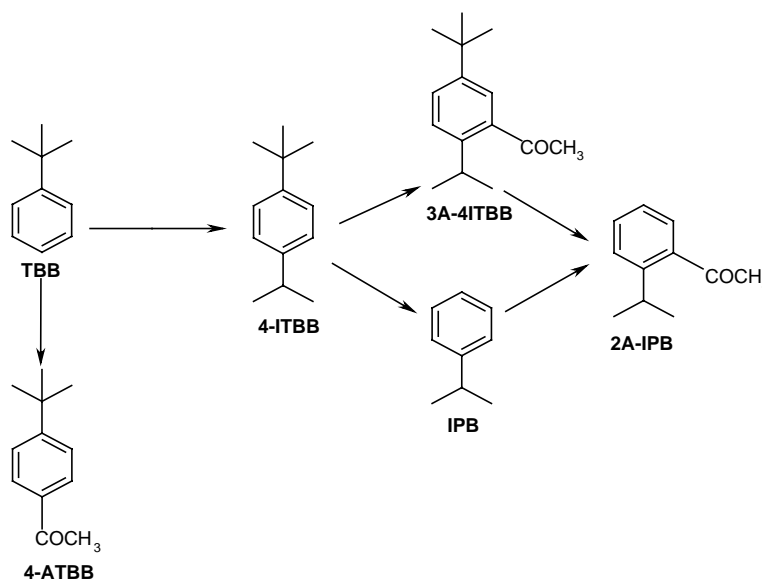
Scheme 1. Acetyl and alkyl derivative of tert-butylbenzene with isopropyl acetate over Al-MCM-41.

Table 3
Catalytic activity of Al-MCM-41 (30 51, 72, and 97) for isopropylation of tert-butylbenzene

Catalyst	Temperature	tert-Butylbenzene conversion (%)	Selectivity to products (%)					
			4-ATBB	4-ITBB	3A-4ITBB	IPB	2A-IPB	Others
Si/Al = 30	200	43.7	25.4	25.7	19.6	16.2	6.1	7.0
	250	40.4	27.7	23.1	20.2	17.9	4.4	6.7
	300	37.6	30.6	19.3	22.4	19.4	2.2	6.1
	350	34.5	31.9	16.9	24.3	20.9	0	6.0
Si/Al = 51	200	41.6	27.8	24.1	20.1	10.7	8.4	8.9
	250	38.9	33.9	22.2	21.4	13.6	3.7	5.2
	300	35.4	32.1	20.3	23.2	16.5	1.1	6.8
	350	31.3	34.4	16.2	25.1	17.9	0	6.4
Si/Al = 72	200	37.5	29.5	20.6	21.2	8.3	9.6	10.8
	250	33.1	31.4	18.5	22.0	10.6	6.8	10.7
	300	30.6	33.1	16.9	24.6	12.3	4.5	8.6
	350	27.2	35.4	13.4	26.0	15.2	2.2	7.8
Si/Al = 97	200	32.3	31.4	18.4	21.5	7.3	9.7	11.7
	250	28.4	33.4	15.4	22.5	9.6	6.5	12.6
	300	25.2	35.1	14.9	25.2	11.5	4.8	8.5
	350	20.9	37.2	11.1	27.8	12.4	2.4	9.1

Feed ratio, 1:3 (TBB:IPA); WHSV, 1.740 h^{-1}.

hydrophobic TBB closer to IPA, facilitating conversion. This high hydrophobic nature of Al-MCM-41 (97) offsets the lack of acid sites in the catalyst. This indicates the role of hydrophobicity of Al-MCM-41 (97). As Al-MCM-41 (97) is more hydrophobic than Al-MCM-41 (30), Al-MCM-41 (97) can preferentially bring hydrophobic TBB and IPA closer. This falls in accordance with the hydrophilic and hydrophobic properties of molecular sieves reaction, as described by Climent et al. [30].

At the feed ratio TBB:IPA of 1:3, IPA is preferentially adsorbed on the catalyst surface leaving TBB in the vapor phase. When TBB diffuses near the layer of isopropyl cation on the catalyst surface, it will get isopropylated selectively on the fourth position to yield 4-ITBB. Further, chemisorption of 4-ITBB over the catalyst active sites yields IPB or 3A-4ITBB. The selectivity to 4-ITBB decreased with the increase in temperature. It might be due to the increase in the selectivity to 3A-4ITBB or increase in the cracking of 4-ITBB on the catalyst active sites yielding IPB. But the selectivity to IPB decreased with the increase in temperature, which evinces the fact that strong acid sites of catalyst are blocked readily, whereas, the weak acid sites remain active
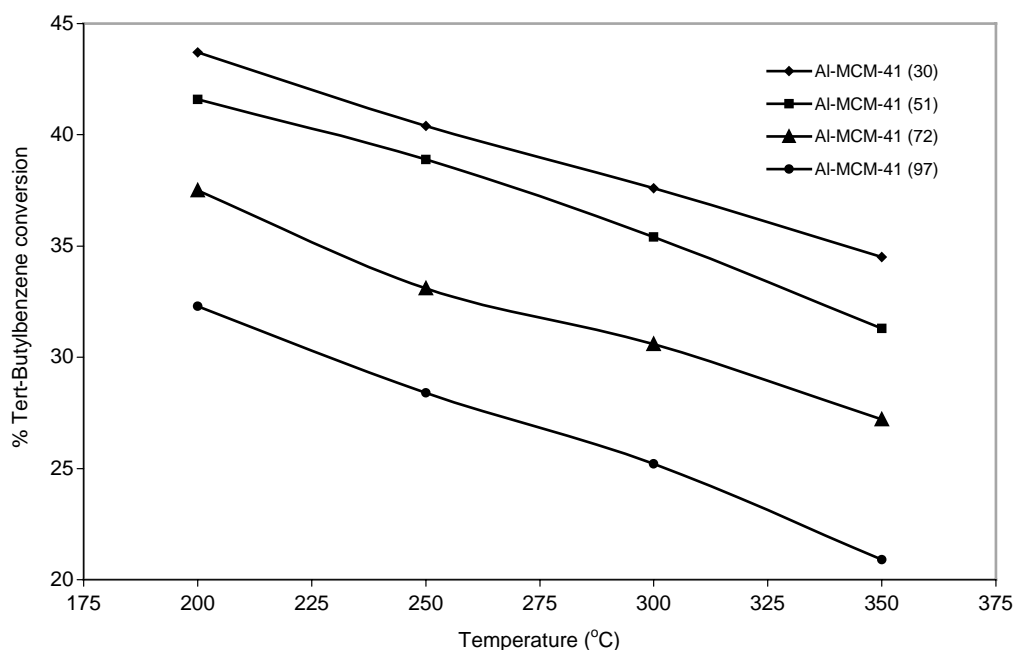

Fig. 1. Comparison of tert-butylbenzene conversion over different catalysts (Si/Al = 30, 51, 72, and 97); feed ratio, 1:3 (TBB:IPA); WHSV, 1.740 h^{-1}.
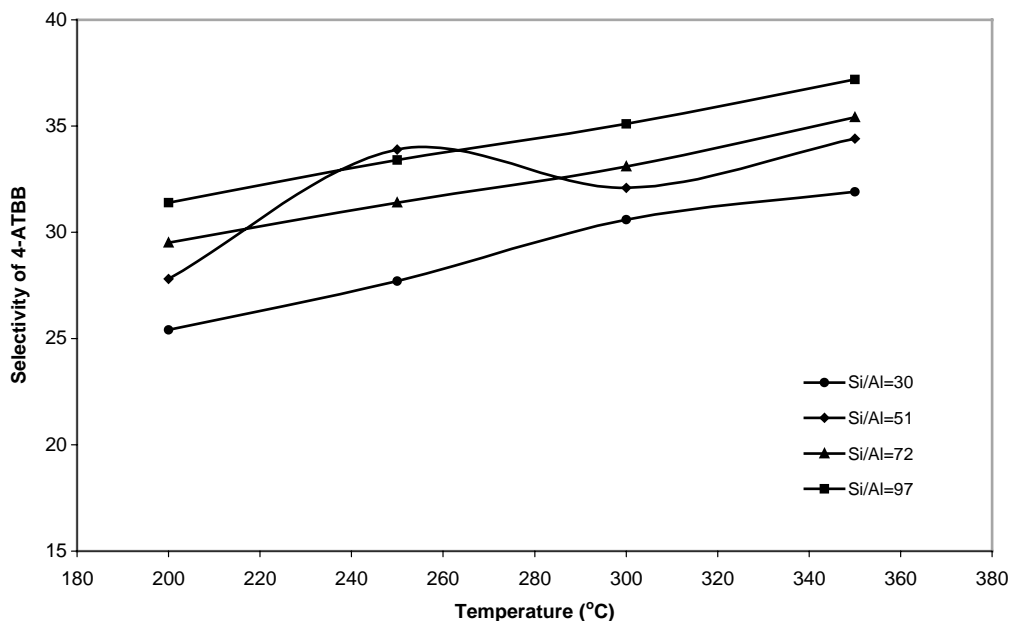
Fig. 2. Selectivity of *p*-acetyl-tert-butylbenzene over different catalysts (Si/Al = 30, 51, 72, and 97); feed ratio, 1:3 (TBB:IPA); WHSV, $1.740 \, h^{-1}$.

for the acylation reaction. It is also reflected in the selectivity to 2A-IPB, which decreased with increase in temperature. During the course of temperature studies, it was found that the selectivity to acetylated product like 4-ATBB and 3A-4ITBB was higher as compared to other products. This indicates that acetylation reaction occurs not only on the defective –OH groups, but also at less acidic bridged hydroxyl groups are involved in the acetylation of the parent TBB and its product members.

The influence of temperature on the selectivity to the products by other catalysts was found to follow similar trends as that of Al-MCM-41 (30). The selectivity to 3A-4ITBB increased with the increase in temperature giving higher yield at each successive higher temperature and at each successive higher ratio when compared to Al-MCM-41 (30). As hydrophobicity increases with silicon content, the other catalysts becomes more hydrophobic than Al-MCM-41 (30). Hence, compared to Al-MCM-41 (30), Al-MCM-41 (97) was found to be more active in transporting more 4-ITBB to 3A-4ITBB.

3.2.4. Influence of feed ratio

The effect of feed ratio TBB:IPA of 1:1, 1:2, and 1:3 on TBB-conversion and product selectivity was studied at

200 °C and the results are presented in Table 4. The conversion increased with increasing IPA in the feed ratio. As the reaction depends both on the formation of isopropyl cation and acetyl cation (or protonated ester), the conversion increases with increasing IPA in the feed ratio. Selectivity to 3A-4ITBB also increased with an increase in the feed ratio. High IPA content in the feed favors both alkylation and acylation. The selectivity to 4-ATBB and 4-ITBB decreased with an increase in the feed ratio (high percentage of IPA), whereas the selectivity to 3A-4ITBB increased. At high feed ratios (high percentage of IPA) multi-alkylation predominantly occurs. In this case, 4-ATBB will not under go further acetylation because the aromatic ring in 4-ATBB gets deactivated by the first acylation leading to the absence of diacetylated product. As a result of which, 4-ITBB will be acetylated to yield 3A-4ITBB. Hence, selectivity to 4-ITBB decreased with an increase in the feed ratio. Similarly, selectivity to 2A-IPB increased with an increase in feed ratio due to the conversion of the same from 4-ITBB increased. It was separately tested for the cracking of TBB at 200 °C for the feed ratio TBB:IPA of 1:3 over the catalyst Al-MCM-41 (30). Significant cracking was observed. Compared to TBB, the product viz., 4-ITBB might have higher tendencies to crack because of the hyperconjugation

Table 4
Effect of feed ratio on isopropylation of tert-butylbenzene over Al-MCM-41 (30)

WHSV (h^{-1})	Feed ratio (TBB:IPA)	tert-Butylbenzene conversion (%)	Selectivity to products (%)					
			4-ATBB	4-ITBB	3A-4ITBB	IPB	2A-IPB	Others
1.738	1:1	10.2	29.1	30.4	10.7	21.4	3.5	4.9
1.740	1:2	24.8	27.9	28.4	14.5	18.1	5.4	5.7
1.741	1:3	42.1	24.5	24.4	20.6	16.4	7.3	6.8

Temperature, 200 °C.

Table 5
Influence of WHSV on tert-butylbenzene conversion and product selectivity

S. No.	WHSV (h^{-1})	tert-Butylbenzene conversion (%)	Selectivity to products (%)					
			4-ATBB	4-ITBB	3A-4ITBB	IPB	2A-IPB	Others
1	1.741	43.7	25.9	24.7	19.9	16.3	5.4	7.8
2	2.612	24.6	33.4	29.8	15.1	14.5	0.6	6.6
3	3.482	10.4	36.5	33.7	11.4	10.3	0	8.1

Feed ratio, 1:3 (TBB:IPA); temperature, 200 °C; catalyst, Al-MCM-41 (30).

Table 6
Effect of time-on-stream on isopropylation of tert-butylbenzene over Al-MCM-41 (30)

S. No.	Time (h)	tert-Butylbenzene conversion (%)	Selectivity to products (%)					
			4-ATBB	4-ITBB	3A-4ITBB	IPB	2A-IPB	Others
1	1	43.2	21.9	28.2	20.8	15.8	5.1	8.2
2	2	37.6	24.3	31.1	20.6	13.2	3.2	7.6
3	3	32.7	25.4	34.7	18.9	11.2	1.4	8.4
4	4	28.6	28.3	37.7	16.4	9.7	0.8	7.1
5	5	24.2	31.2	39.1	14.3	7.9	0	7.5

WHSV, 1.740 h^{-1}; temperature, 200 °C; feed ratio, 1:3 (TBB:IPA).

effect due to the methyne group of the isopropyl group on 4-ITBB.

3.2.5. Influence of WHSV

The effect of flow rate on TBB-conversion and products selectivity was studied at 200 °C with a feed ratio TBB:IPA of 1:3. The WHSV was varied as 1.741, 2.612, and 3.482 h^{-1}. The results are presented in Table 5. A usual expected trend of decrease in conversion with increase in the flow rate was observed. The selectivity to 4-ATBB and 4-ITBB showed increase with increase in the flow rate. The selectivity to IPB and 3A-4ITBB decreased, as both of these were derived from cracking of 4-ITBB. At high flow rate, diffusion of the reactant over the catalyst surface is less probable, hence, subsequent reaction of 4-ITBB to 3A-4ITBB or cracking of former decreases. Also, these reactions are not viable over strong acid sites. Further, decrease in selectivity to 2A-IPB is more pronounced than IPB with increase in the flow rate, as it is more time dependent.

3.2.6. Influence of time-on-stream

The effect of time-on-stream was studied over Al-MCM-41 (30) at 200 °C with the feed ratio TBB:IPA of 1:3 and WHSV 1.740 h^{-1}. The study was conducted for 5 h and the results are presented in Table 6. Gradual decrease in conversion with the increase in time-on-stream was observed. The decrease in conversion with increase in time-on-stream might be attributed to a gradual increase in the blocking of the active sites by polypropene oligomers and coke formation [31]. Selectivity to 4-ITBB increases with time-on-stream, whereas the selectivity to 3A-4ITBB decreases with time-on-stream. This might be due to the rapid blocking of strong active sites than the others. Selectivity to 4-ATBB increased with increase in the stream,

indicating that weak sites were present in the catalyst even after being 5 h on-stream. Selectivity to IPB decreased, whereas the selectivity to 2A-IPB increased with increase in time-on-stream. The selectivity to IPB and 2A-IPB is less than the other products. The study indicated that cracking was not complete even at the end of 5 h on-stream. Again, a salient feature noted here is the cracking of TBB to benzene over fresh catalyst. Hence, the product IPB might be derived from either the cracking of 4-ITBB or rapid isopropylation of benzene with ester; this seems less probable since benzene was not observed as a product.

Another reaction, with a similar trend like that of time-on-stream was carried out for the formation of coke on the catalyst surface. 8.703 g of reactant was fed onto 0.5 g of the Al-MCM-41 (30) catalyst, and this was left on the stream for 5 h. It showed that 6.341 g (72.85%) of reactant was converted to products at the end of 5 h on-stream. Out of the remaining 2.362 g (27.14%) of reactant, an amount of 0.1480 g (1.7%) of the reactant transformed itself into coke. The weight loss of 2.214 g (25.44%) of reactant will be probably due to propene formation.

4. Conclusion

This study incites that isopropylation of aromatics can also be effected with IPA in the vapor phase in addition to isopropyl alcohol or propene. Al-MCM-41 with their mild acid sites are capable of catalyzing this reaction. There are also acetylated products which require to be carefully avoided if selectivity to alkyl aromatics is felt important. In this study, it is proposed that the partly protonated ester takes part in acylation, while strongly protonated ester takes part in alkylation.

Acknowledgements

References

[1] H.G. Franck, J.W. Stadelhofer, Industrial Aromatic Chemistry, Springer, Berlin, 1998.

[2] E. Armengol, A. Corma, H. Garcia, J. Primo, Appl. Catal. A 149 (1997) 411.

[3] P. Andy, J. Garcia-Martinez, G. Lee, H. Gonzalez, C.W. Jones, M.E. Davis, J. Catal. 192 (2000) 215.

[4] P. Botella, A. Corma, J.M. Lopez-Nieto, S. Valencia, R. Jacquot, J. Catal. 195 (2000) 161.

[5] D. Das, S. Cheng, Appl. Catal. A 201 (2000) 159.

[6] U. Freese, F. Heinrich, F. Roessner, Catal. Today 49 (1999) 237.

[7] A.A. O'Kelly, J. Kellett, J. Pluckier, Ind. Eng. Chem. 39 (1947) 154.

[8] P.B. Venuto, L.A. Hamilton, P.S. Landis, J.J. Wise, J. Catal. 5 (1966) 81.

[9] B.D. Flockhart, K.Y. Liew, R.C. Pink, J. Catal. 72 (1981) 314.

[10] P.A. Parikh, N. Subrahmanyam, Y.S. Bhat, A.B. Halgeri, Appl. Catal. A 90 (1992) 1.

[11] K.S. Reddy, B.S. Rao, V.P. Shiralkar, Appl. Catal. A 121 (1995) 191.

[12] J. Cejka, G.A. Kapustin, B. Wichterlova, Appl. Catal. A 108 (1994) 187.

[13] A. Corma, V. Fornes, M.T. Navarro, J. Perezpariente, J. Catal. 148 (1994) 569.

[14] G. Bellussi, G. Pazzuconi, C. Perego, G. Girotti, G. Terzoni, J. Catal. 157 (1995) 227.

[15] K.A. Koyano, T. Tatsumi, J. Chem. Soc., Chem. Commun. (1996) 145.

[16] M. Busio, J. Janchen, J.H.C. van Hooff, Microporous Mater. 5 (1995) 211.

[17] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.C. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.

[18] C-Y. Chen, H-X. Li, M.E. Davis, Microporous Mater. 2 (1993) 17.

[19] X.S. Zhao, G.Q. Lu, G.J. Millar, Catal. Lett. 38 (1996) 33.

[20] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, U.S. Patent no. 50986884, 1992.

[21] J.M. Newmann, M.M.J. Treacy, W.T. Koetsier, C.B. de Gruyter, Proc. R. Soc. London A 420 (1998) 375.

[22] V. Umamaheswari, M. Palanichamy, V. Murugesan, J. Catal. 210 (2002) 367.

[23] T.R. Pauly, Y. Liu, T.J. Pinnavaia, S.J.L. Billinge, T.P. Rieker, J. Am. Chem. Soc. 121 (1999) 8835.

[24] A. Corma, Microporous Mesoporous Mater. 4 (1997) 249.

[25] S. Biz, M.L. Occelli, Catal. Rev. Sci. Eng. 40 (3) (1998) 329.

[26] Y. Sun, Y. Yue, Z. Gao, Appl. Catal. A 161 (1997) 121.

[27] A. Matsumoto, H. Chen, K. Tsutsumi, M. Grun, K. Unger, Microporous Mesoporous Mater. 32 (1999) 55.

[28] H. Kosslick, G. Lischke, B. Parlitz, W. Storek, R. Fricke, Appl. Catal. A 184 (1999) 49.

[29] H. Kosslick, H. Landmesser, R. Fricke, J. Chem. Soc., Faraday Trans. 93 (1997) 1849.

[30] M.J. Climent, A. Corma, S. Iborra, S. Miquel, J. Primo, F. Rey, J. Catal. 183 (1999) 76.

[31] S.K. Badamali, A. Sakthivel, P. Selvam, Catal. Lett. 65 (2000) 153.