

Vapour phase alkylation of ethylbenzene with *t*-butyl alcohol over mesoporous Al-MCM-41 molecular sieves

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Abstract. The alkylation of ethylbenzene with *t*-butyl alcohol was studied over Al-MCM-41 (Si/Al = 50 and 90) and Al, Mg-MCM-41 (Si/(Al + Mg) = 50) in the vapour phase from 200 to 400°C. The products were *p*-*t*-butylethylbenzene (*p*-*t*-BEB), *p*-*t*-butylvinylbenzene (*p*-*t*-BVB) and *m*-*t*-butylethylbenzene (*m*-*t*-BEB). Ethylbenzene conversion decreased with increase in temperature and increase in the ethylbenzene content of the feed. The reaction between the freely diffusing ethylbenzene in the channel and the *t*-butyl cations remaining as charge compensating ions yielded *p*-*t*-BEB. *p*-*t*-BVB, an unexpected product in this investigation, was produced by dehydrogenation of *p*-*t*-BEB over alumina particles present in the channels of the molecular sieves. Adsorption of ethylbenzene on Brønsted acid sites and its subsequent reaction with very closely adsorbed *t*-butyl cations proved to be necessary to obtain *m*-*t*-BEB. Though *m*-*t*-BEB was obtained, the corresponding *m*-*t*-butylvinylbenzene was not observed in this study. Study of time durations indicated rapid and slow catalyst deactivation at lower and higher streams respectively.

Keywords. Mesoporous molecular sieves; Al-MCM-41; ethylbenzene; *t*-butylation; *t*-butyl alcohol.

1. Introduction

Alkylation of aromatic hydrocarbons is a reaction of high commercial significance. Ethylbenzene, isopropylbenzene, isopropyltoluene and C₁₀–C₁₄ linear alkyl benzenes are a few of the many industrially important chemical intermediates obtained by acid-catalysed alkylation of the appropriate aromatics¹. In many commercial plants, alkylation of aromatics is still achieved with mineral acid catalysts such as HF and H₂SO₄. These catalysts pose problems such as difficulty in handling, safety, corrosion, waste disposal and difficulties in product separation. Even heterogeneous catalysts like kieselghur-supported phosphoric acid, used for the production of cumene, are also felt to be undesirable owing to release of acid vapours. The first solid acid catalyst used for the alkylation of benzene with ethylene and propylene was amorphous silica–alumina gel in the year 1942². A wide variety of zeolites have been examined for alkylation since 1960. Zeolites X and Y were found to be more active catalysts for alkylation of benzene with olefins than amorphous silica–alumina gels³. Although zeolites and zeotype molecular

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sieves exhibit better catalytic performance than their corresponding amorphous catalysts, there are problems in the alkylation of alkyl aromatics and phenols with alcohols as the alkylating agents. For example, in the methylation of phenol over Lewis acid ion-exchanged Y and **b**zeolites, the *meta* methylated product was chiefly obtained, although only *para* and *ortho* products were principally required⁴. Similarly, in the ethylation of toluene with ethanol in the vapour phase over NAPO-5 and ZAPO-5 molecular sieves, meta products predominated⁵. Formation of meta product in these reactions was attributed to aryl ring deactivation by adsorption on the Brønsted acid sites of the catalysts. Since these catalysts are microporous materials with more acidic sites, the chances of adsorption of aromatic substrates on the Brønsted acid sites during their diffusion through the pores are expected to be greater. Hence meta substitution increases and is unavoidable on alkylaromatic substrates in zeolites. These problems can be avoided if the recently discovered mesoporous MCM-41 molecular sieves are used as catalysts⁶. They have been shown to exhibit outstanding catalytic behaviour in several acid-catalysed reactions. MCM-41 is reported to be an effective catalyst for the alkylation of benzene to ethyl benzene⁷. Good selectivities have been reported for Al-MCM-41 in the liquid phase alkylation of benzene with propylene compared to the traditional amorphous silica aluminas⁸. Medina-Valtierra *et al*⁹ have reported predominant yield of 4-isopropyltoluene in the alkylation of toluene with isopropanol over MCM-41/gAl₂O₃. The selectivity has been attributed to large pore diameter and few acid sites on the catalyst, and to the easy diffusion that aids escape of the product without multi-substitution. In addition, MCM-41 can provide similar spatial environment for the reactants in the channels as that in the homogeneous solution phase thus aiding the formation of products which are largely kinetic controlled. It is because of these features of MCM-41 that in the present study alkylation of ethylbenzene with *t*-butyl alcohol over Al-MCM-41 molecular sieves has been investigated, and the results obtained are discussed in the following sections. *t*-Butylated ethylbenzenes are the raw materials for the production of *t*-butylated vinylbenzenes which on polymerization produce polymers with enhanced plasticity over the parent polystyrene.

2. Experimental

2.1 Synthesis

The hydrothermal crystallisation procedure described by Beck *et al*⁶ was slightly modified for the preparation of Al-MCM-41 molecular sieves with Si/Al ratios 50 and 90 and Al, Mg-MCM-41 with Si/(Al + Mg) = 50. In a typical synthesis, 10.6 g of sodium silicate nanohydrate (Merck) in water was combined with an appropriate amount of aluminium sulphate and magnesium sulphate (Merck) in solution. It was then acidified with 1 M H₂SO₄ to bring the pH to down 10.5 under vigorous stirring. After 30 min stirring, an aqueous solution of cetyltrimethylammonium bromide (CTAB) (Merck) was added and the surfactant-silicate mixture was stirred for a further 1 h at room temperature. The molar composition of the resultant mixture was SiO₂: 0.2 CTAB: *x* Al₂O₃: *y* MgO: 0.89 H₂SO₄: 120 H₂O (*y* = 0 for Al-MCM-41, *x* varies with Si/Al ratio). The resulting gel was autoclaved and heated for 12 h at 170°C. The solid obtained was filtered and dried at 80°C in the oven. The sample was then calcined at 550°C in air for 5 h in a muffle furnace to expel the template.

2.2 Characterisation

X-ray powder diffraction data for the materials were collected on a Scintag XDS 2000 diffractometer equipped with a Cu-K α radiation source and a liquid nitrogen cooled germanium solid state detector. The samples were scanned from 1 to 10 $^\circ$ (2θ) in steps of 0.02 $^\circ$ with a count time of 15 s at each point. The mid-infrared spectra were recorded on a Nicolet 800 FTIR spectrophotometer by the KBr pellet technique. Thermogravimetric analyses of the samples were carried out on a Mettler TA 3000 thermogravimetric analyser. The samples were heated in air at a rate of 20 $^\circ$ C/min for all data collections from 35 to 700 $^\circ$ C. BET surface area measurements were made using the Sorptomatic 1990 instrument. The samples were outgassed for 16 h under vacuum at 350 $^\circ$ C prior to use.

2.3 Alkylation

The *t*-butylation of ethylbenzene with *t*-butyl alcohol was carried out in a fixed bed continuous downflow glass reactor of 40 cm length and 1 cm internal diameter. About 0.5 g of catalyst was taken in the reactor and the reaction mixture was fed into it by a motor driven syringe pump at predetermined flow rates. Analysis of the products collected for one hour was carried out in a Hewlett Packard gas chromatograph 5890A equipped with a flame ionisation detector (FID) using an OV 17 column and nitrogen as the carrier gas. After completion of each run, the reactor system was flushed with nitrogen to remove the adsorbed molecules and the catalyst was regenerated at 500 $^\circ$ C in a current of moisture-free air for 6 h. Selectivities of the products were calculated using the following equation.

$$\text{Selectivity of the product (\%)} = \frac{\text{product (\%)}}{\text{ethylbenzene derived products (\%)}} \times 100.$$

3. Results and discussion

The X-ray powder diffraction patterns of all the three as-synthesised and calcined materials, shown in figure 1, exhibit a very strong peak at about 1.2 $^\circ$ (2θ) and weak peaks between 2 and 3 $^\circ$ (2θ). These peaks can be indexed for a hexagonal mesophase as these spectral features resemble those reported by Chen *et al*¹⁰. The intensity of the peak at $2\theta=1.2^\circ$ for the calcined samples is more than that of the as-synthesised one due to condensation of defective sites during calcination. The infrared spectra of the as-synthesised samples are shown in figure 2. The broad envelope around 3500 cm^{-1} is due to hydroxyl stretching of water, surface hydroxyl groups and bridged hydroxyl groups. In the spectra of as-synthesised samples there are less intense peaks just below 3000 cm^{-1} which are assigned to symmetric and asymmetric stretching modes of $-\text{CH}_2$ group of the locked-in template which are absent in the spectra of the calcined materials. The corresponding bending mode is observed at 1400 cm^{-1} . The peaks between 500 and 1200 cm^{-1} are assigned to framework vibrations. These spectral features resemble those reported in the literature¹⁰.

The thermograms of the as-synthesised and calcined samples are presented in figure 3. There are three distinct stages of weight loss between 25 and 150, 150 and 400 and above 400 $^\circ$ C. The first weight loss is due to desorption of water, the second due to degradation,

combustion and desorption of imbibed template, and the third due to loss of water molecules via condensation of silanol groups to form siloxane bonds. These data also coincide with the reports of Chen *et al*¹⁰. BET surface area of the three samples Al-

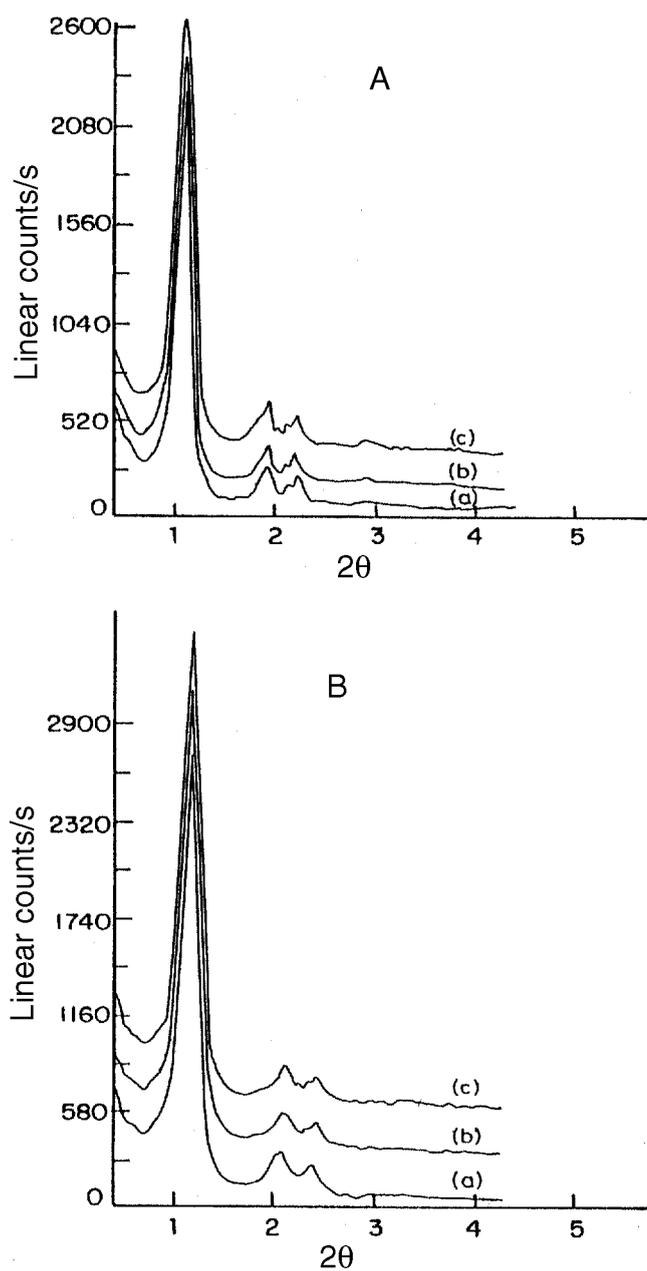


Figure 1. XRD Patterns of (A) as-synthesised and (B) calcined materials. (a) Al-MCM-41 (50), (b) Al-MCM-41 (90) and (c) Al, Mg-MCM-41 (50).

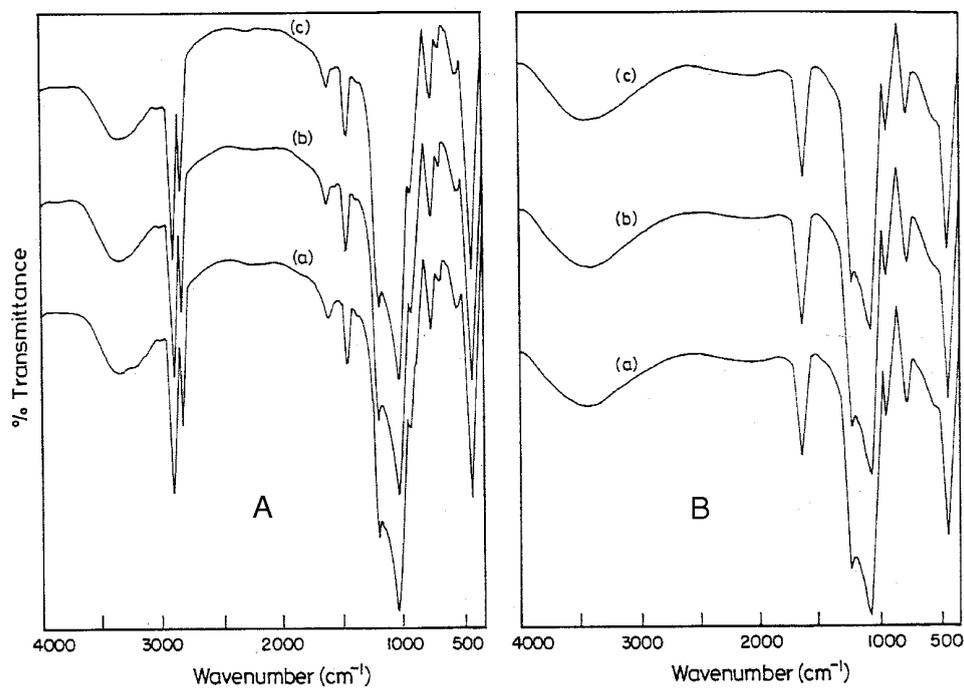


Figure 2. FTIR spectra of (A) as-synthesised and (B) calcined materials. (a) Al-MCM-41 (50), (b) Al-MCM-41 (90) and (c) Al, Mg-MCM-41 (50).

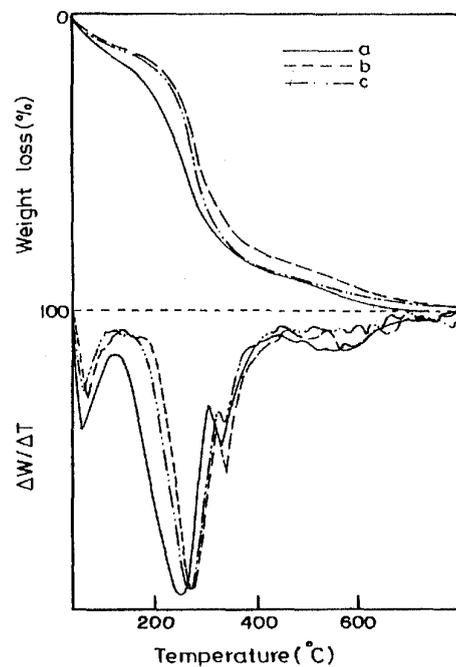


Figure 3. TG and DTG curves of as-synthesised materials. (a) Al-MCM-41 (50), (b) Al-MCM-41 (90) and (c) Al, Mg-MCM-41 (50).

MCM-41 (50), Al-MCM-41 (90) and Al, Mg-MCM-41 (50) measured using the nitrogen physisorption method are 895, 856 and 805 m²/g respectively. Surface areas of the calcined materials are comparable to those previously reported for these kinds of materials⁶.

t-Butylation of ethylbenzene with *t*-butyl alcohol was examined over Al-MCM-41 (50) from 200 to 400°C. The feed ratio of ethyl benzene to *t*-butyl alcohol was initially set at 1:1 and weight hourly space velocity (WHSV) = 2.5 h⁻¹. The results obtained are presented in table 1. The data indicate slight decrease in ethylbenzene conversion with increase in temperature which may be attributed to blocking of active sites by polybutene and/or coke¹¹. The products obtained in this reaction are *p-t*-butylethylbenzene (*p-t*-BEB), *p-t*-butylvinylbenzene (*p-t*-BVB) and *m-t*-butylethylbenzene (*m-t*-BEB). The selectivity of *m-t*-BEB decreases with increase in temperature due to desorption of ethylbenzene. Greater desorption of ethylbenzene with increase in temperature indicates that its adsorption on the catalyst acid sites is weak. Desorption of ethylbenzene alone might be the ultimate cause of decrease in *m-t*-BEB selectivity as this product formation requires close adsorption of both *t*-butyl cation and ethylbenzene. As the adsorption of ethylbenzene on the Brønsted acid sites of the catalyst can occur at *o*- or *p*-positions with respect to the ethyl group, the *meta* position alone becomes available for electrophilic attack with *t*-butyl cation. The other products are *p-t*-BEB and its dehydrogenated product, *p-t*-BVB. The selectivity of the former decreases with increase in temperature but the latter shows the reverse trend. Dehydrogenation of *p-t*-BEB to *p-t*-BVB is expected to occur over alumina particles lying inside the mesopore channel. They are formed by framework leaching of aluminium during calcination of the as-synthesised catalyst to expel the template. Such framework leaching of aluminium has already been reported in the literature¹⁰. The activity of alumina towards dehydrogenation is also reported in the literature¹². The selectivity of *p-t*-BVB increases with increase in temperature, as dehydrogenation is an endothermic process. The increase in *p-t*-BVB selectivity with increase in temperature not only reveals the presence of alumina in the mesopore channel but also that they are not blocked by coke during the reaction. The dehydrogenation of *m-t*-BEB to *m-t*-BVB which was not observed at all temperatures

Table 1. Catalytic activity of Al-MCM-41 (50) for *t*-butylation of ethylbenzene (WHSV = 2.5 h⁻¹).

Mole ratio of the reactants	Temperature (°C)	Ethylbenzene conversion (%)	Selectivity of products (%)		
			<i>m-t</i> -BEB	<i>p-t</i> -BVB	<i>p-t</i> -BEB
1:1	200	61.5	38.2	18.7	43.1
	250	52.7	63.2	17.0	19.8
	300	42.5	48.7	32.3	19.0
	350	19.8	10.6	89.4	–
	400	18	8.9	91.1	–
2:1	200	58.4	10.3	30.5	59.2
	250	54.2	31.9	21.2	46.9
	300	36.2	22.0	42.4	35.6
	350	27.6	21.9	58.6	19.5
	400	11.8	19.6	80.4	–

might be due to the inductive electron-releasing influence of *t*-butyl groups that could deactivate the ethyl groups. Similar effect is also there in *p-t*-BEB but the *t*-butyl group is a little far off and hence the deactivation of ethyl group is not effected.

The influence of reactant feed ratio on ethylbenzene conversion and products selectivity was studied by increasing it from 1:1 to 2:1 with $\text{WHSV} = 2.5 \text{ h}^{-1}$. The results obtained are presented in the same table. There is more decrease in ethylbenzene conversion than for the 1:1 ratio, which is due to greater dilution of *t*-butyl alcohol by ethyl benzene and preferential adsorption of the latter. Hence *t*-butyl alcohol freely diffuses through the pores without getting adsorbed on the Brønsted acid sites of the catalyst. This is also clearly indicated by the greater decrease in selectivity of *m-t*-BEB with increase in temperature. In order to study the influence of contact time on ethylbenzene conversion and product selectivity, WHSV was increased from 2.5 to 4.2 h^{-1} . As expected, the conversion decreases due to faster diffusion of the feed. The selectivity of *m-t*-BEB increases due to reduction in the competition for the *t*-butyl cation by ethylbenzene in the vapour phase (table 2). It is further verified by increasing the feed ratio as 1:3, 1:4, 1:5 and 1:6. The results obtained for these feed ratios are given in the table 3. As the *t*-butyl alcohol content in the feed increases there is a gradual increase in the adsorption of *t*-butyl alcohol along with ethylbenzene. Hence both ethylbenzene conversion and selectivity to *m-t*-BEB increased.

The absence of styrene at all temperatures might be due to its high reactivity with *t*-butyl cation to yield *p-t*-BVB or the inability of ethylbenzene to undergo dehydrogenation to yield styrene. In order to understand which one of these is operating, ethylbenzene alone was passed over Al-MCM-41 (50) at 200°C with $\text{WHSV} = 2.5 \text{ h}^{-1}$. The yield of styrene was 13.5%. Hence styrene might also be formed in the original reaction within the channel which rapidly reacts with *t*-butyl cation to yield *p-t*-BVB.

Table 2. Influence of WHSV on ethylbenzene conversion and product selectivity.

Mole ratio = 1:1, $\text{WHSV} = 4.2 \text{ h}^{-1}$, temperature 200°C

Catalyst	Ethylbenzene conversion (%)	Selectivity of products (%)		
		<i>m-t</i> -BEB	<i>p-t</i> -BVB	<i>p-t</i> -BEB
Al-MCM-41 (50)	59.3	45.4	39.8	14.8
Al-MCM-41 (90)	48.6	66.3	23	10.7
Al, Mg-MCM-41 (50)	60.4	45.2	42.7	12.0

Table 3. Effect of mole ratio on *t*-butylation of ethylbenzene over Al-MCM-41 (50) temperature = 200°C, $\text{WHSV} = 2.5 \text{ h}^{-1}$.

Mole ratio of the reactants	Ethylbenzene conversion (%)	Selectivity of products (%)	
		<i>m-t</i> -BEB	<i>p-t</i> -BVB
1:3	29.7	81.1	18.9
1:4	25.7	94.2	5.8
1:5	19.1	86.4	13.6
1:6	19.9	85.4	14.6

The reaction was also studied over Al-MCM-41 (90). Ethylbenzene to *t*-butyl alcohol feed ratio was initially kept at 1:1 with $\text{WHSV} = 2.5 \text{ h}^{-1}$ and the reaction was studied from 200 to 400°C. The results are presented in table 4. As the density of acid sites is small, the ethylbenzene conversion is less compared to Al-MCM-41 (50). There is a decrease in the selectivity of *p-t*-BEB but with a little maximum at 250°C. The selectivity of *p-t*-BVB increases with increase in temperature. Selectivity of *m-t*-BEB except at 200°C is less compared to Al-MCM-41 (50) illustrating the less number of near acid site pairs which are extremely necessary to adsorb ethyl benzene and *t*-butyl cation very closely to yield this product. It is clearly proved in this study.

If the presence of Brønsted acid sites in close proximity is absolutely necessary to obtain *m-t*-BEB, then use of Al, Mg-MCM-41 (50) should yield more of *m-t*-BEB than Al-MCM-41 (50) as each Mg in Al, Mg-MCM-41 (50) is capable of planting two Brønsted acids closer in the channel of the mesopores. With this idea, this material was also examined for *t*-butylation of ethylbenzene. The results are presented in table 5. There is increase in conversion as well as selectivity of *m-t*-BEB as expected. In addition, it also proves that magnesium is not just entirely buried deep into the wall structure but also planted sufficiently on the surface of channels. When the feed ratio is increased to 2:1 there is decrease in conversion, proving dilution of alcohol and thus reducing its adsorption on Brønsted acid sites. At the feed ratio 1:1, when the WHSV is increased to 4.2 h^{-1} , similar to the earlier observations, there is increase in the selectivity of *m-t*-BEB and decrease in the selectivity of *p-t*-BEB and its dependent product *p-t*-BVB, as illustrated in table 2, thus proving faster diffusion of free ethylbenzene through the channels.

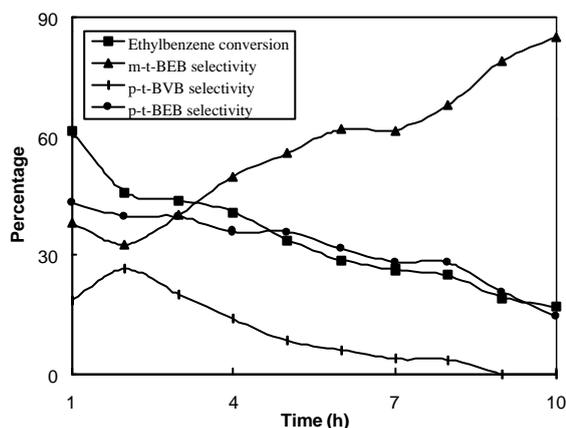
The time on stream study was conducted over Al-MCM-41 (50) at 200°C with feed ratio 2:1 and $\text{WHSV} = 2.5 \text{ h}^{-1}$. The ethylbenzene conversion and products selectivity are illustrated in figure 4. In the early stream, ethylbenzene conversion is high but it decreases with increase in stream. Similarly selectivity to *p-t*-BEB predominates in the early stream but decreases with increase in stream. In the case of *p-t*-BVB the selectivity decreases rapidly with time. The selectivity of *m-t*-BEB is more than that of other products, hence polybutene dimers, trimers etc. are expected to provide a constant barrier for ethylbenzene to react with *t*-butyl cations in the vapour phase. It results in the

Table 4. Catalytic activity of Al-MCM-41 (90) for *t*-butylation of ethylbenzene ($\text{WHSV} = 2.5 \text{ h}^{-1}$).

Mole ratio of the reactants	Temperature (°C)	Ethylbenzene conversion (%)	Selectivity of products (%)		
			<i>m-t</i> -BEB	<i>p-t</i> -BVB	<i>p-t</i> -BEB
1:1	200	52.9	35.0	22.8	42.2
	250	50.0	41.6	30.6	27.8
	300	39.5	23.5	43.8	32.7
	350	38.7	9.0	65.1	25.9
	400	30.2	–	73.5	26.5
2:1	200	48.1	36.2	13.5	50.3
	250	35.4	22.3	31.0	46.6
	300	24.3	25.5	49	25.5
	350	19.2	14.0	56.3	29.7
	400	11.1	–	100.0	–

Table 5. Catalytic activity of Al, Mg-MCM-41 (50) for *t*-butylation of ethylbenzene (WHSV = 2.5 h⁻¹).

Mole ratio of the reactants	Temperature (°C)	Ethylbenzene conversion (%)	Selectivity of products (%)		
			<i>m-t</i> -BEB	<i>p-t</i> -BVB	<i>p-t</i> -BEB
1:1	200	63.1	41.9	11.6	46.5
	250	60.2	48.3	14.5	37.2
	300	47.6	42.2	26.7	31.1
	350	44.8	43.5	32.8	23.7
	400	36.8	35.9	64.1	–
2:1	200	59	35.8	12.5	51.7
	250	49.4	28.2	24.8	47
	300	26.9	17.1	60.2	22.7
	350	27.8	14.5	85.5	–
	400	15.8	11.4	88.6	–

**Figure 4.** Effect of time on stream on Al-MCM-41 (50).

reduction of yield of *p-t*-BEB and *p-t*-BVB and hence indirectly aids formation of more *m-t*-BEB. The lower selectivity of *m-t*-BEB in the early stages but its increase with time confirms the slow and steady formation of polybutenes with stream. This observation imposes the condition that the polybutenes formed in the reaction might not be resting very closely on the catalyst surface but with sufficient space such that ethylbenzene and *t*-butyl alcohol can diffuse through it, themselves get adsorbed on the catalyst surface and react further to yield *m-t*-BEB with greater selectivity.

4. Conclusions

Al-MCM-41 (50), Al-MCM-41 (90) and Al, Mg-MCM-41 (50) are convenient solid acid catalysts for the vapour phase *t*-butylation of ethylbenzene. Dependence of ethylbenzene conversion on the density of acid sites is clearly evident in this study. The necessity of Brønsted acid sites in close proximity for the formation of *m-t*-BEB is vividly illustrated

in this investigation. Presence of sufficient magnesium on the surface of the channels rather than deep within the bulk of the channel is also evident in this study. Formation of *p-t*-BVB by dehydrogenation of *p-t*-BEB over non-framework alumina particles stands as an interesting observation. The combined effect of large pore diameter and scattered distribution of acid sites makes mesoporous molecular sieves convenient alternatives to conventional acid catalysts.

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