

# Comparison of mesoporous Al-MCM-41 molecular sieves in the production of *p*-cymene for isopropylation of toluene

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## Abstract

Mesoporous aluminosilicate Al-MCM-41 with Si/Al = 93 and 104 were synthesized using cetyltrimethylammonium bromide as the structuring agent and the materials were characterized using several techniques. The mesoporous structure was confirmed by X-ray diffraction (XRD) technique. The surface area, pore size and wall thickness was calculated by BET equation and BJH method using nitrogen sorption technique. Fourier transform-infrared (FT-IR) spectroscopy was used in order to obtain information on incorporated aluminum atoms in the mesoporous structure of Al-MCM-41. Thermogravimetric–differential thermal analyzer (TG–DTA) was used to determine the thermal stability of the materials. The effect of reaction temperature, WHSV and isopropanol:toluene ratios on the selectivity of *p*-cymene were studied. The Al-MCM-41 (93) catalyst exhibited excellent selectivity in the production of *p*-cymene by the isopropylation of toluene using isopropanol as the propylating agent. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

There is a considerable demand for large pore size catalysts for the synthesis of large molecules, e.g., *p*-cymene by isopropylation of toluene. This reaction is taken as a model with the aim to identify potential solid acid catalysts for alkylation of industrial interest. The products of the alkylation reaction of isopropanol with toluene are isobutyl benzene and cymenes. *p*-Cymene is an important intermediate used in pharmaceutical industries and for the production of fungicides, pesticides, as flavoring agent and as a heat transfer medium [1].

In many petrochemical plants, these alkylations are still performed with catalysts having certain drawbacks. Often such catalysts are mineral acids, for example, hydrochloric acid containing AlCl<sub>3</sub>, used for the production of ethyl benzene, cumene, linear aromatic benzene and cymenes. This acid gives rise to many problems regarding handling, safety, corrosion and waste disposal. In addition, because the reagents are mixed with acids, separation of the products from the catalyst is often a difficult and energy consuming process. Many of these problems can be solved by supporting the acid catalyst on zeolite β or better by developing new mesoporous molecular sieves MCM-41 [2] and FSM-16 [3], which are very important large pore materials being studied currently as solid-state catalysts. However, as they are pure

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silica materials, lacking sufficient acidity, it is difficult to use them directly as catalysts. Incorporation of aluminum [4–11] and other metals [12–17] into their mesoporous structure has therefore been investigated in order to introduce solid-state acidity and thereby, catalytic function. The typical characteristics of Al-MCM-41, viz., highly ordered mesoporosity, large surface area, high thermal stability and some acidity, allude to the possibility of applying these materials as catalysts in the synthesis and conversion of large molecules.

Corma et al. [5] first reported the details of synthesis and characterization of aluminum incorporated mesoporous materials. However the catalytic activity of the material was low in comparison to the usual silica–alumina catalyst and also the thermal stability was poor. Van Hooff and coworkers [7] also reported the synthesis and characterization of the Al-MCM-41, wherein incorporation of an excess of aluminum (Si/Al ratio = 10) formed an impure crystal phase tridimite and the Lewis acid site prevailed because of the presence of octahedral non-framework aluminum accompanied with the collapse of the structure.

Perego et al. [18] and Cejka et al. [19] have used rich aluminum content of MCM-41, viz., Si/Al = 20.3 and Si/Al = 14.6, 15.0 and 35, respectively, and obtained 85 and 90–97% selectivity of cymenes prepared using propene and toluene in low temperature range of 180–250 °C. However, the percentage of *p*-cymene in the cymenes mixture was only 37–47% (Cejka et al.) and 38% (Perego et al.).

In the present study, synthesis of low aluminum content MCM-41 (Si/Al = 93 and 104) catalysts, their physicochemical characterization and application as catalysts for the selectivity of *p*-cymene produced by the alkylation of toluene using isopropanol has been carried out. Use of low Al content MCM-41 at temperature 275 °C resulted into about 70% yield of cymenes by the isopropylation of toluene using isopropanol but the selectivity for *p*-cymene was as high as 75.3%. Owing to its low cost, and extensive use in industries, isopropanol was chosen instead of propene. The effect of reaction temperature, weight hourly space velocity (WHSV) and isopropanol:toluene ratio on the selectivity of *p*-cymene was investigated.

## 2. Experimental

### 2.1. Chemicals

All the reagents, viz., sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>), aluminum isopropoxide [Al(*i*-OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>], cetyltrimethylammonium bromide (C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>Br<sup>-</sup>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), isopropanol [(CH<sub>3</sub>)<sub>2</sub>-CH-OH] and toluene (C<sub>6</sub>H<sub>5</sub>-CH<sub>3</sub>) were of AR grade purchased from M/S Aldrich, UK.

### 2.2. Synthesis of Al-MCM-41

For the synthesis of the Al-MCM-41 (93), 12.2 g (1 mol) sodium metasilicate (44–47% SiO<sub>2</sub>) dissolved in 50 g of deionized water was mixed with 0.11 g (0.005 mol) of aluminum isopropoxide (dissolved in 10 g of deionized water) solution. This mixture was stirred for 30 min at a speed of about 250 rpm and 100 ml of 1 N of sulfuric acid was added with continuous stirring for another 30 min at a speed of about 250 rpm until gel formation. After that, 7.2 g (0.2 mol) of cetyltrimethylammonium bromide was added drop by drop (30 ml/h) through the dual syringe pump so that the gel was changed into suspension. The suspension was transferred into Teflon-lined steel autoclave and heated to 165 °C for 48 h.

After cooling to room temperature, the material was recovered by filtration, washed with deionized water and ethanol and finally calcined in flowing air at 540 °C for 6 h.

The catalyst Al-MCM-41 (104) was also synthesized in a similar manner wherein only the ratio of sodium metasilicate and aluminum isopropoxide was adjusted appropriately.

### 2.3. Physicochemical characterization

X-ray powder diffraction (XRD) data were collected on a Scintag 2000 diffractometer using Ni-filtered monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.5406$ ). The samples were scanned from  $2\theta = 1-8^\circ$  angle in steps of  $0.5^\circ$  with a count time of 5 s at each point. In order to protect the detector from the high energy of the incident X-ray beam and to resolve a peak at low angles narrowed incident and diffracted beam slits were used in this work.

N<sub>2</sub>-sorption was measured at liquid nitrogen temperature with a NOVA-1000 (Quantachrome, Version 5.01) instrument. Surface area, pore size and wall thickness was obtained from these isotherms using the conventional BET and BJH equations. The calcined samples were outgassed under vacuum at 200 °C for 8 h in flowing argon at a flow rate of 60 ml/min.

Infrared spectra were recorded with a Nicolet impact 410 FT-IR spectrometer in KBr pellet (0.005 g sample with 0.1 g KBr) scan number 36, resolution 4 cm<sup>-1</sup>. The data was treated with the OMNIC software.

Thermogravimetric–differential thermal analysis (TG–DTA) was carried out in a Rheometric Scientific (STA 15H<sup>+</sup>) thermobalance. The amount of as-synthesized sample loaded was 5.9480 mg, and the airflow used was 50 ml/min (1:1 molar ratio). The heating rate was 10 °C/min and the final temperature was 1000 °C.

#### 2.4. Catalytic reactions—*isopropylation of toluene*

Reactions were carried out in an ordinary fixed bed flow-type reaction apparatus. Two gram catalyst packed into a quartz tubular reactor of 6.0 mm inner diameter was pretreated at 500 °C in airflow for 6 h. The liquid reactant was supplied to an evaporator by microdisplacement pump at a WHSV of 2.5 h<sup>-1</sup>, diluted to 1 mol% with air and the vapor introduced into the catalyst bed. In the case of the propylation of toluene, a mixture of isopropanol and toluene were used as the reactants, and the liquid product collected during 1 h was sampled. The percent conversion of toluene was analyzed by gas chromatograph (Hewlett Packard 5890) with FID type detector equipped with a PONA capillary column (50 m long and 0.21 mm OD, coated with a 0.5 mm thick film of stationary phase). The identification of products on conversion of toluene was performed on a Shimadzu GC–MS–QP1000EX (gas chromatography–mass spectrometer).

As the percent conversion of toluene was higher in percent of Al-MCM-41 (93), all other experiments concerning evaluation of the catalyst with respect to isopropylation of toluene were carried out only with Al-MCM-41 (93).

### 3. Results and discussion

#### 3.1. Yield of synthesis

The mass of as-synthesized Al-MCM-41 (93) was found to be 10.2 g, which reduced to 6.3 g on calcinations. The corresponding values for Al-MCM-41 (104) were 8.2 and 5.2 g. Both the syntheses were carried out at pH 10.8 and under hydrothermal conditions.

#### 3.2. XRD

Fig. 1 shows the XRD patterns of calcined Al-MCM-41 samples having Si/Al molar ratio 93 and 104. The X-ray diffractograms of Al-MCM-41 (93) and Al-MCM-41 (104), after calcinations in air at 540 °C for 6 h, contain, a sharp *d*<sub>100</sub> reflection line near  $2\theta = 2.1^\circ$  and  $1.9^\circ$ , respectively. In Al-MCM-41 (104) in addition to the above, a broad peak at  $3.6^\circ$  is obtained. This peak has been attributed to the

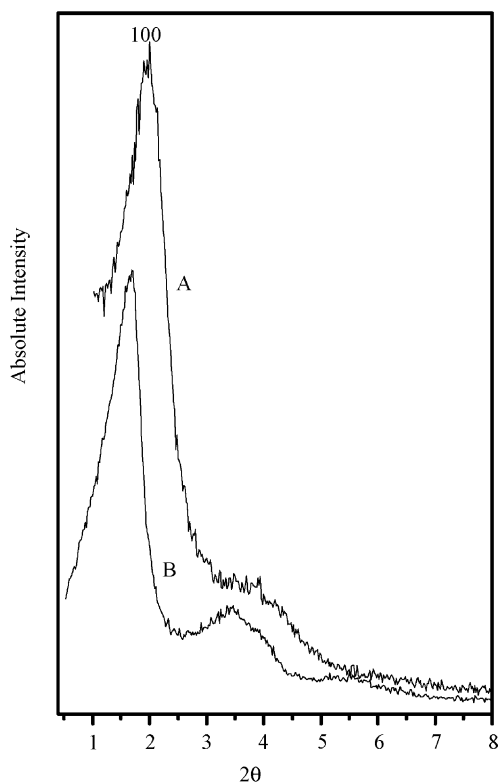


Fig. 1. XRD diffractograms for calcined (A) Al-MCM-41 (93) and (B) Al-MCM-41 (104).

Table 1  
Physicochemical characterization of Al-MCM-41 (93) and Al-MCM-41 (104)

Samples (Si/Al ratio)	<i>d</i> -Spacing value (Å)	Unit cell parameter (Å)	BET surface area (m <sup>2</sup> /g)	Pore size (Å)	Wall thickness (Å)
Al-MCM-41 (Si/Al = 93)	44.6	51	1011	38.2	13.8
Al-MCM-41 (Si/Al = 104)	46.7	54	1099	37.4	15.4

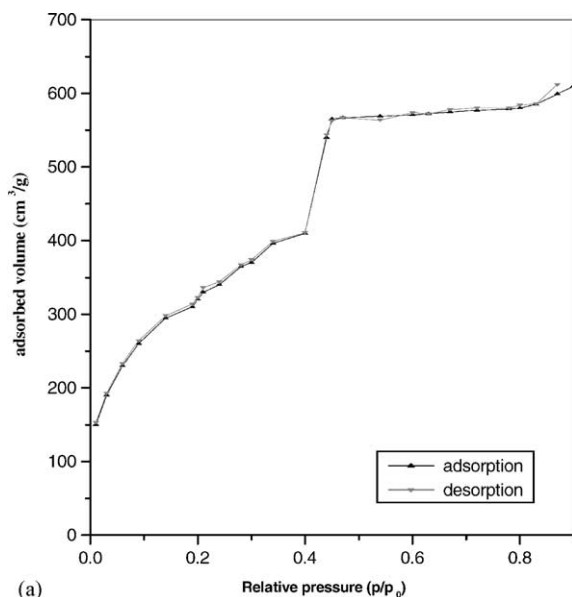
broadening effects of higher reflection lines due to small particles [20]. When using CTMA-Br instead of CTMA-Cl, the  $d_{110}$  line is well resolved indicating the influence of the surfactant counter ion on the solid long-range order. Physicochemical properties of these mesoporous materials are summarized in Table 1. The pore-to-pore distance of Al-MCM-41 could be determined by the XRD patterns. The XRD patterns of calcined Al-MCM-41 (93) with characteristic peaks of hexagonal symmetry and with  $d_{100}$  of 44.60 Å are shown in Fig. 1A. The repeating distance ( $a_0$ ) between pore centers was 51.150 Å. The hexagonal unit cell parameter ( $a_0$ ) was calculated using the following formula from  $d_{100}$ , which was obtained from the peak in the XRD pattern by Bragg's equation ( $2d \sin \theta = \lambda$ , where  $\lambda = 1.5406$  Å for the Cu K $\alpha$  line). The value of  $a_0$  was equal to the internal pore diameter plus one pore wall thickness. In general, at the synthesis condition used, the crystallization reaction is non-stoichiometric and the crystal's Si/Al ratio is always greater than in the hydrogel containing aluminum [21]. Incorporation of aluminum into the silicate framework decreases the size of the unit cell when the source of Al is Al-isopropoxide, and then in general as Al content increases unit cell parameter decreases.

The data obtained for the calcined materials are in good agreement with those reported by Beck et al. [22]. Excess incorporation of aluminum (low Si/Al ratio) might lead to the collapse of the structure, as reported by Kin et al. [23] for Al-MCM-41 (Si/Al = 10) prepared at a pH of 11.

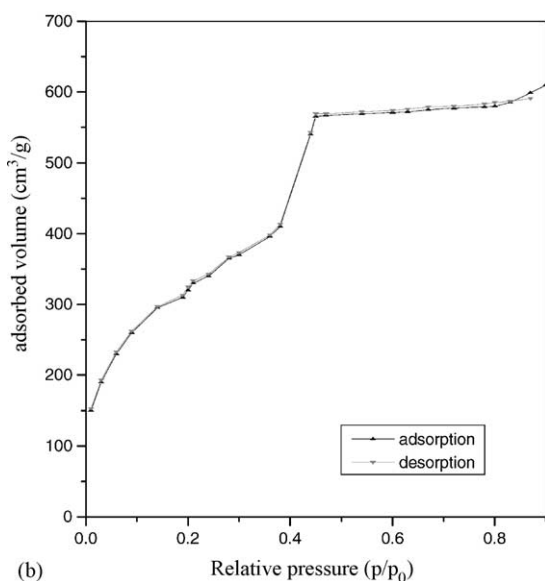
### 3.3. Adsorption isotherm of nitrogen

Fig. 2a and b shows the isotherm of nitrogen adsorption on the calcined Al-MCM-41 (93) and Al-MCM-41 (104) measured at liquid nitrogen temperature (77 K). Three well-defined stages may be identified: (1) a slow increase in nitrogen

uptake at low relative pressure, corresponding to monolayer–multilayer adsorption on the pore walls; (2) a sharp step at intermediate relative pressures indicative of capillary condensation within mesopores; (3) a plateau with a slight inclination at high relative pressures associated with multilayer adsorption on the external surface of the crystals [24]. A fourth stage, characterized by a sharp rise in N<sub>2</sub> uptake as the pressure reaches saturation ( $p/p_0 = 0.9$ ), may be identified in some isotherms. Mesoporous materials with high Al content generally rise the isotherm lines at high pressure which is attributed to the condensation of nitrogen within voids formed by crystal aggregates. It is worthwhile to note that the sharpness and height of the capillary condensation (pore-filling) step in the isotherms is a measure of the pore size uniformity. Departures from a sharp and clearly defined pore-filling step are usually an indication of increase in pore size heterogeneity (i.e., widening of pore size distribution). Both the Al-containing samples exhibit isotherms with a well-developed step in the relative pressure ( $p/p_0$ ) range corresponding from 0.41 to 0.45 (Al-MCM-41 (93)) and from 0.38 to 0.43 (Al-MCM-41 (104)), respectively, characteristic of capillary condensation into uniform mesopores. However, the capillary condensation step is much higher and steep for the Al-MCM-41 (93) than that for the Al-MCM-41 (104). In general the isotherms indicate that all of the samples possess good mesopore structural ordering and narrow pore size distribution and any structural changes resulting from Al incorporation are not necessarily at the expense of pore uniformity. The isotherms also suggest that Al incorporation results in a shift to lower pore size (pore-filling step at lower  $p/p_0$ ) and that the decrease in pore size is greater at higher Al content. It is interesting to note from the isotherms that the presence of Al results in significant adsorption at high partial pressures ( $p/p_0$ ). It is likely that the Al-MCM-41 samples are made up of inhomogeneous particles which gives rise to interparticle



(a)



(b)

Fig. 2. (a) Nitrogen adsorption of Al-MCM-41 (93) and (b) Al-MCM-41 (104).

voids. The surface area, pore size and wall thickness are given in Table 1. The pore size of Al-MCM-41 (93) is higher than that of Al-MCM-41 (104) due to the presence of textural mesoporosity [25]. The pore sizes attributable to framework confined pores of diameter less than 50 Å which is however lower for

Al-MCM-41 materials and decreases with increase in Al-content. (Since the Kelvin equation is not valid for pores below 18 Å, the BJH approach can only be used for mesoporous material.)

### 3.4. FT-IR spectroscopy

Infrared spectroscopy had been used extensively for the characterization of transition-metal cation modified zeolites. In the FT-IR spectrum of calcined siliceous MCM-41, the asymmetric and symmetric stretching vibration bands of framework Si–O–Si bands, assigned by Sohn et al. [26] for zeolites, appeared at 1123 and 814  $\text{cm}^{-1}$ . In as-synthesized Al-MCM-41 (104), the IR spectrum was measured in 400–4000  $\text{cm}^{-1}$  range in a few steps during sample preparation and is shown in Fig. 3. The as-synthesized sample exhibits absorption bands around 2921 and 2851  $\text{cm}^{-1}$  corresponding to n-C–H and d-C–H vibrations of the surfactant molecules. The broad

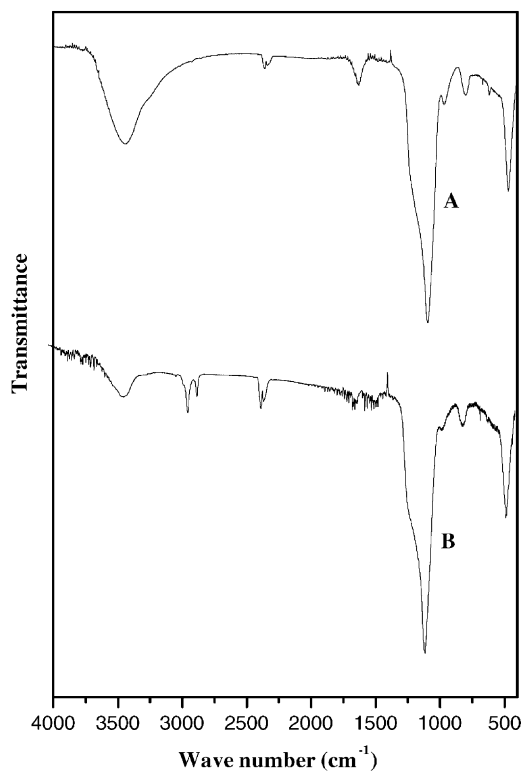


Fig. 3. FT-IR spectra of (A) calcined Al-MCM-41 (93) and (B) as-synthesized Al-MCM-41 (104).

bands around  $3500\text{ cm}^{-1}$  may be attributed to surface silanols and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the adsorption bands at  $1623\text{--}1640\text{ cm}^{-1}$  [27]. The absorption band at  $1057$  and  $1223\text{ cm}^{-1}$  are due to asymmetric stretching vibrations of Si–O–Si bridges, but in the opposite direction are observed for the  $963\text{ cm}^{-1}$  bands due to Si–O–Al vibrations in aluminum incorporation of silanols. By the disappearing peaks at  $2851$  and  $2921\text{ cm}^{-1}$ , one could conclude that calcinations of the original framework were completed and the identity of organic molecule completely disappeared from the calcined Al-MCM-41 (93). The vibration bands of calcined Al-MCM-41 (93) can be shifted from  $1\text{ cm}^{-1}$  into  $3$  or  $5\text{ cm}^{-1}$ , except the vibration bands of  $2921$  and  $2821\text{ cm}^{-1}$  due to removal of organic molecules after calcinations. An FT-IR spectrum of calcined Al-MCM-41 (93) is shown in Fig. 3. Upon introduction of Al, most of the bands shifted to higher wave numbers, consistent with their incorporation in lattice positions. Additionally, an absorption band of  $967\text{ cm}^{-1}$  assigned to a stretching vibration of Si–O–Al linkage was observed. Upon increasing the aluminum content, found an additional broad band around  $3502\text{ cm}^{-1}$ , which was assigned to hydroxyl groups on octahedrally coordinated aluminum species [28].

### 3.5. Thermal analysis

Thermogravimetric analysis of the crystals show distinct weight losses that depend, in part, on framework composition (Table 2). Representative thermograms are given in Fig. 4 (curves A and B). The minor weight loss below  $150^\circ\text{C}$  corresponds to the desorption of physisorbed water (or ethanol) in the voids formed by crystal agglomeration. Weight losses in the  $150\text{--}350^\circ\text{C}$  temperature range are attributed to the decomposition and removal of occluded organics.

Weight losses in this temperature range are not as large as in the parent silicate because of stronger sorbate–sorber interactions at the aluminosilicate surface. In the  $280\text{--}340^\circ\text{C}$  temperature region, the oxidative decomposition of residual organic compounds occurs and accompanied by exotherms whose number and intensity depends on the exotherms on the aluminum content of the crystal. The  $350\text{--}550^\circ\text{C}$  was the region of surfactant associated with Al–O–. There was almost no exothermal peak after  $550^\circ\text{C}$ , which indicated the surfactant had been removed completely. In other words, it could show that the Al-MCM-41 material structure was quite stable because of the straight weight loss line after  $550^\circ\text{C}$ . The total weight loss at  $1000^\circ\text{C}$  of the Al-MCM-41 samples are in the  $41.9\text{--}45.4\%$  range, without any clear dependence on the Si/Al ratio or aluminum source of the sample. However, the distribution of successive weight loss depends on the framework Si/Al ratio [7,29]. Thus, weight loss was higher in the Al-MCM-41 (104) than that in the Al-MCM-41 (93), where the Al content was less in the former than in the later.

### 3.6. Isopropylation of toluene

The isopropylation of toluene with isopropanol is an electrophilic substitution reaction on the aromatic ring. Isopropylation reactions catalyzed by acids are commonly considered as proceeding via carbonium ion type mechanism [30]. The reaction of toluene with isopropanol is given in Fig. 5.

#### 3.6.1. Selectivity of *p*-cymene

When the reaction of isopropylation of toluene was carried out in the presence of Al-MCM-41 (93), the conversion of toluene was  $70.3\%$ , while in the presence of Al-MCM-41 (104) it was only  $65.3\%$ . The selectivity of *p*-cymene for Al-MCM-41 (93) was found to be higher when compared to Al-MCM-41 (104).

Table 2  
Thermogravimetric results (in air) for the Al-MCM-41 (93) and Al-MCM-41 (104)

Samples (Si/Al ratio)	Weight loss (wt.%)			
	Total	50–150 °C	150–350 °C	350–550 °C
Al-MCM-41 (Si/Al = 93)	41.910	3.100	33.21	5.6
Al-MCM-41 (Si/Al = 104)	45.400	4.500	34.60	6.3

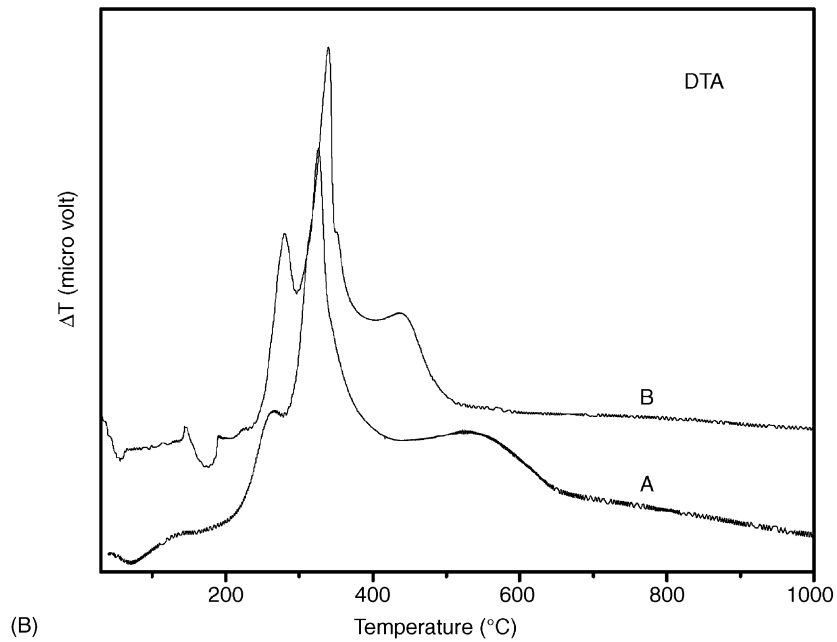
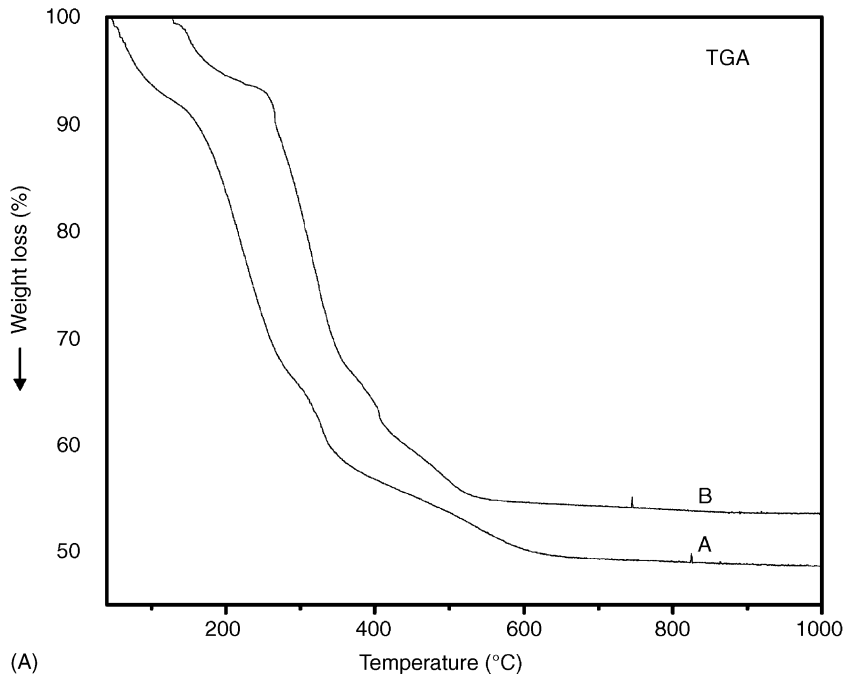


Fig. 4. TG-DTA curves of as-synthesized (A) Al-MCM-41 (93) and (B) Al-MCM-41 (104).



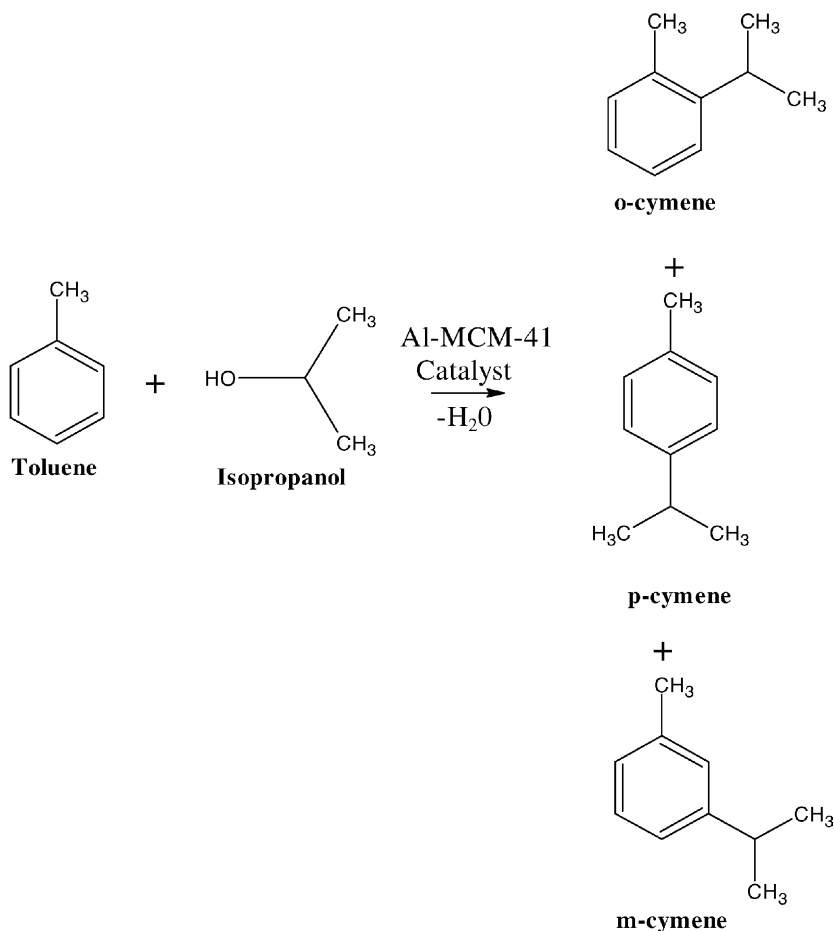


Fig. 5. Reaction of isopropylation of toluene.

The high selectivity of *p*-cymene may be due to the smaller steric hindrance of the methyl group at the *para* position, which is favored from shape selectivity point of view [1]. The higher selectivity of *p*-cymene with Al-MCM-41 (93) than with Al-MCM-41 (104) may be attributed to the higher pore size of Al-MCM-41 (93). This also indicates that the number of Bronsted acid sites in Al-MCM-41 (93) is higher than in Al-MCM-41 (104) [21].

### 3.6.2. Variation with reaction temperature

Vapor phase isopropylation of toluene over Al-MCM-41 (93) and Al-MCM-41 (104) at various reaction temperatures was carried out and the results are presented in Table 3. It may be noted that for both

the catalysts Al-MCM-41 (93) and Al-MCM-41 (104) at 275 °C reaction temperature after 2 h on stream, the toluene conversion was 70.3 and 65.3%, respectively, and the selectivity of *p*-cymene was 75.3 and 71.2%, respectively (Fig. 6). At higher reaction temperature the toluene conversion for both the catalysts was found to decrease. This may be due to deisopropylation and formation of carbocation, which is required for the reaction.

### 3.6.3. Variation with WHSV

Isopropylation of toluene was carried out at 0.25–1.25 h<sup>-1</sup> WHSV for Al-MCM-41 (93) and Al-MCM-41 (104) catalysts at 275 °C. The results of variation of percent conversion with different



Table 3  
Isopropylation of toluene: variation with reaction temperature<sup>a</sup>

Catalysts	Reaction temperature (°C)	TOS (h)	Conversion of toluene (wt.%)	Liquid product selectivity (%)			
				<i>p</i> -Cymene	<i>o</i> -Cymene	<i>m</i> -Cymene	Others
Al-MCM-41 (93)	225	2	48.3	53.1	23.1	23.6	0.2
	250	2	53.0	73.0	23.8	2.7	0.5
	275	2	70.3	75.3	24.0	0.7	–
	300	2	42.1	59.6	30.1	4.5	5.8
	325	2	30.2	48.7	35.0	8.3	8.0
Al-MCM-41 (104)	225	2	35.3	46.1	27.8	25.8	0.3
	250	2	48.1	68.3	28.3	2.7	0.7
	275	2	65.3	71.2	28.4	0.4	–
	300	2	38.1	57.3	35.3	1.4	6.0
	325	2	20.8	44.3	38.3	7.4	10.0

<sup>a</sup> Reaction conditions: TOS, time on stream; WHSV, 0.5 h<sup>-1</sup>; feed composition, 1 mol isopropanol:2 mol toluene.

WHSV are presented for Al-MCM-41 (93) and Al-MCM-41 (104) in Table 4 (Fig. 7). The best WHSV value for this reaction was at 0.5 h<sup>-1</sup>. After 0.5 h<sup>-1</sup> as the WHSV value further increased, the percentage conversion of toluene decreased. This may be due to the deactivation of the catalyst by coking.

#### 3.6.4. Variation with isopropanol:toluene ratio

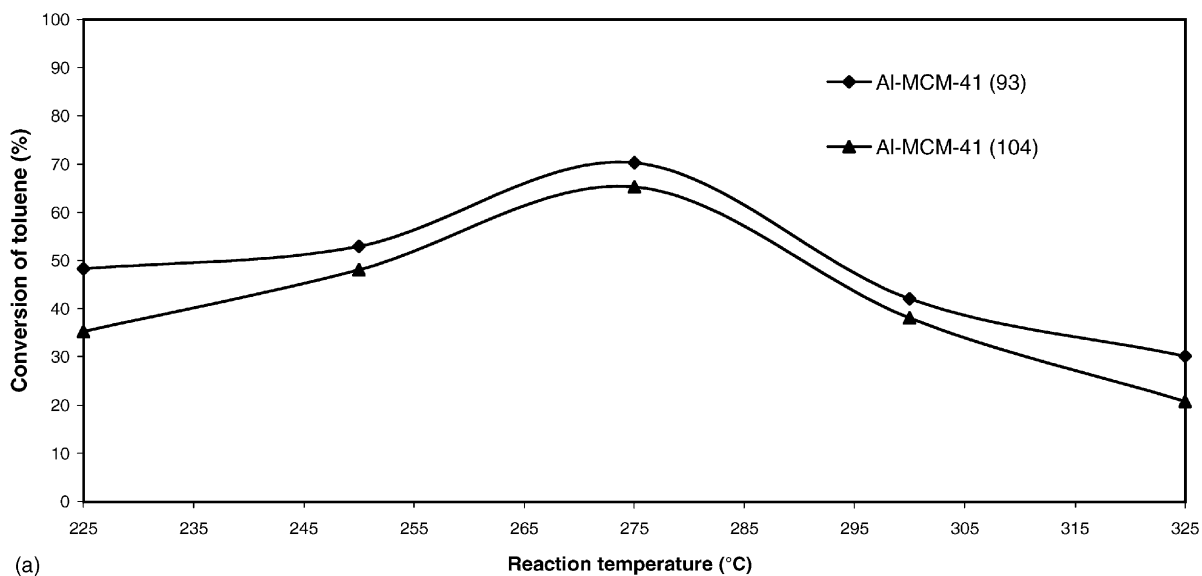
Table 5 summarizes the results of isopropylation reaction carried out with various isopropanol:toluene ratios. In all the cases, *p*-cymene was obtained as the major product along with small amounts of *o*-cymene

and *m*-cymene products. In addition, trace amount of other alkylated products was also observed. It is observed that at reaction temperature of 275 °C on stream at 2 h and at WHSV of 0.5 h<sup>-1</sup>, the highest conversions of toluene and selectivity of *p*-cymene were obtained at isopropanol:toluene ratio of 1:2 as can be seen in Fig. 8a and b, respectively. As the molar ratio of toluene is increased, the percentage conversion of toluene decreased and as the molar ratio of isopropanol is increased the percentage conversion of toluene decreased. This may be due to coking of the catalyst. Hence the optimal molar ratio of isopropanol:toluene is 1:2 at 275 °C reaction temperature.

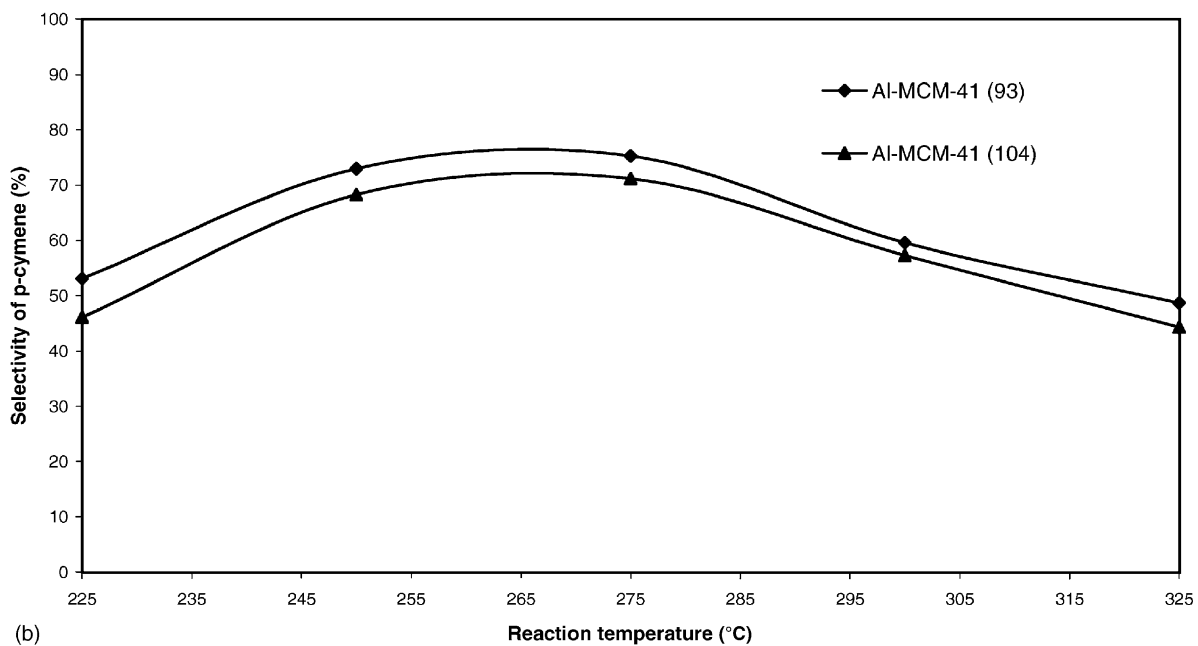
Table 4  
Isopropylation of toluene: variation with WHSV<sup>a</sup>

Catalysts	WHSV (h <sup>-1</sup> )	TOS (h)	Conversion (wt.%)	Liquid product selectivity (%)			
				<i>p</i> -Cymene	<i>o</i> -Cymene	<i>m</i> -Cymene	Others
Al-MCM-41 (93)	0.25	2	60.4	46.1	31.7	10.10	12.00
	0.50	2	70.3	75.3	24.0	0.70	–
	0.75	2	56.0	54.4	24.6	10.50	10.50
	1.00	2	39.9	51.5	28.6	8.60	11.30
	1.25	2	35.9	49.8	29.2	12.50	8.50
Al-MCM-41 (104)	0.25	2	56.4	40.7	28.9	11.7	18.7
	0.50	2	65.3	71.2	28.4	0.4	–
	0.75	2	44.3	50.5	24.4	16.1	9.0
	1.00	2	38.1	48.4	23.1	8.5	20.0
	1.25	2	21.9	42.8	25.3	14.9	17.0

<sup>a</sup> Reaction conditions: TOS, time on stream; reaction temperature, 275 °C; feed composition, 1 mol isopropanol:2 mol toluene.



(a)



(b)

Fig. 6. (a) Variation of percent conversion of toluene with reaction temperature; (b) variation of selectivity of *p*-cymene (%) with reaction temperature.

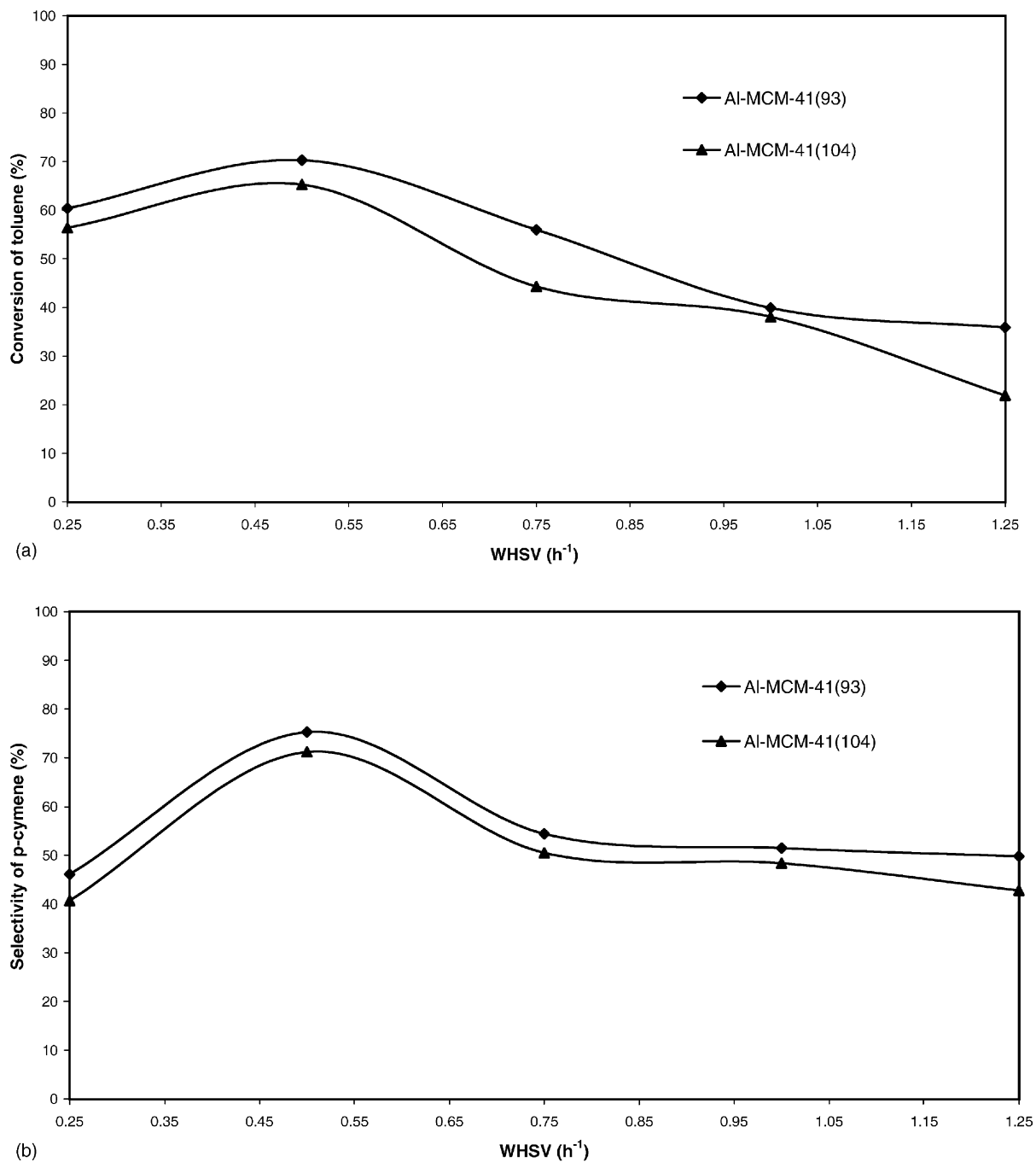


Fig. 7. (a) Variation of percent conversion of toluene with WHSV; (b) variation of selectivity of *p*-cymene (%) with WHSV.

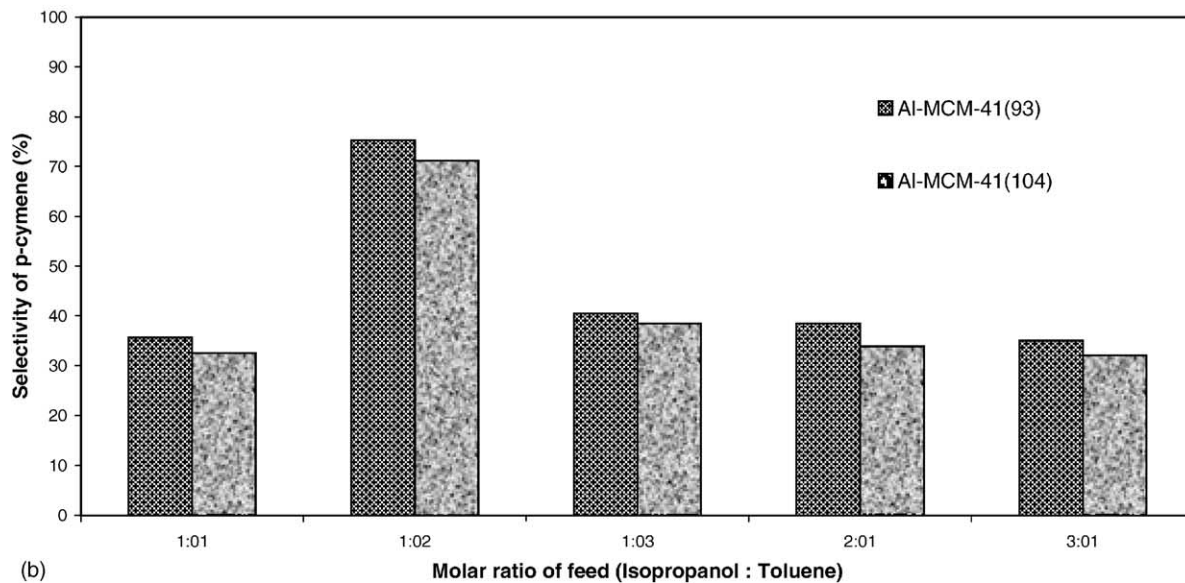
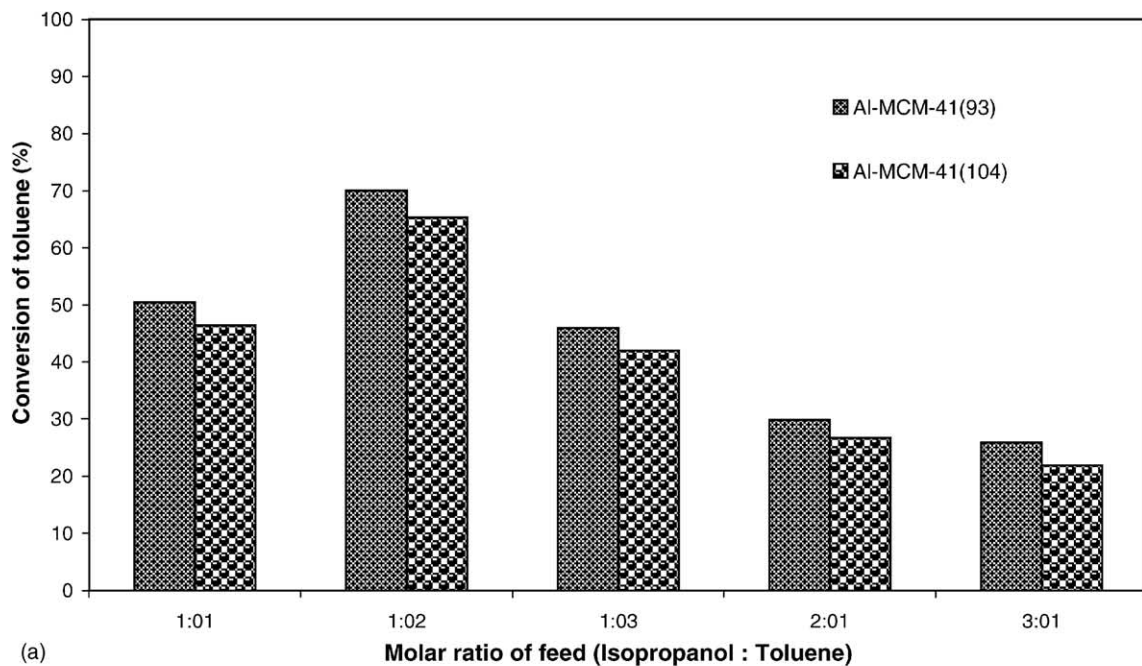


Fig. 8. (a) Variation of percent conversion of toluene with molar ratio of feed (isopropanol:toluene); (b) variation of selectivity of *p*-cymene (%) with molar ratio of feed (isopropanol:toluene).

Table 5

Isopropylation of toluene: variation with molar ratio of feed<sup>a</sup>

Catalysts	Feed molar ratio (isopropanol:toluene)	TOS (h)	Conversion (wt.%)	Liquid product selectivity (%)			
				<i>p</i> -Cymene	<i>o</i> -Cymene	<i>m</i> -Cymene	Others
Al-MCM-41 (93)	1:1	2	50.4	35.7	28.7	8.1	27.5
	1:2	2	70.0	75.3	24.0	0.7	–
	1:3	2	46.0	40.5	25.7	10.5	23.3
	2:1	2	29.9	38.5	25.6	9.5	26.4
	3:1	2	25.9	35.1	26.1	18.5	20.4
Al-MCM-41 (104)	1:1	2	46.4	32.6	25.7	6.3	35.4
	1:2	2	65.3	71.2	28.4	0.4	–
	1:3	2	42.0	38.5	23.1	8.1	30.3
	2:1	2	26.7	33.9	24.7	7.3	34.1
	3:1	2	21.9	32.1	23.9	16.9	27.1

<sup>a</sup> Reaction conditions: TOS, time on stream; reaction temperature, 275 °C; WHSV, 0.5 h<sup>-1</sup>.

#### 4. Conclusions

Mesoporous aluminosilicate molecular sieves Al-MCM-41 with Si/Al = 93 and 104 were synthesized by using sodium metasilicate and Al-isopropoxide as the reagents in sulfuric acid medium and cetyltrimethylammonium bromide as the template. From the physicochemical characterization of the materials it was concluded that both the synthesized catalysts have good Al–O–Si framework, good thermal stability and high surface area. It could be inferred that at molar ratio of 1:2 of isopropanol:toluene, at 275 °C reaction temperature and at 0.5 h<sup>-1</sup> WHSV, there was high selectivity of *p*-cymene (75.3) for Al-MCM-41 (93), though the toluene conversion was only about 70.3%.

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