Journal of Catalysis **210,** 367–374 (2002)
doi:10.1006/jcat.2002.3709

Isopropylation of *m*-Cresol over Mesoporous Al–MCM-41 Molecular Sieves

V. Umamaheswari, M. Palanichamy, and V. Murugesan[1]

Department of Chemistry, Anna University, Chennai-25, India

Received February 19, 2002; revised May 21, 2002; accepted June 4, 2002

Isopropylation of *m*-cresol with isopropyl alcohol was studied using Al–MCM-41 molecular sieves with Si/Al ratios of 59, 103, and 202 at temperature between 250 and 400°C. The products obtained were 2-isopropyl-5-methylphenol (IMP), isopropyl-3-methylphenyl ether (IMPE), and isopropyl-(2-isopropyl-5-methylphenyl) ether (IIMPE). The *m*-cresol conversion increased till 300°C, after which it decreased. The selectivity of 2-isopropyl-5-methylphenol (IMP) was found to be more than that of the other products.

Key Words: **alkylation; *m*-cresol; isopropyl alcohol; Al–MCM-41.**

INTRODUCTION

Alkylation of phenol is an industrially important reaction because many alkylphenols have been used in the manufacture of drugs, pharmaceuticals, dye stuffs, pesticides, paints, and plastics (1). Isopropylation of phenol with ispropyl alcohol over β and Y zeolites was studied by Balasubramanian *et al.* (2). Among the several isopropylation products of methyl phenols, the *m*-cresol-derived 2-isopropyl-5-methylphenol (thymol) is the most important because it is a precursor of menthol (3). Menthol has been used in the manufacture of antiseptic agents, local anesthetics, antibacterial agents, antifungicidal agents, flavors, fragrances, cooling agents, and preservatives (4). Catalysts such as γ-Al_2O_3, aluminium phenolate, and aqueous zinc chloride–hydrogen chloride solution have been used for the isopropylation of *m*-cresol in the liquid phase (5, 6). A small-pore zeolite (erionite), a medium-pore zeolite (ZSM-5), and a large-pore zeolite (mordenite) have been used for such reactions in the gas phase (1). Finely ground synthetic silica–alumina and large-pore Y-type catalysts have been shown to yield 5-isopropyl-3-methylphenol (isothymol) through isomerization and transalkylation activities (7). There are problems due to the formation of undesired alkylates of *m*-cresol in the above-mentioned processes. Mesoporous Al–MCM-41 molecular sieves have become the material of widespread use in recent years in many reactions of industrial importance. In the present investigation, isopropylation of *m*-cresol with isopropanol over Al–MCM-41 materials with $Si/Al = 59, 103$, and 202 was studied. As these materials have very-well-scattered Brønsted acid sites and large-pore diameters with less diffusional constraints, they are expected to discourage consecutive alkylations and deactivation of the catalyst by coke deposition. In addition, unlike microporous zeolites, where simultaneous diffusion of many molecules is prevented, these materials, in contrast, allow simultaneous entry of many reactant molecules into their pores, thereby permitting high conversion.

EXPERIMENTAL

Materials

Al–MCM-41 molecular sieves were prepared according to the following procedure. Sodium silicate (Merck) and aluminium sulfate (Merck) were used as the sources for silicon and aluminum, respectively, with cetyltrimethylammonium bromide (Merck) as the structure-directing template. The mesoporous materials were crystallized by autoclaving the gel of composition, $SiO_2 : x\ Al_2O_3 : 0.2\ CTAB : 0.89\ H_2SO_4 : 120\ H_2O$ (x varies with Si/Al ratio). In a typical synthesis, 10.6 g of sodium silicate nanohydrate in water was combined with an appropriate amount of aluminum sulfate (0.3332, 0.1666, and 0.0833 g for Si/Al gel ratios 50, 100, and 200, respectively) in distilled water and the pH of the solution was adjusted to 10.5 using 1 M sulfuric acid with constant stirring to form a gel. After 15 min, an aqueous solution of CTAB, prepared by dissolving 6.78 g of CTAB, was added to it for 30 min. The resulting mixture was then stirred for 1 h at room temperature. The mixture was then autoclaved and heated for 12 h at 170°C. The solid obtained was filtered and dried at 80°C for 8 h. The sample was then calcined at 550°C in air for 5 h to expel the imprisoned template.

Characterization

The XRD of all the samples were recorded in a Stereoscan diffractometer using nickel-filtered Cu$K\alpha$ radiation and a liquid nitrogen-cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range of 1–40° in steps of 0.02° with a count time of 15 s at each

---

[1] To whom correspondence should be addressed. Fax: 91-44-2200660. E-mail: v_murugu@hotmail.com.

point. Midinfrared spectra of the mesoporous Al–MCM-41 molecular sieves were recorded on a Nicolet (Avatar 360) instrument using KBr pellet technique. About 10 mg of the sample was ground with around 200 mg of spectral-grade KBr to form a mixture which was then made into a pellet using a hydraulic press. This pellet was used to record the infrared spectra in the range 4000–400 cm^{-1}.

Surface area, pore volume, and pore size distribution were measured by nitrogen adsorption at 77 K with an ASAP-2010 porosimeter from Micromeritics Corporation (Norcross, GA). The samples were degassed at 623 K at 10^{-5} torr overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5 by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distributions were estimated using the Barrett, Joyner, Halenda (BJH) algorithm (ASAP 2010 built-in software from Micromeritics). The chemical analysis was performed with an ICP–AES (inductively coupled plasma–atomic emission spectroscopy) Labtum Plasma 8440 instrument.

^{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 and processed with a line broadening of 50 Hz. The chemical shifts were reported with reference to trimethylsilylpropane sulfonic acid (TSP). Solid-state ^{27}Al MAS–NMR measurements were performed on a MSL 400 spectrometer equipped with a magic-angle spinning (MAS) unit. The ^{27}Al MAS–NMR spectra were recorded at a frequency of 104.22 MHz, a spinning rate of 8 KHz with a pulse length of 1.0 μs, a 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 liquid solution of aluminium nitrate.

The acidity of the samples was estimated by infrared spectroscopy using pyridine as probe. The infrared spectra of the samples were recorded at room temperature in a Nicolet 710 instrument using self-supported wafers of 10 mg/cm^2. The calcined samples were outgassed for 8 h at 500°C and 10^{-6} torr. The temperature of the samples was brought down to 30°C and pyridine was then admitted into the cell until complete saturation was ensured. After saturation the samples were outgassed at 423, 520, and 625 K 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 Brønsted and Lewis acid site adsorbed pyridine.

Catalytic Measurements

The reaction was carried out in a fixed-bed, vertical-flow-type reactor made up of a borosil glass tube 40 cm in length and 2 cm in internal diameter. About 0.5 g of particle size ranging from 0.11 to 0.25 mm of the catalyst was placed in the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. The reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. Reactants were fed into the reactor using a syringe infusion pump. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products obtained in the first 10 min were discarded and the product collected after 1 h was analyzed for identification. After each catalytic run the catalyst was regenerated by passing moisture- and carbon dioxide-free air through the reactor for 6 h at 550°C. The liquid products were analyzed using a Hewlett–Packard gas chromatograph 5890 A fitted with a flame ionization detector (FID) and OV 17 column.

RESULTS AND DISCUSSION

Characterization

The XRD powder diffraction patterns of the calcined mesoporous Al–MCM-41 (Si/Al ratios 59, 103, and 202) molecular sieves are shown in the Fig. 1. As displayed in the figure, calcined samples exhibit an intense signal at about 1.8° due to [100] plane and weak signals between 2 and 4° (2θ) due to [110], [200], and [210] planes. These peaks confirm the hexagonal mesophase of the material. The d_{100} spacing and lattice parameter (a_0) calculated as

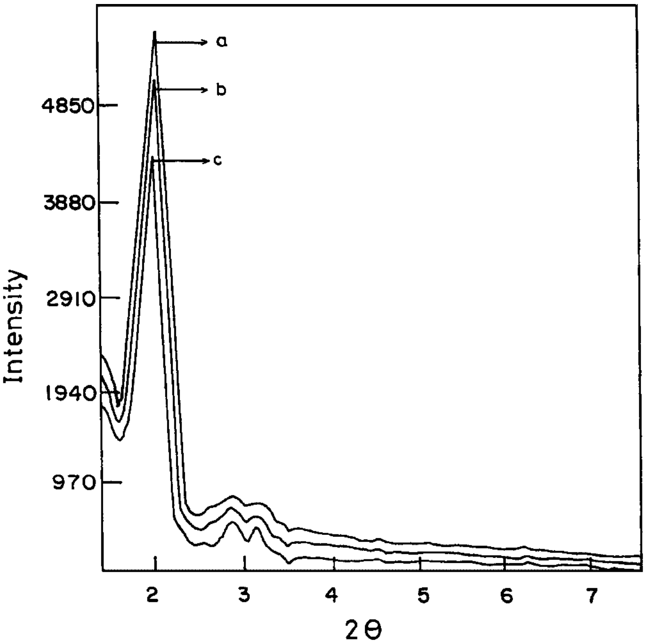


FIG. 1. XRD patterns of calcined mesoporous Al–MCM-41 molecular sieves. (a) Si/Al = 59, (b) Si/Al = 103, and (c) Si/Al = 202.

TABLE 1

XRD d_{100} Spacing and Lattice Parameter a_0

Catalysts	d_{100} (Å)	a_0 (Å)
Al–MCM-41 (59)	37.48	43.27
Al–MCM-41 (103)	39.71	45.85
Al–MCM-41 (202)	47.97	55.39

TABLE 2

Characteristics of Calcined Mesoporous Al–MCM-41 Molecular Sieves

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
Al–MCM-41 (59)	895	0.71	2.41
Al–MCM-41 (103)	904	0.89	3.18
Al–MCM-41 (202)	923	0.91	3.16

per the literature procedure are presented in Table 1. The calcined materials possess well-defined pore structure due to condensation of Si–OH groups. These XRD patterns coincide with the data already reported in the literature for mesoporous aluminosilicate molecular sieves (8–10).

The infrared spectra of the as-synthesised and calcined Al–MCM-41 (Si/Al = 59, 103, and 202) molecular sieves are presented in Figs. 2A and 2B, respectively. 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 (Fig. 2A) of the as-synthesized samples just below 3000 cm^{-1} which

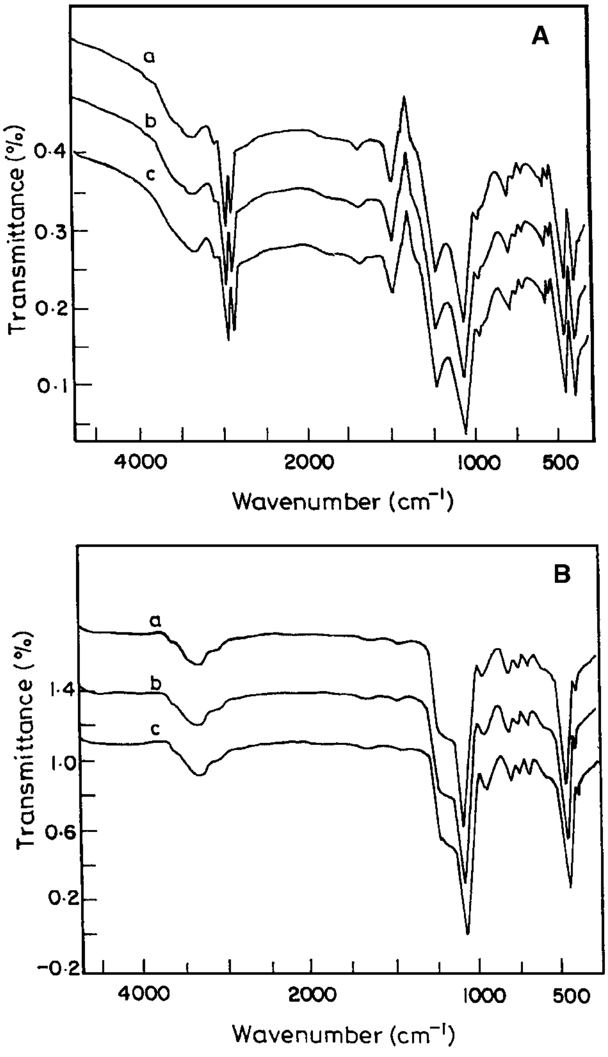


FIG. 2. FTIR spectra of mesoporous Al–MCM-41 molecular sieves. (A) As-synthesised; (B) calcined. (a) Si/Al = 59, (b) Si/Al = 103, and (c) Si/Al = 202.

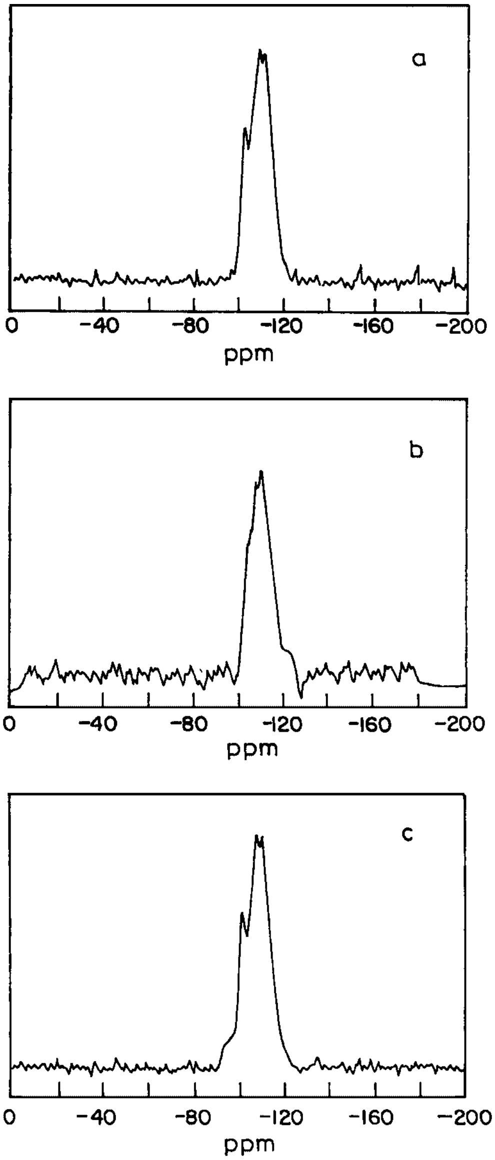


FIG. 3. ^{29}Si MAS–NMR spectra of calcined mesoporous Al–MCM-41 molecular sieves. (a) Si/Al = 59, (b) Si/Al = 103, and (c) Si/Al = 202.

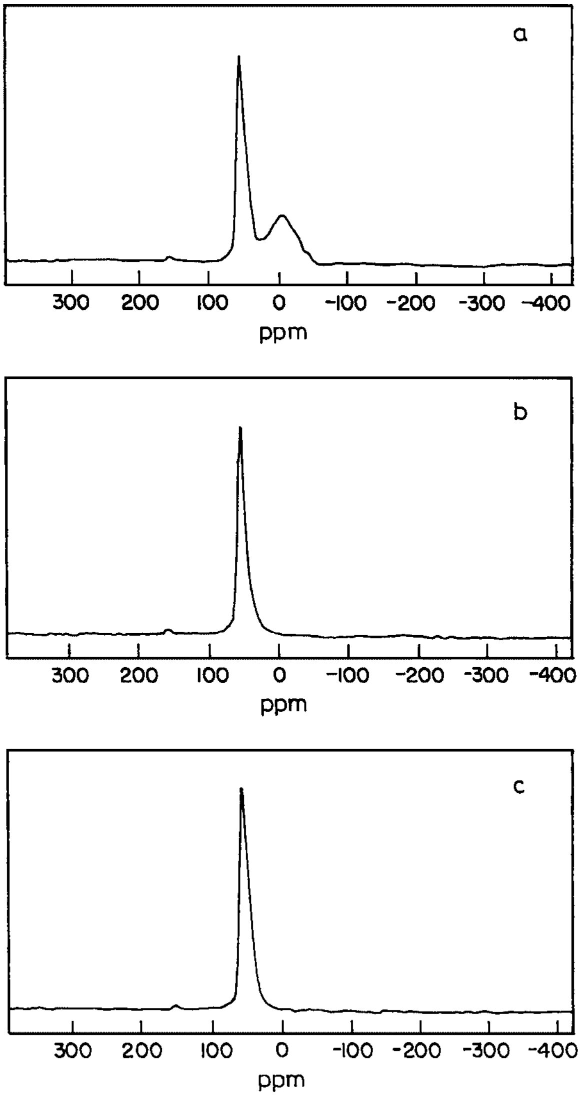


FIG. 4. ^{27}Al MAS–NMR spectra of calcined mesoporous Al–MCM-41 molecular sieves. (a) Si/Al = 59, (b) Si/Al = 103, and (c) Si/Al = 202.

TABLE 3

Si/Al Ratios from ICP–AES Analysis for Mesoporous Molecular Sieves

Catalyst	Si/Al (gel ratio)	Si/Al (ICP)
Al–MCM-41 (59)	50	59
Al–MCM-41 (103)	100	103
Al–MCM-41 (202)	200	202

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 peaks around 1232 and 1081 cm^{-1} are attributed to the asymmetric stretching of T–O–T groups. The symmetric stretching modes of T–O–T groups are observed around 800 and 544 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 the –CH_2 group of the template are absent in the spectra of calcined samples (Fig. 2B). These spectral features resemble those reported by previous workers (8, 10).

BET surface area, pore volume, and pore diameter (BJH method) for calcined materials are presented in Table 2. The surface area and pore volume of the calcined materials are smaller than the already-reported values. The smaller surface area of these materials may be due to their high wall thickness. Though the synthesis procedure is the same for all the materials, the materials cannot be expected to have the same wall thickness at all times.

The ^{29}Si MAS–NMR spectra of the calcined Al–MCM-41 materials are shown in Fig. 3. The spectra show a broad signal at −111 ppm and shoulders from −103 to −108 ppm. The signal at −111 ppm can be assigned to Si(OSi). The shoulders in the range between −103 and −108 ppm in the present case is due to Si(OAl). These spectral features coincide well with those reported by the previous workers (9, 12, 14). The ^{27}Al MAS–NMR spectra of the samples are shown in Fig. 4. The peak around 54.3 ppm can be attributed to the presence of aluminium in tetrahedral coordination (9, 10). The ^{27}Al MAS–NMR of the calcined Al–MCM-41 (59) shows a less intense peak at 0 ppm. This peak is due to the extraframework aluminium species in octahedral coordination and it is expected to arise out of framework dealumination during calcination (14).

The Si/Al ratios of the calcined materials determined using ICP–AES (inductively coupled plasma–atomic emission spectroscopy) analysis are given in Table 3. The Si/Al ratios of the gel are found to be comparable to that obtained by ICP analysis, but for the sample with Si/Al = 59 large deviation from the gel ratio was observed. It may be due to the lower intake of metal ions in the framework. The acidity of the calcined materials was measured by IR spectroscopy using pyridine as probe. The acidity was calculated using the extinction coefficients of the bands of Brønsted and Lewis acid site adsorbed pyridine (15) and the results are presented in Table 4. The samples are found to possess both Brønsted and Lewis acidity. The presence of both the

TABLE 4

Brønsted and Lewis Acidity Values for Mesoporous Molecular Sieves

	425 K		520 K		625 K	
Catalyst	B.A.[a]	L.A.[a]	B.A.[a]	L.A.[a]	B.A.[a]	L.A.[a]
Al–MCM-41 (59)	6.9	9.8	3.1	7.3	0	5.1
Al–MCM-41 (103)	3.5	5.1	1.7	4.1	0	2.5
Al–MCM-41 (202)	1.7	2.4	0.8	2.1	0	1.2

[a] Acidity (μmol py/g catalyst).

acidities in Al–MCM-41 was also reported by Corma *et al.* (16) and Climent *et al.* (17).

Catalytic Reaction

Isopropylation of *m*-cresol with isopropyl alcohol was studied over Al–MCM-41 (59) at 250, 275, 300, 325, 350, 375, and 400°C. The reactants feed ratio (*m*-cresol to isopropyl alcohol) was maintained at 1 : 1 and WHSV was 1.4 h^{-1}. The products are 2-isopropyl-5-methylphenol (IMP), isopropyl-3-methylphenyl ether (IMPE), and isopropyl-(2-isopropyl-5-methylphenyl) ether (IIMPE). *m*-Cresol conversion and selectivity of the products at various temperature are presented in Table 5. The percentage conversion decreases insignificantly with an increase in temperature above 300°C but at 250°C less conversion is observed. The selectivity to IMP is 100% at and above 300°C. The observation of O-alkylation below 300°C and its complete absence above 300°C retaining nearly the same conversion is an important observation in this study. The IMPE selectivity is higher than that of IIMPE, as there is more free *m*-cresol content than IMP in the vapor phase to react with isopropyl cations adsorbed on the surface. Finally the slow decrease in conversion with the increase in temperature could be attributed to the scattered distribution of acid sites of the catalyst that avoids multialkylation leading to coke formation. The large pore diameter of the catalyst also facilitates rapid diffusion of the reactants and products and thereby prevents coke formation.

The lower conversion with Al–MCM-41 (59) may be due to preferential adsorption of *m*-cresol over alcohol on the Brønsted acid sites. Again, at low feed ratio (1 : 1), more alcohol will remain only in the vapor phase. Hence, in order to increase the adsorption of alcohol and consequently increase the *m*-cresol conversion, the feed ratio is increased to 1 : 2. The results are presented in Table 6. As illustrated in the Scheme 1, an isopropyl cation, remaining as the charge-compensating cation reacts with *m*-cresol in the vapor phase to yield IMPE and IMP. The IMP in turn reacts with one more isopropyl cation during its diffusion through the channel to yield IIMPE. The conversion is found to be maximum at 300 and 325°C for WHSV of 1.68 h^{-1}. But 100%

TABLE 5

Influence of Temperature on the Isopropylation of *m*-Cresol with Isopropyl Alcohol

Temperature (°C)	*m*-Cresol conversion (%)	Selectivity of products (%)		
		IMP	IMPE	IIMPE
250	28.1	100.0	—	—
275	35.2	65.3	28.4	6.2
300	36.8	100.0	—	—
325	35.5	100.0	—	—
350	34.7	100.0	—	—
375	34.2	100.0	—	—
400	31.5	100.0	—	—

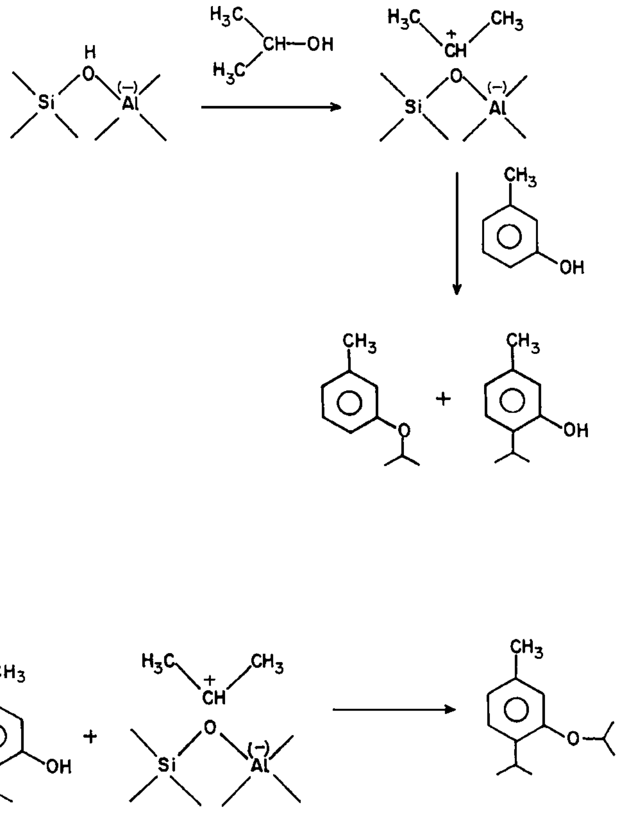
Note. Al–MCM-41 (59). *m*-Cresol: isopropyl alcohol (molar ratio) = 1 : 1. WHSV = 1.4 h^{-1}.

TABLE 6

Influence of WHSV on Isopropylation of *m*-Cresol with Isopropyl Alcohol

WHSV (h^{-1})	Temperature (°C)	*m*-Cresol conversion (%)	Selectivity of products (%)		
			IMP	IMPE	IIMPE
1.68	250	36.5	54.8	25.5	19.7
	275	43.1	59.4	26.2	14.4
	300	45.8	61.5	25.7	12.6
	325	45.5	100.0	—	—
	350	35.8	100.0	—	—
	375	35.4	100.0	—	—
	400	34.5	100.0	—	—
2.8	250	32.2	64.3	27.3	2.7
	275	36.9	58.5	28.2	13.3
	300	40.8	66.7	22.3	11.0
	325	29.8	100.0	—	—
	350	28.7	100.0	—	—
	375	26.0	100.0	—	—
	400	24.2	100.0	—	—

Note. Al–MCM-41 (59). *m*-Cresol : isopropyl alcohol (molar ratio) = 1 : 2.



SCHEME 1

TABLE 7

Influence of Molar Ratio of the Reactants on the Isopropylation of *m*-Cresol with Isopropyl Alcohol

Molar ratio	WHSV (h^{-1})	*m*-Cresol conversion (%)	Selectivity of products (%) IMP	IMPE	IIMPE
1 : 3	1.73	50.4	45.2	37.9	16.9
	2.89	40.2	54.7	32.1	13.2
	4.05	40.0	57.3	30.7	12.0
1 : 4	1.76	55.0	75.3	15.3	9.4
	2.94	46.8	61.8	25.2	13.0
	4.12	39.9	57.9	29.8	12.3

Note. Al–MCM-41 (59). Temperature = 300°C.

selectivity of IMP is observed only above 325°C. The formation of ether is retained even at 300°C for this feed ratio. The observed decrease in selectivity of IMPE is due to an increase in the IMP content in the vapor phase, as revealed by the increase in the selectivity of IIMPE. The appearance of ether products at 300°C with the feed ratio of 1 : 2 may be due to the availability of more isopropyl cations and the requirement of higher temperature for the reaction of isopropyl cation with *m*-cresol or IMP in the vapor phase.

The influence of WHSV was examined at 1.68 and 2.8 h^{-1} at 300°C. The results are presented in Table 7. Independent of the molar ratio of the reactants, the conversion is found to decrease with an increase in WHSV, but the selectivity of IMP is slightly less for the molar ratio 1 : 3. It has been observed that an increase in feed ratio increases the conversion of *m*-cresol, as shown in the Tables 5–8. The conversion increases from 36.8 to 55% at 300°C due to the molar ratio change from 1 : 1 to 1 : 4. At the same time 100% selectivity to IMP is observed only with molar ratios of 1 : 1 and 1 : 2. As the molar ratio and WHSV increase, the selectivity of IMP decreases.

TABLE 8

Isopropylation of *m*-Cresol with Isopropyl Alcohol

Temperature (°C)	*m*-Cresol conversion (%)	Selectivity of products (%) IMP	IMPE	IIMPE
250	41.9	52.0	31.5	16.5
275	40.4	56.2	29.7	14.1
300	55.0	75.3	15.3	9.4
325	52.5	80.7	10.3	9.0
350	47.6	87.2	8.0	4.8
375	42.1	100.0	—	—
400	40.2	100.0	—	—

Note. Al–MCM-41 (59). *m*-Cresol : isopropyl alcohol (molar ratio) = 1 : 4. WHSV = 1.76 h^{-1}.

TABLE 9

Influence of Temperature on Isopropylation of *m*-Cresol with Isopropyl Alcohol

Temperature (°C)	*m*-Cresol conversion (%)	Selectivity of products (%) IMP	IMPE	IIMPE
250	24.9	51.8	48.2	—
275	30.4	100.0	—	—
300	34.7	100.0	—	—
325	34.1	100.0	—	—
350	31.0	100.0	—	—
375	29.4	100.0	—	—
400	26.0	100.0	—	—

Note. Al–MCM-41 (103). *m*-Cresol : isopropyl alcohol (molar ratio) = 1 : 1. WHSV = 1.4 h^{-1}.

As the feed ratio of 1 : 4 and WHSV of 1.76 h^{-1} resulted in higher conversion (55%), the study of influence of temperature on conversion and product selectivity was attempted under the above conditions, and the results are presented in Table 8. At 375°C, the conversion is only 42.1% with 100% selectivity. Comparing this result with that of 1 : 2, it is observed that 45.5% conversion is obtained with 100% selectivity to IMP even at 325°C, confirming the fact that a 1 : 2 molar ratio is advantageous and optimum. A similar study was extended to Al–MCM-41 (103) and this catalyst also exhibited 100% selectivity to IMP at the feed ratio 1 : 1 (Table 9), but the conversion slightly decreased. One would expect that the lower number of acid sites when going from Al–MCM-41 (59) to Al–MCM-41 (103) would confer less activity for the latter than the former. But the activity of the two catalysts remains almost the same, as shown by the data in the Table 9. This demonstrates that besides the number of acid sites, other factors may be the cause for such similar activities. Since the alkylating agent, isopropyl alcohol, is hydrophobic it is necessary to consider the role played by the hydrophilic and hydrophobic properties of the catalysts for adsorption of the two reactants. It could be claimed that Al–MCM-41 (103) is more hydrophobic than Al-MCM (59). Hence, it can adsorb more isopropyl alcohol than Al-MCM (59), thus giving more conversion of *m*-cresol, and bringing the conversion almost close to Al–MCM-41 (59). This trend is similar to hydrophilic and hydrophobic properties of molecular sieves in acetalyzation reaction, as described by Climent *et al.* (17).

When the molar ratio is increased to 1 : 2, although the conversion increases, the selectivity to IMP decreases (Table 10). The selectivity of IMP reached 100% only at 375°C with 30% conversion, which is a disadvantage with this catalyst. Hence an increase of WHSV (2.8 h^{-1}) for this feed ratio gave 100% selectivity of IMP at 325°C but the conversion reached only 27.8%. The studies at feed ratios of 1 : 3 and 1 : 4 for various WHSV at 300°C have been found to show results similar to that of Al–MCM-41 (59) (Table 11).

Though conversion is comparatively less, as expected, Al–MCM-41 (202) shows 100% selectivity to IMP in the

TABLE 10

Influence of WHSV on Isopropylation of *m*-Cresol with Isopropyl Alcohol

WHSV (h^{-1})	Temperature (°C)	*m*-Cresol conversion (%)	Selectivity of products (%) IMP	IMPE	IIMPE
1.68	250	38.7	51.4	29.2	19.4
	275	42.3	51.3	31.2	17.5
	300	45.8	54.1	30.6	15.3
	325	41.2	53.6	33.0	13.4
	350	33.2	62.3	37.7	—
	375	30.0	100.0	—	—
	400	21.4	100.0	—	—
2.8	250	34.2	56.1	31.9	12.0
	275	38.4	56.8	34.4	8.8
	300	40.2	58.5	32.3	9.2
	325	27.8	100.0	—	—
	350	26.0	100.0	—	—
	375	22.4	100.0	—	—
	400	19.7	100.0	—	—

Note. Al–MCM-41 (103). *m*-Cresol : isopropyl alcohol (molar ratio) = 1 : 2.

temperature range 250–400°C for a feed ratio of 1 : 1 (Table 12). An increase in feed ratio to 1 : 2 increases the conversion, but 100% selectivity to IMP could be obtained only at 375°C. When WHSV is increased from 1.68 to 2.80 h^{-1}, 100% selectivity of IMP is attained only at 400°C (Table 13). For the feed ratios 1 : 3 and 1 : 4, 100% selectivity to IMP could not be obtained even at higher temperatures (Table 14), since more isopropyl cations are available for reaction with *m*-cresol and IMP.

Several experiments were carried out and the effect of time on stream for all three catalysts at different temperatures was observed. It is noticed that the rate of deactivation is high at higher temperature. Time-on-stream studies were carried out with catalysts of different Si/Al ratios (59, 103, and 202). The rate of deactivation for the catalysts with different Si/Al ratio follows the order 59 > 103 > 202. The

TABLE 11

Influence of Molar Ratio on Isopropylation of *m*-Cresol with Isopropyl Alcohol

Molar ratio	WHSV (h^{-1})	*m*-Cresol conversion (%)	Selectivity of products (%) IMP	IMPE	IIMPE
1 : 3	1.73	47.3	48.4	38.3	13.3
	2.89	42.6	55.2	33.3	11.5
	4.05	34.5	65.5	23.2	11.3
1 : 4	1.76	50.9	76.2	13.4	10.4
	2.94	39.1	70.8	15.9	13.3
	4.12	34.6	67.1	17.9	15.0

Note. Al–MCM-41 (103). Temperature = 300°C.

TABLE 12

Influence of Temperature on Isopropylation of *m*-Cresol with Isopropyl Alcohol

Temperature (°C)	*m*-Cresol conversion (%)	Selectivity of products (%) IMP	IMPE	IIMPE
250	23.5	100	—	—
275	27.6	100	—	—
300	29.6	100	—	—
325	25.0	100	—	—
350	23.3	100	—	—
375	22.3	100	—	—
400	24.1	100	—	—

Note. Al–MCM-41 (202). *m*-Cresol : isopropyl alcohol (molar ratio) = 1 : 1. WHSV = 1.4 h^{-1}.

TABLE 13

Influence of WHSV on Isopropylation of *m*-Cresol with Isopropyl Alcohol

WHSV (h^{-1})	Temperature (°C)	*m*-Cresol conversion (%)	Selectivity of products (%) IMP	IMPE	IIMPE
1.68	250	34.1	56.3	31.9	11.8
	275	24.9	59.9	31.5	8.6
	300	40.2	54.7	32.1	13.2
	325	38.6	57.5	29.5	13.0
	350	35.0	60.0	40.0	—
	375	28.9	100.0	—	—
	400	21.7	100.0	—	—
2.8	250	24.6	37.8	45.9	16.3
	275	35.5	62.3	28.7	9.0
	300	40.3	58.6	34.5	6.9
	325	38.2	63.4	31.4	5.2
	350	34.5	67.5	32.5	—
	375	26.8	82.1	17.9	—
	400	18.3	100.0	—	—

Note. Al–MCM-41 (202). *m*-Cresol : isopropyl alcohol (molar ratio) = 1 : 2.

TABLE 14

Influence of Molar Ratio on Isopropylation of *m*-Cresol with Isopropyl Alcohol

Molar ratio	WHSV (h^{-1})	*m*-Cresol conversion (%)	Selectivity of products (%) IMP	IMPE	IIMPE
1 : 3	1.73	39.4	58.9	29.4	11.7
	2.89	34.2	65.8	21.0	13.2
	4.05	30.2	71.2	15.6	13.2
1 : 4	1.76	51.0	82.9	—	17.0
	2.94	38.3	87.7	—	12.3
	4.12	36.8	89.1	—	10.9

Note. Al–MCM-41 (202). Temperature = 300°C.

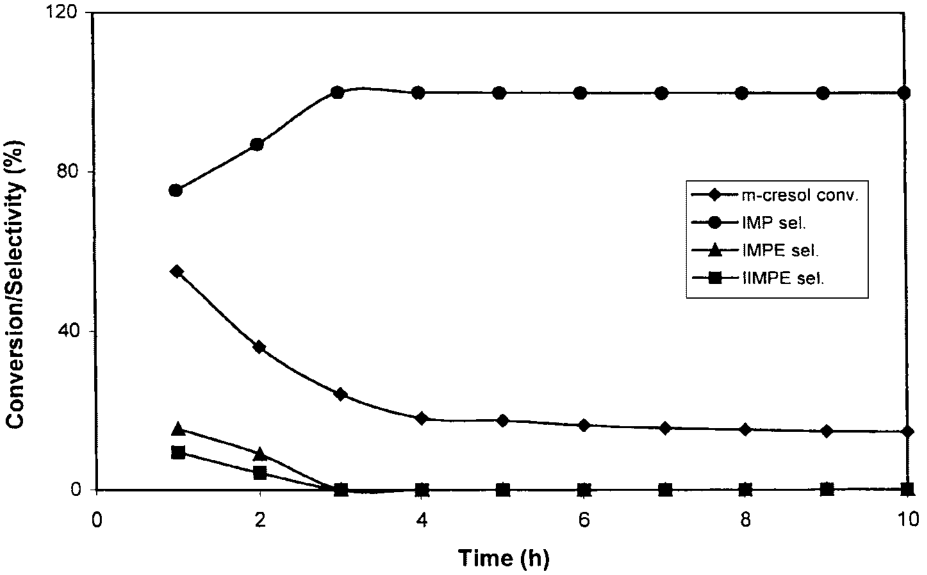


FIG. 5. Study of time on stream over Al–MCM-41 (59). Molar ratio = 1 : 4, temperature = 300°C, and WHSV = 1.76 h^{-1}.

catalyst with the lower Si/Al ratio deactivates faster because of the greater number of acid sites. The experimental results revealed that Al–MCM-41 (59) is found to be a more suitable catalyst than others for isopropylation of *m*-cresol, providing maximum conversion of 55% with 75.3% selectivity to IMP at a feed ratio of 1 : 4 at 300°C and a WHSV of 1.76 h^{-1}. Hence the influence of time on stream was studied over this catalyst at 300°C. The interest in selecting the feed ratio of 1 : 4 is based on the fact that with an increase in time, there could be a gradual increase in the blocking of Brønsted acid sites and hence ultimately fewer acid sites may be left for adsorption. As most of the cresols are left in the vapor state at this stage, the increase in stream facilitates 100% selectivity to IMP, as illustrated in Fig. 5. At this feed ratio, there is a sudden drop in conversion at the end of the third hour, after which conversion remained constant (around 14%) till the end of 10th hour. But the selectivity to IMP remained 100% throughout the stream. All three catalysts were recycled for three times in order to test their activity at 250°C for the title reaction. It was observed that there was no significant loss in activity of any of the three catalysts for this reaction.

CONCLUSION

Of the three catalysts studied for isopropylation of *m*-cresol with isopropyl alcohol in the vapor phase, Al–MCM-41 (59) is observed to be more suitable than Al–MCM-41 (103) and Al–MCM-41 (202). The feed ratio of 1 : 2 is found to be suitable for better conversion and 100% selectivity to IMP. The study of time on stream indicates the retention of activity even after 10 h with the feed ratio of 1 : 4 for nearly 10% conversion. It is concluded that Al–MCM-41 could be a convenient and ecofriendly alternative to the hazardous and highly corrosive mineral acid catalysts for isopropylation of *m*-cresol.

ACKNOWLEDGMENT

The authors express their sincere thanks to the generous financial support of the Department of Science and Technology (DST), Government of India, New Delhi, in the form of a funding project (SP/S1/H-23/96).

REFERENCES

1. Fiege, H., *in* "VLMANN Encyclopedia of Industrial Chemistry" (W. Gehartz, Ed.), pp. 324–332. VCH, Weinheim, 1987.
2. Balasubramanian, V. V., Umamaheswari, V., Palanichamy, M., and Murugesan, V., *in* "Recent Trends in Industrial Catalysis" (V. Murugesan, B. Arabindoo, and M. Palanichamy, Eds.), p. 331. Narosa Publications, New Delhi, 1998.
3. Leffingwell, J. C., and Shackelford, R. E., *Cosmetics Perfumery* **89**(6), 69 (1974).
4. Hopp, R., *Recent Adv. Tobacco Sci.* **19**, 46 (1993).
5. Nitta, M., *Bull. Chem. Soc. Jpn.* **47**, 2360 (1974).
6. Stroh, R., Seydel, R., and Hahn, W., *in* "Newer Methods of Preparative Organic Chemistry" (W. Forest, Ed.), Vol. 2, p. 337. Academic Press, New York, 1963.
7. Klein, A., and Wedemeyer, K., Bayer, DE-OS 2242628, 1972.
8. Chen, C. Y., Li, H. X., and Davis, M. E., *Microporous Mater.* **2**, 17 (1993).
9. Corma, A., *Microporous Mesoporous Mater.* **4**, 249 (1997).
10. Biz, S., and Occelli, M. L., *Catal. Rey.–Sci. Eng.* **40**(3), 329 (1998).
11. Storck, S., Bretinger, H., and Maiera, W. F., *Appl. Catal. A* **174**(1–2), 137 (1998).
12. Sun, Y., Yue, Y., and Gao, Z., *Appl. Catal. A* **161**, 121 (1997).
13. Biz, S., and White, M. G., *J. Phys. Chem. B* **103**, 8432 (1999).
14. Matsumoto, A., Chen, H., Tsutsumi, K., Grun, M., and Unger, K., *Microporous Mesoporous Mater.* **32**, 55 (1999).
15. Emeis, C. A., *J. Catal.* **141**, 347 (1993).
16. Corma, A., Grande, M. S., Gonzalez, A., and Orchilles, A. V., *J. Catal.* **159**, 375 (1996).
17. Climent, M. J., Corma, A., Iborra, S., Miquel, S., Primo, J., and Rey, F., *J. Catal.* **183**, 76 (1999).