

Vapour phase reaction of phenol with ethyl acetate over MCM-41 molecular sieves

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Abstract

The vapour phase reaction of phenol with ethyl acetate was investigated over Al-MCM-41 with Si/Al = 55 and 80, and (Al, Zn)-MCM-41 with Si/(Al + Zn) = 52 at 200, 250, 300, 350 and 400 °C. The products were phenyl acetate (PA), 2-ethylphenol (2-EP), 2-acetylphenol (2-AP) and 4-ethylphenol (4-EP). Phenol conversion increases by increasing temperature up to 350 °C and then decreases at 400 °C. There is no correlation between the acidity and activity of the catalysts. The low activity of (Al, Zn)-MCM-41(52) is due to its high hydrophilicity, which reduces the chemisorption of ethyl acetate on its surface. The low conversion of phenol at low ethyl acetate/phenol feed ratios is attributed to the preferential chemisorption of phenol on the catalyst surface. The decrease in conversion at higher temperature is due to blocking of active sites by coke. This study has revealed that ethyl acetate is an active alkylating reagent for phenol in the vapour phase.

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1. Introduction

Alkylation of phenol and its family members is a reaction of high commercial importance as the products are used in the synthesis of drugs, pharmaceuticals and dyestuffs [1]. Ethylation of phenol is an important reaction as monoethylphenols are used in the production of phenolic resins and in the varnish industry [2]. 2-Ethylphenol (2-EP) and 3-ethylphenol (3-EP) are the starting materials for photochemicals. 4-Ethylphenol (4-EP) is also a starting material for the production of 4-vinylphenol, an intermediate for pharmaceuticals and dyes and various anti-oxidants, which are used in rubber and polymers. Ethylation of phenol with ethanol was studied over Fe₂O₃ catalyst doped with silica and magnesium oxide in the gas phase at 360 °C. 2-EP (60%) and 2,6-diethylphenol (22%) were obtained as products [3]. Ethylation of phenol over Al₂O₃ in the gas phase at 300 °C yielded 2-ethylphenol

and 2,6-diethylphenol [4]. The same reaction showed a decrease in the *ortho*-selectivity and an increase in the yield of 3- and 4-ethylphenols with increasing temperature and contact time [5]. Tanabe and co-worker [6,7] reported that the silica–alumina with higher acid strength was more active but less selective to *ortho*-alkylation due to its amorphous nature. A mixture of isomers with a relatively high proportion of *meta*-product was obtained in the temperature range 400–450 °C [8]. Ethylation of phenol with ethylene in the gas phase was studied on phosphoric acid–SiO₂ catalyst at 420 °C. The products were mixture of isomers of ethylphenol, of which about 44% was 3-ethylphenol [9]. High selectivity to 4-EP (96% at 7% phenol conversion) was obtained when phenol was alkylated with ethylene and water vapour at 400 °C on H-ZSM-5 modified with tetramethoxysilane [10]. Pore size controlled ZSM-5 exhibited about 88% selectivity to *para*-ethylphenol [11]. But none of the above processes is commercialized. 4-EP and 2-EP are being produced industrially by sulphonation of the respective ethylbenzene and alkali fusion of the resulting ethylbenzene sulphonic

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acid, but the process is hazardous. Hence, there is scope for ethylation of phenol with an ecofriendly heterogeneous catalyst.

In our earlier study, alcohols were mainly used as alkylating agents in the alkylation of alkyl aromatics and phenols [12–14]. Recently we reported *iso*-propyl acetate as an active alkylating agent over Al-MCM-41 molecular sieves [15]. It is ascribed that ester adsorption is stronger than the alcohol on the Bronsted acid sites of the catalysts. In continuation of this work, we have investigated ethylation of phenol with ethyl acetate as alkylating agent in the gas phase over Al-MCM-41 molecular sieves. Santacesaria et al. [16,17] have reported competing O- and C-alkylation, the O/C ratio being found to be 2 for alumina, 5 for silica–alumina and 9 for Nafion–H and phosphoric acid at 498 K. But in our studies C-alkylation is observed to be predominant. These results clearly demonstrate that the activity of Al-MCM-41 which is different from either alumina or silica–alumina.

2. Experimental

2.1. Materials and methods

All the reagents, viz. sodium metasilicate, aluminium sulphate, zinc sulphate, cetyltrimethylammonium bromide (CTAB), sulphuric acid, ethyl acetate and phenol were purchased from Merck and used as such. Samples of Al-MCM-41 with Si/Al = 55 and 80 and (Al, Zn)-MCM-41 with Si/(Al + Zn) = 52 were synthesised hydrothermally using a gel composition of $\text{SiO}_2 : x\text{Al}_2\text{O}_3 : 0.2\text{CTAB} : 0.89\text{H}_2\text{SO}_4 : 120\text{H}_2\text{O}$ (x varies with Si/Al and Si/(Al + Zn) ratios). Sodium metasilicate in water was combined with an appropriate amount of zinc sulphate and/or aluminium sulphate in distilled water, and the pH of the solution was adjusted to 10.5 using 1 M sulphuric acid with constant stirring to form a gel. This gel was further homogenised by stirring the mixture for 1 h at room temperature. An aqueous solution of CTAB, prepared by dissolving 6.78 g of CTAB in appropriate amount of distilled water, was added slowly to the gel for a period of about 30 min. The resulting mixture was then stirred for 1 h at room temperature and autoclaved at 170 °C for about 12 h. After crystallization, Al-MCM-41 material was recovered by filtration, washed with distilled water, and dried at 80 °C for 8 h. Mesoporous (Al, Zn)-MCM-41 and Al-MCM-41 catalysts were obtained by removing the occluded surfactant, which filled in the pores, by calcining the samples at 550 °C in air for 6 h.

2.2. Physico-chemical characterisation

Al and Zn contents of (Al, Zn)-MCM-41 and Al content of Al-MCM-41 were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with the Labtam Plasma 8440 instrument. The powder X-ray diffraction patterns of all the samples were recorded with a Siemens

D5005 Stereoscan diffractometer using nickel-filtered Cu K α radiation and a liquid nitrogen-cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range of 0.8–10° in steps of 0.02° with a count time of 10 s at each point.

The acidity of the calcined materials was recorded on a Nicolet Avatar 360 FT-IR spectrophotometer equipped with a high temperature vacuum chamber. Approximately 10 mg of the sample was taken in the sample holder and dehydrated at 500 °C for 6 h under vacuum (10^{-5} mbar). The sample was then cooled and pyridine adsorbed at room temperature. The physically adsorbed pyridine was removed by heating the sample at 150 °C under vacuum (10^{-5} mbar) for 30 min, the removed material was cooled to room temperature, and the spectrum was recorded. The SEM pictures were recorded using a Leoscan scanning electron microscope.

The surface area, pore volume and pore size distribution of the materials were measured by nitrogen physisorption at 77 K using an ASAP-2010 (Norcross, GA, USA) volumetric adsorption analyzer. Before nitrogen adsorption–desorption measurements, the samples were degassed and the specific area of the samples were determined from the linear portion of the BET plots. The pore size distributions were calculated from the desorption branch of N₂ adsorption–desorption isotherms using the Barrett–Joyner–Halenda (BJH) algorithm (ASAP-2010 built-in software from Micromeritics).

²⁹Si MAS-NMR spectra were recorded on a DRX-500FT-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 sulphonic acid. Solid-state ²⁷Al MAS-NMR measurements were performed on a Bruker MSL 400 spectrometer equipped with a magic angle-spinning (MAS) unit. The ²⁷Al MAS-NMR spectra were recorded at a frequency of 104.22 MHz, 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. ²⁷Al MAS-NMR chemical shifts were reported in relation to the liquid solution of aluminium nitrate.

2.3. Catalytic performance — alkylation of phenol

Alkylation of phenol with ethyl acetate was carried out in a fixed-bed, vertical-flow type reactor made up of a glass tube of 40 cm in length and 2 cm in internal diameter. About 0.5 g of the catalyst was placed in the middle of the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. The glass reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller-cum indicator. The reactants were fed into the reactor using a syringe injection pump (sage instruments) that could be operated at

different flow rates. The reaction was carried out at atmospheric pressure. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products collected in the first 10 min were discarded, and the products collected after 1 h were analysed 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 500 °C.

The percent conversion of phenol was analysed on a gas chromatograph (Shimadzu GC-17A) with an FID detector equipped with a 25 m capillary column (cross-linked 5% phenylmethyl polysiloxane). The liquid products were analysed using a Perkin-Elmer Auto System XL gas chromatograph with a Turbo mass spectrometer with helium as carrier gas. As the percentage conversion of phenol was higher with Al-MCM-41(55), all other experiments pertaining to the evaluation of the performance of the catalyst were carried out only with Al-MCM-41(55).

3. Results and discussion

3.1. Characterisation

From ICP-AES analysis, the aluminium and zinc content in (Al, Zn)-MCM-41(52) were found to be 0.053 and 0.057 g, respectively. The aluminium contents in Al-MCM-41(55) and Al-MCM-41(80) were found to be 0.097 and 0.067 g, respectively. XRD powder diffraction patterns of as-synthesised and calcined Al-MCM-41 samples with Si/Al ratios 55 and 80 and (Al, Zn)-MCM-41 with Si/(Al + Zn) ratio 52 are shown in Fig. 1. These XRD patterns coincide with data already reported in the literature [18,19]. The XRD patterns, taken before and after calcination, confirmed the hexagonal phase in the sample. After calcinations, the intense peak was

shifted to higher 2θ value due to pore size contraction. The physical properties of these mesoporous materials are summarized in Table 1. Under the synthesis conditions used, the crystallization reaction was non-stoichiometric and a higher Si/Al ratio was noticed in the crystal [20].

Specific surface area, specific pore volume and pore diameter (BJH method) for the calcined materials are presented in Table 1. The isotherms of nitrogen adsorption for the calcined materials show well-defined stages and they coincide with those already reported in the literature [21]. It is evident from these isotherms (Fig. 2) that high mesostructural ordering and narrow pore size distribution are attained. The surface area of the catalysts decreases in the order Al-MCM-41(80) > Al-MCM-41(55) > (Al, Zn)-MCM-41(52). The pore volume also decreases in the same order due to the presence of textural mesoporosity [22]. The SEM photographs reveal the presence of highly ordered hexagonal crystals of mesoporous molecular sieves (Fig. 3a–c). The pictures also show the orderly growth of pure hexagonal phase with well-defined sides.

The ^{29}Si MAS-NMR spectra of the calcined Al-MCM-41 materials are shown in Fig. 4. The partly resolved signal at –92 ppm is assigned to Q_2 species. This signal is less intense for Al-MCM-41(80) and more intense for Al-MCM-41(55) and (Al, Zn)-MCM-41(52). The other signals appear at –101 (Q_3) and –106, –110 (Q_4) are similar to those reported in the literature [23–25]. The ^{27}Al MAS-NMR spectra of the samples are shown in Fig. 5. The peak around 54.3 ppm is attributed to the presence of aluminium in tetrahedral coordination [23,26]. Al-MCM-41(80) is devoid of any non-framework Al^{3+} (Al_2O_3) as there is no signal at 0 ppm. But Al-MCM-41(55) and (Al, Zn)-MCM-41(52) have such species as there is a broad signal at 0 ppm. The acidity of the calcined materials was measured by FT-IR spectroscopy using pyridine as a probe (Fig. 6). The samples exhibit the

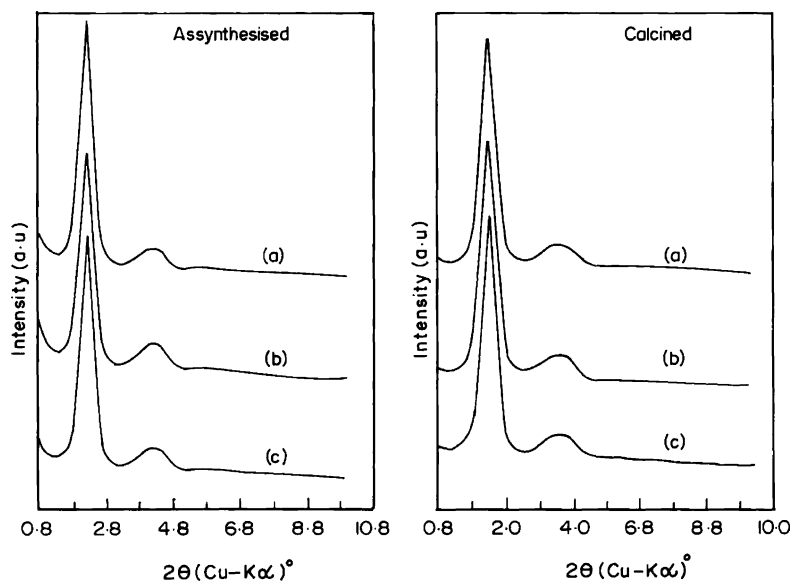


Fig. 1. XRD patterns of as-synthesised, and calcined mesoporous Al-MCM-41 molecular sieves: (a) Si/Al = 80; (b) Si/Al = 55; (c) Si/(Al + Zn) = 52.

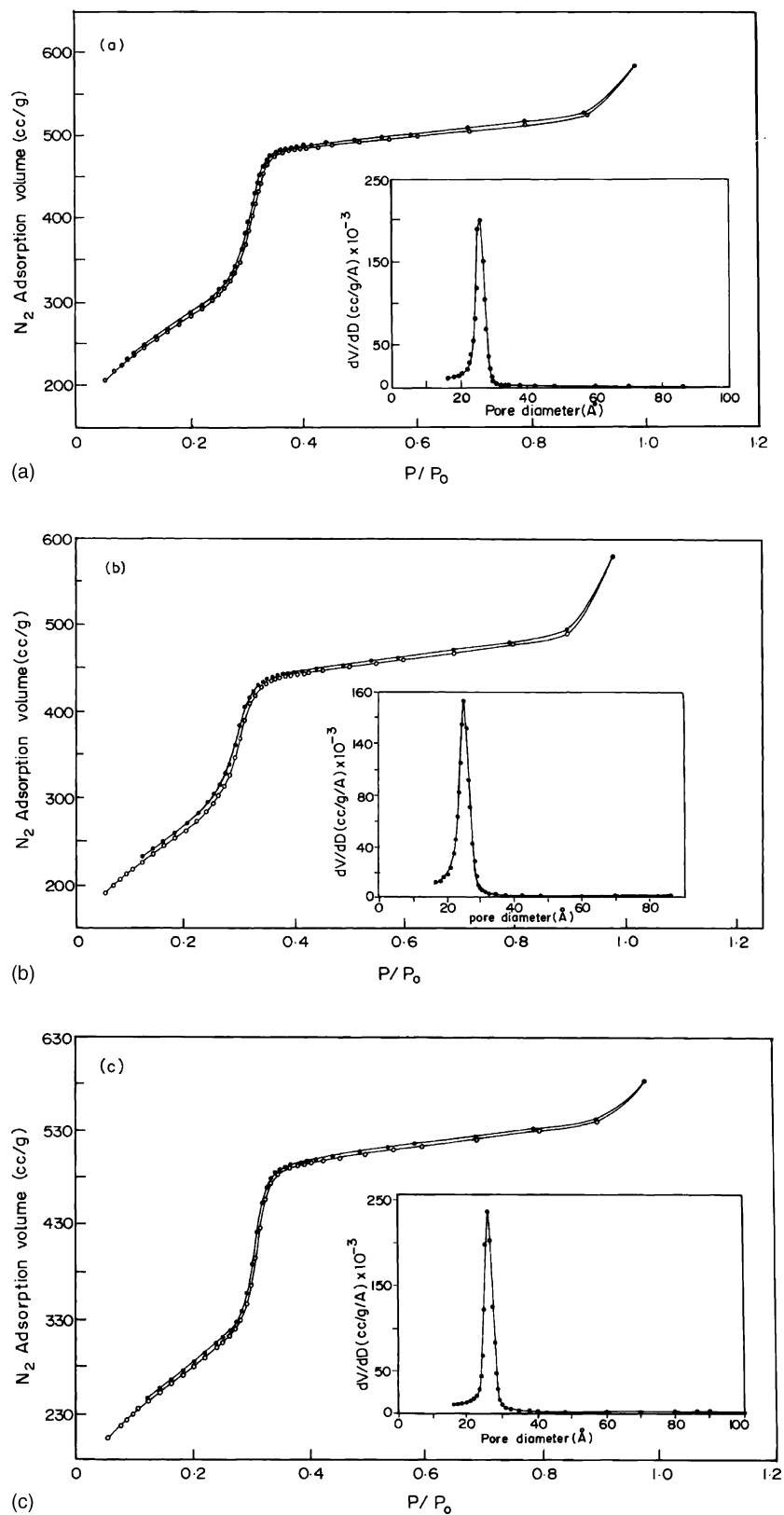


Fig. 2. Adsorption isotherms of Al-MCM-41 molecular sieves: (a) Si/Al = 80; (b) Si/Al = 55; (c) Si/(Al + Zn) = 52.

Table 1
Physico-chemical properties of the catalysts

Catalyst	Si/Al gel ratio	Si/Al (ICP)	d_{100} (Å)	a_0 (Å)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume (Å)	Pore diameter (Å)	Wall thickness (Å)
Al-MCM-41(55)	50	55	41.7	48.1	979	0.68	27.9	20.2
(Al, Zn)-MCM-41(52)	50 ^a	52 ^a	37.5	43.2	930	0.66	28.3	17.6
Al-MCM-41(80)	75	80	38.8	44.7	995	0.64	27.4	19.7

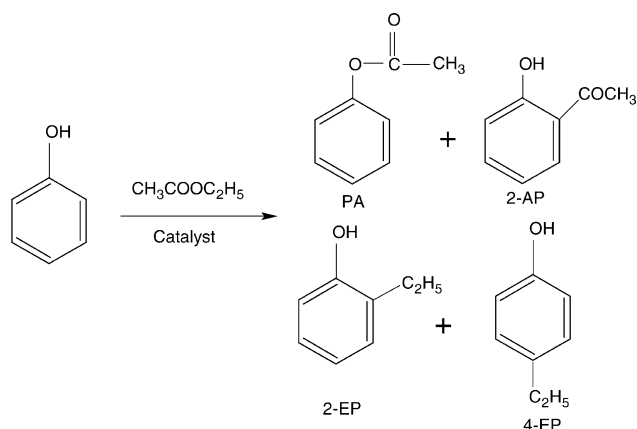
^a Si/(Al + Zn) ratio.

expected bands due to Lewis acid-bound (1450 , 1575 and 1623 cm^{-1}), Bronsted acid-bound (1545 and 1640 cm^{-1}) and both Lewis and Bronsted acid-bound pyridine (1490 cm^{-1}). These data coincide with those reported by Climent et al. [27].

3.2. Alkylation of phenol

3.2.1. Effect of temperature

The vapour phase reaction of phenol with ethyl acetate was conducted over Al-MCM-41(55), Al-MCM-41(80) and (Al, Zn)-MCM-41(52) at 200, 250, 300, 350 and 400 °C. The reaction was investigated by co-feeding phenol and ethyl acetate in the ratio 1:3 and weight hourly space velocity (WHSV) 1.79 h^{-1} (Table 2). The products are phenyl acetate (PA), 2-EP, 2-acetylphenol (2-AP) and 4-EP (Scheme 1). Conversion of phenol was found to be higher over Al-MCM-41(55) than on (Al, Zn)-MCM-41(52) and Al-MCM-41(80). The order of acidity of the catalysts is (Al, Zn)-MCM-41(52) > Al-MCM-41(55) > Al-MCM-41(80). But the conversion does not follow the expected order of acidity of the catalysts. The activity of the catalysts follows the order Al-MCM-41(55) > (Al, Zn)-MCM-41(52) > Al-MCM-41(80). Al-MCM-41(55) is more active than Al-MCM-41(80) due to its dense acid sites. Though (Al, Zn)-MCM-41(52) has higher density of acid sites, the less conversion over this catalyst is attributed to the slight increase in the hydrophilicity on the catalyst surface. Such observation has been already reported by Umamaheswari et al. [13]. Conversion increases by increasing the temperature from 200 to 350 °C, and decreases at 400 °C.



Scheme 1. Reaction of phenol with ethyl acetate.

Phenol competes with ethyl acetate for adsorption on the Bronsted acid sites. At lower temperatures, phenol is adsorbed on the Bronsted acid sites in preference to ethyl acetate, leading to low conversion [9]. Phenol can be adsorbed on the catalyst surface by hydrogen bonding through its -OH group and the bridging oxygen by charge transfer interaction between the aromatic ring and Bronsted acid sites. Similar trend in the adsorption of ethylbenzene on Bronsted acid sites at lower temperature is also reported by our group [14]. At higher temperatures, phenol can be easily desorbed, thus facilitating more adsorption of ethyl acetate. This has been observed up to 350 °C. At 400 °C, the conversion is low due to blocking of more number of active sites by coke. Temperature dependence of selectivity in the adsorption of reactants has already been proposed in our earlier studies [13]. Coke formation is a common phenomenon in the alkylation of phenol and its derivatives [2]. Such coke formation is observed right from 200 °C in the present study. Significant decrease in conversion over Al-MCM-41(55) and (Al, Zn)-MCM-41(52) at 400 °C compared to Al-MCM-41(80) is due to the difference in the density of acid sites of the catalysts. Al-MCM-41(80) with lower acid site density is slowly deactivated at 400 °C as it does not promote multialkylation leading to coke formation as rapidly as Al-MCM-41(55) and (Al, Zn)-MCM-41(52).

Table 2 illustrates the results of the effect of temperature on products selectivity over all the catalysts. The selectivity to PA decreases gradually with increase in temperature. Sakthivel et al. [28] reported acid sites of different strength on the surface of MCM-41. Ethyl acetate is free to chemisorb on all these sites. The electrophilic attack of ethyl cation is accounted for by assuming the chemisorption of ethyl acetate on strong acid sites. If chemisorption occurs on weak acid sites or defective sites, it cannot promote ethylation but can promote only acylation. As the temperature increases, chemisorption of ethyl acetate on weak acid/defective sites decreases and consequently the selectivity to PA decreases with increasing temperature. The selectivity to 2-EP increases with increase in temperature over all the catalysts. At low temperature, phenol is more susceptible to chemisorption on strong acid sites and at higher temperature it gets desorbed. Higher temperature facilitates chemisorption of ethyl acetate on strong acid sites and thereby increasing the selectivity to 2-EP. The selectivity to 2-AP decreases with increase in temperature. This product may be formed by direct C-acylation at the *ortho*-position of the ring or by the Fries rearrangement of previously formed PA. Since increase in temperature will reduce chemisorption of ethyl acetate on weak acid/defective sites,

Table 2
Effect of temperature on phenol conversion and product selectivity

Catalysts	Reaction temperature (°C)	Conversion of phenol (%)	Product selectivity (%)			
			PA	2-EP	2-AP	4-EP
Al-MCM-41(55)	200	63.7	25.9	45.7	17.8	10.6
	250	68.1	20.3	53.6	16.2	9.9
	300	76.3	17.3	69.2	13.5	0
	350	85.5	16.0	71.3	12.7	0
	400	71.2	13.5	76.9	9.6	0
(Al, Zn)-MCM-41(52)	200	56.2	24.9	45.2	20.1	9.8
	250	60.9	23.5	49.1	19.8	7.6
	300	62.8	21.9	57.3	17.6	3.2
	350	79.4	20.4	61.0	16.5	2.1
	400	67.5	17.7	67.4	14.9	0
Al-MCM-41(80)	200	40.6	21.1	49.8	17.7	11.4
	250	46.4	20.6	52.7	15.8	10.9
	300	58.7	19.7	57.1	13.6	9.6
	350	68.6	17.0	63.3	11.4	8.3
	400	66.5	14.3	70.0	10.8	4.9

Note: Phenol:ethyl acetate (feed ratio) = 1:3. WHSV = 1.79 h⁻¹.

there should be reduced formation of PA. Hence, further rearrangement to give 2-AP is also less favoured. Chemisorption of ethyl acetate on moderate acid sites may be important for C-acylation. Hence, with increase in temperature adsorption of ethyl acetate on these sites for direct ring acylation is hindered. So the increase in temperature decreases the selectivity of 2-AP.

The selectivity to 4-EP is high at low temperature but decreases gradually or disappear ultimately with increase in temperature. The mode of chemisorption of phenol on the Bronsted acid sites of the catalysts may lead to the high selectivity to 4-EP at low temperature, and low selectivity at high temperature. At lower temperatures, the acid sites of the catalysts are free and hence adsorption of phenol on strong acid sites of the catalysts can occur through its π electronic cloud of the ring. This mode of adsorption can activate both *ortho*- and *para*-positions equally for electrophilic reaction. So, 4-EP has sufficient selectivity at 200 °C over all the catalysts. At high temperatures, there is blocking of active sites by coke in addition to reduced chemisorption of phenol. Hence, the reaction of phenol with ethyl cation can occur only in the vapour phase. Phenol approaches ethyl cation on the surface through its –OH group pointing towards the channel surface. This orientation of phenol will make the *ortho*-position more susceptible to the electrophilic reaction with ethyl cation. Hence, 4-EP selectivity decreases at high temperature whereas the selectivity to 2-EP is increased.

3.2.2. Effect of feed ratio

The effect of the feed ratio on conversion of phenol and products selectivity was studied at 350 °C over Al-MCM-41(55). The feed ratio was varied from 1:1 to 1:3 (Table 3). Phenol conversion increases with increase in ethyl acetate content in the feed. Since the temperature is high, ethyl acetate is adsorbed in preference to phenol. Hence, even at the

Table 3
Effect of feed ratio on phenol conversion and product selectivity

Feed ratio	Conversion of phenol (%)	Product selectivity (%)			
		PA	2-EP	2-AP	4-EP
1:1	70.9	14.8	74.3	10.9	0
1:2	85.5	17.3	69.2	13.5	0
1:3	88.4	21.1	63.3	15.6	0

Note: Al-MCM-41(55), temperature = 350 °C.

low feed ratio (1:1), there is about 71% conversion. At the 1:3 feed ratio, the conversion is about 88% due to increased adsorption of ethyl acetate. The percentage increase in conversion is only 3% when the feed ratio changes from 1:2 to 1:3, showing that saturation point has almost reached even at 1:2 feed ratio. But the effect of dilution of phenol in the vapour phase with high content of ethyl acetate is not observed even at 1:3 feed ratio; the conversion does not decrease. The dependence of feed ratio in the adsorption of *m*-cresol on Bronsted acid sites were reported earlier [13]. The dominant product is 2-EP, but the selectivity decreases slightly with increase in ethyl acetate content in the feed. This may be accounted for by presuming that nearly all strong acid sites that favour *ortho*-ethylation are used for chemisorption of ethyl acetate. Increase in the selectivity to PA is observed with increase in ethyl acetate content in the feed. Hence, weak acid sites that favour acylation would also acquire chances of adsorption of ethyl acetate with its high content in the feed. This could also be the reason for the increase in the selectivity to 2-AP with increasing ethyl acetate in the feed.

3.2.3. Effect of WHSV

The effect of WHSV on phenol conversion and products selectivity was examined over Al-MCM-41(55) at 350 °C with feed ratio 1:3 (phenol:ethyl acetate). The results are

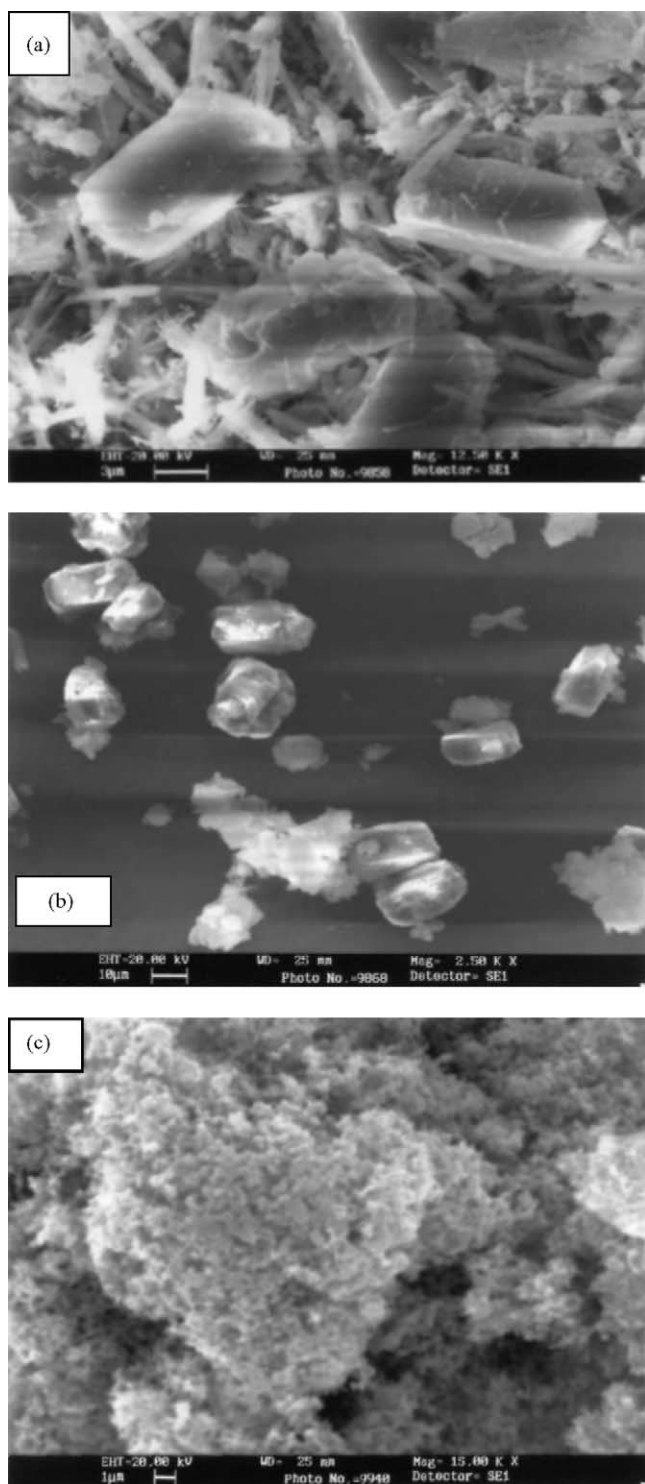


Fig. 3. SEM pictures of calcined mesoporous Al-MCM-41 molecular sieves: (a) Si/Al = 80; (b) Si/Al = 55; (c) Si/(Al + Zn) = 52.

presented in Table 4. As expected, phenol conversion decreases with increase in WHSV [11]. The selectivity to 2-EP decreases with increase in WHSV, which may be attributed to either decreased chemisorption of ethyl acetate on more acidic Bronsted acidic sites or fast diffusion of phenol. This will cause significant reduction in the electrophilic reaction

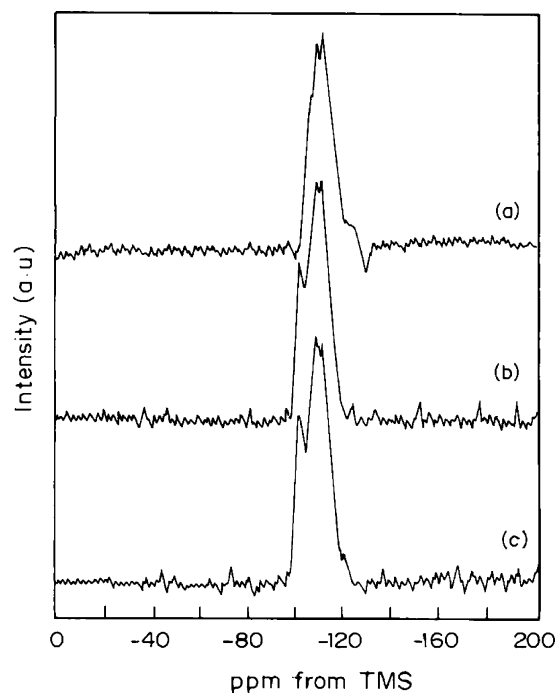


Fig. 4. ^{29}Si MAS-NMR spectra of Al-MCM-41: (a) Si/Al = 80; (b) Si/Al = 55; (c) Si/(Al + Zn) = 52.

of phenol with chemisorbed ethyl acetate. As ethyl acetate is hydrophobic in nature, its adsorption on the Bronsted acid sites of Al-MCM-41(55) is less probable because of its hydrophilic property. The selectivity to phenyl acetate increases

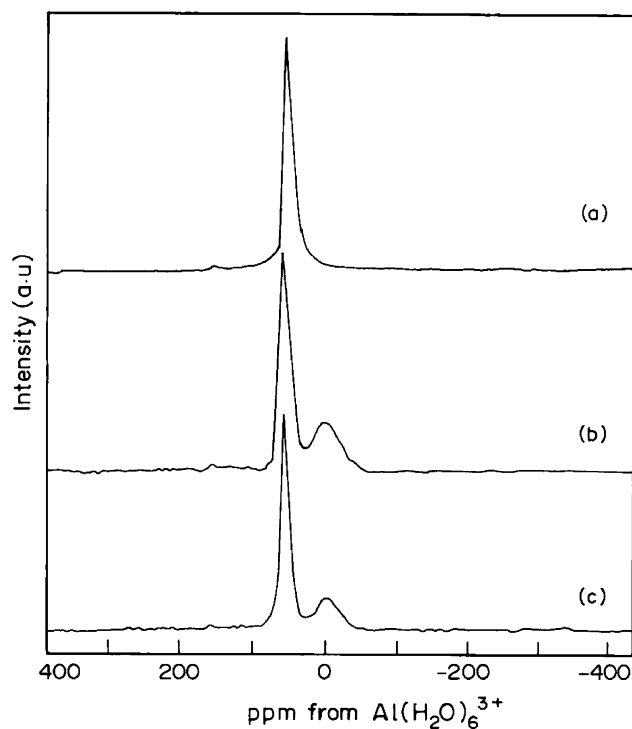


Fig. 5. ^{27}Al MAS-NMR spectra of Al-MCM-41: (a) Si/Al = 80; (b) Si/Al = 55; (c) Si/(Al + Zn) = 52.

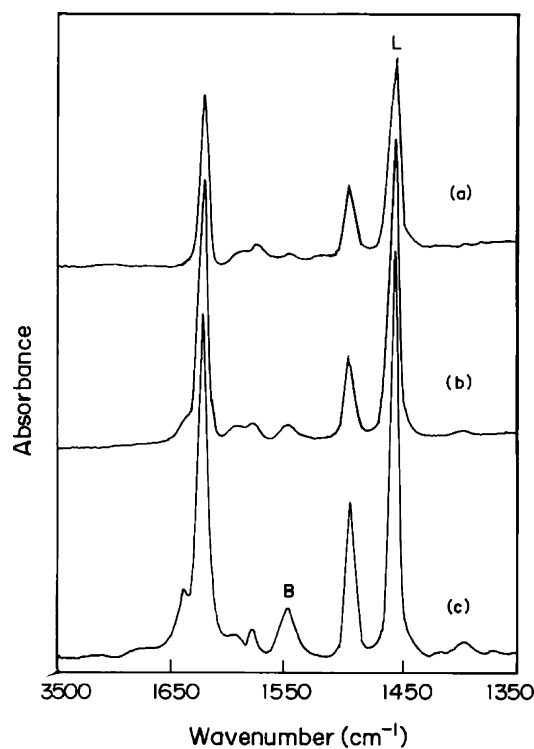


Fig. 6. Bronsted and Lewis acidity of Al-MCM-41: (a) Si/Al = 80; (b) Si/Al = 55; (c) Si/(Al + Zn) = 52.

Table 4
Effect of WHSV on phenol conversion and product selectivity

WHSV (h^{-1})	Conversion of phenol (%)	Product selectivity (%)			
		PA	2-EP	2-AP	4-EP
1.79	88.4	21.1	63.3	15.6	0
2.68	72.3	22.8	60.1	17.1	0
3.57	65.1	24.6	57.4	18.0	0

Note: Al-MCM-41(55); phenol:ethyl acetate (feed ratio) = 1:3; temperature = 350°C .

slightly with increase in WHSV. The formation of 2-AP is either through direct C-acylation or through the Fries rearrangement of PA. These two are parallel reactions as reported by Subba Rao et al. [29]. In order to check this, PA was used alone as the feed and examined over Al-MCM-41(55) at 350°C with WHSV 1.79 h^{-1} . The selectivity to 2-AP is about 40.8% confirming the existence of the Fries rearrangement of PA to 2-AP. The selectivity to 2-AP slightly increases with increase in WHSV. Hence, it could not be exclusively formed by the rearrangement of PA, which is a time dependent process. But there might be direct C-acylation of phenol to yield 2-AP. This study reveals the optimum WHSV (1.79 h^{-1}) for alkylation of phenol with ethyl acetate. A test run was carried out at optimized condition of temperature (350°C), feed ratio (1:3)

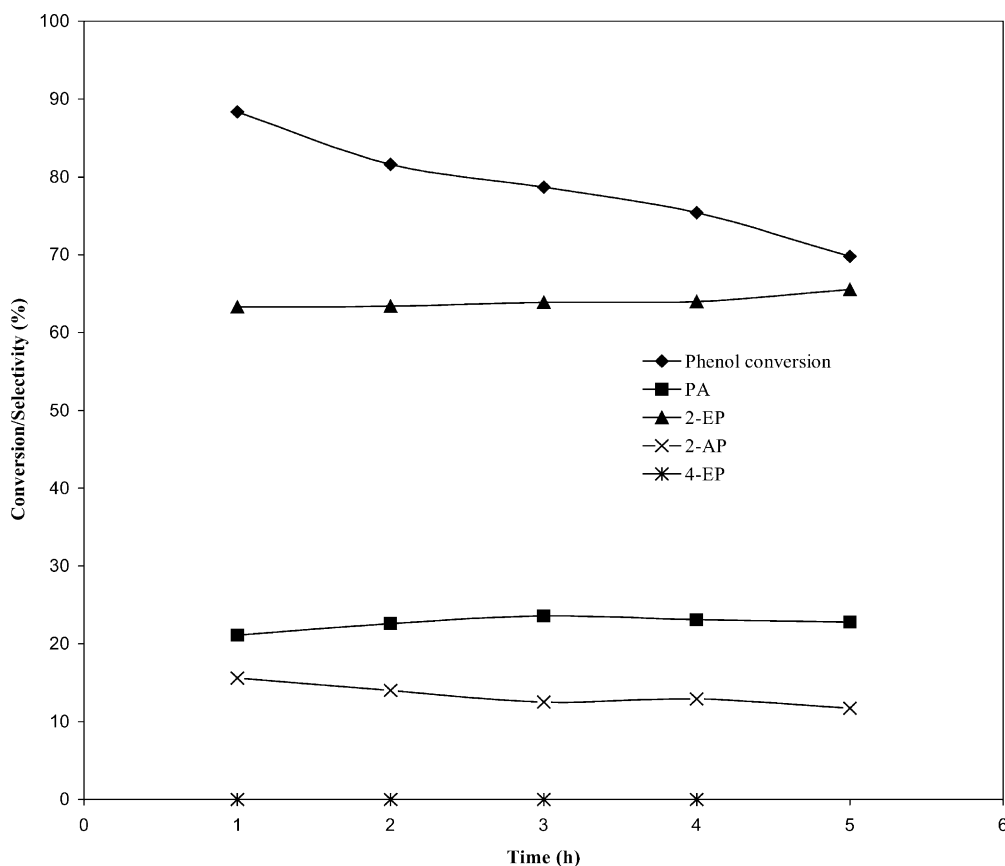


Fig. 7. Study of time on stream over Al-MCM-41(55). Molar ratio = 1:3; temperature = 350°C ; WHSV = 1.79 h^{-1} .

and WHSV (1.79 h^{-1}) in order to find out the material balance in the reaction. The percentage of coke formed is found to be 13%.

3.2.4. Effect of time on stream

The effect of time on stream was examined on the activity of Al-MCM-41(55) at 350°C with a feed ratio 1:3 and WHSV 1.79 h^{-1} . The study was carried out for 5 h and the results are illustrated in Fig. 7. The conversion gradually decreases with increase in time on stream due to gradual increase in the blocking of active sites by coke. But the decrease is less than 10% for the entire 5 h stream. This is due to large pore diameter that permits the products to diffuse out fast avoiding multialkylation leading to coke. The selectivity to 2-EP remains the same although there is a slight increase with increase in time on stream, indicating that a similar mechanism of ethylation prevailed during the entire stream. The selectivity to PA is about 20% and this remains nearly the same although a little increase is observed with increase in time on stream. The selectivity to 2-AP shows a decreasing trend with increase in time on stream. This observation suggests that the formation of 2-AP can also occur through the rearrangement of PA. Once PA is formed it goes to other active sites to undergo rearrangement to yield 2-AP. Therefore, the sites on which PA is formed may not be active enough for subsequent adsorption and rearrangement to yield 2-AP. But the sites for rearrangement may not be freely available as in the beginning of the stream due to slight coke formation.

4. Conclusions

The study of vapour phase reaction of phenol with ethyl acetate reveals: (i) the capability of ethyl acetate functioning both as an alkylating and acylating agent; (ii) ethylation is more predominant than acylation; (iii) *ortho*-ethylation is more predominant than *para*-ethylation; and (iv) absence of multialkylated products. Among the catalysts studied Al-MCM-41(55) is found to be more active than the other catalysts. At the optimal feed ratio and WHSV, phenol conversion is found to be 85.5% at 350°C with high selectivity to 2-EP (63.3%). Time on stream study indicates very slow deactivation of the catalysts with time and maintenance of nearly the same selectivity to the products throughout the stream.

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