

Mesoporous material as catalyst for the production of fine chemical: Synthesis of dimethyl phthalate assisted by hydrophobic nature MCM-41

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Received 31 October 2004; received in revised form 24 March 2005; accepted 24 June 2005

Available online 5 August 2005

Abstract

Aluminum, iron and zinc containing MCM-41 molecular sieves were prepared by the hydrothermal method. The catalyst was characterized by the XRD, BET (surface area), FT-IR and ²⁹Si, ²⁷Al MAS-NMR techniques. The catalytic activity of these molecular sieves was tested with esterification reaction used with phthalic anhydride (PAH) and methanol (MeOH) in the autoclave at 135 °C, 150 °C and 175 °C. Conversion increases with an increase in temperature and mole ratio. The activity of these catalysts followed the order: Al-MCM-41 (112) > Fe-MCM-41 (115) > Al-MCM-41 (70) > Al-MCM-41 (52) > Fe-MCM-41 (61) > Al, Zn-MCM-41 (104) > Al-MCM-41 (30). The reaction yielded both monomethyl phthalate (MMP) and dimethyl phthalate (DMP). The nature of the catalyst sites has been proposed using with water as an impurity. The selectivity of the dimethyl phthalate increases with increase in temperature and mole ratio. The weight of the catalyst was optimized at 0.07 g. The hydrophilic and hydrophobic nature of the catalyst has been explained by the influence of water and the external surface acidity also facilitates the reaction and this has been confirmed by the supporting reaction.

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Keywords: MCM-41; Conversion; Hydrophobicity; Dimethyl phthalate; Monomethyl phthalate

1. Introduction

In recent days, the role of catalysts has been in focus because of its commercial value. Esters, which include a wide category of organic compounds, ranging from aliphatic to aromatic, are important intermediates in the synthesis of fine chemicals, drugs, plasticisers, food preservatives, solvents, perfumery, cosmetics, chiral-auxiliaries, agrochemicals and also as precursors for a gamut of pharmaceuticals [1]. Thorat et al. also studied the reaction with super acid catalyst [2], Ma et al. studied with zeolites [3], Arabi et al. studied with HPA [4] and Zhao studied with aluminophosphate molecular sieves [5]. Though, the previous methods has many of the disadvantages, like lower conversion, consumption of higher energy for high yield, diffusion and reusability of the catalyst.

The catalyst has an important role in many reactions, such as: alkylation, acylation, cyclization, Aldol condensation, Knoevenagel condensation, oxidation, reduction, isomerization, disproportionation, polymerization, esterification, protection, deprotection and acetalization, etc. The catalyst catalyzes the reaction by its active sites (Brönsted; Lewis acid sites) and the type of requirement of the site is dependent on the type of the reaction. Generally, the esterification of alcohols by carboxylic acids using the Brönsted acidity (viz. mineral acids) is well known [6]. Lewis acid sites are involved to generate the olefins as a side product from the alcohols like *tert*-butanol and isopropyl alcohol, which undergo dehydration even at room temperature to yield *iso*-butylene and propene. Apart from the catalyst sites, the catalysts itself create many problems to the environment.

The conventional method for the esterification reaction is carried out using mineral acids, such as sulfuric acid, hydrochloric acid, orthophosphoric acid and some of the

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Lewis acid-based catalyst, like tin octoate. These mineral acids are corrosive, non-ecofriendly and virulent, which need to be neutralized after the completion of reaction [7–11]. In the case of metal-containing Lewis acid catalyst, the metal must be removed carefully after the reaction [12]. The important drawback of the butyl ester synthesis is the use of acid halide as an esterification agent, which yields highly toxic gaseous hydrogen halide as by-product, in stoichiometric quantities. Apart from this, the catalyst is also soluble in water, which is the main by-product of esterification reaction. Hence, separation of catalyst from product becomes quite difficult and expensive. Hence, there is a need to develop an environmentally benign method for the esterification of acids using more active, selective and reusable solid acid catalyst. Ion-exchange resin [13] and supported heteropolyacids [14] are some of the active heterogeneous catalysts reported in the literature. But low thermal stability and low surface area are the common disadvantages of heteropolyacids, as solid catalyst.

The esterification of *tert*-butanol, using solid acid catalyst like activated basic alumina, at mild conditions (at room temperature under argon) gave a good yield of *tert*-butyl ester, but the amount of catalyst relative to the reactants used by Nagasawa et al. was very large (catalyst/reactants weight ratio = 2.1 ± 0.4) [11,15]. It is not of practical interest to use such a large amount of catalyst, and moreover, the removal of high-molecular weight products which adsorbed on the catalyst is quite difficult and expensive too. Expenditure for the reaction also depends on the method of reaction. In the esterification reaction using alcohol, water is formed as a by-product, thereby requiring azeotropic distillation to remove water during the reaction [16].

These hectic procedures have been thwarted by the use of mesoporous heterogeneous catalyst Al-MCM-41. They are easily separated from the product and reactants by filtration and are also regenerated easily [17]. Al-MCM-41 (112) has higher activity than other Si/Al ratios. Michel et al. [14] reported a very low activity for MCM-41 (Si/Al = 16) and ascribed it to its low acid strength. It can be pointed out that very low activity, as reported earlier, may be construed due to the 'dealumination' process, as well as by the collapse of the pores, due to the presence of larger amount of aluminium. The failure in the result is not acquired due to acid strength of the catalyst, but due to the hydrophilic nature of the MCM-41. In condensation reaction (like esterification reactions), the catalyst requires more specific properties to facilitate product formation.

Lower % of aluminium containing Al-MCM-41 (112) has higher hydrophobic nature and higher hydrothermal stability towards water that is formed during the reaction. Higher hydrophobic nature prevents ester hydrolysis, which in turn prevents the backward reaction. Less acidic MCM-41 does not have extra-framework Lewis acid aluminium, which reduces the dehydration of alcohols. Hence, it avoids some of the by-products, thereby improving the reaction selectivity. This reaction gives maximum conver-

sion of 99.1 wt.% and selectivity to DMP is 100% at 150 °C.

2. Experimental

2.1. Synthesis of catalytic materials

The hydrothermal crystallization procedure reported by Beck et al. [18] was adopted for the synthesis MCM-41 (Si/Al = 30, 52, 70, 112; Si/Fe = 61, 115; Si/Al + Zn = 104) molecular sieves. In a typical synthesis, 10.6 g of sodium silicate nanohydrate (Merck) in demineralized water was combined with the appropriate amount of aluminum sulphate, as aluminum source and/or ferric nitrate used for the source of iron, and zinc sulphate used for the source of zinc. It was then acidified with 1 M H₂SO₄ to bring down the pH to 10.5 under vigorous stirring. After 30 min of stirring, an aqueous solution of cetyltrimethylammonium bromide (CTAB) (Merck) was added and the surfactant silicate mixture was stirred for further 30 min at room temperature. The molar composition of the resultant mixture was SiO₂:0.2CTAB:XAl₂O₃:0.89H₂SO₄:120H₂O (*X* varies with the Si/Al ratio). The resultant gel was autoclaved and heated for 48 h at 145 °C. The solid obtained was filtered and dried at 100 °C in air. The sample was then calcined at 525 °C in air for 5 h in a muffle furnace to expel the template.

2.2. Characterization

The XRD powder diffraction patterns of the calcined mesoporous MCM-41 (Si/Al = 30, 52, 70, 112; Si/Fe = 61, 115; Si/Al + Zn = 104) molecular sieves were obtained from 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 0.8–9.8° in the steps of 0.02° with a count time of 15 s at each point for MCM-41 molecular sieves. Surface area, pore-volume and pore-size distribution were measured by nitrogen adsorption at 77 K with ASAP-2010 porosimeter from Micromeritics Corporation Norcross, GA. The samples were degassed at 623 K and 10⁻⁵ Torr overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen 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 distribution was estimated using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) built-in software from Micromeritics. Mid-IR spectra of the mesoporous Al-MCM-41 molecular sieves were collected on Nicolote (Avatar 360) instrument using KBr pellet technique. About 10 mg of the sample was ground with about 200 mg of spectral grade KBr to form a pellet under hydraulic pressure to record the IR spectrum in the range 4000–400 cm⁻¹. ²⁹Si 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 $2.50 \mu\text{s}$ (45° pulse), delay time of 10 s and spectral width of 335 ppm. Two thousand scans were acquired with reference to trimethylsilylpropanesulfonic acid (TSP). Solid-state ^{27}Al MAS-NMR spectra were recorded at a frequency of 104.22 MHz, spinning rate of 8 KHz, a pulse length of $1.0 \mu\text{s}$, delay time of 0.2 s and a spectral width of 330 ppm. The total number of scans was 150 and the line broadening was 50 Hz. The ^{27}Al chemical shifts were reported in relation to the solution of aluminum nitrate.

2.3. Catalytic runs

Esterification reactions were carried out under batch reaction condition, using an autoclave in the temperature range of $135\text{--}170^\circ\text{C}$, at autogenous pressure conditions. A typical reaction mixture in the reactor contained 0.3804 g of PAH and MeOH. To this mixture, 0.04 g of a freshly activated catalyst was added. Activation of the catalyst was done by calcination at 525°C in air for 5 h. The autoclave temperature was

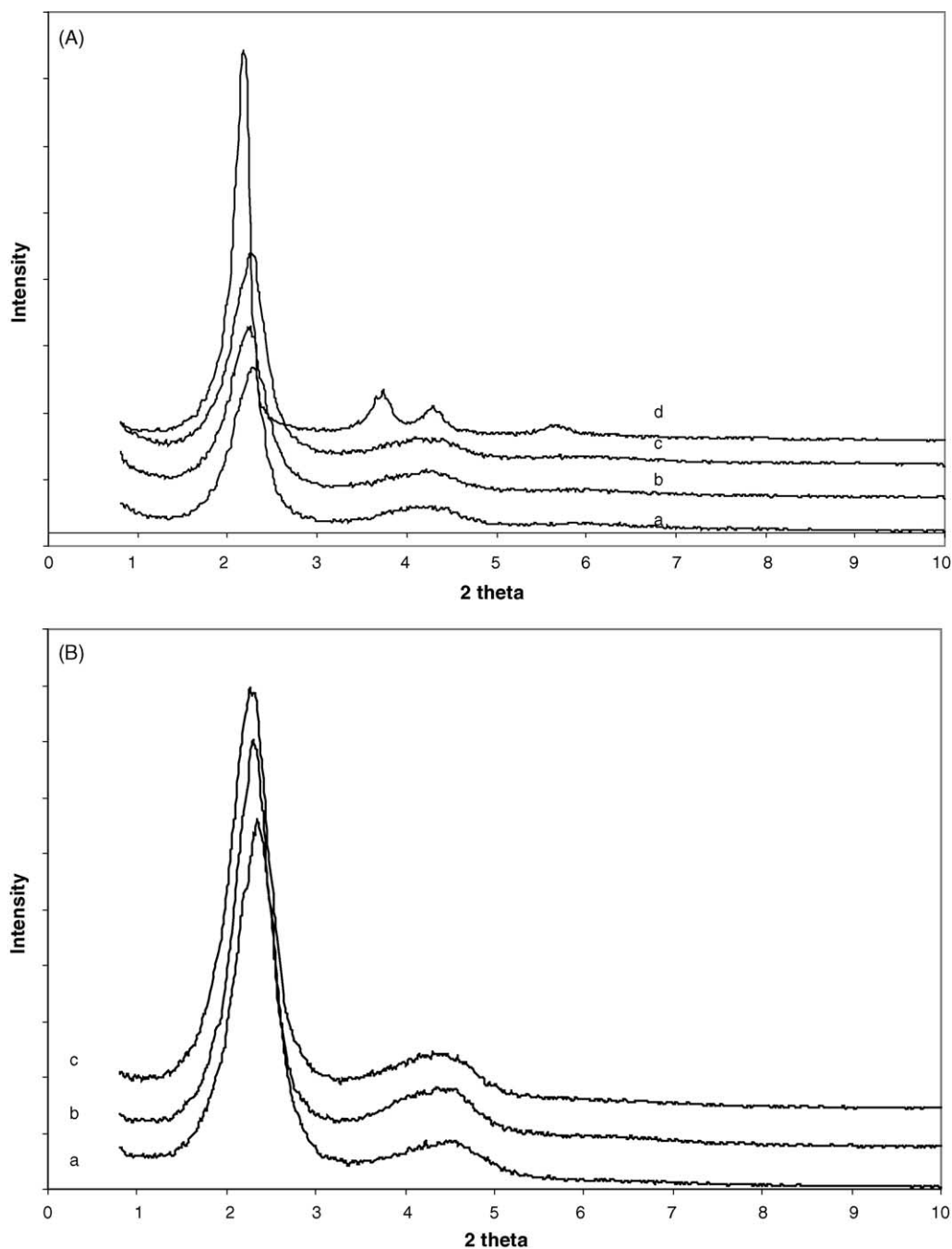


Fig. 1. (A) X-ray diffraction pattern of MCM-41 molecular sieves obtained after calcination: (a) Al-MCM-41 (30), (b) Al-MCM-41 (52), (c) Al-MCM-41 (70), (d) Al-MCM-41 (112). (B) X-ray diffraction pattern of MCM-41 molecular sieves obtained after calcinations: (a) Al, Zn-MCM-41 (104), (b) Fe-MCM-41 (61), (c) Fe-MCM-41 (115).

then slowly raised to 135 °C, 150 °C and 175 °C as required and maintained at the desired temperature during the reaction period of 7 h. The effect of the reaction period, the molar ratios of the reactants, and the amount of catalyst required on PAH-conversion and product selectivity are studied.

2.4. Acidity measurements

The acidity measurements of Al, Fe and Zn containing MCM-41 materials were analyzed by both TPD of NH₃ with TGA method. About 1.0 g of the sample was packed in a quartz tube and the initial flushing was carried out with dry nitrogen for 3 h. Then the system was evacuated (1.999×10^{-3} N/m²) at 550 °C for 5 h and cooled to room temperature. Passing the ammonia vapors over the catalyst bed has carried out the ammonia adsorption. After adsorption, the system was evacuated to remove the physisorbed ammonia, and again ammonia was passed through the system. The adsorption and evacuation processes were repeated five times for saturating the molecular sieves. The extent of ammonia adsorbed over each catalyst was measured by TGA in a TA 3000 Mettler system. Nitrogen, as purge gas, was passed during desorption of ammonia. The TGA study was conducted at a heating rate of 10 °C/min up to 600 °C.

2.5. Analysis of the product

Analysis of the products collected from autoclave was carried out in a gas chromatograph (Shimadzu GC-17A, DB-5 5 capillary column) and nitrogen as the carrier gas. The identification of products was performed on Shimadzu

GC-MS-QP 5000 with a PE-5 capillary column; scan mode 40–400 amu.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The powder XRD patterns of the calcined mesoporous catalyst (Fig. 1(A) and (B)), confirm the hexagonal mesophase of these samples by the typical intense diffraction peak of [1 0 0] plane [19–21]. The d_{100} spacing and the lattice parameter (a_0) calculated as per the procedure, mentioned by the previous literature, are presented in Table 1. The calcined materials possess well-defined pore structure due to the condensation of Si–OH groups. These XRD patterns coincide well with the data already reported for mesoporous aluminosilicate molecular sieves [22].

3.1.2. Nitrogen adsorption isotherms

BET surface areas, pore size and pore volume for calcined materials are presented in Table 2. Adsorption and desorption isotherms, and pore-size distribution for calcined materials (BJH method), are shown in Figs. 2 and 3; they coincide with the reported values [23,24].

3.1.3. Thermal analysis

The thermal properties of the samples were investigated by TGA. The initial weight loss up to 120 °C is due to desorption of physically adsorbed water. The weight loss from 120 °C to

Table 1
Textural properties of the catalysts

Catalysts	Si/Al + Zn	Si/Fe + Al	Si/Fe	Si/Al	Si/Zn	Calcined		TPD of NH ₃ (mmol/g)		Total acidity (mmol/g)
						d_{100}	Unit cell, a_0 (nm)	LT-peak	HT-peak	
Al-MCM-41 (30)	0	0	0	30	0	38.86	4.49	0.238	0.189	0.427
Al-MCM-41 (52)	0	0	0	52	0	39.16	4.52	0.152	0.149	0.301
Al-MCM-41 (70)	0	0	0	70	0	39.16	4.52	0.145	0.101	0.246
Al-MCM-41 (112)	0	0	0	112	0	40.60	4.69	0.128	0.067	0.195
Fe-MCM-41 (61)	0	0	61	0	0	38.47	4.42	0.136	0.117	0.253
Fe-MCM-41 (115)	0	0	115	0	0	37.45	4.32	0.113	0.072	0.185
Al, Zn-MCM-41 (104)	104	0	0	50	54	37.81	4.36	0.233	0.178	0.411

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

Catalysts	Surface area (m ² /g)	Surface area BJH _{Ads} (m ² /g)	Surface area BJH _{Des} (m ² /g)	Pore size BJH _{Ads} (nm)	Pore size BJH _{Des} (nm)	Pore volume BJH _{Ads} (cm ³ /g)	Pore volume BJH _{Des} (cm ³ /g)
Al-MCM-41 (30)	931.6	1117	1066	2.667	2.647	0.777	0.756
Al-MCM-41 (52)	949.9	1106	1127	3.194	3.263	0.978	0.972
Al-MCM-41 (70)	955.3	1167	1154	3.469	3.476	0.969	0.962
Al-MCM-41 (112)	1015	1205	1198	3.482	3.452	0.997	0.992
Fe-MCM-41 (61)	995.6	1225	1194	2.489	2.485	0.938	0.918
Fe-MCM-41 (115)	1051	1293	1251	2.623	2.611	0.956	0.934
Al, Zn-MCM-41 (104)	901.8	1131	1127	2.594	2.576	0.757	0.724

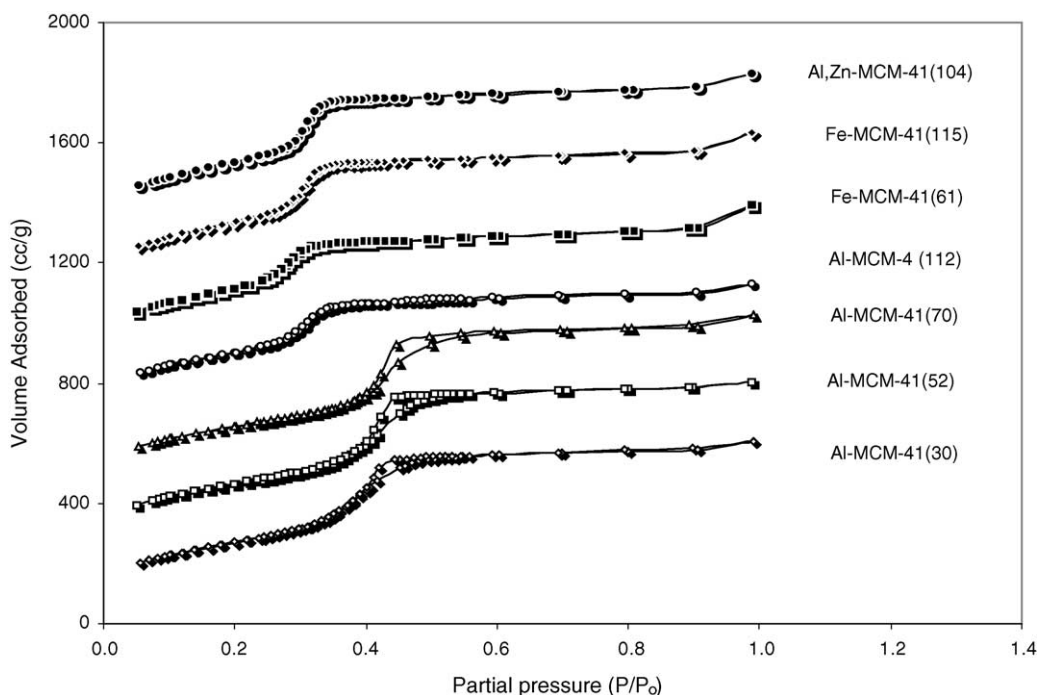


Fig. 2. Adsorption isotherms of Al, Zn and Fe-MCM-41 molecular sieves.

350 °C is due to organic template. The oxidative desorption of the organic template takes place at 180 °C and the minute quantity of weight loss above 350–550 °C is related to water loss from the condensation of adjacent Si–OH groups to form siloxane bonds [19]. The individual values of weight losses for all the four catalysts are presented in Table 3.

3.1.4. ^{29}Si , ^{27}Al MAS–NMR

The ^{27}Al MAS–NMR spectra of the samples are shown in Fig. 4. The peak around ~ 52 ppm is attributed to the presence of aluminum in tetrahedral coordination [25,26]. ^{27}Al MAS–NMR of the calcined Al-MCM-41 (30, 52, 70) and Al, Zn-MCM-41 (104) shows a less-intense peak

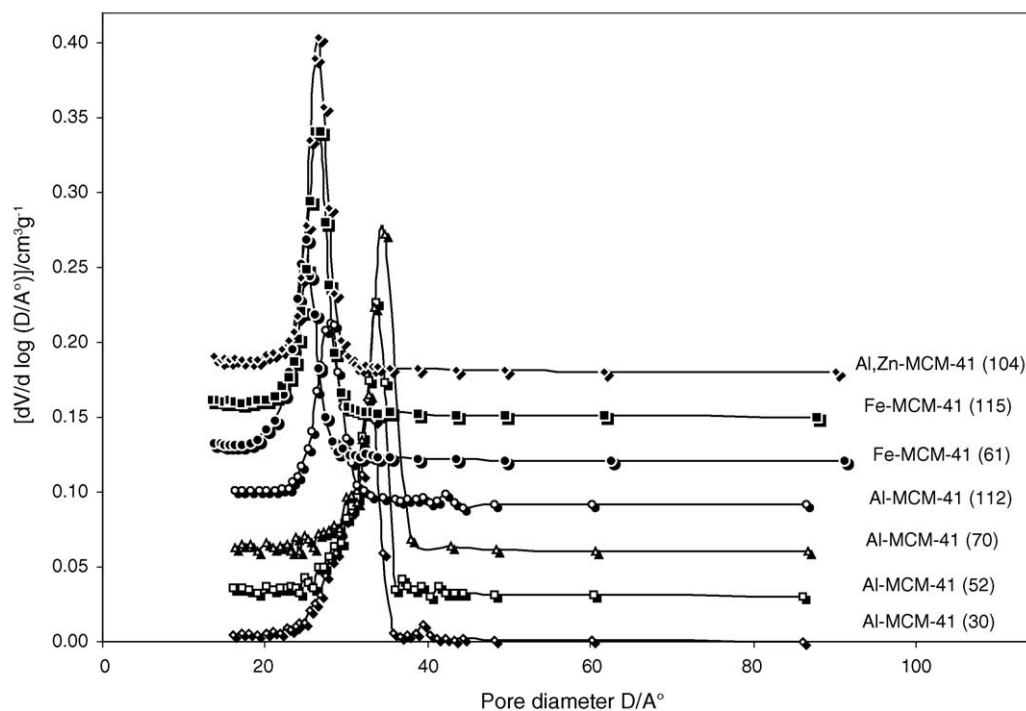


Fig. 3. Pore-size distribution in Al, Zn and Fe-MCM-41 (adsorption isotherms).

Table 3

TGA and DTA, and ^{27}Al , ^{29}Si MAS–NMR spectral data of uncalcined mesoporous molecular sieves: Al-MCM-41 (30, 52, 70 and 112), Fe-MCM-41 (61, 115) and Al, Zn-MCM-41 (104)

Catalyst	Weight loss (wt.%)				^{27}Al MAS–NMR (ppm)		^{29}Si MAS–NMR (ppm)
	Total	43–120 °C	120–350 °C	350–680 °C	Tetrahedral co-ordination	Octahedral co-ordination	
Al-MCM-41 (30)	45.91	3.89	32.32	9.70	+53.17	+1.42	–108.41
Al-MCM-41 (52)	47.27	5.09	29.71	12.47	+53.62	+0.00	–108.72
Al-MCM-41 (70)	46.87	4.77	33.58	8.52	+53.41	+1.81	–109.24
Al-MCM-41 (112)	48.23	5.26	31.75	11.22	+51.81	No signal	–108.29
Fe-MCM-41 (61)	45.91	5.24	30.15	10.52	–	–	–
Fe-MCM-41 (115)	47.82	3.95	34.60	9.27	–	–	–
Al, Zn-MCM-41 (104)	47.58	4.29	33.89	9.40	+52.91	+1.54	–108.34

at ~ 0 ppm. This peak is due to the extra-framework aluminum species in octahedral co-ordination and it is expected to arise out of the framework dealumination during calcination [28]. The ^{29}Si MAS–NMR spectra of the calcined MCM-41 materials are shown in Fig. 5. The broad signal at -111 ppm in the spectra can be assigned to $\text{Si}(\text{OSi})_4$. The shoulder in the range between -103 ppm and -108 ppm is due to $\text{Si}(\text{OAl})$. These spectral features

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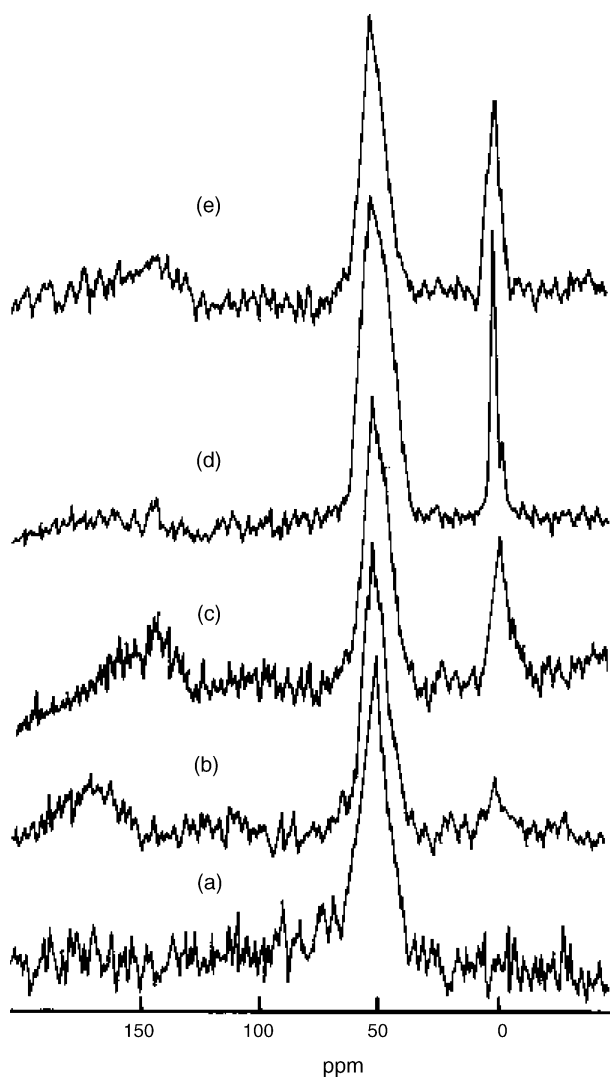


Fig. 4. ^{27}Al MAS–NMR spectra of calcined mesoporous MCM-41 molecular sieves: (a) Al-MCM-41 (112), (b) Al-MCM-41 (70), (c) Al-MCM-41 (52), (d) Al-MCM-41 (30), (e) Al, Zn-MCM-41 (104).

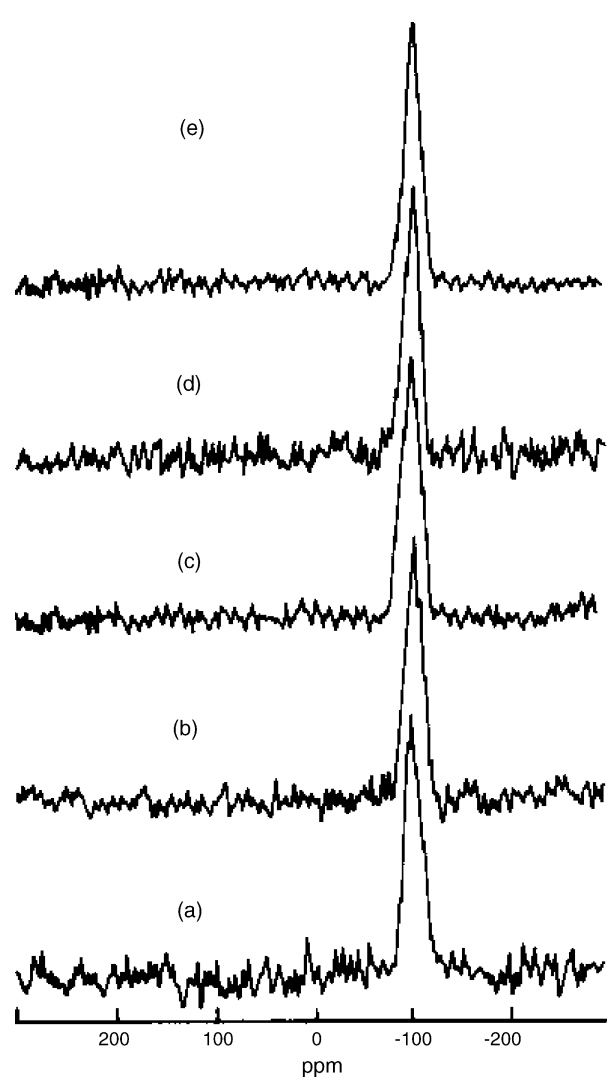


Fig. 5. ^{29}Si MAS–NMR spectra of calcined mesoporous MCM-41 molecular sieves: (a) Al-MCM-41 (112), (b) Al-MCM-41 (70), (c) Al-MCM-41 (52), (d) Al-MCM-41 (30), (e) Al, Zn-MCM-41 (104).

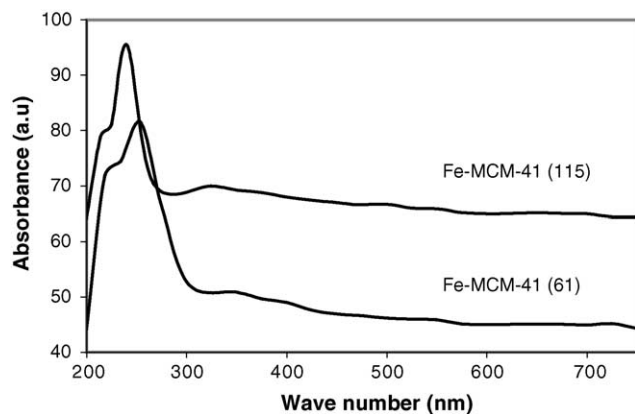


Fig. 6. Diffuse reflectance UV-vis spectra of Fe-MCM-41 catalysts.

coincide well with those reported by previous workers [25,27,28].

3.1.5. ICP-AES analysis

The aluminum content in Al-MCM-41 for various Si/Al ratios, 30, 52, 70 and 112, was recorded using ICP-AES with Allied Analytical ICAP 9000. The results of Si/Al ratios of the materials are given in Table 1.

3.1.6. TPD studies

The total acidity of all the catalytic materials was measured by TPD of ammonia by TGA method. The desorption temperature and amount of ammonia desorbed are considered as indexes of acid strength and total number of acid sites, respectively. [29] The amounts of ammonia desorbed and desorption temperature of all the catalytic materials are presented in Table 1. It is observed that two major weight losses occurred over all the catalysts at lower and higher temperature ranges, which may be due to the desorption of ammonia adsorbed on weak- and strong-acid sites, respectively. The first and second weight losses occurred between 200–225 °C and 385–420 °C, respectively, for all the catalytic systems.

3.1.7. DRS-UV measurements

The appearance of the two prominent absorption bands in DRUV-vis spectra (Fig. 6), i.e. a strong band at 250 nm associated with a shoulder around 215 nm accounts for the charge-transfer (CT) transitions involving Fe(III) in $(\text{FeO}_4)^-$ tetrahedral geometry [30]. This is further supported by the appearance of weak d-d transitions between 300 nm [31]. However, upon calcination, the CT bands are shifted to higher wavelengths along with broadening of d-d bands, suggesting partial breaking of Si-O-Fe framework linkage [30].

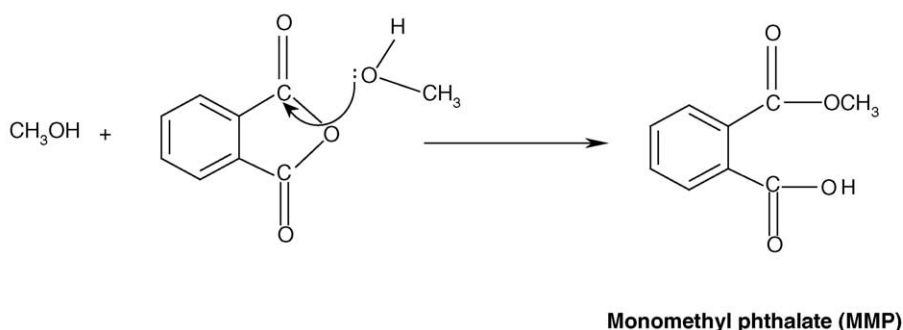
3.2. Application of aluminium, iron, zinc containing MCM-41 catalysts for the esterification of phthalic anhydride

3.2.1. Esterification

The esterification of PAH with MeOH is an electrophilic substitution reaction on the carbonyl group, which is relatively slow and needs activation, either by high temperature or by a sufficient amount of catalyst to achieve significant amount of the yield of the product. The effect of various parameters on the esterification reaction is discussed later.

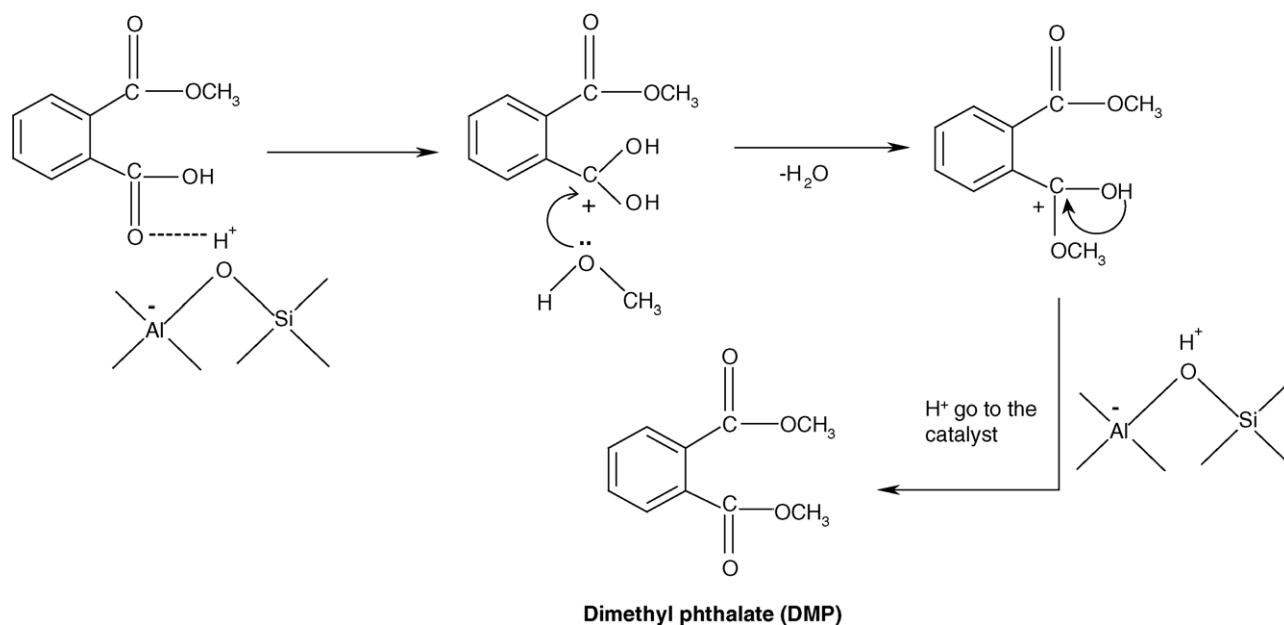
3.2.1.1. Reaction mechanism. In the first step of the reaction, the catalyst does not allow the formation of monoester. Hence, for the formation of monoester, the reaction undergoes a catalyst-independent pathway. The literature says that the first step is the fast, non-catalytic, first-order reaction of phthalic anhydride with one molecule of methanol [32]. The cleavage of the anhydride group due to the attack of MeOH on the carbonyl group of the PAH, leads to the formation of MMP. Hence, acidity does not facilitate the conversion, whereas more appropriately, MMP formation is facilitated by temperature. The second step is the condensation reaction, which is carried out by the catalyst. [32] The condensation reactions are facilitated by the simultaneous distillation of water from the reaction medium. Otherwise, the water molecules, which are formed during the reaction, get adsorbed on the surface of the catalyst retarding the forward reaction.

Catalyst independent



Scheme 1. Monoester formation in the catalyst-independent path mechanism.

Catalyst dependent path



Scheme 2. Diester formation over Brønsted acid sites in the catalyst-dependent path mechanism.

3.2.2. Reaction follows the decreasing order of catalyst with respect to acidity

The activity of these catalysts followed the order Al-MCM-41 (112) > Fe-MCM-41 (115) > Al-MCM-41 (70) > Al-MCM-41 (52) > Fe-MCM-41 (61) > Al, Zn-MCM-

41 (104) > Al-MCM-41 (30) (Table 6). The order of the catalyst clearly indicates that the conversion is inversely proportional to the acidity of the catalyst. Shifting of the reaction towards the right hand side is due to hydrophobic nature rather than the acidity of the catalyst. As mentioned

Table 4
Influence of mole ratio at 135 °C over various aluminium, iron, zinc containing MCM-41 molecular sieves

Mole ratio	Catalyst	Conversion	Selectivity to phthalic anhydride (%)	
			DMP	MMP
1:4	Al-MCM-41 (30)	10.1	19.8	80.2
1:6		15.3	34.4	65.6
1:8		20.9	35.8	64.2
1:4	Al-MCM-41 (52)	15.0	23.5	76.5
1:6		17.4	41.2	58.8
1:8		22.2	50.2	49.8
1:4	Al-MCM-41 (70)	22.5	45.2	54.8
1:6		29.1	49.8	50.2
1:8		33.8	51.2	48.8
1:4	Al-MCM-41 (112)	29.1	50.2	49.8
1:6		34.4	61.2	38.8
1:8		39.9	70.5	29.5
1:4	Fe-MCM-41 (61)	13.5	21.3	78.7
1:6		16.2	40.2	59.8
1:8		21.1	48.7	51.3
1:4	Fe-MCM-41 (115)	28.9	49.5	50.5
1:6		31.2	57.2	42.8
1:8		35.6	64.2	35.8
1:4	Al, Zn-MCM-41 (104)	12.3	20.5	79.5
1:6		16.2	38.6	61.4
1:8		20.5	47.2	52.8

Reaction conditions: temperature = 135 °C; weight of the catalyst = 0.04 g; reaction period = 7 h; pressure = autogenous pressure; reactor = autoclave.

Table 5
Influence of mole ratio at 150 °C over various aluminium, iron, zinc containing MCM-41 molecular sieves

Mole ratio	Catalyst	Conversion	Selectivity to phthalic anhydride (%)	
			DMP	MMP
1:4	Al-MCM-41 (30)	34.7	59.2	40.8
1:6		41.3	63.5	36.5
1:8		55.2	75.6	24.4
1:4	Al-MCM-41 (52)	49.7	76.9	23.1
1:6		52.2	85.2	14.8
1:8		61.8	82.8	17.2
1:4	Al-MCM-41 (70)	58.8	82.3	17.7
1:6		67.1	88.2	11.8
1:8		77.4	91.2	8.8
1:4	Al-MCM-41 (112)	68.1	95.4	4.6
1:6		73.6	97.6	2.4
1:8		80.1	98.7	1.3
1:4	Fe-MCM-41 (61)	45.2	74.4	25.6
1:6		50.6	82.6	17.4
1:8		59.9	88.2	11.8
1:4	Fe-MCM-41 (115)	60.2	92.2	7.8
1:6		71.1	95.2	4.8
1:8		78.6	97.7	2.3
1:4	Al, Zn-MCM-41 (104)	40.2	70.2	29.8
1:6		48.6	75.2	24.8
1:8		57.5	81.6	18.4

Reaction conditions: temperature = 150 °C; weight of the catalyst = 0.04 g; reaction period = 7 h; pressure = autogenous pressure; reactor = autoclave.

Table 6
Influence of mole ratio at 175 °C over various aluminium, iron, zinc containing MCM-41 molecular sieves

Mole ratio	Catalyst	Conversion	Selectivity to phthalic anhydride (%)	
			DMP	MMP
1:4	Al-MCM-41 (30)	80.8	89.7	10.3
1:6		82.5	91.2	8.8
1:8		85.1	95.4	4.6
1:4	Al-MCM-41 (52)	85.4	90.2	9.8
1:6		86.4	92.3	7.7
1:8		89.6	95.7	4.3
1:4	Al-MCM-41 (70)	88.3	92.3	7.7
1:6		90.2	94.7	5.3
1:8		92.5	95.7	4.3
1:4	Al-MCM-41 (112)	90.3	97.5	2.5
1:6		91.1	98.7	1.3
1:8		94.6	99.4	0.6
1:4	Fe-MCM-41 (61)	80.5	87.5	12.5
1:6		84.1	89.2	10.8
1:8		85.5	94.1	5.9
1:4	Fe-MCM-41 (115)	87.5	91.2	8.8
1:6		90.2	94.7	5.3
1:8		93.6	97.5	2.5
1:4	Al, Zn-MCM-41 (104)	78.5	82.1	17.9
1:6		85.2	85.3	14.7
1:8		88.2	92.5	7.5

Reaction conditions: temperature = 175 °C; weight of the catalyst = 0.04 g; reaction period = 7 h; pressure = autogenous pressure; reactor = 10 ml autoclave.

earlier, the first step in the scheme has been facilitated by temperature rather than the catalyst active sites (Scheme 1), and in the second step, MMP condenses with MeOH to form DMP (Scheme 2).

3.2.3. Variation with reaction temperature

Liquid-phase esterification of PAH over MCM-41 (Si/Al = 30, 52, 70, 112; Si/Fe = 61, 104; Si/Al + Zn = 104) was carried out at various reaction temperatures ranging from 135 °C to 175 °C and with mole ratios 1:4, 1:6 and 1:8 (PAH:MeOH). The reaction conditions and conversion with respect to PAH over various metal containing MCM-41 with different ratios and the conversion and selectivity of the product are given in the Tables 4–6, and the selectivity to DMP is shown in Fig. 7. Influence of acidity on MCM-41 can be explained in comparison with both Si/Al = 30 and 112 ratios and the results are presented in Table 4.

Initially, Al-MCM-41 (30), which gives 13.3 wt.% conversion, has 64.5% higher Brönsted acidity than that of Al-MCM-41 (112) which gives 29.1 wt.% conversion at 135 °C; mole ratio = 1:4 (PAH:MeOH). Al-MCM-41 (112) gives 15.8 wt.% higher conversion than Al-MCM-41 (30). Secondly, Al-MCM-41 (30) shows a selectivity of 35.8% to DMP at 135 °C, mole ratio = 1:4 (PAH:MeOH), whereas Al-MCM-41 (112) shows 70.5% selectivity to DMP at the same conditions. In this reaction, the DMP is formed in the second step. So, it can be clearly concluded that the condensation process is facile by the specific property of the catalyst and not due to the acidity of the cata-

lyst. Further comparison is made, based on the temperature study.

Generally, conversion increases with an increase in temperature. The same reaction trend has been observed in this reaction also. The conversion of PAH over Al-MCM-41 (112), with a mole ratio of 1:4 (PAH:MeOH) is 90.3 wt.% at 175 °C, whereas at 135 °C, PAH-conversion is 29.1 wt.%. In the case of selectivity to DMP was 97.5% out of the 90.3 wt.% PAH-conversion at 175 °C, whereas at 135 °C, the selectivity to DMP was found to be only 50.2 wt.% out of the 29.1 wt.% PAH-conversion. Hence, this confirms that the temperature enhances the PAH-conversion and the DMP-selectivity of condensation reaction.

3.2.4. Defective acid sites facilitates the reaction

Defective acid sites also involve in the reaction; this can be confirmed further by the two separate mock reactions. The two autoclave reactions were conducted under same conditions (catalyst = Al-MCM-41 (52); mole ratio = 1:8 (PAH:MeOH); temperature = 150 °C; weight of the catalyst = 0.04 g, reaction period = 7 h), one containing ground and another with un-ground catalyst. The results of the reaction were as expected. The ground catalyst showed better conversion. It gave 66.4 wt.% conversion and selectivity of the DMP and MMP were 86.2% and 13.8%, respectively. Un-ground catalyst showed quite lesser conversion. It gave 60.2 wt.% conversion, and selectivity of the DMP and MMP were 83.1% and 16.9%, respectively. These results apparently explained two aspects. Firstly, the external surface area

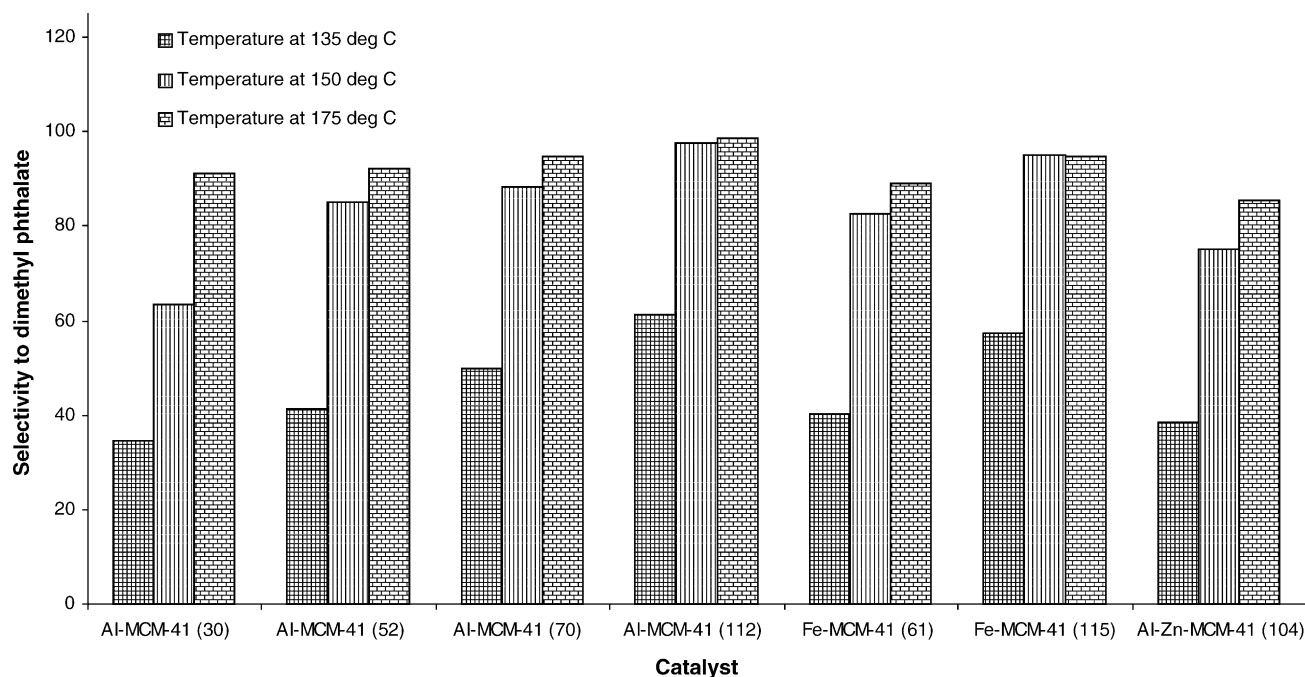


Fig. 7. Variation of selectivity to dimethyl phthalate (%) with reaction temperature over MCM-41: (Si/Al = 30, 52, 70, 112; Si/Fe = 61, 104; Si/Al + Zn = 104). Reaction conditions: weight of the catalyst = 0.04 g; reaction period = 7 h; pressure = autogenous pressure; reactor = 10 ml autoclave.

Table 7
Test-reaction data (with and without aluminium-containing catalyst) are presented

Catalyst	Conversion (wt.%)	Selectivity to phthalic anhydride (wt.%)	
		DEP	MEP
Without catalyst	64.2	14.6	85.4
Amorphous SiO ₂	68.1	18.7	81.3
Si-MCM-41	75.4	11.4	88.6

Reaction conditions: temperature = 150 °C; mole ratio = 1:8 (PAH:EtOH); weight of the catalyst = 0.04 g; reaction period = 7 h; pressure = autogeneous pressure; reactor = 10 ml autoclave.

of the powdered catalyst was high (particle size was less in the ground catalyst than the un-ground catalyst). Secondly, the external surface has lesser acidity (Si–OH has proton strongly bonded with oxygen atom due to electron-withdrawing tendency of the silicon), which increased the conversion to significant value. The ground catalyst showed 6.2% higher conversion due to the external and defective silanol groups. From the above discussion, it is confirmed that the reaction also occurs on the surface of the catalyst, apart from reaction which occurred inside the pores.

The reaction was also studied in the absence of catalyst and also in the presence of amorphous silica and Si-MCM-41 at 150 °C; their results are presented in the Table 7. This study was undertaken in order to establish the temperature effect and the catalytic activity of silanol defects. The conversion was found to be 64.2% in the absence of the catalyst, and in the presence of amorphous silica and Si-MCM-41, the conversion were 3.8% and 11.2% higher, respectively. This study establishes the activity of the silanol defects and also confirms the formation of MMP. The formation of MMP is only due to the influence of temperature, whereas the formation of DMP requires sufficient number of Brönsted active sites. Hence, the test reaction confirms the reaction occurred in the pores rather than the external surface of the catalyst.

Table 8
Influence of hydrophobic nature of the catalyst over Al-MCM-41 (Si/Al = 30, 112) molecular sieves

Weight of the catalyst	Water (ml)	Conversion (%)	Selectivity to phthalic anhydride (%)	
			DMP	MMP
Al-MCM-41 (112)	0.0	68.9	85.9	14.1
	0.05	59.8	68.2	31.8
	0.10	54.8	69.7	30.3
	0.15	51.2	59.4	40.6
	0.20	47.9	51.8	48.2
Al-MCM-41 (30)	0.0	34.4	57.2	42.8
	0.05	20.6	45.4	54.6
	0.10	12.9	20.9	79.1
	0.15	7.3	11.2	88.8
	0.20	3.1	5.6	94.4

Reaction conditions: temperature = 150 °C; mole ratio = 1:6 (PAH:MeOH); weight of the catalyst = 0.04 g; reaction period = 7 h; pressure = autogenous pressure; reactor = 10 ml autoclave.

3.2.5. Discussion of hydrophilic and hydrophobic nature of the catalyst

The aim of this particular experiment is to explain the hydrophobic nature of the catalyst, as described by Climent et al. [33]. The esterification of PAH involves a less hydrophilic reactant and a more hydrophilic MeOH with highly hydrophobic Al-MCM-41 (114) as catalyst. It is also necessary to consider the role played by the hydrophilic–hydrophobic properties of the catalyst on the relative adsorption of the two reactants. In this sense, it has been claimed [34,35] that silica MCM-41 materials are hydrophobic as they adsorb a much larger amount of cyclohexane than water. Ma et al. reported that strong acid sites enhance the hydrophilicity of the catalyst. They confirmed the results with dealumination process and they proposed that the framework dealuminated catalyst has more hydrophobic nature than the parent catalyst [3]. Palani and Pandurangan recently reported that more hydrophobic Al-MCM-41 (100) was found to be more active than other catalysts with less Si/Al ratios [36].

If this is the case, then it can be expected that the higher Al content containing MCM-41, adsorbs the more hydrophilic reactant than the other reactant. Hence, one of the reactants closer than the other has been influencing negatively the diffusion and the diffusion–adsorption–desorption rates of reactants and products. Change in Si/Al ratio in the framework of the catalyst can change this behavior. Then, with the increasing Si/Al ratio of the MCM-41, the hydrophobicity of the catalyst also tends to increase and the adsorption of the aliphatic alcohol, as well as desorption and diffusion of products will occur in larger extent, improving the catalyst behavior of the mesoporous material. The above statement indicates that the catalysts having lower Si/Al ratio does not provide surface for hydrophobic reactant.

3.2.6. Influence of water as an impurity

If the above statement is important for the conversion of PAH, then the reaction with high % of MeOH should show better conversion than with low % of MeOH over higher Si/Al ratio of the catalyst. Whereas, if same reaction is carried out

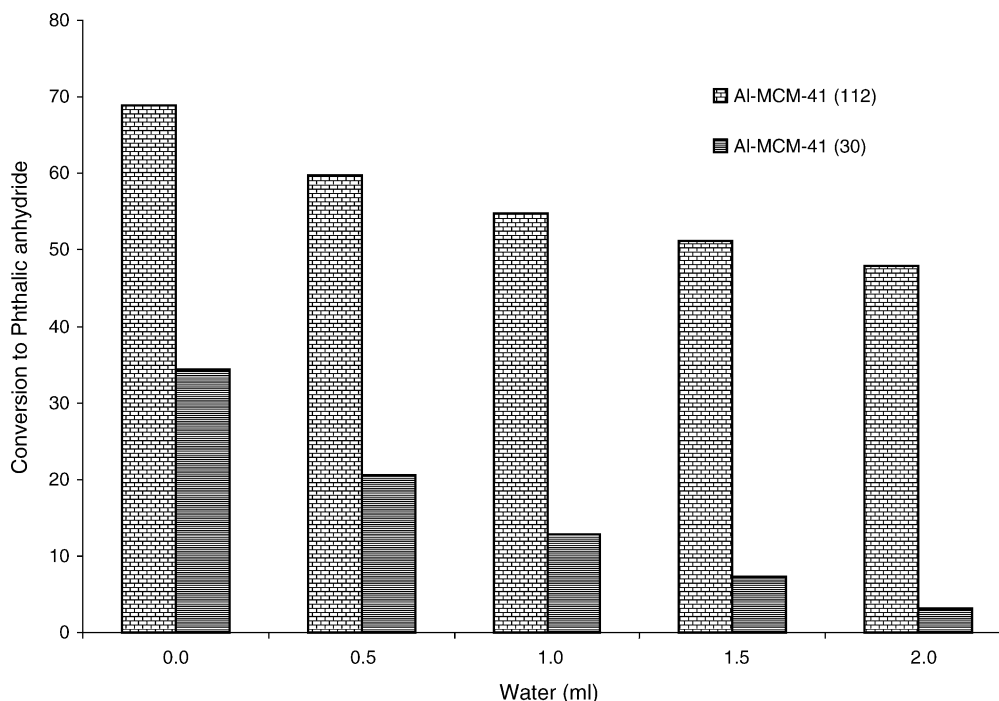


Fig. 8. Variation of selectivity to dimethyl phthalate (%) with various quantity of water over Al-MCM-41 (Si/Al=112). Reaction conditions: temperature = 150 °C; mole ratio = 1:6 (PAH:MeOH); weight of the catalyst = 0.04 g; reaction period = 7 h; pressure = autogenous pressure; reactor = 10 ml autoclave.

over lower Si/Al ratio, the catalyst should show decrease in conversion, compared to the conversion of the reaction carried out at lower mole ratios. The former statement lies in good agreement with the results, but the latter one does not coincide with the data obtained. This clearly indicates that formation of water largely influences the reaction. The catalyst having lower Si/Al ratio chemisorbs the water molecule due to its hydrophilicity. Therefore, the reactions carried out with increased mole ratio of alcohol over both the high and low Si/Al catalyst show high conversions.

The influence of water has been confirmed by the test reaction using water as an impurity, and the results are presented in the Table 8 and conversion is shown in Fig. 8. This reaction was carried out over Al-MCM-41 (Si/Al = 30 and 112); weight of the catalyst = 0.04 g; temperature = 150 °C; mole ratio = 1:6. Conversion decreases gradually with increasing water content. Al-MCM-41 (112) gives a conversion of 68.9 wt.% in a reaction containing 0 ml water. When 0.05 ml (~76000 ppm) of water was added to the reaction, the conversion fell to 59.8 wt.%. 0.05 ml water reduces the conversion up to 9.1 wt.% (13.2% less). But 34.4 wt.% of conversion was observed over Al-MCM-41 (30) for the water-less reaction. The reaction containing 0.05 ml (~76000 ppm) of water as an impurity shows 20.6 wt.% conversion. Hence, 0.05 ml of water has an impurity which decreases the conversion upto 13.8 wt.% (40.1% less).

The influence of 0.05 ml water on Al-MCM-41 (30) reduces conversion to 40.1%. Whereas, the decrease in con-

version observed over Al-MCM-41 (112) was only 13.2%. It clearly indicates that higher % of aluminum in catalyst creates strong hydrophilicity, facilitating chemisorption of water on the active sites, thus, decreasing the conversion. From this reaction, it can be concluded that lower % of aluminium contained MCM-41 shows better activity.

3.2.7. Influence of reaction time

The effect of the reaction time in the esterification of PAH by MeOH on Al-MCM-41 (Si/Al = 112) was studied at 150 °C using reactant mole ratio of 1:6 (PAH:MeOH). Conversion with respect to PAH is presented in Fig. 9. The increasing trend in conversion was observed from the 1st hour to the 10th hour. In first hour of the reaction, conversion of 13.7 wt.% was observed. As the reaction time increased, conversion too increased gradually. At the tenth hour, the reaction shows maximum conversion of 85.7 wt.% and selectivity to DMP shows 98.8%. The observations followed the usual trend of the reaction.

3.2.8. Influence of the amount of the catalyst

It is not of practical interest at all to use large amount of catalyst, as the removal of adsorbed high-molecular weight products from the catalyst is quite expensive [37]. Hence, the amount of catalyst with respect to the amount of reactant was optimized. Fig. 10 shows selectivity to DMP, and Table 9 shows the effect of amount of catalyst on the conversion and selectivity of MMP and DMP, respectively. Catalyst

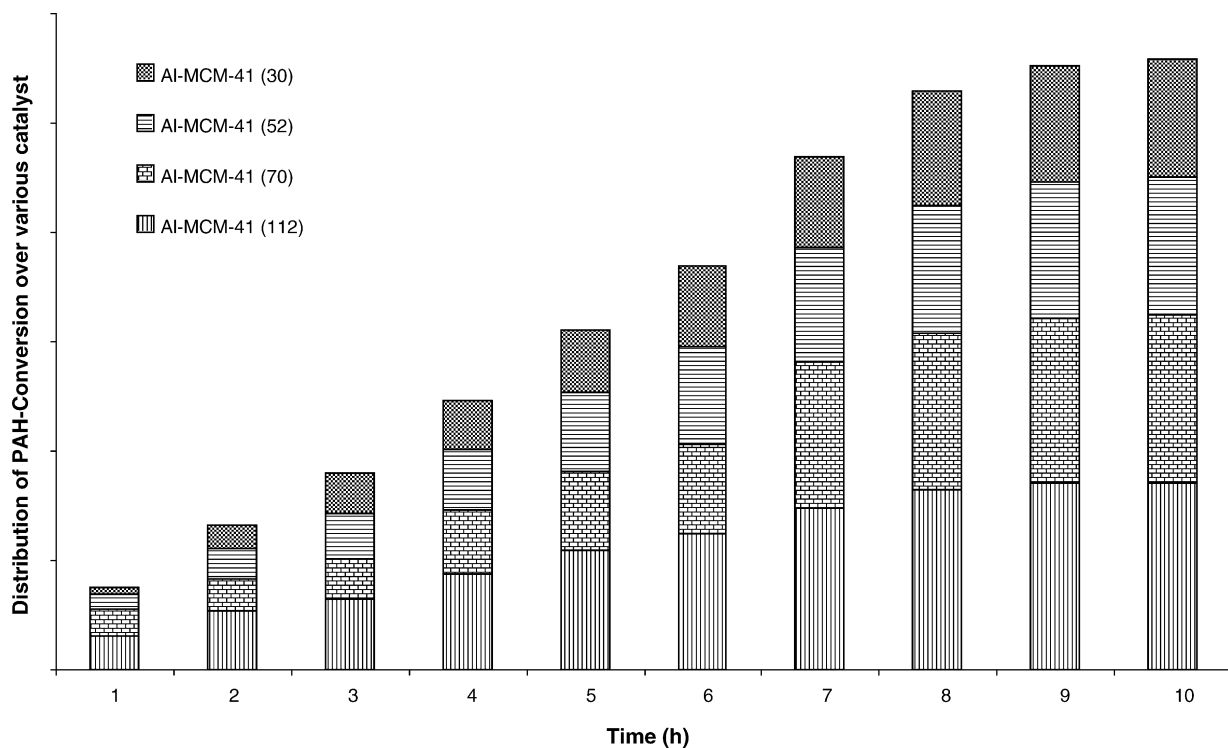


Fig. 9. Influence of time on phthalic anhydride with methanol over Al-MCM-41 (Si/Al=30, 52, 70, 112) molecular sieves. Reaction conditions: temperature = 150 °C; mole ratio = 1:6 (PAH:MeOH); weight of the catalyst = 0.04 g; reaction period = 1–10 h; pressure = autogeneous pressure; reactor = 10 ml autoclave.

amount varied from 0.02 g to 0.1 g, temperature at 150 °C; mole ratio 1:4 (PAH:MeOH) and the reaction time was 7 h. As proposed in the literature, the yield of the reaction accelerated with an increase in the amount of the catalyst. Conver-

sion increases from 0.02 g (61.4 wt.%) to 0.07 g (84.6 wt.%), optimized at 0.07 g and then shows the decrease till 0.1 g (58.9 wt.%). When the catalyst amount was increased from 0.02 g to 0.07 g, the availability of large surface area and the

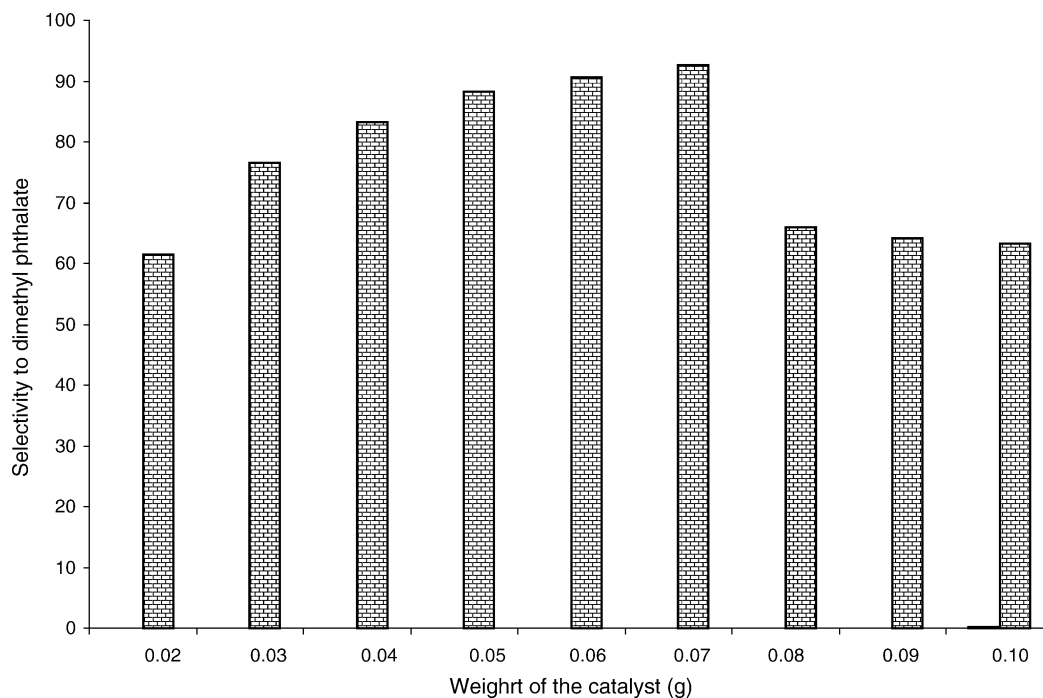


Fig. 10. Variation of selectivity to dimethyl phthalate (%) with weight of the catalyst over Al-MCM-41 (Si/Al=112). Reaction conditions: temperature = 150 °C; mole ratio = 1:4; weight of the catalyst = 0.04–0.1 g; reaction period = 7 h; pressure = autogeneous pressure; reactor = 10 ml autoclave.

Table 9
Influence of weight of the catalyst over Al-MCM-41 (112) molecular sieves

S. no.	Weight of the catalyst	Conversion	Selectivity to phthalic anhydride (%)	
			DMP	MMP
1	0.02	61.4	61.4	38.6
2	0.03	67.2	76.6	23.4
3	0.04	71.8	83.3	16.7
4	0.05	78.4	88.3	11.7
5	0.06	81.8	90.7	9.3
6	0.07	84.6	92.6	7.4
7	0.08	82.0	66.0	34.0
8	0.09	63.6	64.2	35.8
9	0.10	58.9	63.2	36.8

Reaction condition: temperature = 150 °C; mole ratio = 1:4 (PAH:MeOH); weight of the catalyst = 0.04–0.10 g; reaction period = 7 h; pressure = autogenous pressure; reactor = 10 ml autoclave.

extensively dispersed active sites enhanced the accessibility of large number of reactant molecules. Further increase in the amount of catalyst from 0.08 g to 0.10 g, then decreases the conversion gradually. With an excess amount of catalyst, the number of catalytic sites is increased, and hence, MeOH (solvent-cum-reactant) molecules easily get adsorbed on to the active site. Thus, the MeOH molecules now act only as the reactant and cease to act as the solvent (lower % of MeOH present in the reaction). The dearth of solvent molecules, which brings out the reactant–product mixture out of the catalyst pores, clogs the pores, decelerating further reaction in the same pores attributing to the decrease in conversion. This has been confirmed by a test reaction.

The reaction conditions are Al-MCM-41 (112) with weight of 0.1 g; mole ratio = 1:8 (PAH:MeOH); temperature = 150 °C; reaction period = 7 h. It gives 90.2 wt.% conversion and selectivity to DMP is 92.5%, while for MMP is 7.5%.

Secondly, Al-MCM-41 (112) with weight of 0.04 g; mole ratio = 1:8 (PAH:MeOH); temperature = 150 °C; reaction period = 7 h (data from Table 5), shows 80.1 wt.% conversion. The excess of MeOH acts as solvent and diffuses the products from the pores of the catalyst, thus increasing the trend in conversion.

3.2.9. Influence of mole ratio of the reactants

The influence of mole ratio of the reactants on conversion and selectivity to both MMP and DMP, respectively, were studied over Al-MCM-41 (112) with reaction period of 10 h. Various mole ratios of PAH:MeOH (1:4, 1:6, 1:8, 1:10, 1:12, 1:14) were studied at 150 °C. The conversion and the product selectivity are shown in Table 10, and selectivity of DMP is presented in the Fig. 11. The PAH-conversion increased upto 1:10 mole ratio and then it decreased gradually. DMP was observed as the most selective product than the MMP [38]. The conversion of PAH is 88.2 wt.% for

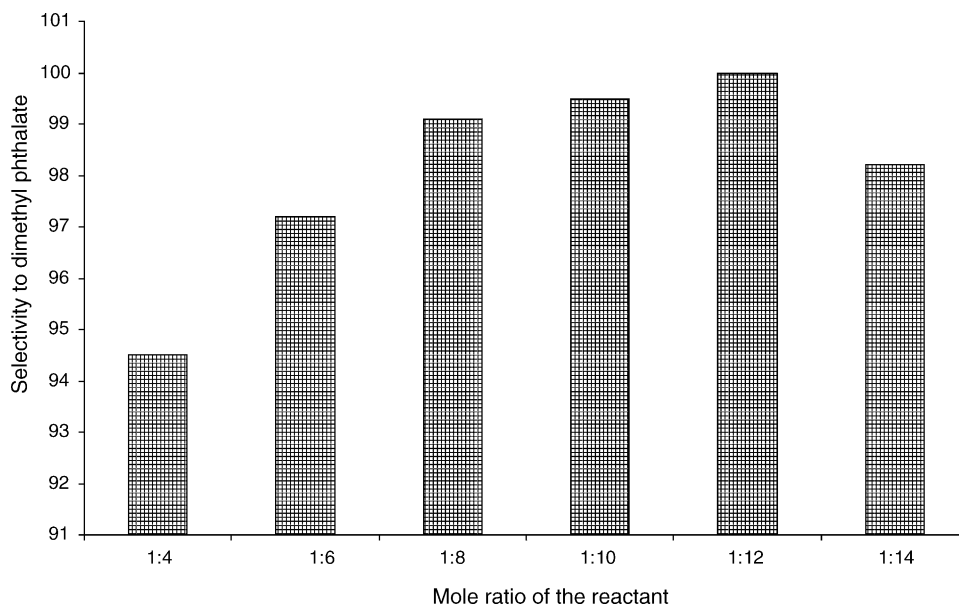


Fig. 11. Variation of selectivity to dimethyl phthalate (%) with mole ratio (PAH:MEOH) over Al-MCM-41 (Si/Al=112). Reaction conditions: temperature = 150 °C; weight of the catalyst = 0.07 g; reaction period = 10 h; mole ratio = 1:4–1:14; pressure = autogeneous pressure; reactor = 10 ml autoclave.

Table 10

Influence of mole ratio of phthalic anhydride with methanol over Al-MCM-41 (112) molecular sieves

Mole ratio (PAH:MeOH)	Conversion	Selectivity to phthalic anhydride (%)	
		DMP	MMP
1:4	88.2	94.5	5.5
1:6	92.5	97.2	2.8
1:8	94.9	99.1	0.9
1:10	97.2	99.5	0.5
1:12	99.1	100	–
1:14	96.1	98.2	1.8

Reaction conditions: temperature = 150 °C; weight of the catalyst = 0.07 g; reaction period = 10 h; pressure = autogenous pressure; reactor = 10 ml autoclave.

a mole ratio of 1:4. With further increase in mole ratio, conversion reaches 99.1% at mole ratio of 1:10. Increase in mole ratio of the reactant from 1:8 to 1:10 shows only 1.2 wt.% increase in conversion. The conversion decreases when mole ratio is above 1:10 (PAH:MeOH). Increasing the mole ratio from 1:4 to 1:10 (PAH:MeOH) reactant molecules will be present around the active sites of catalyst surface, promoting the conversion upto optimum level. Above the optimum mole ratio (1:10), availability of PAH on the catalyst surface decreases gradually that reduces the PAH-conversion.

4. Conclusion

Through this study, it can be inferred that Al-MCM-41 catalyst could be the convenient eco-friendly alternative to the conventional hazardous mineral acid catalyst for esterification reactions. Iron and zinc containing MCM-41 shows less activity due to higher acidity. The reaction confirms that catalyst repels water by its hydrophobic nature and shifts the reaction towards the right hand side. The higher % of alcohol also decreases the conversion and the higher amount of catalyst blocks the reactant. Maximum conversion and products selectivity can be attained at the end of 10 h at 150 °C, which can be achieved sufficiently only by the specific nature of the solid acid catalyst.

Acknowledgements

One of the authors, Dr. A. Pandurangan, gratefully acknowledges the BRNS funding agency for the financial support. Mr. S. Udayakumar thanks the BARC for SRF scholarship.

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