

Esterification of terephthalic acid with methanol over mesoporous Al-MCM-41 molecular sieves

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Abstract

Esterification of terephthalic acid with methanol was carried out over Al-MCM-41 (Si/Al = 25, 50, 75 and 100) molecular sieves in the vapour phase (with respect to methanol) at 200, 250, 300 and 350 °C, and under autogenous pressure conditions at 200 °C. The vapour phase reaction showed 90% conversion at 300 °C over Al-MCM-41 (100) with 100% selectivity to dimethyl terephthalate (DMT). Under the autogenous pressure, the reaction yielded about 95% DMT over Al-MCM-41 (100). The catalytic role of Al-MCM-41 was established by comparing activity with Si-MCM-41. The effects of various reaction parameters such as temperature, terephthalic acid loading, methanol flow rate, and catalyst weight on conversion were studied and the results discussed.

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Keywords: Al-MCM-41; Esterification; Terephthalic acid; Methanol; Dimethyl terephthalate

1. Introduction

Esterification of terephthalic acid with methanol is an industrially important process. The product, dimethyl terephthalate (DMT), is used in the production of poly(ethyleneterephthalate) (PET) [1,2]. World DMT/TPA capacity was over 75 million metric tons as of 1 January 2004. Much of the growth in capacity has been in East Asia as countries such as Taiwan, the Republic of Korea and China have become internally sufficient in polyester terephthalate fibers, films and solid-state resins. Esterification of carboxylic acid with alcohols has been generally carried out over homogeneous mineral acid catalysts such as sulphuric acid [3]. But there are drawbacks such as corrosion of reaction vessels, the disposal of liquid acid catalysts and separation of products from the catalysts. Therefore, the replacement of liquid acid catalysts by solid acid catalysts can make the work up procedures easier and the catalysts are also environmental friendly. Many reports are available for esterification of carboxylic acid with alcohol using solid acid catalysts [4–13]. Recently Al-MCM-41 has been employed as catalysts for broad range of reactions

such as alkylation, acylation, esterification and etherification [14–21]. Based on these reports, the title reaction was carried out over Al-MCM-41 (Si/Al = 25, 50, 75 and 100) in the liquid as well as in the vapour phase. Terephthalic acid is generally produced by oxidation of *p*-xylene and subsequent esterification with methanol to obtain dimethyl terephthalate. In the Amoco process, liquid phase oxidation of *p*-xylene to terephthalic acid was carried out with a soluble manganese-cobalt catalyst using compressed air as oxidant [22]. Terephthalic acid was then esterified in another reactor with methanol at 250–350 °C. This process is used for the purification of terephthalic acid. In 1947, a patent was applied for the production of DMT with terephthalic acid and methanol at a temperature of about 225–350 °C under super atmospheric pressure in the presence of catalysts consisting of zinc oxides, lead oxides, etc. [23]. The above batch process may be replaced by vapour phase reaction (with respect to methanol) at convenient temperatures below its sublimation (402 °C). In the present study the technique for esterification of terephthalic acid adapted by Meyer et al. [24] was slightly modified and employed. But Al-MCM-41 molecular sieves have been used as the catalysts in the present work. In addition, the reaction has been studied over Al-MCM-41 under autogenous condition and the results are discussed in the following sections.

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2. Experimental

2.1. Chemical reagents

Sodium meta silicate, aluminium sulphate, cetyltrimethylammonium bromide, sulphuric acid and terephthalic acid were purchased from Merck and were used as such. Methanol was refluxed over CaO for 6 h and distilled before use.

2.2. Catalyst preparation

Al-MCM-41 molecular sieves with Si/Al ratio 25, 50, 75 and 100 were prepared by the following method [25]. In a typical synthesis 10.6 g of sodium meta silicate in demineralised water was combined with appropriate amount of aluminium sulphate. It was then acidified with 2 M H₂SO₄ to bring down the pH to 10.5 under stirring. After 30 min of stirring, an aqueous solution of cetyltrimethylammonium bromide (CTAB) was added and the resultant gel was stirred for 45 min at room temperature. The molar composition of the resultant gel was SiO₂; xAl₂O₃; 0.2CTAB; 0.89H₂SO₄; 120H₂O (x various with Si/Al ratios). The gel was autoclaved and kept at 145 °C for 48 h. The solid obtained was filtered, washed with distilled water, and dried at 100 °C in air. The as-synthesised sample was then calcined at 550 °C in air for 6 h to remove the template.

2.3. Characterisation

X-ray diffraction (XRD) measurements were conducted on a Siemens D5005 diffractometer using Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation. The diffractograms were recorded in the 2θ range of 0–10° in steps of 0.02° with a count time of 15 s. 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. FT-IR spectra of the molecular sieves were collected on Nicolet (Avatar 360) instrument using KBr pellet technique. Solid-state ²⁷Al MAS-NMR spectra were recorded using Bruker MSL 400 spectrometer equipped with a magic angle-spinning (MAS) unit to analyse the aluminium environment.

The acidity of the material was analysed by pyridine adsorption followed by FT-IR spectroscopy. The catalyst sample (10–15 mg) was finely grounded and was pressed for 2 min at 10 t/cm² pressure under vacuum into a self-supporting wafer. The wafers were calcined under vacuum ($133.322 \times 10^{-3} \text{ N/m}^2$) at 500 °C for 2 h, followed by exposure to pyridine vapour at

ambient temperature for 2 h to allow the pyridine to permeate the samples. After adsorption of the pyridine vapours on the wafer, the physisorbed pyridine molecules have been expelled using high vacuum for 30 min. After expelled physisorbed vapours on the catalyst wafer it was placed in the FT-IR cell and the spectrum was recorded on a Nicolet 800 (Avatar 360) FT-IR spectrometer.

2.4. Reaction procedure

The reaction was carried out in a fixed bed, continuous flow glass reactor of 40 cm length and 1 cm internal diameter. About 0.4 g of catalyst mixed with terephthalic acid was taken in a reactor tube. A motor driven syringe pump was used to feed methanol. After completion of each run, the reaction system was flushed with nitrogen to expel the reactant and products, then the products were analysed by gas chromatograph (HP-5890) with FID detector and OV-17 column. The products were confirmed using authentic samples and by FT-IR and NMR techniques. After each catalytic run, moisture and carbon dioxide free air was passed through the reactor for 6 h at 500 °C. The conversion of terephthalic acid was computed from the following equation.

Conversion of terephthalic acid

$$= \frac{\text{DMT}(\text{theoretical}) - \text{DMT}(\text{experimental})}{\text{DMT}(\text{theoretical})} \times 100$$

For reactions under autogenous condition, the catalyst, terephthalic acid and methanol were taken together in a 15 ml autoclave and heated in an oven at constant temperature for a definite time interval. The products were analysed as discussed above.

3. Results and discussion

3.1. Characterisation

The XRD patterns of as-synthesised and calcined mesoporous catalysts show a sharp reflection at $d[100]$ ascribed to the hexagonal structure of the mesopore. The weak broad signals appear at $[110]$ and $[200]$ reflections indicate the presence of the long-range order structure and regular mesoporous structure. The unit cell parameters of as-synthesised and calcined Al-MCM-41 catalysts are given in Table 1. The data obtained are in good agreement with those reported by Beck et al. [25].

Nitrogen adsorption isotherms revealed three different well-defined stages. The computed BET surface areas pore size and

Table 1
Physical characteristics of Al-MCM-41 (25), Al-MCM-41 (50), Al-MCM-41 (75), Al-MCM-41 (100) catalysts

Catalysts	Calcined		Uncalcined		Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
	d_{100} (Å)	Unit cell (nm)	d_{100} (Å)	Unit cell (nm)			
Al-MCM-41 (25)	37.81	4.37	38.47	4.44	951	3.485	0.964
Al-MCM-41 (50)	37.45	4.32	38.47	4.44	982	3.190	0.970
Al-MCM-41 (75)	37.45	4.32	38.19	4.41	1035	2.661	0.952
Al-MCM-41 (100)	37.81	4.36	38.19	4.41	1042	2.665	0.952

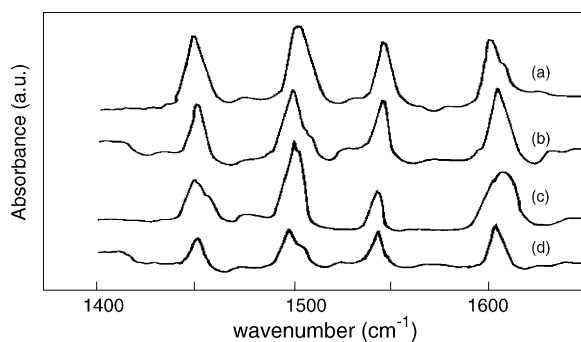


Fig. 1. FT-IR spectrum of (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75), (d) Al-MCM-41 (100) catalysts containing adsorbed pyridine.

pore volume are presented in Table 1. The isotherms show well-defined stages and they coincide with those already reported in the literature [26].

The FT-IR spectra of the as-synthesised and calcined Al-MCM-41 materials are shown. The broad envelope around 3500 cm^{-1} is due to O–H stretch of water, surface hydroxyl groups and bridged hydroxyl groups. There are less intense peaks just below 3000 cm^{-1} in the spectra of the as-synthesised samples, which are assigned to symmetric and asymmetric stretching modes of the $-\text{CH}_2$ group of the locked-in template. The intense peak at 1123 cm^{-1} is due to the asymmetric stretching of T–O–T groups. The symmetric stretching modes of T–O–T groups are observed around 800 cm^{-1} and the peak at 460 cm^{-1} is due to the bending mode of T–O–T group. These spectral features resemble those reported by the previous workers [27].

The FT-IR spectra of Al-MCM-41 (25, 50, 75 and 100) containing adsorbed pyridine are presented in Fig. 1 and the quantitative data of the relative acidity of the Al-MCM-41 samples are presented in Table 2. The peak at 1545 cm^{-1} in all the spectra with intensities decreasing from Si/Al (25) to Si/Al (100) is assigned to pyridine adsorbed on the Bronsted acid sites of the catalysts. The peak at 1455 and 1620 cm^{-1} whose intensity decreases from Si/Al (25) to Si/Al (100) is assigned to the pyridine adsorbed on the Lewis acid sites. It suggests the presence of more amount of non-framework aluminium in Al-MCM-41 (25). The peak at 1500 cm^{-1} indicates the pyridine adsorbed on both Bronsted and Lewis acid sites. The intensities of the peaks due to pyridine adsorbed on Bronsted acid sites correlate with Si/Al ratio of the catalysts [28].

^{27}Al MAS-NMR spectra of samples are presented in Fig. 2. The peak at 53.7 ppm in all the spectra is assigned to tetrahedrally

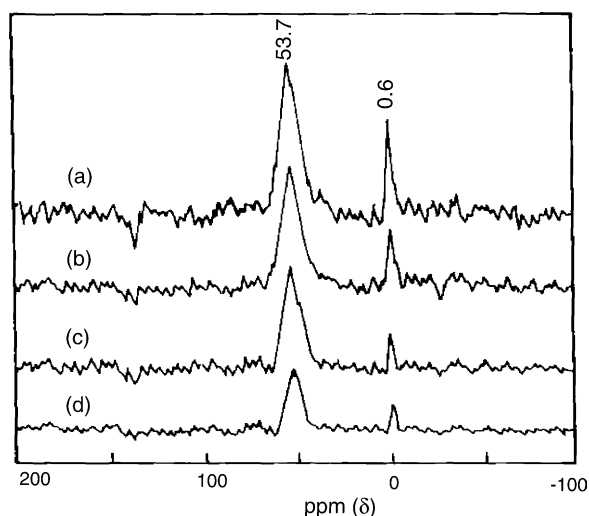


Fig. 2. ^{27}Al MAS-NMR spectrum of Al-MCM-41 molecular sieves after calcinations: (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75), (d) Al-MCM-41 (100).

co-ordinated framework aluminium, and the peak at 0.6 ppm is assigned to octahedral non-framework aluminium species. Chakraborty et al. [29] reported water co-ordinated framework aluminium could also produce peak around 0 ppm .

3.2. Esterification in the vapour phase

The vapour phase esterification of terephthalic acid with methanol was studied at $200, 250, 300$ and $350\text{ }^\circ\text{C}$. 0.5 g terephthalic acid was mixed with 0.4 g of catalyst and the mixture was contacted with methanol vapours at a flow rate of 3.5 ml/h for 3 h . This technique is quite different from the conventional vapour phase reaction that involves the use of liquid reactants. The results are illustrated in Fig. 3. The data show a linear trend of increase in conversion with temperature for all the catalysts. DMT was the only product observed in the reaction and mono methyl terephthalate (MMT) was not observed indicating MMT rapidly undergoes subsequent esterification to DMT. As the melting point of terephthalic acid is $427\text{ }^\circ\text{C}$, there might not be acid independent esterification on the surface. On the other hand, terephthalic acid may be leached out by methanol vapours and subsequently esterified over the acid sites Al-MCM-41.

Table 2
Bronsted and Lewis acidity values of mesoporous molecular sieves

Catalysts	423 K	
	BA ^a	LA ^a
Al-MCM-41 (25)	7.8	9.0
Al-MCM-41 (50)	7.0	8.9
Al-MCM-41 (75)	3.6	5.5
Al-MCM-41 (100)	3.4	1.1

^a Acidity ($\mu\text{mol py/g}$ catalyst).

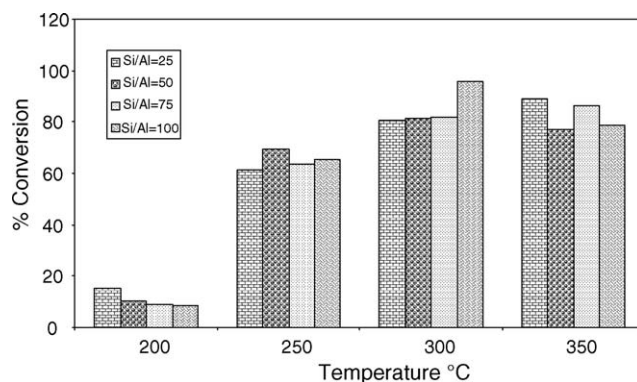


Fig. 3. Effect of temperature in the vapour phase over Al-MCM-41 catalysts.

Table 3
Effect of terephthalic acid content over Al-MCM-41 (100) in the vapour phase at 300 °C

Weight of terephthalic acid	% Conversion
0.5	95.5
1.0	82.0
1.5	60.0

Amount of catalyst = 0.4 g, methanol feed rate = 3.5 ml/h, temperature = 300 °C, time = 3 h, selectivity = 100% (DMT).

In order to verify this, the reaction was also studied over Si-MCM-41 under similar conditions (300 °C with flow rate of 3.5 ml/h for 3 h) and the conversion obtained was only 35%. Thus, the esterification is catalysed by more acidic sites of Al-MCM-41 than the defective sites of Si-MCM-41. The reaction was also studied at 300 °C without catalyst the conversion was found to be 21%, which is 69%, less than in the presence of the catalyst. Hence, it is established that the reaction mainly occurs over the acidic sites of Al-MCM-41 molecular sieves.

In order to establish that the reaction occurs mainly over the acid sites lying inside the pore of Al-MCM-41, the reaction was also studied over amorphous silica–alumina catalyst. The conversion was only 40.6%. Hence, methanol leaching of terephthalic acid and the esterification of the same within the pores of Al-MCM-41 might be the actual sequence of the process in this study.

The effect of terephthalic acid content on conversion and product selectivity was studied with 0.5, 1.0 and 1.5 g of terephthalic acid over Al-MCM-41 (100) with methanol flow rate 3.5 ml/h for 3 h. The results are presented in Table 3. Conversion decreased with increase in the weight of terephthalic acid, and the selectivity to DMT remained at 100%. The decrease in conversion might be due to decrease in the amount of methanol accessibility to every terephthalic acid crystals to leach out. In order to verify this, the reaction was studied by varying the methanol flow rate at 300 °C (Table 4). The conversion increased with increase in the flow rate from 1.5 to 2.5 ml/h. Hence at the flow rate 2.5 ml/h there might be an increased amount of alcohol accessibility to every terephthalic acid crystals for leaching out, i.e. there could still sufficient attraction between terephthalic acid and methanol that could facilitate leaching out process. Although this observation is in line with our view, further increase in the flow rate from 3.5 to 4.5 ml/h, decrease in conversion was observed. Hence, rapid diffusion might not leach out terephthalic acid for esterification.

Table 4
Effect of methanol feed over Al-MCM-41 (100) in the vapour phase at 300 °C

Methanol feed (ml/h)	% Conversion
1.5	66
2.5	97
3.5	95.5
4.5	92

Terephthalic acid = 0.5 g, catalyst weight = 0.4 g, temperature = 300 °C, time = 3 h, selectivity = 100% (DMT).

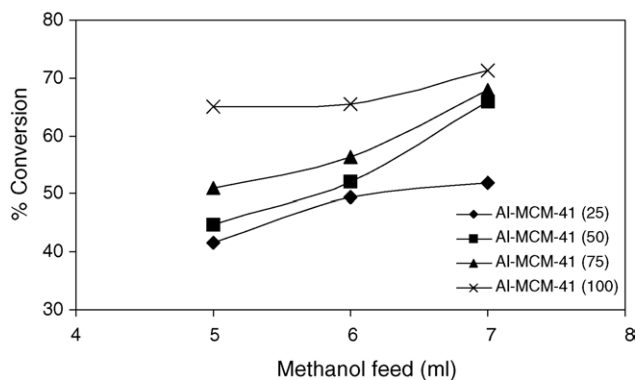


Fig. 4. Effect of methanol content over Al-MCM-41 (25), Al-MCM-41 (50), Al-MCM-41 (75), Al-MCM-41 (100) in the liquid phase under autogenous conditions.

3.3. Reaction under autogenous pressure

The reaction was also studied under autogenous pressure by autoclaving the reactants and the catalysts at 200 °C. The conversion of terephthalic acid and the product selectivity are illustrated in Fig. 4. The conversion increased with increase in methanol content over all the catalysts in line with our view. Hence, there is more leaching of terephthalic acid with methanol, similar to the above discussion. It could be suggested that the activation of terephthalic acid by protonation on the surface followed by nucleophilic attack on it by methanol (Eley–Rideal mechanism) could be operated in both the liquid and vapour phase reactions. In order to justify this, the reaction was also studied under autogenous pressure at 200 °C without the catalyst. The conversion was 26%, which is 79% less than that in the presence of the catalyst, thus establishing the Eley–Rideal mechanism involving protonation of terephthalic acid and subsequent nucleophilic attack on it by methanol. Among the catalysts studied Al-MCM-41 (100) was observed to be more active than others. Hence, the Bronsted acid sites of this catalyst are to be more acidic than the other catalysts.

3.3.1. Effect of time on stream

The effect of time-on-stream on terephthalic acid conversion was studied at 200 °C over Al-MCM-41 (100) under autogenous pressure. The results of the conversion and product selectivity are presented in Table 5. The conversion increased with time thus establishing time dependent nature of the reaction. There are sequences of steps like leaching at the outermost surface of every particles, their diffusion into the mesopores, their chemisorption on the Bronsted acid sites, nucleophilic attack on them by methanol to yield ester and desorption of DMT. The reaction reached a maximum conversion of about 90% at the end of 8–9 h. Coke is not observed in the entire reaction time. The selectivity to DMT remained 100%. Since the reaction was suggested to attain equilibrium at the end of 8–9 h, the reverse reaction, viz., hydrolysis of DMT to terephthalic acid could also occur on the catalyst surface. However, the higher conversion obtained with high Si/Al ratio throughout the reaction can be attributed due to its high hydrophobic nature of the catalyst; with which it repel

Table 5

Effect of time-on-stream over Al-MCM-41 (100) in the liquid phase under auto-genous conditions at 200 °C

Time (h)	% Conversion
1	28
2	49
3	65
4	71.4
5	73.5
6	75
7	78
8	80.9
9	81

Terephthalic acid = 0.5 g, catalyst weight = 0.4 g, temperature = 200 °C, selectivity = 100% (DMT).

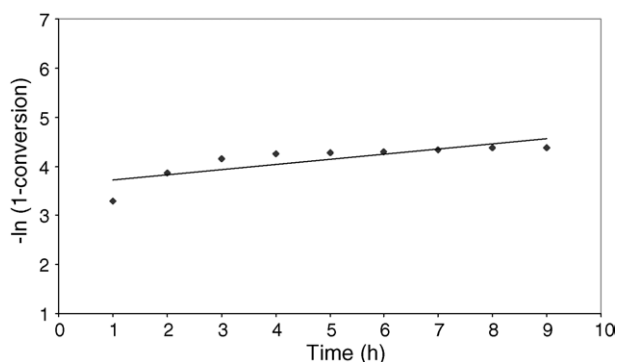


Fig. 5. Determination of rate constant value in the liquid phase at 200 °C under autogenous conditions.

Table 6

Effect of catalyst amount over Al-MCM-41 (100) in the liquid phase under autogenous conditions at 200 °C

Weight of the catalyst	% Conversion
0.5	80.9
1.0	82.4
1.5	83.4
2.0	92.0

Terephthalic acid = 0.5 g, methanol = 7 ml, temperature = 200 °C, time = 8 h, selectivity = 100% (DMT).

the water out of the pores thereby thwarting the hydrolysis of DMT to terephthalic acid.

In order to verify that the reaction is diffusion controlled, the rate constant has been determined by plotting conversion versus time. Pseudo first-order rate constant is evaluated and the results are presented in Fig. 5. The rate constant value is found to be 0.1049 in line with our view. The effect of catalyst amount on the conversion and product selectivity was also studied over Al-MCM-41 (100) at 200 °C (Table 6). The conversion increased with increase in the amount of the catalyst due to increase in the number of active sites.

4. Conclusion

Esterification of terephthalic acid with methanol was carried out over Al-MCM-41 molecular sieves both in the vapour phase and in the liquid phase under autogenous pressure. The

reaction was shown to occur by leaching of terephthalic acid by methanol and subsequent adsorption on Bronsted acid sites following Eley–Rideal mechanism. Mono methyl terephthalate was not observed and hence esterification of one carbonyl group might not be influenced by other. Liquid phase reaction under autogenous condition gave higher conversion than vapour phase reaction. The requirement of more acidic sites was established by running the reaction over Al-MCM-41 and Si-MCM-41. Compared to conventional methods in which hazardous mineral acid and metal oxides of less surface area are used, the present technique is better as it involves high surface Al-MCM-41 molecular sieves and eco-friendly nature.

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