

# Esterification of Phthalic Anhydride over Al-MCM-48 Molecular Sieve

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**Abstract—** Mesoporous Al-MCM-48(Si/Al = 25, 50, 75 and 100) and Al,Mg-MCM-48 (Si/(Al+Mg) = 25 and 50) were synthesized hydrothermally and characterized by XRD, SEM, TEM and BET. The orderly arrangement of mesopores was clearly evident from TEM images in all the samples. Their catalytic activity was tested in the esterification of phthalic anhydride with isopropanol at 120 °C. Phthalic anhydride rapidly reacted with isopropanol to form monoisopropyl phthalate (MIPP) even in the absence of a catalyst. But the subsequent reaction of MIPP with isopropanol to form diisopropyl phthalate (DIPP) was found to be catalyst dependent. Based on the MIPP conversion, Al-MCM-48(25) is found to be more active than others which is due to the presence of more density of acid sites. Phthalic acid was not observed in the reaction and hence the released water during the course of the reaction is not used to bring hydrolysis of MIPP. As the subsequent esterification of MIPP proceeded even in the absence of catalyst, the carbonyl group of the ester is suggested to activate the adjacent carboxyl group in the MIPP. A separate reaction with Si-MCM-48 gave conversion slightly higher than the catalyst independent route. It is attributed to reactants organizing property of Si-MCM-48.

**Keywords:** MCM-48; esterification; phthalic anhydride; MIPP; DIPP

## I. INTRODUCTION

Generally phthalic esters are liquid and they resemble very much like vegetable oils. They act as softener for hard plastics like polyvinyl chloride. Dialkylphthalates in general and diisopropylphthalate in particular is a commercially important plasticizer. Diisopropylphthalate has been prepared by the esterification of phthalic acid or phthalic anhydride with isopropanol using hazardous mineral acid catalysts. Hence, the use of eco-friendly solid acid catalysts such as zeolites are advantageous. But zeolites have diffusion constrain for both reactants and products. In this context the use of mesoporous solid acid catalysts is suggested to be quite good as the reactants and products can freely diffuse in and out of the pores respectively. They also have high surface area (about 1000 m<sup>2</sup>/g), high thermal stability (> 700 °C) and large pore size (> 20 Å). Mesoporous MCM-41 has been reported as active catalyst for the esterification of phthalic anhydride with methanol [1]. Friedel-Crafts alkylation and acylation are also found to be successful over MCM-41 [2, 3]. Koster et al. [4] reported esterification of acetic acid with ethanol over MCM-41. Bhagiyalakshmi et al. [5] have reported esterification of maleic anhydride with methanol.

MCM-48, yet another mesoporous material like MCM-41, has three dimensional cross-linked pores. It has higher surface area than MCM-41. Such three dimensional cross-linked pores are advantageous as the contact time of the reactants are increased, and largely suppressed the coke forming reactions. In addition the acid sites are very well scattered. So unlike MCM-41 where the pores are not cross-linked, every active site in MCM-48 can be considered to exhibit the same probability for adsorbing the reactants to catalyze the reaction. The catalytic activity of Al-MCM-48 has already reported in the literature [6-9]. It is reported that only Bronsted acid sites are the active sites. Based on the previous reports, in the present study we synthesized Al-MCM-48(Si/Al = 25, 50, 75 and 100) and Al,Mg-MCM-48(25 and 50) and tested their catalytic activity in the esterification of phthalic anhydride with isopropanol in the liquid phase.

## II. EXPERIMENTAL METHODS

### A. Preparation of the catalysts

Tetraethylorthosilicate (TEOS; Merck), aluminium hydroxide (Merck) and magnesium acetate (Merck) were used as the sources for silicon, aluminium and magnesium respectively. N-hexadecyltriethyl ammonium bromide (Merck) was used as the structure directing agent. Other chemicals such as sodium hydroxide, phthalic anhydride and isopropanol were of Merck samples and used as such without further purification

In a typical synthesis of sodium form of Al-MCM-48, TEOS was added slowly to a solution of N-hexadecyltriethylammonium bromide dissolved in distilled water. Sodium hydroxide (1M) was added to it and the pH was raised to 11.6. The gel was then stirred for 30 min at room temperature (solution I). The required amount of aluminium hydroxide in 31.2 ml water was stirred for 2 h at 80 °C (solution II). The aluminium hydroxide solution (II) was added slowly to solution I under constant stirring. The resulting mixture was then stirred for 1 h at room temperature. The mixture was transferred to a 500 ml autoclave and kept in an air oven at 100 °C for 72 h. The samples were labeled as Al-MCM-48 (x) where x denotes Si/Al molar ratio. The solid product obtained was washed with distilled water and dried at 100 °C. The dried material was calcined at 550 °C for 1h in nitrogen atmosphere followed by 6 h in air to remove the organic template. The Na form of Al-MCM-48 was converted to H form by repeated ion exchange with 1M ammonium nitrate followed by calcination at 550 °C for 6 h in air. Al,Mg-MCM-48 with Si/(Al+Mg) ratios of 25 and 50 were synthesized by adopting the same procedure with magnesium acetate as the source for magnesium.

### B. Characterization

The X-ray diffraction (XRD) patterns of calcined Al-MCM-48 and Al,Mg-MCM-48 were recorded on a PANalytical X'Pert Pro X-ray diffractometer using CuK $\alpha$  radiation. The low angle diffractograms were recorded in the 2 $\theta$  range 1.0-10° with a 2 $\theta$  step size of 0.01° and a step time of 10 s at each point. Surface area measurement of all the catalysts was carried out by nitrogen adsorption at 77 K on a ASAP-2010 porosimeter from Micromeritics Corporation (Norcross, GA, USA). Before nitrogen adsorption-desorption measurements, the samples were degassed for 3 h at 250 °C under vacuum (10<sup>-5</sup> mbar) in the degas port of the adsorption analyzer.

Scanning electron microscopic (SEM) images were recorded in a SEM (Hitachi S-4500LV) instrument and TEM images were recorded using a high resolution TEM instrument (JEOL 3010 electron microscope) operated at 300 kV. The powder samples were softly grounded in an agate mortar and dispersed in acetone in an ultrasonic bath for several minutes. A few drops were then deposited on a 200 mesh copper grid covered with a holey carbon film. Macrostructures of the solids were imaged directly by conventional method and also using CRISP computer program.

### C. Catalytic studies

Esterification of phthalic anhydride with isopropanol was carried out in liquid phase. Phthalic anhydride (1 mol), isopropanol (5 mol) and catalyst (0.05 g) were taken in a 50 ml round bottom flask fitted with a reflux condenser. The flask with its contents placed in an oil bath was heated at a constant temperature and simultaneously stirred magnetically. Aliquots of the hot mixture were withdrawn at regular intervals to monitor the progress of the reaction. The samples were centrifuged and the centrifugates were analyzed with a Shimadzu GC-17A gas chromatograph using a DB-5 capillary column (30m X 0.25mm X 0.25  $\mu$ m) equipped with a flame ionization detector. The identification of products was also made using GC-MS Perkin Elmer Auto System XL gas chromatograph (Perkin-Elmer elite series PE-5 capillary column, 30m X 0.25mm X 1  $\mu$ m) equipped with a Turbo Mass Spectrometer (EI, 70 eV) using helium as the carrier gas at a flow rate of 1ml/min.

## III. RESULTS AND DISCUSSIONS

### A. XRD

The XRD patterns of Al-MCM-48(Si/Al = 25, 50, 75 and 100) and Al,Mg-MCM-48 Si/(Al+Mg) = 25 and 50) are shown in Fig. 1. In all the spectra the pattern due to (211) plane is clearly seen but the pattern due to (220) is not well resolved. Zhao et al. [10] reported well resolved patterns for MCM-48. But such well resolved patterns are not seen for the present materials. The patterns due to (420) and (332) are overlapped in all the spectra without enough resolution. Similar spectra were also reported by Huang et al. [11]. The intensity of the pattern due to (211) is less for all magnesium incorporated molecular sieves than aluminium incorporated molecular sieves. In the spectra of Al-MCM-48 the intensity of the pattern due to (211) increased with increase in Si/Al ratio of the materials. Hence aluminium is suggested to have retardation influence on the orderly arrangement of pores. But TEM results indicated very orderly arrangement of pores. Hence within the material there may be some distortion in order to reduce the intensity of the XRD patterns.

## B. BET

The  $N_2$  adsorption-desorption isotherms of Al-MCM-48(Si/Al = 25, 50, 75 and 100) and Al,Mg-MCM-48(Si/(Al+Mg) = 25 and 50) are shown in Fig. 1. All the isotherms exhibited the characteristics of type IV adsorption isotherm [12]. There are two hysteresis loops in all the isotherms, the first one occurred at low  $p/p_0$  due to condensation of nitrogen in the capillary and the second one at high  $p/p_0$  due to condensation in the voids formed between the particles [13]. Based on the positions it could be presumed that the size of voids may be larger in dimension than the pore size. Comparison of the height due to pore condensation illustrates that the pore volume of Al-MCM-48 is higher than that of Al,Mg-MCM-48. The sharpness of pore size condensation suggests uniform pore size distribution [12]. A general conclusion drawn is a decrease in all these parameters with the increase in the metal content of the molecular sieves. Generally when silicon is substituted by aluminium or magnesium, it could be expected an increase in all these parameters because of higher bond angles of aluminium and magnesium tetrahedra than silicon tetrahedra. But the observed values are not in accordance with our expectation. When aluminium or magnesium is planted on the framework, the latter carries negative charges; a unit negative charge for each aluminium and two unites of negative charges for each magnesium. With this negative charge the framework can move close to the surface of the micelle rods that carries positive charge. Such a close approach is suggested to be main cause for the decrease in all these parameters with the increase in metal content

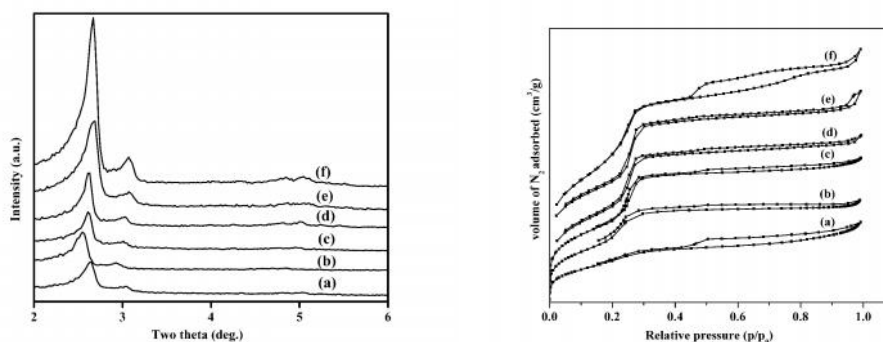


Fig. 1 XRD and BET patterns of calcined (a) Al,Mg-MCM-48(25), (b) Al,Mg-MCM-48(50), (c) Al-MCM-48(25), (d) Al-MCM-48(50), (e) Al-MCM-48(75) and (f) Al-MCM-48(100).

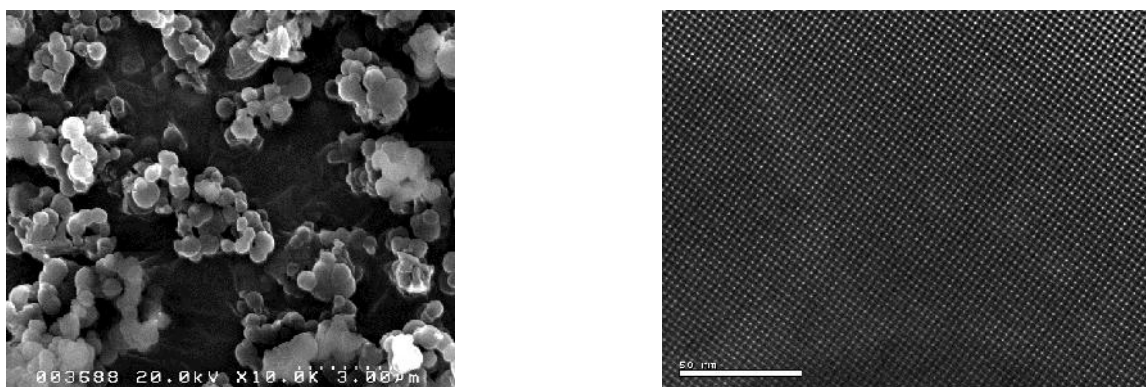


Fig. 2 SEM and TEM patterns of calcined (a) Al-MCM-48(25)

## C. SEM and TEM

The SEM picture of Al-MCM-48(25) is shown on above Fig. 2. It shows particles of spherical morphologies and such similar morphologies have already been reported in the literature [14]. The particles are of different sizes but other phases are not present. The TEM picture of Al-MCM-48(25) is shown in Fig. 2. The pores are arranged orderly illustrating textural uniformity. Similar images are also reported in the literature [14].

#### D. CATALYTIC STUDIES

Esterification of phthalic anhydride with isopropanol was carried out over Al-MCM-48(Si/Al = 25, 50, 75 and 100) and Al,Mg-MCM-48(Si/(Al+Mg) = 25, 50) in the liquid phase. The results are presented in Table 1. The major products are found to be monoisopropyl phthalate (MIPP) and diisopropyl phthalate (DIPP). The conversion results of phthalic anhydride and monoisopropyl phthalate (MIPP) and product selectivity are presented in Table 1. The conversion of phthalic anhydride is found to be 100% over all the catalysts, as the reaction of phthalic anhydride with isopropanol is instantaneous and catalyst independent. This is similar to the reported esterification of maleic anhydride with methanol [5]. But the conversion of monobutyl phthalate to di-butyl phthalate is catalyst dependent which decreased with increase in the Si/Al ratio of the catalysts. But the esterification of acids with alcohols over zeolites it was observed that the yield of esters increased with increase in the Si/Al ratio of the catalysts. This is due to rapid expulsion of water out of the pores of high hydrophobic character [5]. This observation is quite contradicting the present results. Al-MCM-48(25) with high hydrophilic character showed higher conversion than catalysts of high hydrophobic character. Similar results are also obtained over Al,Mg-MCM-48 catalysts. Since the materials are mesoporous and the acid sites are well scattered over the surface, it could be more appropriate to consider them as hydrophobic. Hence, it is the number of acid sites that is the main criterion for conversion. Under this context it is understandable for the high conversion of monoisobutyl phthalate over Al-MCM-48(25). The selectivity of DIPP over Al-MCM-48 (25) is found to be 96%, which decreased with increase in the Si/Al ratio of the catalysts. Similar trend was also observed over Al,Mg-MCM-48 catalysts. Hence the concept of hydrophobicity of catalysts in the high Si/Al ratio is again not applicable to account for the decrease in the selectivity of DIPP with increase in the Si/Al ratio of the catalysts.

Generally esterification is an equilibrium reaction catalyzed by mineral acid catalysts and hence 100% conversion is not easy to attain under ordinary condition. But in the present reaction with hydrophobic heterogeneous catalysts, the active sites are located in the hydrophobic regions. When MIPP is esterified, the released water will be repelled away from the hydrophobic regions and so it can not acquire activation to hydrolyze both MIPP and DIPP. Hence 100% conversion may not be an unusual observation over solid acids in general and mesoporous materials in particular. So the concept of esterification and hydrolysis catalyzed by mineral acid catalysts can not be as such applied to heterogeneous catalysts while interpreting the results of conversion.

The effect of feed ratio on the conversion of MIPP and product selectivity was studied at 1:1, 1:3, 1:5, 2:1 and 4:1 over Al-MCM-48 (25) at 120 °C and the results are presented in Table 2. As expected, the conversion of MIPP with 1:1 feed ratio was almost nil whereas it was very much significant (88%) with selectivity of DIPP (89%) at 1:3. Similarly the conversion of MIPP was almost nil at 2:1 and 4:1 feed ratios. This observation is the prerequisite to confirm that mono esterification of phthalic anhydride does not require any catalyst. The 100% selectivity of MIPP at 1:1, 2:1 and 4:1 also confirms our view that Bronsted acid sites are located in the hydrophobic regions and hence accessibility of water to such regions may not be feasible to hydrolyze MIPP to phthalic acid. Based on the conversion and product selectivity, the feed ratio of 1:5 was found to be better than others. It is presumed that MIPP may be rapidly chemisorbed on the active sites of the catalyst, and isopropanol slowly attacks MIPP to give DIPP. This assumption is confirmed by the increase in conversion with increase in isopropanol content in the feed.

The effect of reaction time on MIPP conversion and selectivity to DIPP was studied by conducting the reaction for 3, 6, 8, 12 and 18 h with the feed ratio 1:5 at 120 °C. The results are presented in Table 3. Both MIPP conversion and selectivity to DIPP increased with increase in reaction time but the increase was not significant at 18 h. The same reaction was also carried out over Si-MCM-48 for 12 h with 1:5 feed ratio at 120 °C. In addition, the results obtained in the absence of catalyst are also presented. The conversion of MIPP is found to be much less over Si-MCM-48 illustrating the requirement of more acidic catalysts. But the conversion is slightly higher than in the absence of the catalyst. Hence, siliceous materials may possess the organizing effect of reactants, and promote the catalysts independent route to give more conversion. Since the conversion of MIPP is not to zero in the absence of catalyst, there is a possibility for activation of COOH group by the adjacent ester group. In order to establish the fact, esterification of benzoic acid was studied with isopropanol in the absence of catalyst for a reaction period of 12 h under the same condition. It was observed that the conversion was 20% less than the conversion of MIPP thus confirming our view.

**Table 2.** Effect of temperature on reactant conversion and product selectivity

Catalyst	Temperature (°C)	Conversion (%)		Product selectivity (%)	
		Phthalic anhydride	MIPP	DIPP	MIPP
Al-MCM-48(25)	80	100	91.4	91.5	8.5
	100	100	92.8	93.2	6.8
	120	100	95.2	96.1	3.9
	150	100	94.5	95.9	4.1
Al-MCM-48(50)	80	100	88.7	90.8	9.2
	100	100	90.2	91.7	8.3
	120	100	91.3	93.0	7
	150	100	91.2	94.3	5.7
Al-MCM-48(75)	80	100	84.9	88.2	11.8
	100	100	86.4	89.7	10.3
	120	100	89.0	91.2	8.8
	150	100	88.7	90.9	9.1
Al-MCM-48(100)	80	100	80.7	86.3	13.7
	100	100	84.5	87.9	12.1
	120	100	86.1	89.4	10.6
	150	100	85.9	88.7	11.3
AlMgMCM-48(25)	80	100	89.4	91.2	8.8
	100	100	91.2	92.4	7.6
	120	100	92.1	94.5	5.5
	150	100	91.7	93.7	6.3
AlMgMCM-48(50)	80	100	85.9	85.9	14.1
	100	100	86.7	87.7	12.3
	120	100	87.5	88.6	11.4
	150	100	88.2	88.1	11.9

Reaction condition: Catalyst amount 0.05 g; Feed ratio 1:5 (phthalic anhydride: isopropanol); Time 12 h

**Table 3.** Effect of Feed ratio on reactant conversion and product selectivity

Feed ratio	Conversion (%)		Product selectivity (%)	
	Phthalic anhydride	MIPP	DIPP	MIPP
1:1	100	76.0	0.0	100
1:3	100	88.0	89.0	4
1:5	100	95.2	96.0	4
2:1	100	0.0	0.0	100
4:1	100	0.0	0.0	100

Reaction condition: Catalyst Al-MCM-48(25); Catalyst amount 0.05 g; Temperature 120 °C; Time 12 h

**Table 4.** Effect of time on stream on reactant conversion and product selectivity

Time (h)	Conversion (%)		Product selectivity (%)	
	Phthalic anhydride	MIPP	DIPP	MIPP
3	100	67.0	72	28
6	100	76.0	79	21
8	100	82.0	87	13
12	100	93.2	96	4
18	100	89.0	91	9

Reaction condition: Catalyst Al-MCM-48 (25) Catalyst amount 0.05 g; Temperature 120 °C; Feed ratio 1:5 (phthalic anhydride: isopropanol)

#### IV Conclusion

Mesoporous Al-MCM-48 and Al,Mg-MCM-48 molecular sieves were synthesized hydrothermally and characterized. The orderly arrangement of pores in them was confirmed by XRD and TEM images. Their catalytic activity was tested in the esterification of phthalic anhydride and isopropanol. The monoesterification of phthalic anhydride is very rapid and catalyst independent but the subsequent esterification of MIPP to DIPP is catalyzed one. In the esterification of MIPP it is presumed that MIPP is activated by chemisorption and free isopropanol attacks on it to give DIPP. As the reaction occurred even in the absence of catalyst, the carboxyl group of MIPP is suggested to be activated by the adjacent ester group. Since the conversion of MIPP is slightly higher over siliceous MCM-41 than in the absence of catalyst, the later may have good reactants organizing property (i.e) the catalyst can bring the reactants close and allow them to react further on its surface. Hence mesoporous Al-MCM-48 may be a convenient and ecofriendly solid acid catalyst for the esterification of phthalic anhydride with isopropanol to diisopropyl phthalate.

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