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Synthesis of mesoporous zeolites and their application for catalytic conversion of polycyclic aromatic hydrocarbons

Kondam Madhusudan Reddy, Chunshan Song *

Fuel Science Program, Department of Materials Science and Engineering 209 Academic Projects building, The Pennsylvania State University, University Park, PA 16802, USA

Abstract

Three series of mesoporous aluminosilicate (Al-MCM-41) samples were synthesized using different aluminum sources including aluminum isopropoxide, pseudo boehmite and aluminum sulfate. Their catalytic activities were tested in the conversion of aromatic hydrocarbons including hydrocracking of 1,3,5-triisopropylbenzene, alkylation of naphthalene, and hydrogenation of naphthalene and phenanthrene. The three series of Al-MCM-41 samples behaved differently in acting as acidic catalysts and as supports. The Al-MCM-41 synthesized using aluminum isopropoxide was found to be the most promising acidic catalyst and good support for Pt catalyst.

Keywords: Mesoporous molecular sieves; Al-MCM-41; Hydrocracking; Isopropylation; Hydrogenation; Polycyclic aromatic hydrocarbons

1. Introduction

Microporous molecular sieve catalysts such as zeolite Y and ZSM-5 are widely used catalysts in acid-catalyzed reactions for the production of fuels, petrochemicals, and fine chemicals [1–3]. However, their applications are limited to relatively small molecules as their pore size is restricted to micropore size range (usually < 1.4 nm). With the growing demand for treating heavier feeds, as well as for synthesis of large molecules for producing commodity and fine chemicals, it is necessary to develop catalysts with larger pores. Recently, Mobil researchers have reported a new series of mesoporous molecular sieves [4,5]: MCM-41 is one of the members of this extensive family of mesoporous series possessing a hexagonal array of uniform mesopores. Many reports have since appeared on synthesis and characterization of these new materials [6–11]. The pore dimensions of these materials can be tailored (in the range of 1.5–10.0 nm or more) through the choice of surfactant and auxiliary chemicals as templates and crystallization conditions in the synthesis procedure. The BET surface area of these materials is usually more than 1000 m^2/g with high sorption capacities of 0.7 ml/g and greater. Moreover, these materials can be synthesized in a large range of framework Si/Al ratios and therefore can develop acid sites of different strength.

However, information on the method of introducing aluminum into the framework of

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* Corresponding author.

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MCM-41 and the catalytic activity of the resulting Al-MCM-41 is still limited. Our work focuses on the synthesis and catalytic applications of Al-MCM-41. This work is motivated by the need for more efficient upgrading of heavy oils and coal-derived liquids to produce clean transportation fuels, particularly thermally stable jet fuels. In this paper, we report the synthesis of three series of Al-MCM-41 samples using different aluminum sources and their application for catalytic conversion of polycyclic aromatic hydrocarbons as model compounds.

2. Experimental

The mesoporous aluminosilicate molecular sieves, Al-MCM-41, were synthesized hydrothermally in 100 ml Teflon-lined autoclaves from a mixture of reactants with the following composition: $50SiO_2–\chi Al_2O_3–2.19(TMA)_2O–15.62(CTMA)Br–3165H_2O$; where $\chi = 0.5$ and 1.0, TMA and CTMA stand for tetramethylammonium and cetyltrimethylammonium, respectively. Three series of samples with varying Si/Al ratios were synthesized using different aluminum sources (aluminum isopropoxide, pseudo boehmite and aluminum sulfate). Prior to catalytic runs, the organic template from the as-synthesized solids was removed by calcining the samples in a tubular furnace at 550°C for 1 h in nitrogen and 6 h in air flow. The Al-MCM-41 samples were characterized by chemical analysis, X-ray diffraction, nitrogen adsorption, thermogravimetric analysis, and solid state NMR. More details for synthesis and characterization are given elsewhere [11].

The calcined samples were ion-exchanged with ammonium nitrate (0.5 M) at 90°C. The protonated form was then obtained by calcining these ammonium ion-exchanged samples at 480°C for 3 h. The Pt-loaded catalysts (3 wt% Pt) were prepared by incipient wetness impregnation on protonated MCM-41, with the required amount of hexachloroplatonic acid ($H_2PtCl_6 \cdot H_2O$,from Aldrich) solution, followed by calcination in air at 450°C for 3 h.

The catalytic properties of the mesoporous zeolites were tested for the following reactions: (1) hydrocracking of 1,3,5-triisopropylbenzene (TIPB), (2) isopropylation of naphthalene, and (3) hydrogenation of naphthalene and phenanthrene. All the chemicals were of reagent grade from Aldrich and used as supplied. A 30 ml stainless-steel tubing bomb batch reactor was used for all the experiments. During the reaction, reactors were heated in a fluidized sandbath under vertical shaking (240 cycles/min). The standard reactor charge was 0.10 g of catalyst and 1.0 g of reactant and other reaction conditions are given in appropriate tables for individual reactions. At the end of the reaction, the reactor was quenched in a cold water bath. The reaction products were collected in acetone solution and analyzed by GC (Perkin-Elmer 8500) using DB-17 fused silica capillary column. The products were identified by GC-MS (Hewlett-Packard 5890II GC coupled with a mass selective detector). More analytical details may be found elsewhere [12,13].

Table 1
Synthesis and physical characteristics of mesoporous zeolites Al-MCM-41

Sample	Al source	SiO_2/Al_2O_3 (mole ratio)		BET surface area (m^2/g)	Pore diam. from sorption (Å)
		Input	Output		
MRK9a	Al isopropoxide	100	88.4	1147	27.7
MRK9b	Al isopropoxide	50	53.8	1206	28.0
MRK10a	Catapal B	100	95.5	1010	21.9
MRK10b	Catapal B	50	44.3		
MRK11a	Al sulfate	100	164.6	834	25.4
MRK11b	Al sulfate	50	87.4		

3. Results and discussions

We have synthesized three series of mesoporous Al-MCM-41 samples using aluminum isopropoxide, pseudo boehmite (Catapal B), and aluminum sulfate, with feed Si/Al ratios of 50 and 25. Some synthesis parameters and the physical characteristics of the resulting Al-MCM-41 are shown in Table 1. The crystallinity, the incorporation of aluminum in framework and the acidity were studied by XRD, nitrogen sorption, thermal desorption of *n*-butylamine on samples, ^{27}Al MAS NMR. A typical XRD pattern of Al-MCM-41 (MRK10b) is shown in Fig. 1. X-ray diffraction patterns showed that all the samples are well crystallized and phase pure with a very strong peak and three weak peaks [4,5]. It was observed from nitrogen sorption and XRD studies that the samples prepared with aluminum sulfate are less crystalline compared to the other two series of samples. However, the incorporation of aluminum in framework was found to be more effective with aluminum isopropoxide and aluminum sulfate, compared to pseudo boehmite. The aluminum incorporation was characterized by increase in the interplanar *d*-spacings from XRD and was confirmed by the peak corresponding to Al in tetrahedral coordination in ^{27}Al MAS NMR. The acidity due to the presence of aluminum in the framework was determined by a thermal desorption of *n*-butylamine on the samples. As the aluminum incorporation is higher in samples prepared with aluminum isopropoxide and aluminum sulfate, they have shown higher acidity compared to the samples prepared with pseudo boehmite. More detailed results on the synthesis and characterization of Al-MCM-41 samples are described elsewhere [11].

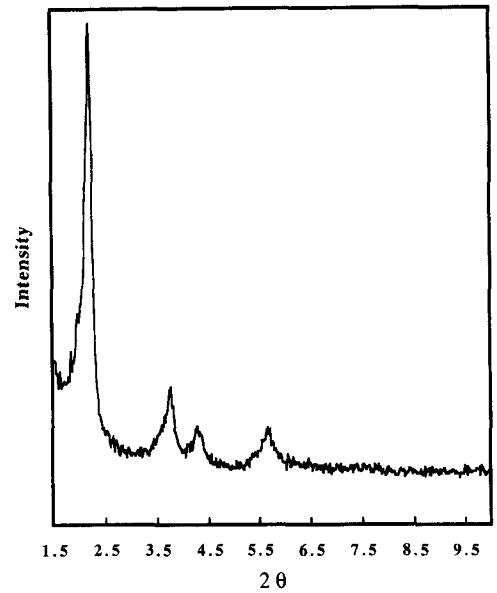

Fig. 1. A typical X-ray powder diffraction pattern of Al-MCM-41 molecular sieve. This sample corresponds to MRK10b in Table 1.

Catalytic test results for the hydrocracking of TIPB, isopropylation of naphthalene, and hydro-

Table 2

Hydrocracking of 1,3,5-triisopropylbenzene over Al-MCM-41 catalysts. Reaction conditions: 0.1 g catalyst, 1.0 g triisopropylbenzene, 1500 psi H_2 pressure, 350°C for 2 h or 300°C for 30 min

	Al-MCM-41 catalysts					
	None [a]	H/MRK9b [b]	H/MRK10b [b]	H/MRK11b [b]	H/MRK9b [a]	Pt/MRK9b [a]
Conversion (wt%, based on feed)	0.4	47.5	29.2	43.5	77.1	100.0
Liquid products (wt%)						
1,3,5-triisopropylbenzene	99.6	52.5	70.8	56.5	22.9	0
isopropylbenzene	0.0	1.5	0.7	1.3	8.2	0
1,3-diisopropylbenzene	0.3	15.1	13.1	15.6	28.5	0
1,4-diisopropylbenzene	0	4.8	3.4	5.0	8.1	0
benzene and others [c]	0	4.4	3.2	4.6	2.9	19.8
Total liquid products (wt%)	99.9	78.3	91.2	83.0	70.6	19.8

[a] 350°C for 2 h.

[b] 300°C for 30 min.

[c] Benzene and alkylbenzenes.

genation of naphthalene and phenanthrene are summarized in Table 2, Table 3, Tables 4 and 5. The general observation is that the synthesized Al-MCM-41 can be used as a catalyst for acid-catalyzed reactions, and as a support for hydrogenation and hydrocracking catalysts.

Table 2 shows the results of hydrocracking of a bulky molecule. TIPB, over mesoporous zeolite catalysts at 350 and 300°C. Without a catalyst, the conversion of TIPB was negligible, even at higher temperature (350°C) with longer reaction time (2 h). The protonated catalysts, H/Al-MCM-41, showed significant catalytic activity for runs both at 300 and 350°C. The main liquid products with H/Al-MCM-41 are mono- and di-substituted isopropylbenzenes. The main gaseous products are propane and propylene. There is some difference in the catalytic activity of the protonated Al-MCM-41 catalysts prepared with different aluminum sources. The samples prepared with aluminum isopropoxide (MRK9b) and aluminum sulfate (MRK11b) showed higher activity compared to the one prepared with pseudo boehmite (MRK10b). The TIPB conversion at 300°C decreased in the following order with respect to the catalysts: H/MRK9b > H/MRK11b > H/MRK10b. This order is consistent with that of framework aluminum incorporation in these samples. In the experiments with H/Al-MCM-41, the catalytic TIPB hydrocracking is exclusively due to the acidic sites. It is apparent from the above results that there is clear difference in the acid characteristics between the Al-MCM-41 samples. It should be mentioned that 1,4-diisopropylbenzene was also detected in the liquid product, which was formed during TIPB hydrocracking.

We also examined TIPB hydrocracking at 350°C using H/Al-MCM-41 sample prepared from aluminum isopropoxide (MRK9b) with and without platinum loading. TIPB hydrocracking at 350°C for 2 h afforded substantially higher conversion than that at 300°C for 30 min, as might be expected. Loading Pt on Al-MCM-41 resulted in a highly active hydrocracking catalyst, which gave 100% conversion of TIPB compared to a 77% conversion over the catalyst without Pt at 350°C. It is interesting to note that diisopropylbenzene was the major product with H/Al-MCM-41 catalyst, but disappeared with Pt/Al-MCM-41 catalyst. This may be due to the hydrogenation promoted by Pt which leads to further cracking, which is known for zeolite-supported Pt catalysts. The above results show that Al-MCM-41 catalysts are also good catalysts for hydrocracking. though they are less acidic compared to the well-known microporous Y-zeolites. The data with Pt/Al-MCM-41 catalyst indicate that loading platinum on mesoporous zeolites can produce excellent hydrocracking catalysts. A major advantage of mesoporous Al-MCM-41 catalysts is that they are capable of converting very large molecules,

Table 3
Isopropylation of naphthalene over Al-MCM-41 catalysts. Reaction conditions: 0.1 g catalyst, 1.0 g naphthalene, 150 psi propylene, 200°C for 2 h

	Al-MCM-41 catalysts			
	H/MRK9b	Pt/MRK9b	Pt/MRK10b	Pt/MRK11b
Naphthalene conv.(%)	92.5	96.6	37.4	90.2
Product selectivity (wt%)				
2-isopropylnaphthalene	11.8	9.1	24.6	11.6
1-isopropylnaphthalene	16.3	9.9	56.2	20.3
diisopropylnaphthalenes	42.1	39.2	16.4	42.2
2,6-diisopropylnaphthalene	3.2	4.9	0.8	2.1
2,7-diisopropylnaphthalene	4.0	3.8	0.8	2.1
triisopropylnaphthalenes	25.4	34.3	2.5	22.3
tetraisopropylnaphthalenes	4.4	7.5	0.3	3.6

whose sizes are too large to enter the pores of microporous zeolites.

Table 3 presents the product analyses of isopropylation of naphthalene using propylene over mesoporous zeolite catalysts. The alkylation reaction was used as a probe reaction, because it is known to occur on acid sites in zeolites. All the catalysts showed catalytic activity for naphthalene alkylation, and the main products are mono-, di-, tri- and tetra-isopropylnaphthlenes. It is worthy noting that the α-substitution proceeded in preference to β-substitution over all the H/Al-MCM-41 and Pt/Al-MCM-41 catalysts. Moreover, tri- and tetra-isopropylnaphthalene are formed in large quantities which is a clear indication of easy diffusion of large molecules in the Al-MCM-41 catalysts. Since the electron density of α-position in naphthalene is higher than that β-position [12], α-substitution is favored kinetically provided that there is enough space inside the pore channel for the formation of bulky transition state and the out-of-pore diffusion of the 1-isopropylnaphthalene and its derivatives. In the runs with microporous mordenite catalysts under comparable conditions, the formation of such bulky molecules as α-substituted isopropylnaphthalenes as well as tri- and tetra-isopropylnaphthalenes is very limited due to the steric restrictions of the small micropores [12,13]. These results once again indicate that the diffusion and conversion of large-sized molecules can readily occur in the mesopore channel of Al-MCM-41 catalysts, which are not easy within the pore channel of microporous zeolites.

Table 3 also shows the effect of Pt loading on the mesoporous zeolite prepared from Al isopropoxide. Both the protonated neat-H/Al-MCM-41 and Pt/Al-MCM-41 catalyst showed good activity in the reaction of isopropylation of naphthalene. In general, the catalytic activity and selectivity of the two catalysts appeared to be similar to each other. The Pt-containing catalyst yielded somewhat less mono- and di-isopropylnaphthalenes and more tri- and tetra-isopropylnaphthalenes.

There is also a significant difference in catalytic activity among the Al-MCM-41 catalysts prepared using different aluminum sources. The MCM-41 catalyst prepared with pseudo beohmite was not as active as the other two MCM-41 catalysts, as can be seen from Table 3. It indicates that the catalyst prepared with pseudo beohmite is less acidic, which again confirms the poor incorporation of aluminum in the framework compared to the other two catalysts. In alkylation reactions over zeolites, the type of alkylating agent is also known to have an effect. For example, the alkylation with alcohols was found to be less efficient compared with alkenes in terms of conversion [13]. Similar results were observed with these mesoporous molecular sieves. The conversion of naphthalene to isopropylnaphthalenes was found to be less when isopropanol was used as an alkylating agent compared to propylene. This could be due to the inhibition of catalytic activity by the water formed in the alkylation with alcohol.

Table 4 presents the results of naphthalene hydrogenation. Al-MCM-41 supported Pt catalysts are very active for the hydrogenation. The conversion was almost 100% with all the catalysts. However, the type of Al-MCM-41 supports significantly effects the selectivity of Pt

Table 4
Naphthalene hydrogenation over Pt/Al-MCM-41 catalysts. Reaction conditions: 0.1 g catalyst, 1.0 g naphthalene, 1000 psi H_2 pressure, 200°C for 1 h

Catalyst	Naphthalene conv.(%)	Product selectivity (wt%) tetralin	*t*-decalin	*c*-decalin	Total decalins	*t*-/*c*-decalins
Pt/MRK9b	100.0	0.2	33.2	66.6	99.8	0.497
Pt/MRK10b	99.7	25.5	18.0	56.5	74.5	0.319
Pt/MRK11b	100.0	0.0	32.3	67.7	100.0	0.476

catalysts. When the support was Al-MCM-41 prepared with pseudo beohmite, there was a large amount of intermediate product tetralin. On the other hand, with the Pt catalysts supported on the Al-MCM-41 samples prepared with aluminum isopropoxide and aluminum sulfate, the conversion of tetralin to decalin was almost complete. The *t*-decalin/*c*-decalin ratios for all the MCM-41 catalysts are low, especially in the case of the Al-MCM-41 catalyst prepared with pseudo beohmite the ratio is lower compared to the earlier results reported for mordenite-supported Pt catalysts [14,15]. Our earlier results indicate that the isomerization of *c*-decalin to *t*-decalin takes place on acid sites. Moreover, this isomerization was promoted strongly when Pt was loaded on mordenite [15]. In this context, MCM-41 samples are less acidic as compared to mordenite, the difference in *t*-/*c*-decalin ratios reflect the different characteristics between Pt-loaded mordenite and Al-MCM-41 catalysts. Moreover, this ratio is very low for the Al-MCM-41 catalyst prepared with pseudo beohmite because of the poor incorporation of aluminum in the framework, leading to poor acidity.

Table 5 shows the product analyses in hydrogenation of phenanthrene over three different Pt-loaded Al-MCM-41 catalysts. They are all active but their product selectivities are different. The products were mainly di-, tetra- and octa-hydrophenanthrenes. The phenanthrene conversion and the yields of *sym*-octahydrophenanthrene decreased in the following order with respect to the Al source used for preparing Al-MCM-41: pseudo boehmite (MRK10b) > Al isopropoxide (MRK9b) > Al sulfate (MRK11b). This order is different from that observed for naphthalene hydrogenation (Table 4). The *sym*-octahydroanthracene was also detected, which is a product from isomerization of *sym*-octahydrophenanthrene. Song and Moffatt [16] have found that this type of isomerization reaction, denoted as ring-shift isomerization, occurs over Y and mordenite catalysts at low temperatures. They concluded that the isomerization occurs on acid sites. The present results for hydrogenation of phenanthrene showed that isomerization of *sym*-octahydrophenanthrene also occurred during hydrogenation, but it is not occurring as effectively as on Y and mordenite zeolites. Probably MCM-41 catalysts are not as acidic as microporous zeolites, especially the MCM-41 catalyst prepared with pseudo beohmite. Chen et al. [6] and Corma et al. [8] also noted the relatively lower acidity of MCM-41 compared to mordenite and Y-zeolites.

We also analyzed the particle size of the Pt in the supported catalysts. Fig. 2 shows the X-ray diffraction patterns of Pt-loaded MCM-41 catalysts. It is noticeable from the peak intensities and their widths that Pt particle size is more or less similar in all the samples. The Pt particle

Table 5
Hydrogenation of phenanthrene over Pt/Al-MCM-41 catalysts.Reaction conditions: 0.1 g catalyst, 1.0 g phenanthrene, 1500 psi H_2 pressure, 300°C for 2 h

	Al-MCM-41 catalysts		
	Pt/MRK9b	Pt/MRK10b	Pt/MRK11b
Phenanthrene conv. (%)	79.6	88.0	66.6
Product selectivity (wt%)			
1,2,3,4-tetrahydrophenanthrene (THP)	7.1	6.8	14.8
9,10-dihydrophenanthrene (DHP)	41.8	45.5	54.4
sym-octahydrophenanthrene (*sym*-OHP)	14.9	31.3	13.3
sym-octahydroanthracene (*sym*-OHA)	16.9	1.4	7.7
unsym-octahydrophenanthrene (*unsym*-OHP)	15.4	13.0	9.6
tetradecahydrophenanthrenes (TDHP)	3.9	2.0	0.2
sym-OHA/*sym*-OHP	1.13	0.05	0.58

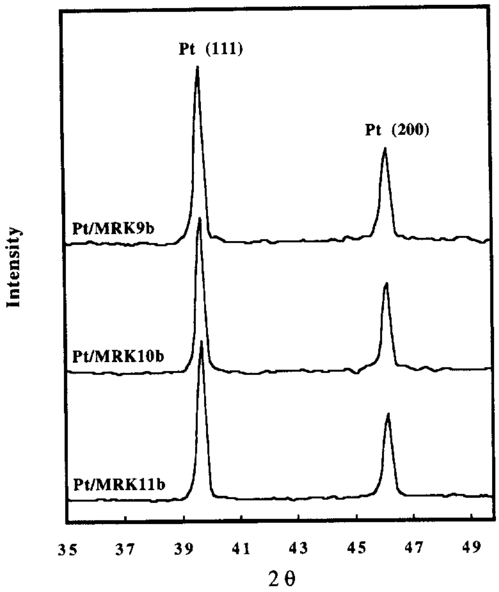

Fig. 2. X-ray diffraction patterns (in Pt range) of Pt loaded Al-MCM-41 catalysts.

size was calculated using the Scherrer equation [17] from the XRD data, which was about 1700 Å for all the three different samples. The XRD data also support the earlier discussion on alkylation (Table 2) in that the difference in catalytic activities of Pt-loaded Al-MCM-41 are due mainly to the differences in the acidity of the samples. Schmitz and Song [14] observed that the particle size of Pt was different for mordenite and Y-zeolites and their different Si/Al ratio analogs. The Pt particle size was found to be different for different types of mordenite and Y-zeolite supports even though the same procedure has been used for Pt loading. It was also observed that the activities and selectivities of these catalysts vary with the type of support for hydrogenation of naphthalene [14]. However, the present results indicate a close similarity of Pt particles on the three different Al-MCM-41 supports. On the other hand, since the Pt particle size determined from XRD is two orders of magnitude larger than the pore size of Al-MCM-41, it is likely that some of the pores are blocked. However, the XRD can only detect the particles larger than ~ 30 Å. The presence of fine particles inside the pores cannot be ruled out by XRD data.

4. Conclusions

The results of this work, though still preliminary, have clearly demonstrated the potential of mesoporous zeolites, Al-MCM-41, as acidic catalysts themselves and as supports for hydrogenation and hydrocracking catalysts. We observed that mesoporous zeolite catalysts are capable of converting bulky aromatic hydrocarbons. The activity of the mesoporous zeolites can be significantly different, depending on the synthesis conditions, especially with respect to the source of aluminum. The catalysts prepared with aluminum isopropoxide and aluminum sulfate were found to be more active for acid catalyzed reactions, compared to the ones prepared with pseudo boehmite. Pt loading on Al-MCM-41 results in active catalysts for hydrogenation and hydrocracking of large aromatic molecules.

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