Synthesis of mesoporous molecular sieves: influence of aluminum source on Al incorporation in MCM-41

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Received 13 June 1995; accepted 12 September 1995

Three series of mesoporous aluminosilicate molecular sieves, MCM-41, with various Si/Al ratios were synthesized using different aluminum sources (aluminum isopropoxide, pseudo boehmite and aluminum sulfate). XRD analysis, temperature programmed desorption of *n*-butylamine, ^{27}Al and ^{29}Si MAS NMR, and catalytic alkylation test indicated that aluminum isopropoxide is a better source for incorporating aluminum in the framework of MCM-41 type molecular sieves with better crystallinity and acid characteristics.

Keywords: mesoporous materials; MCM-41, synthesis; aluminum source

1. Introduction

Conventional microporous zeolite catalysts often suffer from diffusion limitation when applied to fuel and petrochemical processing. Due to the increasing demand for processing heavy oils with large-pore catalysts, it has become important to develop mesoporous molecular sieve catalysts. Such catalysts also have potential for more efficient catalytic upgrading of coal derived liquids to produce transportation fuels, particularly advanced thermally stable jet fuels.

Recently a new family of mesoporous molecular sieves denoted as M41S was invented by Mobil researchers [1,2]. One member of this series, MCM-41, possesses a regular array of uniform and one-dimensional mesopores that can be tuned to the desired pore diameter in the range of 15 to 100 Å. Since the discovery of these new materials, research has been directed towards the creation of new mesoporous materials with greater structural and chemical diversity. It has been reported that it is possible to incorporate elements like aluminum, titanium and vanadium into the framework of these materials [1–11]. To date, however, the incorporation of these elements in the framework, particularly aluminum atoms, in the mesoporous materials have not been firmly established. Davis et al. reported synthesis and characterization of MCM-41 materials using pseudo boehmite and sodium aluminate and found that aluminum incorporation is better with sodium aluminate than with pseudo boehmite [3,4]. Corma et al. have reached similar conclusion from their studies on acidity and stability of MCM-41 aluminosilicates [5]. Chmelka et al. suggested that syntheses using monomeric aluminum precursors can yield stable MCM-41 samples with controlled incorporation of aluminum into the framework [6]. Recently, Borade and Clearfield have reported the synthesis of aluminum rich MCM-41 using sodium aluminate [7]. Our preliminary work has shown that the type of aluminum compounds used in the hydrothermal synthesis affects the Al content and catalytic properties of the resulting MCM-41 type mesoporous materials [11].

From the above studies, it seems that the source of aluminum has a significant effect on the incorporation of aluminum in the framework and the properties of the resulting materials. Therefore, it is important to study the influence of the type of aluminum source compounds in the hydrothermal synthesis of mesoporous materials. In this paper we report the synthesis and characterization of MCM-41 materials using three aluminum sources of different nature (aluminum isopropoxide, pseudo boehmite and aluminum sulfate).

2. Experimental

Cab-O-Sil fumed silica (Cabot Corporation), tetramethylammonium silicate solution (0.5 TMA/SiO$_2$, 10 wt% silica, Sachem Inc.), sodium silicate (containing 14 wt% NaOH and 27 wt% silica, Aldrich) cetyltrimethylammonium bromide (Aldrich), aluminum isopropoxide (Aldrich), pseudo boehmite (75% alumina, Catapal B, Vista Chemicals), aluminum sulfate (Strem Chemicals, 98+%) and deionized water were used as the reagents.

The mesoporous materials were synthesized from a mixture of reactants with the following composition: $50SiO_2–xAl_2O_3–4.32Na_2O–2.19(TMA)_2O–15.62(CTMA)Br–3165H_2O$; where $x = 0.5$, 1.0 and 2.0. In a typical synthesis, 4.0 g of Cab-O-Sil fumed silica was dissolved in 25.7 g of deionized water under stirring for 15 min (solution A). A solution of 11.6 g TMA-silicate

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was mixed with 5.5 g sodium silicate, stirred for 10 min, and combined with the above solution A, followed by 15 min stirring using a magnetic stirrer. Then the cetyltrimethylammonium bromide solution (12.9 g CTMABr and 87 g deionized water) was added to the mixture. After 20 min stirring of the above mixture, a given amount of aluminum source was added. The resulting mixture was stirred for another 15 min and the gel preparation is complete here. This gel was measured for its pH value, and then transferred into a Teflon lined stainless-steel autoclave (100 ml) and heated statically at 100°C for crystallization under autogeneous pressure in an oven for 24 h. After crystallization, the solid product was recovered by filtration, washed with deionized water and dried at 100°C. The organic template was removed by calcining the samples at 550°C with slow heating rate of 5°C/min in inert atmosphere of flowing nitrogen for 1 h then in flowing air for another 5 h. TGA of calcined MCM-41 samples in air at high temperatures up to 1000°C did not show any weight loss, which indicates that the organic template has been removed completely during the calcination. The ammonium form of MCM-41 was obtained by ion exchange with 0.5 M ammonium nitrate solution at 90°C. The protonated form was then obtained by calcining the ammonium form at 480°C for 3 h in an air flow.

The Al-containing MCM-41 samples were characterized by a number of analytical techniques including chemical analysis, X-ray diffraction, N_2 adsorption, thermogravimetric analysis, and solid state NMR. X-ray diffraction patterns were obtained on Phillips Automated Powder Diffractometer using Cu K_α radiation. Calcined MCM-41 samples were characterized by nitrogen adsorption at liquid nitrogen temperature using a Quantachrome automated adsorption apparatus (Autosorb 1), from which BET surface areas and pore size data were obtained.

Thermogravimetric analysis (TGA) was performed on a Mettler TG50 thermobalance. TGA was used in two types of experiments, one for examining the removal of organic matter from as-synthesized MCM-41 samples, the other for comparing the acidic properties of the proton-form MCM-41 samples. Therefore, the samples were examined by TGA at different heating rates in different atmospheres. TGA of the as-synthesized MCM-41 samples was conducted under calcination conditions. Characterization of relative acidity of MCM-41 molecular sieves was performed by temperature programmed desorption of *n*-butylamine on the TGA apparatus. A flow system was designed with heating and evacuation capability for the preparation of *n*-butylamine adsorbed samples. The samples (in their protonic forms) were degassed prior to adsorption under vacuum at 450°C for 2 h, then the *n*-butylamine vapor (generated by nitrogen bubbling of the liquid) was passed through the sample with flow rate of about 100 cm^3/min using nitrogen as a carrier at room temperature for about 1 h. The base-covered samples were then transferred to the thermal analyzer. Nitrogen was used as purge gas and was maintained (60 cm^3/min) at room temperature for 30 min before thermal analysis was started. TGA data were obtained from about 30 to 700°C at the heating rate of 10°C/min.

The ^{29}Si and ^{27}Al MAS NMR spectra of as-synthesized MCM-41 samples were recorded on a CMX 300 Chemagnetics solid state NMR spectrometer, using 7 mm o.d. zirconia rotor with a spinning speed of 3.5 kHz using dehydrated compressed air as driving gas. Single pulse excitation was used. All spectra were recorded at room temperature. The ^{27}Al NMR spectra were recorded at a frequency of 77.485 MHz with a pulse length of 2 μs (pulse width $B_1 = 31.25$ kHz), and a pulse delay of 2 s. The ^{29}Si NMR spectra were recorded at a frequency of 59.075 MHz with a pulse length of 4 μs ($B_1 = 45.45$ kHz) and a pulse delay of 30 s. The chemical shifts were measured with respect to TMS for ^{29}Si and $Al(H_2O)_6^{3+}$ for ^{27}Al.

Isopropylation of naphthalene over MCM-41 catalysts was carried out at 200°C for 2 h in horizontal tubing-bomb reactors, using the procedure described elsewhere [13], with 0.1 g of catalyst, 1.0 g of naphthalene, under 150 psi propylene initial pressure. Products were analyzed by gas chromatography (Perkin-Elmer 8500) and GC/MS using DB-17 fused silica capillary column using *n*-nonane as an internal standard.

3. Results and discussion

Three series of Al-containing MCM-41 samples were synthesized under the conditions tabulated in table 1, using three different aluminum sources (aluminum isopropoxide, pseudo boehmite and aluminum sulfate) with the feed Si/Al ratios of 50, 25, and 12.5. The physico-chemical properties of the synthesized MCM-41 samples are presented in table 2. Initial Si/Al molar ratios taken while synthesizing samples and the ratios obtained from the crystalline solid products are different from each other. The Si/Al molar ratios of the MCM-41 prepared with aluminum isopropoxide and pseudo boehmite (table 2) are lower than the corresponding feed

Table 1
Synthesis conditions for Al-MCM-41 samples

Sample	Source of Al	Feed SiO_2/Al_2O_3	pH of the gel
AI1	Al isopropoxide	100	11.93
AI2	Al isopropoxide	50	12.02
AI3	Al isopropoxide	25	12.07
PB1	pseudo boehmite	100	11.87
PB2	pseudo boehmite	50	11.88
PB3	pseudo boehmite	25	11.86
AS1	Al sulfate	100	11.77
AS2	Al sulfate	50	11.64
AS3	Al sulfate	25	11.52

Table 2
Physico-chemical properties of synthesized Al-MCM-41 samples

Sample	SiO_2/Al_2O_3	XRD parameters		BET surface area (m^2/g)	Pore size from sorption (Å)
		peak[a] intensity	d_{100} spacings (Å)		
AI1	88.4	2967	37.4	1147	27.67
AI2	46.8	2906	38.7	1206	28.02
AI3	27.4	2272	37.9	1020	28.46
PB1	95.5	3642	32.9	1010	21.92
PB2	44.3	3216	34.2	–	–
PB3	18.4	2722	34.7	–	–
AS1	164.6	2511	35.6	834	25.38
AS2	87.4	2204	37.7	–	–
AS3	39.5	583	38.1	–	–

[a] Peak due to the 100 reflection.

ratios (table 1), which is common for the synthesis of high silica molecular sieves. The molecular sieve samples prepared with aluminum sulfate, however, show exceptionally higher SiO_2/Al_2O_3 ratios compared to the corresponding feed ratios. The reason for this lower degree of Al in the solid product is not yet clear. It may be due to lower reactivity of the Al species in the gel prepared from aluminum sulfate. Zeolites normally incorporate all of the aluminum present in the reaction mixture leaving varying amounts of silica or silicate in solution according to the factors such as the hydroxide concentration and the presence of various inorganic and organic cations in the reaction mixture [14].

X-ray diffraction patterns of all the samples before and after calcination were obtained. Fig. 1 shows the XRD patterns of three calcined MCM-41 samples prepared with different aluminum sources. Like the samples shown in fig. 1, almost all the calcined samples are well crystallized and phase pure (no other crystalline phase) with a very strong peak and three weak peaks, as also observed in previous studies [1,2]. The major XRD peak (100 reflection) intensities and d_{100} spacing values are shown in table 2. On the basis of Bragg equation dictating the correlation between d spacing, X-ray wavelength and diffraction angle, it is clear from the two theta values in fig. 1 that the d spacing values increase in the following order according to the aluminum source at feed Si/Al ratio of 50: pseudo boehmite (32.9 Å) < Al sulfate (35.6 Å) < Al isopropoxide (37.4 Å). In fact, this order is generally true for all but one sample listed in table 2. It should also be mentioned that non-calcined samples show some extra small peaks which disappeared upon calcination. This could be due to the presence of large amounts of surfactants, about 50 wt% within the channels. It was also observed that XRD patterns of calcined samples exhibit peaks with increased intensity and a shift to lower two theta compared to the XRD of as-synthesized samples. Similar trends were observed in previous studies and it was pointed out that calcination leads to a contraction of unit cell accompanied by a loss in silanol density via condensation of Si-OH groups [3].

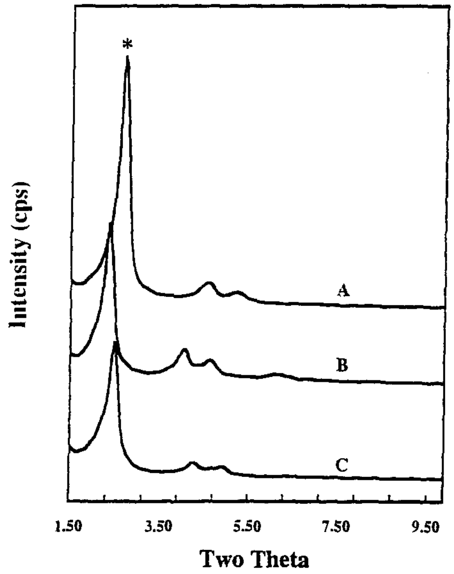

Fig. 1. X-ray diffraction patterns of samples prepared using (A) pseudo boehmite (PB1), (B) Al isopropoxide (AI1) and (C) Al sulfate (AS1). (*) Peak due to 100 reflection.

Fig. 2 depicts the influence of the feed Si/Al ratio on the XRD peak intensity of 100 plane, which reflects on crystallinity of the materials, for three series of MCM-41 samples prepared using different aluminum sources. Within each series of samples, a decrease in Si/Al ratio decreased the intensity of the main XRD peak, indicating that increasing Al content of the feed hindered crystallization process. Therefore, fig. 2 shows that the level of crystallinity decreases upon increasing the aluminum content in the feed. It is a known phenomenon for synthesis of high silica molecular sieves that the more aluminum in the gel, the more difficult to crystallize because of stability reasons. However, the decreasing extent of crystallinity with increasing feed Al content also appears to depend on the type of aluminum source, as can be seen from fig. 2. This may be attributable to the different reactivities of the Al species in the gels formed with the three aluminum sources toward bonding with Si species during the gelation process. The nature of the resulting

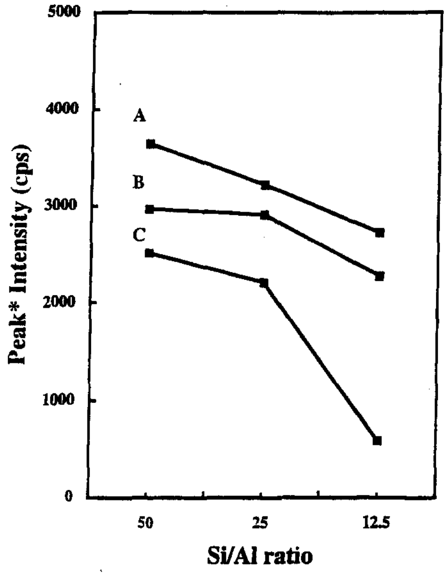

Fig. 2. Comparison of crystallinity with varying Si/Al ratios of samples prepared using different Al sources. (A) Pseudo boehmite, (B) Al isopropoxide and (C) Al sulfate. (*) Peak due to 100 reflection.

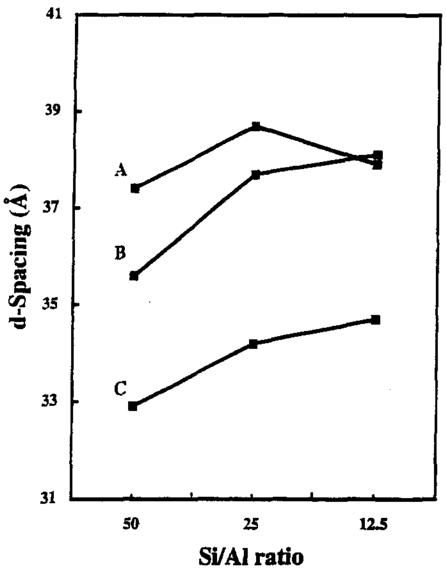

Fig. 3. Comparison of unit cell expansion (d_{100} spacings) of samples prepared using different Al sources with varying Si/Al ratios. (A) Al isopropoxide, (B) Al sulfate and (C) pseudo boehmite.

gel influences the crystallinity and amount of aluminum incorporation in the framework. It seems that aluminum isopropoxide reacted more readily with silica, as compared with aluminum sulfate. As shown in table 1, the pH of the gel prepared with aluminum sulfate at any given feed Si/Al ratio was lower than that with aluminum isopropoxide. This low pH may be the reason why the crystallinity is lower for the samples prepared with aluminum sulfate relative to those prepared with aluminum isopropoxide. The samples prepared with pseudo boehmite show high crystallinity, almost the same as the sample prepared without aluminum. In this case, there was no change in pH of the resulting gel upon increasing the aluminum content. It suggests that most of the Al species in the alumina were not reacting with silica during the gelation process.

We also examined the sequence of gel preparation with respect to the timing of aluminum addition. For all the samples described above, the Al source was added to the silicon source before addition of organic template. In an alternative procedure, we added the Al source after the addition of the template to the mixture. However, the resulting materials were found in XRD analysis to be poorly crystallined. Therefore, this alternative procedure was abandoned.

Fig. 3 shows a plot of *d* spacing versus the feed Si/Al ratio for all three series of calcined MCM-41 samples. The *d* spacing value increased with decreasing Si/Al ratio for all but one samples. For MCM-41 type mesoporous molecular sieves, *d* spacing of the crystal structure can be correlated to hexagonal unit cell parameter by $a = 2d_{100}/\sqrt{3}$ [1,2]. Therefore, fig. 3 indicates that increase in aluminum content in the gel increases the unit cell parameter. The increase in unit cell size is due to the incorporation of large aluminum ions (Al^{3+} ion radius = 0.50 Å) as compared to silicon (Si^{4+} ion radius = 0.41 Å) in the framework that leads to an expansion of unit cell. The length of Al–O bond (1.75 Å) is longer than that of Si–O bond (1.60 Å) [7]. Our results indicate that the order of expansion of unit cell with increasing aluminum content using three different sources is aluminum isopropoxide > aluminumsulfate > pseudo boehmite alumina. This order also represents the order of the aluminum incorporation in the MCM-41 framework. This can be attributed to the difference in the nature of gels obtained with different aluminum sources effecting the crystallization process.

The nitrogen adsorption isotherms (at liquid nitrogen temperature) of all the calcined MCM-41 samples showed similar type isotherms, irrespective of source of aluminum used in synthesis. These isotherms are characteristic of mesoporous materials with uniform pore size [1,2,15] with an inflection characteristic of capillary condensation within the pores. The relative pressure at which this inflection occurs increases with the diameter of the pores [2]. For our samples, it occurred at p/p^0 in between 0.20 and 0.40. The average pore diameters calculated using the BJH model [16] are given in table 2 which are in the same order of *d* spacings.

In general, all the calcined MCM-41 samples show a unimodal pore size distribution, with a unique peak centered in between 20 and 30 Å. BET surface areas also clearly confirm the results of crystallinity comparison. As shown in table 2, the MCM-41 samples, AI1 to AI3, prepared with aluminum isopropoxide displayed higher BET surface areas (1020–1147 m^2/g), and larger pore diameters (27.7–28.5 Å) than the other two series of samples. The MCM-41 sample prepared with pseudo boehmite, PB1, has higher BET surface area (1010 m^2/g) but smaller pore diameter (22.2 Å) than the one prepared with aluminum sulfate, AS1 (834 m^2/g, 25.4 Å). Therefore, at the same feed Si/Al ratio of 50, the pore diameter of the synthesized MCM-41 samples increases in the following order with respect to aluminum source: pseudo boehmite alumina < aluminum sulfate < aluminum isopropoxide.

Thermogravimetric analysis in combination with XRD results showed that samples are thermally stable at least at our calcination conditions. The organic template is decomposed below 823 K leaving well crystalline mesoporous materials. The weight loss for all the samples was in the range of about 50–70 wt% which indicates that as-synthesized samples contain large amounts of organic templates because of the presence of mesopores with large void volume. For example, from TGA of the three as-synthesized samples PB2, AS2 and AI2 (table 1), the weight loss values below 125°C (atributed to water removal) were 2.1, 4.6, and 3.7 wt%, respectively; the amounts of weight loss due to organic template removal (125–550°C) were 66.4, 64.1, and 51.3 wt%, respectively.

Temperature-programmed desorption of *n*-butylamine has been conducted on TGA to characterize the acidity of the samples. Ghosh and Curthoys compared the acidity of a hydrogen mordenite and two dealuminated hydrogen mordenite zeolites using TGA [17]. Here we compared the relative acidity of protonated MCM-41 samples prepared using different aluminum sources by TGA. As shown in fig. 4, the TGA curves indicate that most of the adsorbed *n*-butylamine is desorbed below 200°C. This low temperature desorption compared to mordenite could be due to low acid strength and the presence of mesopores made diffusion easy. From the weight losses due to *n*-butylamine desorption (presuming *n*-butylamine adsorption was done at completely dry conditions), it is also clear that MCM-41 samples prepared with aluminum isopropoxide and aluminum sulfate adsorbed more *n*-butylamine (about 18 wt%) whereas the sample prepared with pseudo boehmite adsorbed less *n*-butylamine (about 10 wt%). These results indicate that the first two samples adsorbed more base, hence they are more acidic than the last one, which again confirms that aluminum incorporation is better for the first two samples. Our preliminary TPD results indicate that compared to a hydrogen Y-zeolite (SiO_2/Al_2O_3: 5) and a hydrogen mordenite (SiO_2/Al_2O_3: 38), there are fewer strong acid sites in the MCM-41 samples. In terms of the relative amount of *n*-butylamine desorption in the temperature range of 340–500°C, the qualitative order of acidity is HY > HM > protonated MCM-41.

Figs. 5–7 illustrate the ^{29}Si and ^{27}Al MAS NMR spectra of as-synthesized MCM-41 mesoporous molecular sieves. From the ^{27}Al MAS NMR spectra in fig. 5, it is clear that samples prepared with aluminum isopropoxide (fig. 5A) and aluminum sulfate (fig. 5C) exhibit mainly a single peak at around 50 ppm (fig. 5). This peak is due to tetrahedral Al in the framework [3–8]. The peak at 0 ppm corresponding to octahedral Al species [7,8] is very small in these samples. These results clearly indicate that nearly all the Al atoms in these two as-synthesized MCM-41 materials with aluminum isopropoxide and aluminum sulfate are present in a tetrahedral environment. By contrast, the ^{27}Al MAS NMR spectrum of MCM-41 sample (fig. 5B) prepared using

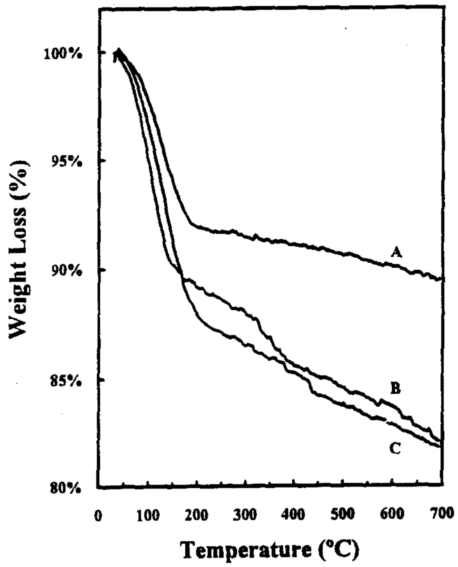

Fig. 4. TGA of *n*-butylamine pre-adsorbed samples prepared using different Al sources. (A) Pseudo boehmite (PB2), (B) Al isopropoxide (AI2) and (C) Al sulfate (AS2).

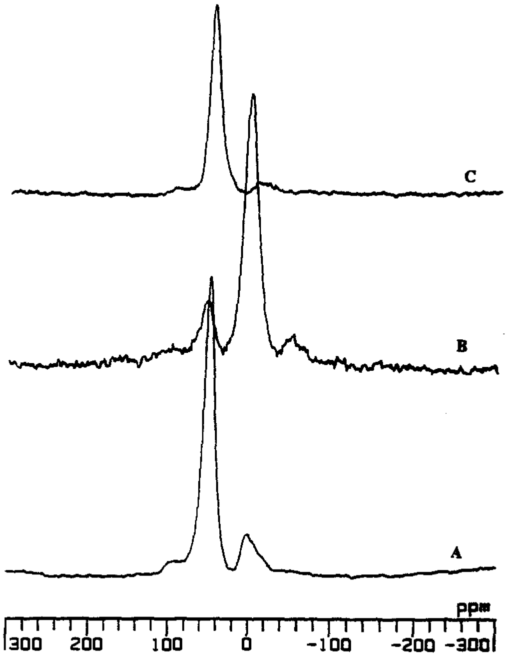

Fig. 5. ^{27}Al MAS NMR spectra of samples prepared using different Al sources. (A) Al isopropoxide (AI2), (B) pseudo boehmite (PB2) and (C) Al sulfate (AS2).

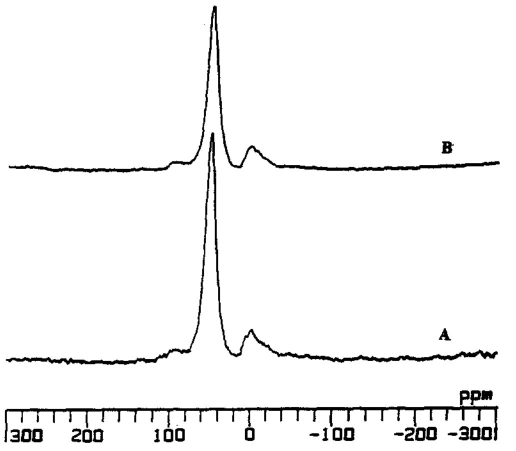

Fig. 6. ^{27}Al MAS NMR spectra of samples prepared using Al isopropoxide with SiO_2/Al_2O_3 ratio of (A) 100 and (B) 50.

pseudo boehmite alumina, which was also used in previous studies [1,2], shows a very large peak at 0 ppm corresponding to octahedral Al species, with only a small peak at around 50 ppm corresponding to tetrahedral Al species. Therefore, most of Al species in this sample are extra-framework Al, probably amorphous alumina occluded in the pores. Similar results were observed by Davis et al. [3] for their samples prepared with pseudo boehmite as Al source. These results clearly indicate that pseudo boehmite is not a good source to incorporate Al in the framework (tetrahedral Al species). Aluminum isopropoxide and aluminum sulfate are better sources for incorporation of aluminum in the framework.

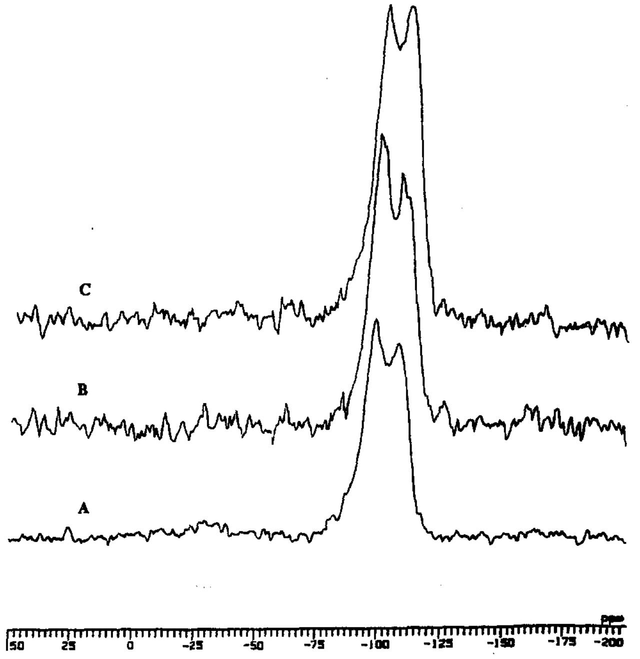

Fig. 7. ^{29}Si MAS NMR spectra of samples prepared using different Al sources with SiO_2/Al_2O_3 ratio of 50: (A) Al isopropoxide (AI2), (B) Al sulfate (AS2) and (C) pseudo boehmite (PB2).

Fig. 6 compares the ^{27}Al MAS NMR spectra for the samples prepared with the same source, aluminum isopropoxide, with two different Si/Al ratios. It shows that decreasing the Si/Al ratio from 50 to 25 did not change the Al symmetry much, which indicates that it is possible to incorporate most of the aluminum even with increasing Al contents. Recently Borade et al. [7] synthesized MCM-41 molecular sieves with Si/Al ratios as low as 2 without observing the presence of octahedral Al using sodium aluminate as aluminum source. Fig. 7 illustrates the ^{29}Si MAS NMR of the samples prepared with three different sources. The three samples showed two major peaks at around −99 and −108 ppm, which correspond to two different Si species. There are differences in the signal/noise ratio and relative intensity of −99 and −108 ppm peaks between the three spectra in fig. 7. Probably, the −99 and −108 ppm peaks correspond to the Si(1Al, 3Si) and Si(0Al, 4Si) species, respectively, in the framework, as also reported by Kolodziejski et al. [8]. The relative intensity of the −99 ppm peak is higher with the samples prepared from Al isopropoxide and Al sulfate than with the sample from pseudo boehmite, being consistent with ^{27}Al NMR and XRD data.

It should also be mentioned that for ^{27}Al NMR spectra in both figs. 5 and 6, spinning sidebands (SSBs) from tetrahedral Al are small, as can be seen in the downfield SSB at about 95 ppm in figs. 5A and 5C and fig. 6. The upfield tetrahedral SSB is also present near 4 ppm in figs. 5A and 5C, but is buried under the wide octahedral resonance at about 0 ppm. In fig. 5B, the spectrum is dominated by the octahedral resonance at 0 ppm and its SSBs at about −52 ppm and 54 ppm. The tetrahedral resonance is only a part of the 54 ppm peak.

We also performed naphthalene alkylation with propylene as a probe reaction to examine the acidic catalytic properties of the MCM-41 samples. In the reaction of isopropylation of naphthalene all the MCM-41 catalytsts are found to possess certain activity like other zeolite-based catalysts examined in our previous work [13]. The naphthalene conversion over catalysts prepared with aluminum propoxide (AI2), pseudo boehmite (PB2) and aluminum sulfate (AS2) were 96, 37 and 90 wt% respectively. Apparently, the MCM-41 catalysts prepared with aluminum propoxide and aluminum sulfate are much better than that with pseudo boehmite. Since the alkylation over zeolites is known to occur on acid sites, it is understood that the catalyst prepared with pseudo boehmite is less acidic, which again confirms the poor incorporation of aluminum in the framework compared to the other two MCM-41 catalysts. In addition, because of the mesopores, the products selectivities with MCM-41 catalysts are different from those with proton-form mordenite catalysts [13]. As expected, it was observed that tri and tetra isopropyl naphthalene are formed in large quantities with MCM-41, which is a clear indication of non selective nature of these mesoporous materials compared with microporous zeolites [13].

4. Conclusions

In conclusion, it is possible to synthesize phase pure mesoporous aluminosilicate molecular sieves, MCM-41, with varying Si/Al ratios by using different aluminum sources. The Al-MCM-41 samples prepared using aluminum isopropoxide and pseudo boehmite have better crystallinity compared to the one with aluminum sulfate probably due to the lower pH of the resulting gel. It is also clear from the XRD, TPD of *n*-butylamine, solid state NMR and catalytic evaluation that both aluminum isopropoxide and aluminum sulfate are good sources to incorporate aluminum in the framework leading to better acidity hence the catalytic activity. However, in terms of better crystallinity and higher level of Al incorporation, aluminum isopropoxide is better than aluminum sulfate as the Al source for synthesizing MCM-41.

Acknowledgement

We are very grateful to Professor Harold Schobert of PSU for his encouragement and support. This work was jointly supported by the US Department of Energy and the US Air Force. We would like to thank Mr. M.E. Harrison III of USAF and Dr. S. Rogers of DOE for their support. We also thank Dr. A. Benesi of PSU for performing the NMR analysis and for helpful discussions on the NMR spectra.

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