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Synthesis of aluminum rich MCM-41

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The synthesis of MCM-41 mesoporous compounds with Si/Al ratios as low as 2 without observing the presence of octahedral Al in ^{27}Al MAS NMR is reported. FTIR spectra of chemisorbed pyridine indicated that MCM-41 materials in their protonated form exhibit both Brønsted and Lewis acid sites.

Keywords: MCM-41 synthesis; NMR; FTIR

1. Introduction

The discovery of a new family of mesoporous materials designated as M41S by scientists at Mobil Oil Corporation has opened a new era in the hydrothermal synthesis of porous materials [1,2]. MCM-41 is one of the members of this family. The novelty of MCM-41 type compounds is not only that these materials have well defined pore sizes that can be tuned to the desired pore size in the range of 20–100 Å but also that these materials exhibit high thermal stability, a property which is one of the major requirements of an industrial catalyst. There are few reports in the open literature that describe the synthesis of MCM-41 material using different sources of silicon and aluminum and surfactant [1–7]. Davis et al. [8,9] reported the synthesis and characterization of MCM-41 materials synthesized using HiSil and tetramethylammonium silicate as sources of silicon and pseudo boehmite and sodium aluminate as sources of aluminum. From their studies they concluded that, using sodium aluminate as the aluminum reagent, MCM-41 can be prepared with Si/Al ratio as low as 29 without observing octahedral Al in ^{27}Al MAS NMR and such is not the case with pseudo boehmite. More recently, Schmidt and co-workers [6] reported the synthesis of MCM-41 with Si/Al ratio of 4 using sodium silicate and sodium aluminate as sources of Si and Al, respectively. However, the ^{27}Al MAS NMR study indicated that the MCM-41 sample with Si/Al ratio 4 contains significant quantities of Al with octahedral coordination. In this report we describe the synthesis of MCM-41 material with Si/Al ratios near 2 without observing octahedral Al in ^{27}Al MAS NMR.

2. Experimental

The fumed silica (Sigma, S-5130), sodium aluminate (28.4% Na_2O, 46.8% Al_2O_3, 24.8% H_2O), cetyltrimethylammonium chloride (CTMACl, TCI), tetramethylammonium hydroxide pentahydrate (TMAOH, Aldrich), sodium hydroxide (J.T. Baker) and deionized water were used as the reagents.

The starting reaction mixture had a chemical composition $1SiO_2$–(0–0.25) Al_2O_3–0.23CTMACl–0.11Na_2O–0.089TMAOH–125H_2O. The synthesis procedure was as follows: The mixture A was obtained by dissolving TMAOH in deionized water followed by addition of fumed silica. This mixture was stirred for 10–15 min. The mixture B was prepared by dissolving sodium aluminate in deionized water to which was added NaOH and then CTMACl. This mixture was also stirred for 10–15 min. Finally, mixture A was added to mixture B and then the whole mixture was stirred for another 15 min using a magnetic stirrer. When the stirring was complete, the pH was measured and then the mixture was transferred into a teflon lined stainless steel autoclave of 1 ℓ capacity. The autoclave was closed and kept in an oven at 100°C for crystallization under autogenous pressure for 16–70 h. The crystallization process was terminated by quenching the autoclave in cold water. The solid product was recovered by filtration and washed with hot deionized water and dried at $\sim$ 100°C overnight. The organic matter was removed by calcining the sample at 550°C for 10 h. The NH_4^+-form of MCM-41 was obtained by repeated ion exchange with 2 M NH_4Cl solution at 80°C. The protonated form was then obtained by calcining the NH_4^+ form at 550°C for 10 h.

The synthesized samples were characterized by X-ray diffraction, thermogravimetric analysis, bulk and surface analysis. X-ray powder diffraction patterns were obtained with a Rigaku RU 200 automated powder diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). The TGA analysis was carried out by using a Du Pont (model 951) thermal analyzer. About 20 mg of the sample was placed in a quartz bucket and was heated at a heating rate of 10°C/min in the presence of a N_2 atmosphere. Chemical analysis was performed for Si and Al by Galbraith Laboratories, Knoxville, TN, USA. The ^{29}Si and ^{27}Al MAS NMR spectra were recorded on a Bruker MSL 300 spectrophotometer. The magnetic field was 7.046 T. The sample material was contained in a zirconia rotor and the rotor was spun near 3.5 kHz with dry air as driving gas. Chemical shifts were recorded with respect to TMS for ^{29}Si and $Al(H_2O)_6^{3+}$ for ^{27}Al. All spectra were recorded at room temperature. The IR spectra were recorded on a Digilab FTS-40 spectrometer in the range 4000–400 cm^{-1} using a 2 cm^{-1} resolution. The protonated form of the sample was pressed into a self-supporting wafer and was activated under vacuum near 425°C. Then the sample was cooled down to 50°C and exposed to pyridine vapors. Finally, physisorbed pyridine was desorbed at 150°C under vacuum. The details of the procedure are available elsewhere [10].

3. Results and discussion

Fig. 1 shows X-ray powder diffraction patterns of as-synthesized MCM-41 materials with different Si/Al ratios. The X-ray powder diffraction pattern of MCM-41 synthesized in the absence of aluminum corresponds to that reported for the all silica MCM-41 [1–4]. This compound exhibits a very strong reflection at 36.2 Å and very weak reflections at 21.2, 18.6 and 14.1 Å. It is important to mention that depending on the synthesis conditions, type of silicon and aluminum sources and drying temperature used the position of the main peak may vary significantly. With a decrease in the Si/Al ratio or increase in the aluminum content the main intense peak shifts towards higher *d*-spacing (see fig. 1). This suggests that there is an increase in the interplanar distance or, in other words, an increase in the pore size of the MCM-41 material. In addition to this the main peak becomes broader and less intense (as compared to the all silica MCM-41) which signifies the poorly crystalline nature of the material. Moreover, the weak reflections become much weaker and were not seen in the case of MCM-41 with Si/Al $\approx$ 2. Similar kinds of observations have been made by Corma et al. [11] for their MCM-41 material when the Si/Al ratio was decreased from 100 to 14. Recently, Pinnavaia et al. [12] synthesized hexagonal mesoporous silica (designated as HMS) and its titanium-substituted derivative using dodecylamine as a template. They observed

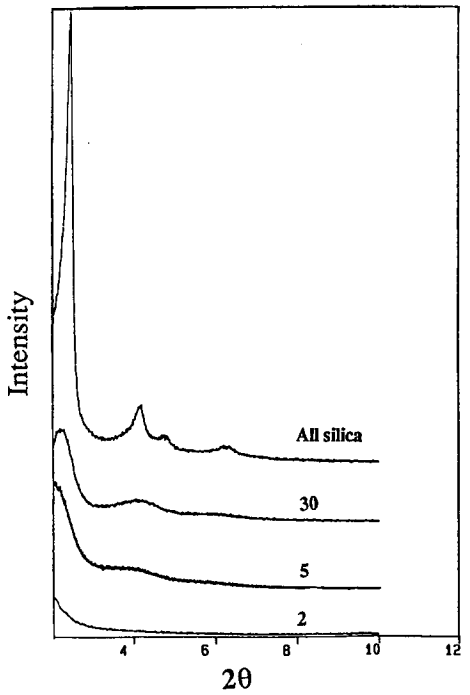

Fig. 1. X-ray powder diffraction patterns of as-synthesized MCM-41 mesoporous materials. Figures indicate Si/Al ratios in the starting reaction mixture.

that higher order Bragg reflections were not resolved in the XRD patterns of HMS and Ti-HMS materials. By studying electron diffraction, transmission electron micrograph and scanning electron microscopy, Pinnavaia et al. [12] suggested that even though HMS and Ti-HMS show single reflection, these materials exhibit crystallographic symmetry analogous to MCM-41 phases and the diffuse scattering at 2 theta, 5° may arise from broadening of *hk*0 reflections due to finite size effects. The observed increase in the interplanar spacing can be explained on the basis of replacement of shorter Si–O bonds (1.60 Å) by longer Al–O bonds (1.75 Å) in the MCM-41 structure. Beck et al. [2] reported the formation of unstable lamellar material during their MCM-41 preparations under certain conditions. The formation of unstable lamellar material during our synthesis is rejected mainly because as-synthesized lamellar material shows [2] well defined XRD peaks at $d = 36.2$, 17.9 and 11.9 Å and upon calcination this material loses almost all its crystallinity. All materials of the present study upon calcination showed rather an improved crystallinity with respect to the (100) reflection. Fig. 2 shows TGA curves for the MCM-41 samples of the present study. In agreement with the literature [2,8] our all silica MCM-41 material showed a 4.8% weight loss (25–125°C) due to water and a 49.0% weight loss (125–1000°C) due to organic matter. The MCM-41 sample with Si/Al = 2 showed a 26.7% weight loss due to water and 13.6% due to organic. We have observed that with the incorporation of Al atoms in the MCM-41 framework the amount of water desorbed increases and that of the organic content decreases. The Si/Al ratios determined by chemical analysis and XPS methods were 2.3 and 1.96, respectively.

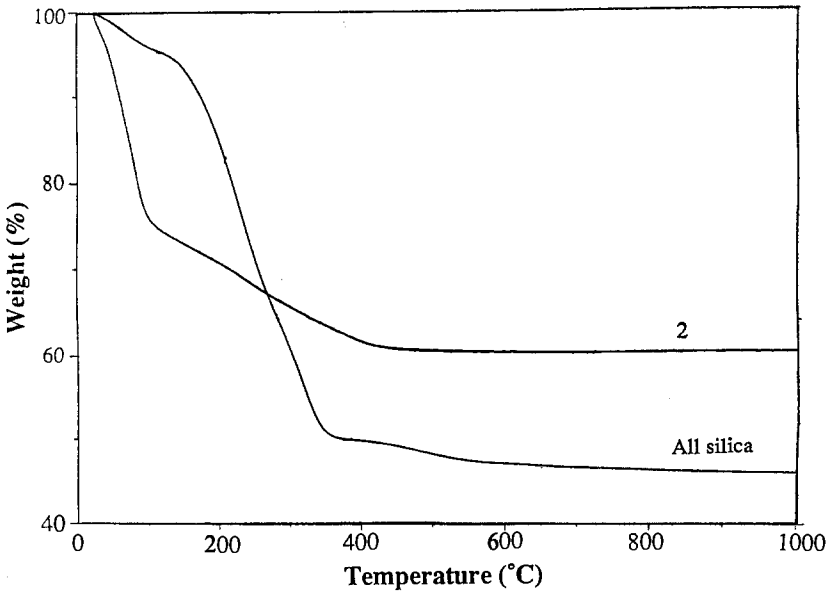

Fig. 2. TGA curves of as-synthesized MCM-41. Figures indicate Si/Al ratios in the starting reaction mixture.

Fig. 3 illustrates the ^{27}Al NMR spectrum of as-synthesized MCM-41 material with Si/Al ratio $\sim$ 2. It is clearly seen that at such a high Al content this material exhibits a single peak at 54.7 ppm. No peak at 0 ppm corresponding to octahedral Al species is detected in this sample confirming that all Al atoms in the as-synthesized MCM-41 material are present in a tetrahedral environment [8]. This peak was found to be somewhat broader when compared with the ^{27}Al NMR spectrum of ZSM-5 zeolite. The broadening of the peak may be an indication of the presence of some of the Al species in distorted tetrahedral environments. The ^{29}Si NMR spectrum of the as-synthesized sample did not give any meaningful information in terms of its aluminum environment. A broad peak with peak maximum at −92 ppm was observed. The FTIR spectra in the hydroxyl region were very diffused and did not give any meaningful information. Fig. 4 shows the IR spectra of an MCM-41 sample with Si/Al ratio 2 in the region 1575–1425 cm^{-1} after pyridine chemisorption. This region shows three IR bands at 1575, 1490, 1455 cm^{-1}. The band at 1575 cm^{-1} is due to the formation of pyridinium ions on Brønsted acid sites, the band at 1490 cm^{-1} is due to pyridine interacting with both Brønsted and Lewis acid sites and the band at 1455 cm^{-1} is due to the pyridine chemisorption on Lewis acid sites. The Brønsted-to-Lewis acid ratio determined from the intensities of these bands was found to be 0.41. From the FTIR study it is concluded that the MCM-41 material contains both Brønsted and Lewis acid sites. The observed Brønsted-to-Lewis ratio is significantly lower than one which suggests that during various pretreatments (such as calcination) the MCM-41 sample has undergone dehydroxylation to a significant extent that resulted in the destruction of some of the Brønsted acid sites and generation of Lewis acid sites. These findings are very similar to the observations made by Corma et al. [11] for their MCM-41 sample having Si/Al ratio 14. The TGA study of NH_4^+-exchanged MCM-41 sample showed that about 92% of total Al species are associated with either Brønsted and or Lewis acid sites. The catalytic activity study indicated that these materials are not active for *n*-hexane cracking reaction under our experimental conditions. The reaction conditions used were: reaction temperature = 350°C, sample weight

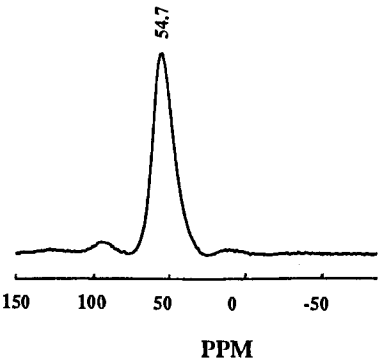

Fig. 3. ^{27}Al MAS NMR spectrum of MCM-41 with Si/Al = 2.

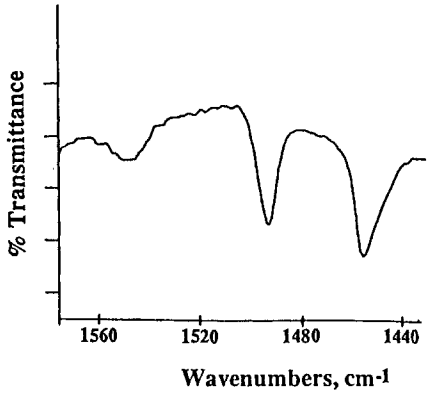

Fig. 4. FTIR spectra in the region 1575–1425 cm^{-1} for MCM-41 (Si/Al = 2) after pyridine chemisorption.

= 40 mg, total flow N_2 + *n*-hexane = ~ 27 ml/min, $P_{n\text{-hexane}}$ = 47.6 Torr. Over ZSM-5 catalyst (Si/Al = 18), about 98 μmol of *n*-hexane were converted per min per g of the zeolite.

From this study we conclude that, using the present procedure, MCM-41 material can be synthesized with Si/Al ratio as low as 2 without observing the presence of octahedral Al in the ^{27}Al NMR spectrum.

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