Room-temperature formation of thermally stable aluminium-rich mesoporous MCM-41

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The room-temperature (RT) synthesis of MCM-41 mesoporous compounds with high substitution levels of aluminium (Si/Al = 1.5) is achieved in a minimum time of synthesis. The compound shows similar characteristics to hydrothermally synthesized materials. ^{27}Al NMR study confirms the presence of tetrahedral aluminium in as-synthesized material as well as in the calcined material without observing the presence of octahedral aluminium after calcination.

Keywords: RT synthesis, thermal analysis, NMR

1. Introduction

The recent synthesis of a family of silica-based mesoporous molecular sieve materials (designated M41S) [1,2] has attracted considerable interest because of the potential of these materials, and it is now recognized that there are a variety of routes by which they can be prepared [3–5]. The catalytic properties of mesoporous molecular sieves rely on the presence of the active sites in their framework. In the case of MCM-41, active sites are generated by the incorporation of the heteroatom (e.g., Al, Ti). In particular, Brønsted-acid sites are introduced by isomorphous substitution of the Al for Si, which is achieved by the hydrothermal synthesis in which charged quaternary ammonium micelles are used as template for charged aluminosilicate inorganic precursor [6–8]. Previously, the formation of a templated aluminosilicate MCM-41 at 25 °C was reported briefly by Stucky et al. [9], who noted a lack of hydrothermal, thermal and mechanical stability for this compound compared to that obtained by the hydrothermal preparation. We report here the formation of MCM-41 containing higher substitution levels of aluminium at room temperature and minimum time of synthesis. The thermal stability of the compound and the short reaction time make it a point of considerable interest.

2. Experimental

The starting reaction mixture had a chemical composition SiO_2 : 0.66 Al_2O_3 : 0.25 $C_{16}H_{33}N(CH_3)_3Cl$: 0.23 Na_2O : 107 H_2O. The synthesized mixture was prepared using tetraethylorthosilicate (TEOS, Nacalai Tesque, Inc., Japan), sodium aluminate (30% Na_2O, 35% Al_2O_3, CicaReagents, Kanto Chemicals, Japan), cetyltrimethylammonium chloride (Merck), sodium hydroxide and deionized water.

The synthesis procedure was as follows. 1.92 g cetyltrimethylammonium chloride was added to the deionized water and stirred until a clear solution was obtained. Then a solution of sodium hydroxide was added to the mixture, and the mixture was stirred for a few minutes (≈120 min). The required amount of sodium aluminate was dissolved in water and then slowly added to the solution, stirring was continued until homogeneity was achieved. To this clear solution, 5 g of TEOS was added under stirring conditions. After a few minutes, a solid product was formed. The resultant product was washed thoroughly with deionized water. The sample was dried exclusively at room temperature prior to characterization. The organic matter was removed by calcining the sample at 600 °C for 10 h.

The synthesized sample was characterized by X-ray diffraction, thermogravimetric analysis, chemical and spectroscopic analysis (e.g., IR, XPS, etc.). X-ray diffraction patterns of the sample were recorded on a Rigaku RAD-X system using monochromatized Cu Kα radiation. The TG analysis was carried out by using a Rigaku Thermoflex TAS200 unit. (About 10 mg of the sample was placed in a platinum pan and was heated at a heating rate of 10 °C/min.) Chemical analysis was performed for Si, Al by XPS. The ^{29}Si and ^{27}Al MAS NMR spectra were recorded on a Varian INOVA 500 NMR spectrometer with CPIMS probe. All spectra were recorded at room temperature.

3. Results and discussion

X-ray powder diffraction patterns of as-synthesized (different time) and calcined materials are presented in figure 1. The figure indicates that, with increase in the aging time, surfactant micelles were coated with aluminium-containing silica and, after aging, the coating was accomplished and

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the reflection from the free surfactant disappeared. The higher aluminium content leads to shifting of the main intense peak towards the higher d spacing indicating an increase in the pore size of the material. This compound exhibits very strong reflections towards lower 2θ value. It is very important to mention that the main peak of this type of compound varies significantly with the synthesis conditions. An extraneous peak attributed to the organic material is observed in the 5 min product, but, with increasing time, this becomes less intense and was not seen in the final material. Corma et al. [10] observed that, with decreasing the Si content (Si/Al = 100–114), the weaker reflection was absent in the higher aluminium content material. Thermogravimetry analysis showed (figure 2) that the heating of the sample leads to the release of small amounts of water, which was almost completed at 150 °C, and then it exhibits several steps. The process is strongly exothermic and corresponds to the decomposition of embedded template. At the temperature of 600 °C, all of the template is released from the pore system. The Si/Al ratios determined by the chemical analysis and XPS methods were 1.8 and 1.64, respectively. A N_2-adsorption isotherm was run on the calcined material. The material showed a reversible isotherm with type IV characteristics associated with MCM-41 [11] (figure 3). The BET surface area was calculated by fitting the straight part of the $p/x(p - p_0)$ vs. p/p_0 curve (1071 $m^2\,g^{-1}$). This surface area was within the range expected for the mesoporous materials. In contrast to zeolites, no structure-sensitive absorption band was observed in the IR spectrum of the MCM-41. The IR spectra in the 400–1800 cm^{-1} region contain a series of bands that are characteristic of the SiO_4 tetrahedron and its modification by the aluminium substitution (1060 cm^{-1}). The spectra are very similar to those of amorphous silica. After calcination at 300 °C, the band at 1487 cm^{-1} (CH_3) disappeared indicating that cetyl branch of the template has been cracked and removed from the sample. But the appearance of the band at 1620 cm^{-1} indicating the R–NH_3^+ of protonated amine showed the decomposition of template occurs through a Hoffmann reaction. Finally, heating at 600 °C totally removes the template. The ^{29}Si and ^{27}Al NMR spectra were recorded at room temperature. The broad ^{29}Si spectra of as-synthesized and calcined MCM-41 (figure 3) were identical with those of amorphous silica. This indicates that the

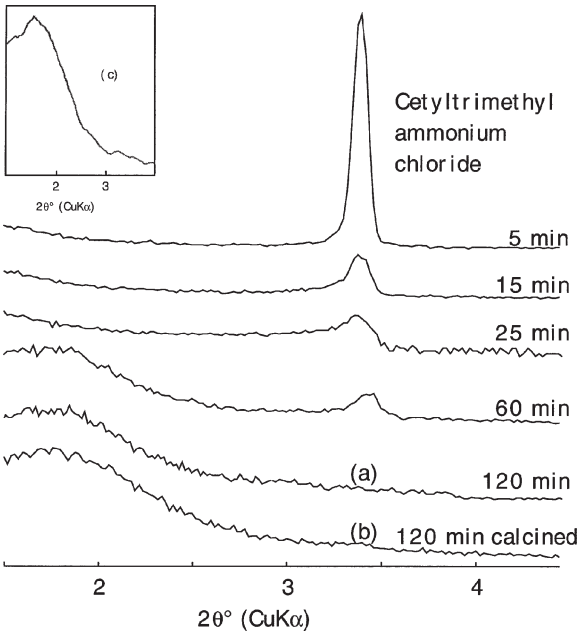

Figure 1. Powder X-ray diffraction pattern of the MCM-41 sample: (a) as-synthesized, (b) calcined, (c) lower angle diffraction.

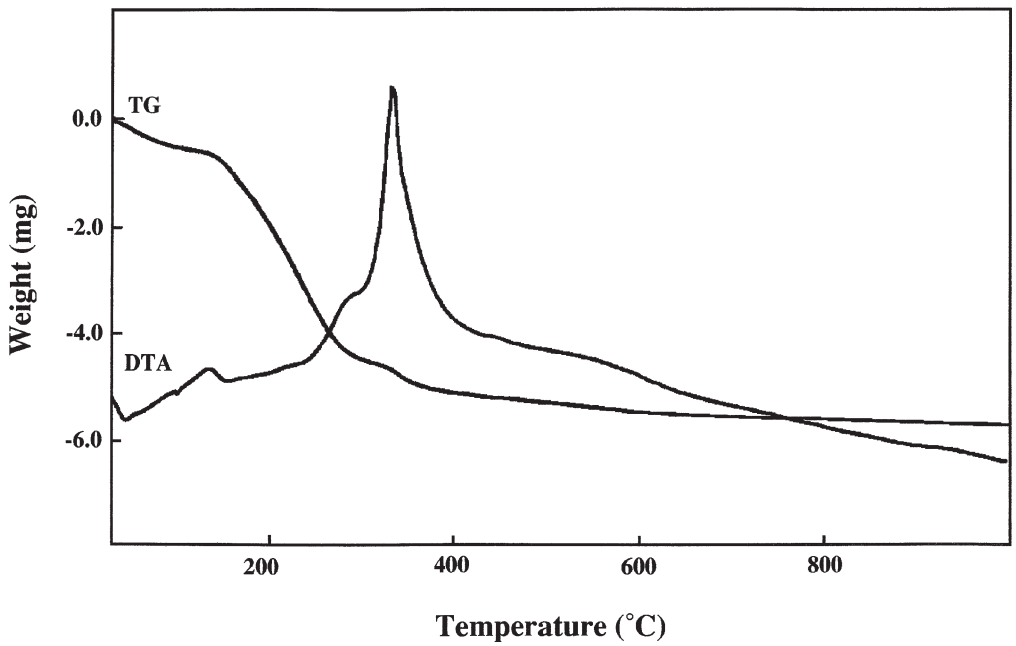

Figure 2. TG-DTA curve of as-synthesized Al-MCM-41 sample.

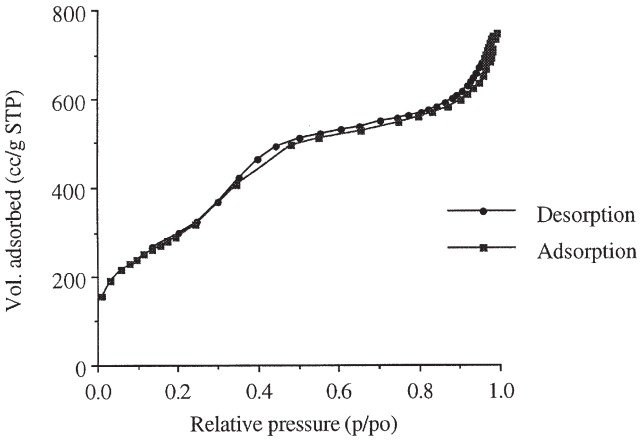

Figure 3. N_2-sorption isotherm taken for calcined material.

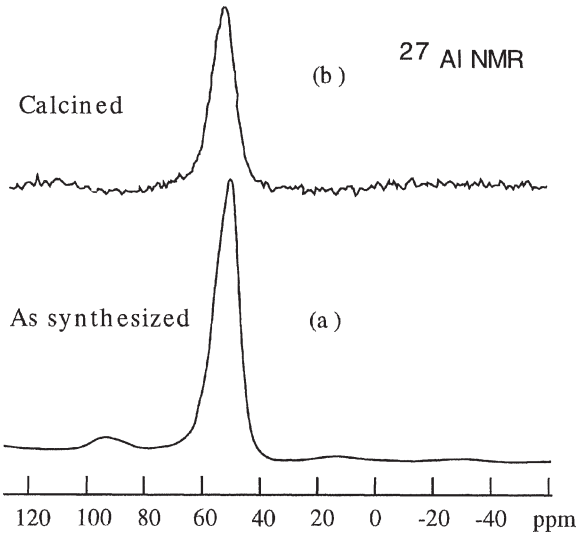

Figure 4. ^{27}Al NMR spectra of aluminosilicate MCM-41: (a) as-synthesized, (b) calcined.

local arrangement of Si–O–Si bonds in the pore walls is irregular, and that a wide range of bond angles are present. This ^{29}Si spectrum did not give any meaningful data in terms of aluminium environment. The ^{27}Al NMR analysis of the as-synthesized material (figure 4) suggests that all the aluminium observed in the sample is tetrahedrally coordinated, as represented by the resonance at 55.0 ppm. This means that aluminium from the synthesis gel is incorporated exclusively into the framework. The peak is found to be somewhat broadened in comparison to the ^{27}Al NMR of ZSM-5. The broadening may be due to the presence of aluminium species in distorted tetrahedral environments. Upon calcination at 600 °C to remove the template, there is no change in the peak position. At the same time, there is no evidence of the appearance of a peak at 0 ppm corresponding to the octahedrally coordinated aluminium confirming that all the aluminium atoms are in the tetrahedral position. This indicates that the transformation of the original tetrahedrally coordinated aluminium into the lower symmetry, as described by the previous author [12,13], has been prevented absolutely.

The MCM-41 appears as an ordered silica alumina with uniform mesoporosity. The as-synthesized sample, as well as calcined sample, has totality of aluminium in framework tetrahedral position. A catalytic study indicates that this material is active for dehydrogenation of cumene using pulse microreactor at the temperature of 500 °C with a flow of helium, but which needs further study.

In conclusion, for the first time, the detailed synthesis of well organized aluminium-containing MCM-41 material of silica to alumina ratio as low as Si/Al = 1.5 at room temperature and minimum synthesis time, while only observing tetrahedrally coordinated aluminium after calcination, is reported. During the removal of template by calcination, the aluminium is sustained in its position. This may be ascribed to the existence of sodium ions compensating the negative charge on the pore walls even after the removal of the organic cations by calcination.

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