Disintegration of Mesoporous Structures of MCM-41 and MCM-48 in Water

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It has been found that mesoporous structures of MCM-41 and MCM-48 disintegrate readily in distilled water around 370 K, while the structures can be stable in 100%-steam of 1 atmospheric pressure at much higher temperatures around 820 K. Thus, the structure disintegration is thermodynamically more favorable in water than under the steaming condition. X-ray powder diffraction and magic angle spinning ^{29}Si NMR spectroscopy indicate that the disintegration of the mesoporous structures in water occurs due to silicate hydrolysis.

Introduction

The recent discovery of MCM-41 and MCM-48 by scientists at the Mobil Co.[1,2] led to a great focusing of new possibilities of the mesoporous molecular sieves, with pore diameters ranging 2-10 nm, as hosts, adsorbents and catalysts for large species that did not enter conventional zeolite pores. The incorporation of aluminum in the siliceous framework of the materials promoted further the possibility of applications requiring acid sites and ion exchange sites.[3,4] Moreover, the structure of the MCM-41 was stable under heating conditions up to 1170 K in air or O_2 containing as much as 2.3 kPa water vapor.[4,5] The mesoporous structure was also stable during heating in 100%-steam of 1 atmospheric pressure at 820 K.

However, in spite of all the above merits, we have found that the MCM-41 material has a critical weakness in the hydrothermal stability. The material showed destruction of its characteristic X-ray powder diffraction (XRD) pattern during storage in humid air and experiments in aqueous solutions. MCM-48 also showed similar disintegration of the structure in water. The poor hydrothermal stability of the mesoporous structures at low temperature can be a serious limitation on applications of the new materials.

In the present paper, we report on the details of the mesoporous structure disintegration at low temperature, not only to give useful information for proper applications of the materials but also to stimulate researches on the development of mesoporous molecular sieves with improved hydrothermal stability.

Experimental Section

Three hydrothermal procedures described in Refs. 2, 4 and 5 were used to synthesize pure-silica MCM-41 samples, respectively. In the first procedure,[5] the MCM-41 was crystallized from a gel composition of 4 SiO_2 : 1 hexadecyltrimethylammonium chloride (HTACl) : 1 Na_2O : 0.15 $(NH_4)_2O$: 200 H_2O at 370 K using sodium silicate as a silica source. In the second procedure,[2] tetraethylorthosilicate and silica gel were used as silica sources to obtain a gel composition of 2 SiO_2 : 0.7 HTACl : 0.3 HTAOH : 52 H_2O. The HTAOH was obtained by ion exchanging HTACl with an anion exchange resin. In the third procedure,[4] a sodium silicate solution with a Na/Si ratio of 0.5 was used to obtain a gel composition of 4 SiO_2 : 1 HTACl : 1 Na_2O : 0.15 $(NH_4)_2O$: 200 H_2O. Major difference between this procedure and the first procedure was that pH of reaction mixture was adjusted to 10.2 three times with acetic acid during hydrothermal crystallization. The samples are designated SiMCM-41A, B and C, respectively. Another sample with a Si/Al ratio of 30 (AlMCM-41) was also obtained by adding aqueous solution of sodium aluminate into the gel for the synthesis of the SiMCM-41C. MCM-48 was synthesized with a gel composition of 1 SiO_2 : 0.05 Na_2O : 0.65 HTABr : 52 H_2O, using the procedure in Ref. 6. The reaction temperatures for the above sample preparation were between 370 and 390 K. All products were washed thoroughly with doubly distilled water at room temperature and dried using oven at 370 K before calcination. The calcination was carried out in O_2 flow during heating to 813 K over 10 h and maintaining at 813 K for 4 h. The products after calcination were immediately washed again in distilled water and then quickly placed in an oven to dry for 2 h at 370 K.

Hydrothermal stability of the samples was investigated by measuring the intensity decrease in XRD diffractogram during heating in doubly distilled water or other aqueous solutions. The sample to liquid ratio was fixed as 1 L g^{-1}. Samples after the heating in the liquids were filtered, washed in doubly distilled water, and immediately placed in oven to dry for 2 h at 400 K. XRD patterns were obtained from the dried samples, with a Cu K_α X-ray source using a Rigaku D/MAX-III (3 kW) instrument. Magic angle spinning (MAS) ^{29}Si NMR spectra were obtained after the samples were quickly hydrated at 296 K, with a Bruker AM 300 instrument operating at 78.2 MHz. Relaxation delay for the ^{29}Si NMR was given as 5 s. Sample spinning rate for the NMR was 3.5 kHz.

Results and Discussion

Figure 1 displays XRD patterns for the SiMCM-41 and MCM-48 structures against heating temperatures of the materials in water. The XRD patterns for the calcined MCM-

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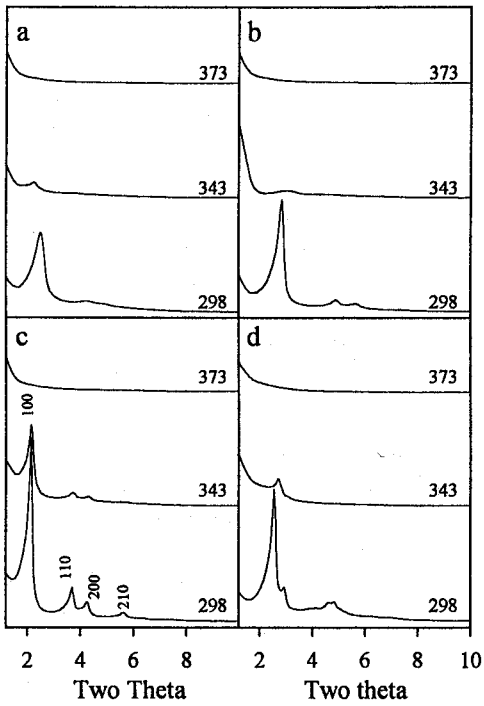

Figure 1. XRD patterns of mesoporous materials: (a) SiMCM-41A; (b) SiMCM-41B; (c) SiMCM-41C; (d) MCM-48. The XRD patterns were obtained with Cu K_α X-ray source using Rigaku D/MAX-III (3 kW) instrument, after the samples were heated in distilled water for 12 h. Numbers denote the heating temperatures in kelvin.

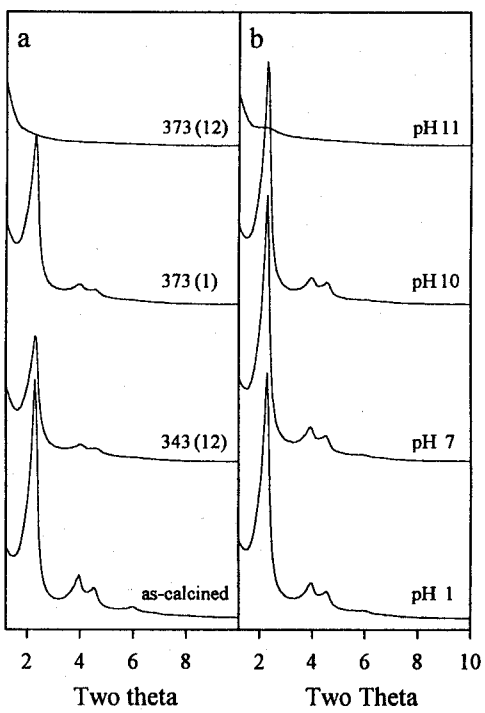

Figure 2. XRD patterns of AlMCM-41: (a) after the sample was heated in distilled water. Numbers before parentheses indicate the heating temperatures in kelvin and the numbers in the parentheses denote the heating times (hour). (b) after the sample was slurred in the aqueous solution with various pH. pH of the solution was adjusted by adding HCl and NaOH in doubly distilled water.

41 samples before the heating in water show four diffraction lines characteristic of the hexagonal structure of MCM-41. The XRD pattern for the MCM-48 sample agrees with the cubic $I_a\bar{3}_d$ structure known in the literature.[1,2,6] No distinct changes in the structures are indicated by the XRD lines during 12 h in distilled water at room temperature. As the water temperature was increased to 343 K, the intensity of the XRD patterns decreased conspicuously. The SiMCM-41C showed better stability than the other pure-silica samples. The stability difference is consistent with previous conclusion[4,7] that the stability of MCM-41 can be enhanced by repeated pH adjustment to around 11 during hydrothermal synthesis, due to an equilibrium shift of the synthesis reaction toward the silicate condensation. However, all the structures disappeared completely during the heating at 373 K.

Figure 2 illustrates the effects of solution temperature and pH on the structure of AlMCM-41. Figure 2(a) is very similar to Figure 1(c), indicating that the structure of the AlMCM-41 sample also disintegrated in water at 373 K. The XRD patterns in Figure 2(b) were obtained after placing the AlMCM-41 sample for 12 h in aqueous solutions at room temperature. pH of the solution was adjusted by adding HCl or NaOH in doubly distilled water. The results in Figure 2(b) shows that the MCM-41 structure was stable for 12 h in the aqueous solutions with pH=1-10, above which the structure disintegration occurred seriously. No significant changes in the structure were detected when the AlMCM-41 sample was gently stirred in 0.1-0.5 M aqueous solutions of $NaNO_3$ for 12 h and subsequently washed with doubly

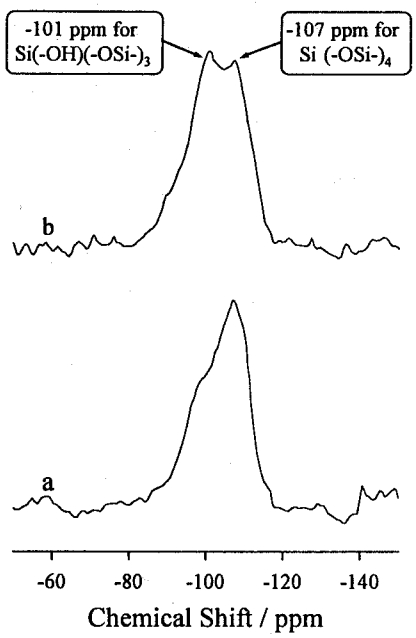

Figure 3. Magic angle spinning (MAS) ^{29}Si NMR spectra: (a) as-calcined SiMCM-41C; (b) SiMCM-41C, heated in distilled water at 373 K for 12 h. ^{29}Si MAS NMR spectra were obtained after the samples were quickly hydrated at 296 K with a Bruker AM 300 instrument operating at 78.2 MHz. Relaxation delay fot the ^{29}Si NMR was given as 5 s. Sample spinning rate for the NMR was 3.5 kHz.

distilled water. However, as the stirring in the $NaNO_3$ solution for 1 h and subsequent washing were repeated 4 times in order to increase the Na^+ ion exchange level, the XRD patterns decreased in intensity very seriously. Thus, the structure disintegration also depended on the ion exchange level.[4]

MAS ^{29}Si NMR spectra displayed for SiMCM-41 and MCM-48 in Figure 3 show significant increases in the intensity ratio between $Si(\text{-}OSi\text{-})_3OH$ and $Si(\text{-}OSi\text{-})_4$ tetrahedral silicon atoms after the heating for 12 h in water, indicating that the structure disintegration occurred with hydrolysis of Si-O-Si linkages in the structures. Amorphous frameworks of the mesoporous materials are believed to be easily attacked by the hydrolysis, compared with completely cross-linked aluminosilicate frameworks in zeolites. The hydrolysis seems to result in the structure disintegration through opening of Si-O-Si linkages in the structures.

The poor hydrothermal stability of MCM-41 in distilled water at 373 K seemed to disagree with our previous results showing excellent stability at high temperatures up to 980 K in O_2 flow containing 2.3 kPa water vapor.[4] In order to investigate the stability difference under the different conditions, we obtained a XRD pattern of the pure-silica MCM-41 sample after heating for 2 h through steam (100% H_2O) flow at 873 K. The XRD pattern of the heated sample was very similar to Figure 1(c), which indicated that the mesoporous structure was maintained during the steaming condition at 873 K. MCM-48 also exhibited similar hydrothermal behavior. Thus, the mesoporous structures were indeed more stable under the steaming conditions at the high temperatures than in distilled water at 373 K.

There are many reports on catalytic applications of MCM-41 type materials in the literature.[8~11] However, the currently available mesoporous materials are expected to lose the catalytic activity repidly with time, under such circumstances as containing water. For ultimate successful commercial use of the MCM-41 type materials, it is very critical to improve the hydrothermal stability by post-synthesis modification, or opimization of the synthesis procedures. Alternatively, it may be considered to find other mesoporous with greatly improved stability.

Conclusion

The structures of all MCM-41 and MCM-48 samples avaiable in the present work disintegrated in aqueous solution or water around 373 K, more or less readily depending on the synthesis methods and pH of the solution. Repeated adjustment of pH to 10.2 during hydrothermal crystallization of MCM-41 following the procedure of Ryoo and Kim[4,7] increased the hydrothermal stability significantly. However, the mesoporous structure was completely lost during the overnight-heating in water at 373 K, due to silicate hydrolysis. Contrary to the structure disintegration at 373 K, the mesoporous structures were stable under 100%-steaming conditions around 873 K. Thus, the silicate hydrolysis of the mesoporous materials was thermodynamically more favorable in water at 373 K than in steam at 873 K.

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