Mechanochemical Collapse of M41S Mesoporous Molecular Sieves through Hydrolysis of Siloxane Bonds

Takashi Tatsumi,* Keiko A. Koyano, Yoshinori Tanaka,† and Shinichi Nakata†
Engineering Research Institute, School of Engineering, The University of Tokyo, Yayoi, Tokyo 113
†*Chiyoda Corporation, Moriya-cho, Kanagawa-ku, Yokohama 221*

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The structural collapse of mesoporous molecular sieves MCM-48 and MCM-41 materials by mechanical compression was found to occur mechanochemically through the hydrolysis of Si-O-Si bonds. Their ordered structures were well retained by compressing the samples under dry N_2.

Recent discovery of a new family of mesoporous molecular sieves named M41S has been receiving much attention. The M41S family is classified into several members: MCM-41 (hexagonal), MCM-48 (cubic) and other species.[1] These materials have uniform pores, and their pore size can be tailored in the range from1.6 nm to 10 nm through the choice of surfactant as the template, auxiliary chemicals and reaction conditions. Inagaki *et al.* also reported the synthesis of highly ordered mesoporous molecular sieve with a similar hexagonal array of uniform channels; this material obtained from kanemite was named FSM-16.[2] These mesoporous materials have been made good use of as supports, adsorbent, and catalysts.[3]

Mechanical stability is an important property for various applications, since compaction is an element in the handling of powdery materials for industrial use. Recently, Gusev *et al.* reported that the ordered mesoporous structure of pure silica MCM-41 was mechanically unstable compared to zeolites, silica gels and alumina.[4] It has been recently shown that FSM-16 crystals also become less ordered by pressing.[5] Here we report that the structural collapse of mesoporous molecular sieves MCM-48 and MCM-41 materials by mechanical compression occurs mechanochemically through the hydrolysis of Si-O-Si bonds.

For the preparation of pure-silica MCM-48, an aqueous solution of cetyltrimethylammonium chloride / hydroxide (CTMACl/OH, Cl/OH = 70/30) was added dropwise to tetraethyl orthosilicate (TEOS) under vigorous stirring at 278 K. After stirred for 1 h, the mixture was heated at 358 K for 4 h to remove the ethanol produced in the hydrolysis of the TEOS. The resultant gel was poured into a Teflon bottle, and heated under static conditions at 373 K for 10 days. After hydrothermal treatment, the solids were filtrated, washed, dried, and finally calcined in air at 813 K for 6 h. The molar composition of the gels subjected to hydrothermal synthesis was as follows: $SiO_2 \cdot$ CTMA $\cdot$ $46.5H_2O$. For the synthesis of pure-silica MCM-41, fumed silica (Aerosil 200, Nippon Aerosil) and dodecyltrimethylammonium bromide (DTMABr) were used as an Si source and template, respectively. The procedure was based on the method reported by Reddy *et al.*[6] Fumed silica was dissolved in a NaOH solution and stirred for 30 min. Then DTMABr was added to the mixture, which was stirred for 1 h. The resulting mixture was hydrothermally treated at 373 K for 6 days. The following steps were the same as described above for the synthesis of pure-silica MCM-48. The molar composition of the gels subjected to hydrothermal synthesis was as follows: $SiO_2 \cdot 0.5$DTMA $\cdot 0.17Na_2O \cdot 30H_2O$.

Mechanical stability of MCM-41 and MCM-48 was investigated as follows: all the samples were calcined in air at 813 K for 6 h immediately before compression. The samples (0.1 g) were pressed in a steel die of 20 mm diameter by a pressing apparatus under air or dry nitrogen for 10 min. X-ray powder diffraction (XRD) patterns were taken on a Rigaku Rint 2400 diffractometer using CuK_α radiation. Nitrogen adsorption measurements were performed on a Belsorp 28SA analyzer. The solid-state NMR measurements were performed on a JEOL JNM-GX270 spectrometer equipped with a magic angle spinning (MAS) unit. Measurement conditions were as follows: the resonance frequency, 53.54 MHz; pulse width, 6 μs; pulse delay 7 s; spinning speed, 5.5 kHz; standard, $(CH_3)_4Si$.

The XRD pattern of synthesized pure silica MCM-48 materials matched well that reported by Vartuli *et al.*[1] As shown in Figure 1, the calcined sample exhibited a very strong peak at *d* spacing of 3.56 nm and medium or weak peaks at *d* spacings of 3.10, 2.34, 2.18, 1.95, 1.86, 1.79 and 1.72 nm. These eight peaks were indexed on a cubic unit cell with a = 8.72 nm. The N_2 adsorption isotherm of this sample was characteristic of mesoporous materials with uniform pore size. The average pore diameter determined by the Dolimore-Heal method was 2.52 nm.

Figure 1a shows the XRD patterns of MCM-48 compressed at varying pressure under air. The intensities of all the diffraction peaks were markedly decreased with increaing pressure. Simultaneously the steep increase in N_2 adsorption at p/p_0 around 0.3 due to the ordered cubic mesoporous structure faded and the amount of adsorbed N_2 reduced. Table 1 summarizes the effects of compression on the surface area and pore volume as well as the d_{211} peak height. These results are similar to those reported for pure-silica MCM-41[4] and for FSM-16.[5]

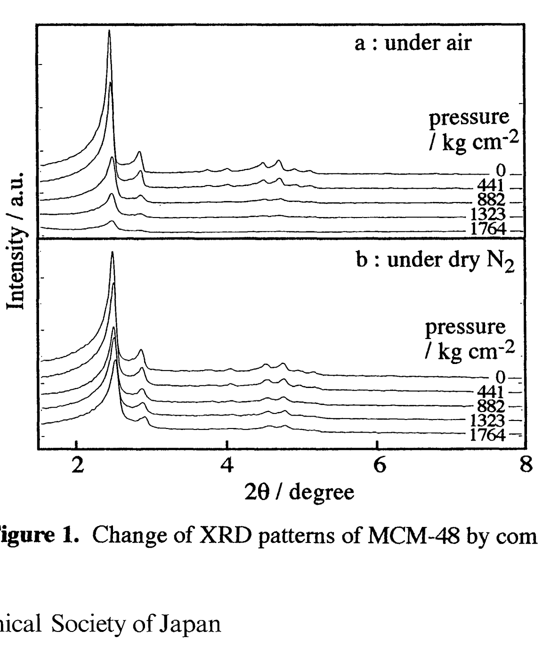

Figure 1. Change of XRD patterns of MCM-48 by compression.

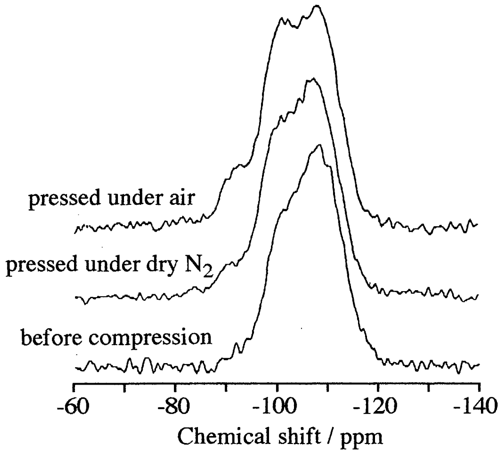

Figure 2. ^{29}Si MAS NMR spectra of MCM-48 before and after compression.

The mechanical stability of the MCM-48 material was similarly tested under dry N_2. As shown in Figure 1b, the structure of the MCM-48 sample was found much more resistant to compression under dry N_2 than under air. The results are also listed in Table 1. Although the structure was appreciably affected by mechanical compression at low pressures, the structural destruction proceeded barely with further increasing pressures; the X-ray diffraction patterns characteristic of the cubic structure and the step of the N_2 adsorption isotherms were well retained after compression at 1764 kg/cm^2.

In order to obtain detailed information on the structural change, ^{29}Si MAS NMR spectra of the MCM-48 samples were taken before and after compression at 1764 kg/cm^2 (Figure 2). The sample before compression exhibited two broad resonances, at -110 ppm for the Q^4 environment and at -100 ppm for the Q^3 environment together with a shoulder ascribable to the Q^2 species. By applying pressure under air, the Q^3 and Q^2 species were increased at the expense of Q^4, as shown in Table 2. This is analogous to the IR observation by Ishikawa *et al.*,[5] who reported that the surface SiOH groups of FSM-16 increased with increasing applied pressure. On the other hand, the increase in the intensity of Q^3 and Q^2 species was suppressed for the compression under dry N_2. Thus it is conceivable that the compression under air promoted the cleavage of the $\equiv$Si-O-Si$\equiv$ bonds by adsorbed water, leading to the formation of silanol groups. In contrast, the structure of MCM-48 only slowly destroyed under air without mechanical compression; upon exposure to the water vapor over saturated aqueous solution of NH_4Cl at room temperature for 20 days and for 90 days, the d_{211} peak height decreased by 36% and by 65%, respectively. This structural change was also accompanied with the increase in the Q^3 and Q^2 environments. Therefore it is concluded that the structural change was remarkably promoted by compression and that the reaction expressed by eq. 1 occurred mechanochemically.

$$\equiv\text{Si-O-Si}\equiv \;+\; H_2O \;\xrightarrow{\text{Mechanical compression}}\; 2\equiv\text{Si-OH} \qquad (1)$$

The lattice of the structure may be strained by pressing and then made susceptible to hydrolysis; MCM-48 adsorbed relatively large amount of water (e.g., 32% over saturated aqueous solution of NH_4Cl at room temperature). When water was absent, however, the cleavage of siloxane bonds hardly occurred, resulting in the retention of the ordered structure.

Table 1. Effect of atmosphere during compression on mechanical stability of pure silica MCM-48

Atmosphere	under air			under N_2		
Pressure /kg cm^{-2}	d_{211} peak height^a	S.A.^{b} /m^{2}g^{-1}	P.V.^{c} /cm^3 g^{-1}	d_{211} peak height^a	S.A.^{b} /m^{2}g^{-1}	P.V.^{c} /cm^3 g^{-1}
0	100	1074	0.89	100	1074	0.89
441	76	815	0.68	86	967	0.80
882	34	652	0.51	63	824	0.62
1323	19	484	0.32	65	858	0.65
1764	10	382	0.17	59	854	0.62

^{a}Relative; 100 before compression. ^{b}BET surface area. ^{c}Pore volume.

Table 2. ^{29}Si MAS NMR data for pure silica MCM-48

		Si/ mole %	
Compression Conditions	Q^2	Q^3	Q^4
Before compression	3.4	33	64
1764 kg/cm^2 under air	9.8	38	53
1764 kg/cm^2 under dry N_2	6.4	32	62

Similar retardation of structural change by applying pressure under dry N_2 was also observed for pure silica MCM-41. The BET surface area, the pore volume, and the average pore diameter of the MCM-41 sample before compression were 1110 m^2/g, 0.81 cm^3/g, and 2.12 nm, respectively. By compression at 1764 kg/cm^2, the d_{100} peak height, the BET surface area, and the pore volume decreased by 14%, 21%, and 27%, respectively, under dry N_2, while they decreased by 47%, 33%, and 40%, respectively under air. As to the relative stability of MCM-48 and MCM-41, further experiments will be required, since the two materials used in this study are different in the pore size and adsoprtion amount of water, which depends also on the humidity of air.

The noticeable loss of the regularity of the structures by applying pressure under dry N_2 as well will be due to the incomplete removal of adsorbed water and/or adventitious moisture during the compression measurements.

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