Increased Stability of Organically Modified MCM-41 Synthesized by a One-step Procedure

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Organically functionalized mesoporous silica MCM-41 materials synthesized by a one-step procedure are found to be structurally more stable than the unfunctionalized ones. This increased stability can be ascribed to the increase in hydrophobicity.

Recently, a new family of mesoporous molecular sieves such as MCM-41 has been receiving much attention. These mesoporous materials have found feasible for adsorbents, supports, and catalysts. However, the range of application has been limited by the instability of the structure of the mesoporous molecular sieves. Kim *et al.* claimed that MCM-41 has low hydrothermal stability.[1] The regular structure of FSM-16, from which the surfactant was removed by HCl treatment, disappeared on exposure to water vapor at room temperature.[2] Furthermore, these materials are mechanically unstable compared to other materials such as alumina and silica gels.[3,4] We have found that the structure collapse of mesoporous molecular sieve materials by mechanical compaction occurs mechanochemically through the hydrolysis of Si-O-Si bond in the presence of adsorbed water.[5]

Organically functionalized derivatives of such mesoporous materials can be produced by grafting of suitable moieties onto the surface of preformed mesoporous silica.[6] Recently we have reported that trimethylsilylation of mesoporous silicas is effective in enhancing their stability to moisiture and compaction through increasing their hydrophobicity.[7] An alternate organic-functionalization of mesoporous silicas have been attained by a one-step synthesis procedure through the co-condensation of tetraethoxysilane (TEOS) and organoalkoxysilane.[8-11] To our best knowledge, however, there is no report on the stability of organically functionalized mesoporous silica synthesized by a one-step procedure. Here we will show the improved stability of the regular structure of the methyl- and vinyl-modified MCM-41 type silica.

The standard synthesis method is as follows: an aqueous solution of NaOH / hexadecyltrimethylammonium bromide (C_{16}TMABr) was added to a mixture of TEOS and either methyltriethoxysilane (MTES) or vinyltriethoxysilane (VTES) under vigorous stirring, and the mixture (0.80 TEOS : 0.20 organosilane : 0.12 C_{16}TMABr : 0.50 NaOH : 130 H_2O) was stirred for 3 days at room temperature. Hydrothermal treatment (T) at 87℃ for 1 day which followed the 2-day stirring at room temperature and pH adjustment (A) to 10.2 after 24 h of stirring at room temperature have been also provided as variation methods to give MCM-41-MTES-T and MCM-41-A or MCM-41-MTES-A, respectively. Combination of the pH adjustment and the hydrothermal treatment was also applied and the obtained sample was denoted as MCM-41-MTES-AT. Additionally, MCM-41-40MTES was prepared from the gel with the increased MTES/TEOS ratio of 40/60. All crystallized products were filtered, washed, and dried. The organic templates were removed by an acid extraction method using 1 M HCl solution in ethanol at 80 ℃ for about 16 h. Stability of these samples was evaluated through exposure to moisture over a saturated aqueous solution of NH_4Cl at room temperature for various days, followed by XRD measurement for the intensity changes. Mechanical stability was investigated by pressing the samples in a steel die at various pressures, followed by XRD measurement.

The XRD patterns of the organically functionalized samples from which the surfactant was removed by the acid extraction exhibited d_{100}, d_{110} and d_{200} reflections, indicating a hexagonal arrangement of channels. The extraction seems complete, as confirmed by the absence of nitrogen in an elemental analysis. ^{13}C-CP/MAS and ^{29}Si-MAS NMR were recorded on JEOL JNM-Λ-400WB and JNM-GX270 spectrometers operating at frequencies of 100.53 and 53.54 MHz, respectively. Chemical shifts were referenced to external tetramethylsilane (TMS) for both ^{13}C and ^{29}Si. Spinning rates of 5.2 and 3.5 kHz, recycle delay times of 4.0 and 7.0 s, pulse widths of 5.0 and 6.0 μs, and 1000 and 15000 to 20000 scans were taken for ^{13}C and ^{29}Si, respectively. The ^{1}H contact time in the ^{13}C-CP/MAS NMR measurements was 3 ms. The incorporation of organic groups

Table 1. Physical data for MCM-41 and organically functionalized MCM-41

Sample	Pore size[a] / Å	Pore volume / cm^3 g^{-1}	BET surface area / m^2 g^{-1}	Peak intensity of (100) reflection	Organosiloxane incorporation / %
MCM-41	27	1.25	1271	80	0
MCM-41-A	25	1.12	831	100	0
MCM-41-MTES	21	0.82	927	65	12.5
MCM-41-VTES	21	0.81	943	78	n.d.[b]
MCM-41-MTES-A	21	0.93	1063	65	n.d.[b]
MCM-41-MTES-T	21	0.94	941	73	11.8
MCM-41-MTES-AT	21	1.08	1012	99	16.1
MCM-41-40MTES	19	0.51	1005	29	34.8

[a] Measured by using the Dolimore-Heal method. [b] Not determined.

was indicated by the ^{13}C MAS NMR; the peak of the organic group directly bonded to Si appeared at -7.3 ppm for the methyl group and at 134.4 and 128.9 ppm for the vinyl group. The physical data for the MCM-41 samples are shown in Table 1. It was observed that the pore size and the pore volume decreased by the incorporation of organic groups. Their decrease was remarkable when the MTES/TEOS ratio was increased to 40/60.

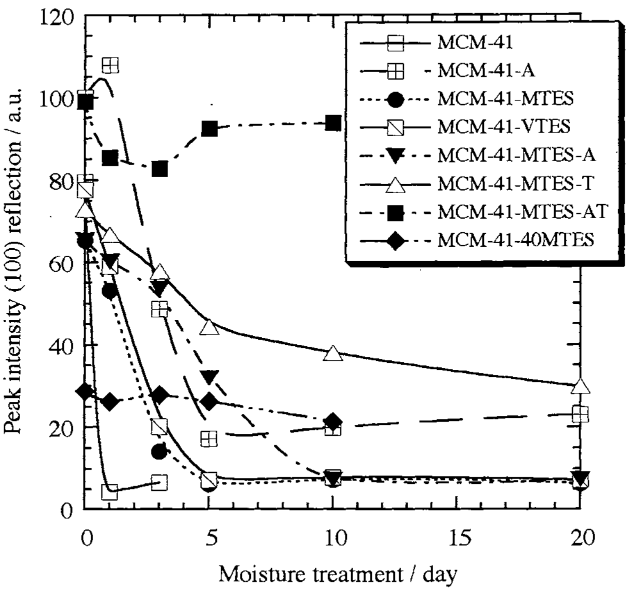

Figure 1. Stability to moisture of MCM-41 and organically functionalized MCM-41.

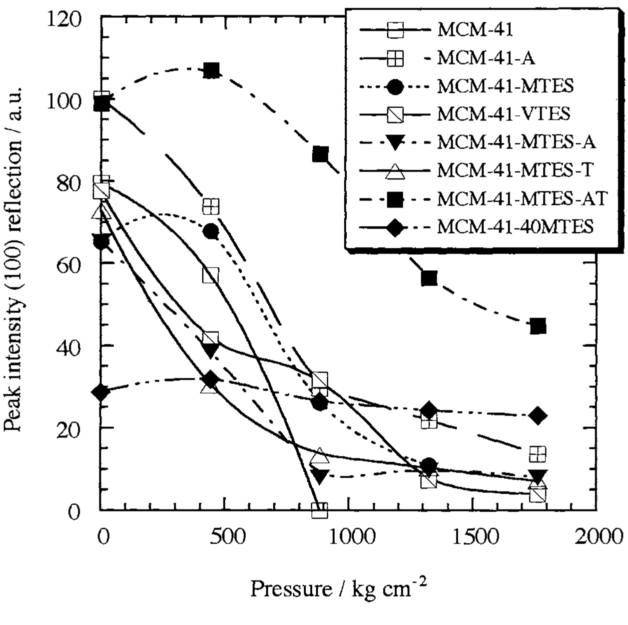

Figure 2. Mechanochemical stability of MCM-41 and organically functionalized MCM-41.

The high surface area was maintained for all the samples. ^{29}Si NMR spectra of the organically functionalized samples show five peaks centered at -110, -101, -92, -65, -53 ppm which can be assigned to $Si(OSi)_4$ [Q^4], $HOSi(OSi)_3$ [Q^3], $(HO)_2Si(OSi)_2$ [Q^2], $MeSi(OSi)_3$ [T^3], and $Me(HO)Si(OSi)_2$ [T^2], respectively. The extent of organosiloxane incorporation was determined from the combined peak intensity of (T^2 and T^3) divided by the total peak intensity due to T^m and Q^n species. It is noteworthy that to date methyl-functionalized MCM-41 materials have not been reported.

Figure 1 shows the change in the d_{100} reflection intensity of MCM-41 materials during moisture treatment. Organically functionalized samples exhibited high stability compared to the pure silica MCM-41, synthesized at room temperature and acid-treated for surfactant removal, which lost the regularity very rapidly. The increased MTES/TEOS ratio resulted in increased stability, although the material, MCM-41-40MTES, had low regularity. When the combination of the pH adjustment and the hydrothermal treatment was applied, stability has been dramatically improved. This is probably due to the enhancement of the condensation of silicates as evidenced by the decrease in (Q^2 + Q^3)/Q^4 and T^2/T^3 of ^{29}Si NMR spectra (data not shown) and H_2O adsorption measurements (see below). As shown in Figure 2, the mechanical stability was also improved by organic functionalization of MCM-41, especially for MCM-41-40MTES and MCM-41-MTES-AT.

H_2O adsorption isotherms of selected samples have been measured. The amount of monolayer adsorption of H_2O (molecules / nm^2) was estimated from the BET plot of H_2O adsorption isotherms and the BET surface area measured by N_2 adsorption. The hydrophilic site decreased in the following order: MCM-41 (2.80 H_2O/nm^2) > MCM-41-MTES (1.89 H_2O/nm^2) > MCM-41-MTES-AT (1.59 H_2O/nm^2) > MCM-41-40MTES (0.76 H_2O/nm^2). This order is in agreement with the order of stability to moisture or compaction. Thus the improved stability of the organically functionalized MCM-41 can be ascribed to the increase in hydrophobicity.

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