Postsynthesis Hydrothermal Restructuring of M41S Mesoporous Molecular Sieves in Water

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A high-quality Si−MCM-41 was prepared with the composition of SiO_2, 0.2; TEAOH, 0.25; CTMABr, 35 in H_2O using fumed silica as the silica source. The quality of the compounds was assessed using different analytical techniques such as XRD, N_2 adsorption−desorption measurement, UV−vis absorption, FTIR, and ^{29}Si MAS NMR. The quality of M41S mesoporous materials, synthesized using a single $C_{16}TMA^+$ surfactant, could be further improved by a postsynthesis hydrothermal treatment of the as-synthesized materials in water. In comparison with the ordinary preparation, the water-treated materials exhibited a higher long-distance order, a higher BET surface area, and a larger pore size. The postsynthesis water treatment method provided an easy and mild way to prepare high-quality M41S molecular sieves with the pore size controllable by altering either the treatment time or the temperature. The postsynthesis treatment also enhanced the stability, especially the hydrothermal stability, of Si−MCM-41. The ^{29}Si MAS NMR results demonstrated that the water treatment promoted the wall polymerization or local atomic arrangement. It was suggested that the pH lowering of synthesis mixture by replacing the mother liquor with water played a crucial role in the restructuring toward a high-quality Si−MCM-41. The quality of Ti−MCM-41, Al−MCM-41, and Si−MCM-48 was also improved by a similar postsynthesis hydrothermal treatment.

1. Introduction

The M41S family of mesoporous molecular sieves, especially MCM-41 and MCM-48, has been attracting considerable attention since their discovery.[1] Owning to their high surface area and highly ordered mesopores (20−100 Å), they have found potential applications as catalysts,[2,3] absorbents,[4] and hosts for various kinds of molecules.[5,6] It is recognized that the thermal and hydrothermal stability is a crucial parameter to the practical applications of these mesoporous materials. Pure siliceous MCM-41 is stable when heated to 850 °C in air or 800 °C in air with low water vapor pressure.[7] However, the mesoporous structure gets collapsed when it is mechanically compressed in the presence of adsorbed water or after a long-time exposure to water vapor at room temperature.[8−10] The hydrothermal stability of MCM-41 is poor in water,[11] and also the mesoporous structure is completely lost upon boiling in water for 2 days.[12] Since the instability of these materials imposes a strict limitation on their applications, there are enormous efforts being devoted to the improvement of the stability of M41S mesoporous materials. By the addition of some sodium salts such as sodium chloride during synthesis, or by ion exchange with Na^+, K^+, Ca^{2+}, and Y^{3+}, the hydrothermal stability of the resulting MCM-41 could be enhanced.[13,14] The postsynthesis grafting of calcined sample using some metal alkoxides has also been found to increase the thermal stability of MCM-41 materials, with the introduction of a new element.[15] More recently, postsynthesis silylation has been reported to enhance the hydrothermal stability of mesoporous materials due to the increase in hydrophobicity.[16,17]

However, it is more desirable to prepare a stable mesoporous material by a direct synthesis. The technique of increasing the wall thickness and wall polymerization is commonly used. By controlling the pH of the initial synthesis mixture, a Si−MCM-41 with a wall thickness of 16 Å was prepared.[18] Recently, a Si−MCM-41 with a wall thickness as high as 26.8 Å was prepared at 165 °C, and this material could be calcined at 1000 °C with little structure damage.[19,20] Apart from the technique of controlling the synthesis conditions, a postsynthesis treatment of as-synthesized sample can further improve the quality of the MCM-41. Taking into account the pH increment during synthesis, pH adjustments using some acids have been shown to significantly increase the inherent long-range order of MCM-41 and hence improve the stability.[21,22] A more simple method has been addressed recently;[23] that is, a low-temperature and low-pH water treatment improved the product quality and enlarged the pore size of the Si−MCM-41, which was synthesized by using mixed surfactants containing gemini $C_{m−s−m}$ molecules. This provided a convenient and mild way to prepare high quality and large pore mesoporous materials. Unfortunately, this method was found to be effective only to the Si−MCM-41, which was synthesized using a complex gemini $C_{m−s−m}$ surfactant.

In the present investigation, we have found that a postsynthesis hydrothermal treatment in water also improved the quality of the MCM-41 and MCM-48 prepared by using a common $C_{16}TMA^+$ surfactant. The pore size, quality, and stability of Si−MCM-41 were increased upon such a restructuring in water. A high-quality Si−MCM-41 has been prepared by a postsynthesis water treatment and could be calcined at 1000 °C in air or heated in boiling water without suffering from significant structure damage. The beneficial effect of a postsynthesis hydrothermal treatment on the qualities of other M41S materials

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such as Ti−MCM-41, Al−MCM-41, and Si−MCM-48 has also been investigated. The mechanism of the postsynthesis hydrothermal restructuring has been investigated by ^{29}Si MAS NMR.

2. Experimental Section

2.1. Chemicals. Tetraethyl orthosilicate (TEOS), 20 wt % tetraethylammonium hydroxide (TEAOH) aqueous solution, cetyltrimethylammonium bromide (CTMABr), titanium isopropoxide, and sodium aluminate were from Wako Pure Chemicals Industries Ltd., Japan. Fumed silica was from Sigma, and colloidal silica was from Nissan Chemical Industrial Ltd. Millipore treated water was used.

2.2. Normal Synthesis of MCM-41 and Si−MCM-48. For the synthesis of pure siliceous MCM-41 (Si−MCM-41), a gel mixture with the composition SiO_2, 0.2; TEAOH, 0.25; CTMABr, 35 in H_2O was used. A detailed preparation procedure can be described as follows. A 40.4 g amount of water and 6.2 g of CTMABr were mixed and stirred at room temperature until all the CTMABr was dissolved. Then, to this mixture, 10 g of 20% TEAOH solution was added. Finally, 4.1 g of fumed silica was introduced. The mixture was kept stirring at 70 °C for 2 h and aged at room temperature for 24 h. Then, it was transferred into a Teflon-lined autoclave and synthesized at 150 °C for 48 h under autogenous pressure. After the autoclave was cooled to room temperature, the as-synthesized MCM-41 material was filtered, washed with plenty of Millipore water, air-dried, and finally calcined in air at 550 °C for 9 h with a heating rate of 1 °C/min. Ti- and Al-containing MCM-41 (Ti−MCM-41 and Al−MCM-41) were also prepared in a similar way by the addition of an appropriate amount of titanium isopropoxide or sodium aluminate into the synthesis mixture following the introduction of fumed silica, and finally, the pH was adjusted to 11 using a 1 M H_2SO_4 solution. The synthesis temperature was 120 °C for both Al−MCM-41 and Ti−MCM-41.

A Si−MCM-48 sample was prepared using a recipe similar to that reported in the literature.[24] A mixture of TEOS, CTMABr, NaOH, and water with the composition SiO_2, 0.6; CTMABr, 0.5; NaOH, 60 in H_2O was stirred at room temperature for 2 h and then transferred into an autoclave and heated at 110 °C for 48 h. The final product was washed with water, dried at room temperature, and calcined in air at 550 °C for 9 h. The MCM-41 and Si−MCM-48 samples prepared following the above procedures were regarded as normal samples.

2.3. Postsynthesis Hydrothermal Restructuring. The postsynthesis hydrothermal treatment was carried out by replacing the mother liquor with pure water after the normal synthesis. Typically, after the synthesis gel mixture was heated at 150 °C for 24 or 48 h, the autoclave was cooled to about 30−35 °C. The as-synthesized Si−MCM-41 was separated from the mother solution by filtration mixed with a certain amount of pure water, which was equivalent to about 10 mL of water per gram of dried uncalcined sample, transferred into an autoclave, and kept in the oven maintained at 150 °C again for different periods of time. Finally, the solid product was filtered, washed, dried, and calcined as in the normal preparation. Samples prepared by the two-step method (first synthesis in the mother liquor, then in water) were referred to water-treated samples, and the second step was defined as water treatment.

2.4. Characterization. BET surface area and pore size were obtained from N_2 adsorption isotherms measured at −196 °C using a Bellsorp36 instrument. Prior to N_2 adsorption, the sample was degassed at 350 °C for at least 2 h to achieve a final pressure of 1.5×10^{-3} Torr. For the calculation of pore size of MCM-41 mesoporous materials, it is known that the BJH method
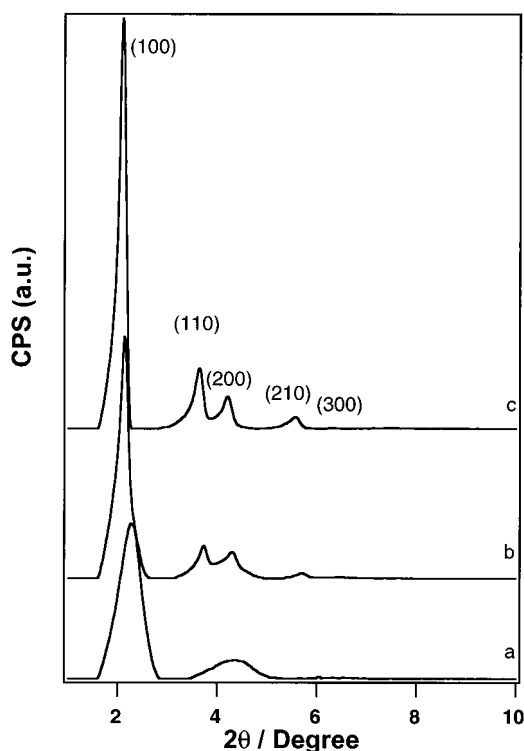
Figure 1. XRD spectra of calcined Si−MCM-41 prepared from different silica sources: (a) TEOS; (b) colloidal silica; (c) fumed silica.

underestimates the pore size.[25,26] Therefore, the primary pore size (ω) was calculated according to a more precise method described elsewhere;[27−30] that is, $\omega = cd(\rho V_p)^{1/2}/(1 + \rho V_p)^{1/2}$, where $c = 1.213$, $\rho = 2.2$ g/cm^3, d is the lattice spacing of d_{100}, and V_p is the primary mesopore volume. For samples with the presence of a noticeable amount of micropores, the primary pore size was calculated according to $\omega = cdV_p^{1/2}/(1/\rho + V_p + V_{mi})^{1/2}$, where V_{mi} is the micropore volume.

XRD spectra were recorded in the 2θ range $1-10°$ using a MXP powder diffractometer with a Cu Kα radiation operated at 40 kV and 40 mA. A step size of 0.01° and a scanning speed of 1° 2θ/min were used. UV−vis absorption spectra were recorded using a U-3000 spectrophotometer in the similar way as reported previously for solid samples.[31] The pure siliceous ZSM-5 was used as the reference. FTIR study was performed using a JASCO FTIR-620 spectrometer with a resolution of 4 cm^{-1} and 16 scans. The KBr technique with a sample to KBr weight ratio of 1:150 was used.

The [29]Si magic-angle spinning (MAS) NMR spectra were measured using a Bruker AMX-500 spectrometer with zirconia rotors spun in air at 4000 Hz. Data were acquired at 99.4 MHz and 10 s recycle delays. The chemical shifts are given in ppm using tetramethylsilane (TMS) as a standard material.

3. Results and Discussion

3.1. Influences of Silica Source. The quality of the Si−MCM-41 strongly depends on the type of silica source used. Figure 1 shows the XRD spectra of the Si−MCM-41 prepared from the three mostly used silica sources, that is, TEOS, colloidal silica, and fumed silica, respectively. It can be seen that, when TEOS is used, the XRD pattern of the sample shows a poor resolution for the (110) and (200) diffraction peaks. Interestingly, the XRD pattern is similar to that of KIT-1,[32] which possesses a shorter distance order compared to that of MCM-41. However, the N_2 adsorption results indicated that this material is not much different in both the pore size and surface

TABLE 1: Characteristics of Normally Prepared and Water-Treated Si−MCM-41 Samples[a]

time (h)	unit cell a_0 (Å)	BET surface area (m²/g)	primary pore diameter (Å)	wall thickness (Å)
		Normal Synthesis at 150 °C		
24	37.9	933	30	7.9
48	42.2	1018	34	8.2
72	45.5	969	37	8.5
120	48.1	400	34	14.1
		Water Treated at 150 °C		
24	47.6	978	39	8.6
72	50.5	792	41	9.5
		Normal Synthesis at 165 °C		
24	40.4	812	32	8.4
48	48.3	720	38	10.3
72	52.3	547	41	11.3
120	54.8	313	38	16.8
		Water Treated at 165 °C		
24	53.6	728	43	10.6
72	58.8	468	45	13.8

[a] Water-treatment was started after 48 h normal synthesis.

area from the MCM-41 material, which has a well XRD resolution. One tentative interpretation is that less oligomerized silicate anions are formed after the hydrolysis of TEOS. These small silicate anions are not readily polymerized further under the synthesis conditions. Therefore, the final product is composed of small MCM-41 particles, which renders a short-distance order. On the other hand, the XRD of the Si−MCM-41 from fumed silica showed all the peaks corresponding to (100), (110) and (200), the (210) and (300) planes, which is indicative of a high long-distance order. Hence, it can be inferred from Figure 1 that the fumed silica is the best silica source for the preparation of high-quality Si−MCM-41 molecular sieve under our experimental conditions. The high quality of Si−MCM-41 from using fumed silica can be attributed to the high degree of polymerization of silicate. Furthermore, since the fumed silica itself is composed of large oligomeric silica particles, it would also contribute to the high quality of Si−MCM-41.

3.2. Postsynthesis Hydrothermal Restructuring of M41S Mesoporous Materials. When the as-synthesized Si−MCM-41 was hydrothermally treated with water, the XRD intensity as well as the unit cell parameter was found to increase. However, it is known that prolonging the synthesis time also increases the pore size even in the normal synthesis.[20,29,30,33,34] To demonstrate the superiority of the water treatment method over the ordinary synthesis, two parallel experiments were carried out under similar synthesis conditions. During synthesis, a part of the solid product was removed at some stages of synthesis for assessment and heating of the remaining synthesis mixture was continued.

From Table 1, it can be seen that, in the normal synthesis at 150 °C, the pore size increases with the synthesis time at the initial stage of synthesis but no increment is observed if the synthesis time exceeds 72 h and the wall thickness increases at the expense of BET surface area. In contrast, the water-treated sample exhibits a higher BET surface area and a larger pore size even after 3 days of treatment. The increment of the unit cell parameter a_0 and pore size is always larger for the water-treated sample than for that of the normally prepared samples at the same synthesis period. The differences are more pronounced if the synthesis time is prolonged. One may notice that the pore size expands only by about 7−8 Å after a 3 day water treatment. However, the most apparent advantage of the postsynthesis water treatment is the significant improvement
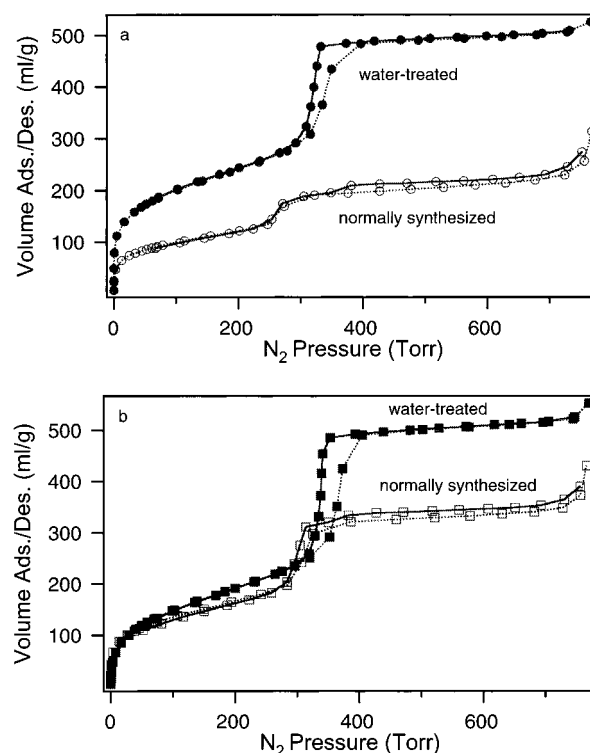

Figure 2. N_2 adsorption−desorption isotherms of the normally synthesized and water-treated Si−MCM-41 samples after a total of 5 days synthesis or treatment at 150 °C (a) or 165 °C (b).

in product quality, compared to the normal synthesis method. A comparison of XRD patterns shows that the water-treated Si−MCM-41 exhibits much higher XRD intensities than that does normally prepared sample (Figure 1S and 2S of the Supporting Information). Figure 2 shows the N_2 adsorption−desorption isotherms of the representative normally synthesized and water-treated Si−MCM-41 samples. It can be seen that the water-treated samples show steep hysteresis sides for both adsorption and desorption (at 300~400 Torr), attesting the presence of well-ordered mesopores. On the other hand, the hysteresis is less steep and small in the normally synthesized samples, indicating a poor quality of the material. Another interesting observation is that the volume of N_2 adsorption (at ~ 300 Torr) is very high (~ 500 mL/g) on the water-treated samples compared with that of normally synthesized samples (~200−300 mL/g). The t-plot analysis of the N_2 adsorption results revealed that a noticeable amount of micropores are present in the normally synthesized samples while it is almost negligible for the water-treated samples.

Besides the strategy of controlling the water treatment time, it has also been found that the pore size of the Si−MCM-41 can be controlled while maintaining the high long-distance order just by altering the water-treatment temperature. It can be seen from Figure 3 that, for the sample synthesized at 120 °C, the postsynthesis water treatments at 120, 150, and 165 °C for 24 h resulted in an increase in the d_{100} spacing from 31 to 34, 40, and 47 Å, respectively. However, if the temperature exceeded 180 °C, the structure deteriorated, since the intensity of (100) peak decreased considerably and the (110) and (200) peaks diminished. This is possibly caused by the decomposition of the surfactant at 180 °C. It has also been noticed that there is not much difference in the long-distance order or the d_{100} spacing between the Si−MCM-41 samples whether they were finally treated in water at 165 °C for 24 h, regardless whether the samples were initially synthesized at 120, 150, or 165 °C. From

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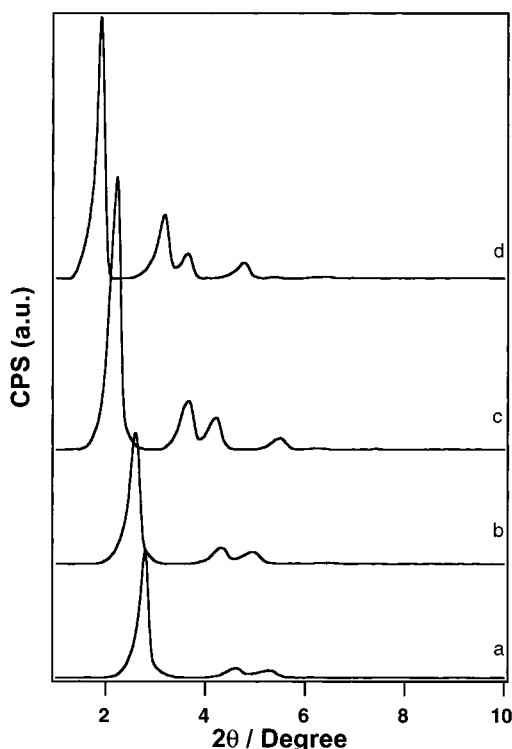
Figure 3. XRD spectra of calcined Si−MCM-41 (a) synthesized at 120 °C for 72 h, or treated in water at (b) 120 °C, (c) 150 °C, and (d) 165 °C for 24 h following the normal synthesis at 120 °C for 48 h.

the above results, it is clear that the water treatment time and temperature are the crucial factors in determining the property of the final product.

The postsynthesis hydrothermal treatment also improves the quality of Si−MCM-41 that was synthesized using other recipes, although the initial product quality was not as good as that obtained using the optimal recipe mentioned above. When TEOS or colloidal silica was used, or when NaOH was used instead of an organic tetraalkylammonium base, increments of unit cell parameter and enhancement of the long-distance order were also observed (Figure 3S of the Supporting Information). A phase transformation from lamellar to hexagonal during the restructuring in water has also been observed which is similar to that noticed upon pH adjustment.[35] This means that the postsynthesis water treatment is widely applicable to the further improvement of the quality of Si−MCM-41 irrespective of the synthesis history of the sample.

Another important aspect of this investigation is that the postsynthesis water treatment also resulted in an improvement in the quality of mesoporous molecular sieves other than pure siliceous MCM-41. Table 2 shows that the long-distance order is enhanced and the unit cell parameter is increased upon a water treatment as short as 24 h for both Ti−MCM-41 and Al−MCM-41 samples. The improvement is more significant if the treatment time is prolonged or the treatment temperature is increased. For the Ti−MCM-41 samples with a Si/Ti ratio of l0, the water treatment resulted in an increase in the intensity ratio of the IR band at 965 cm^{-1} to that at 1080 cm^{-1} (I_{965}/I_{1080}) from 0.39 to 0.60. The band at 965 cm^{-1} is associated with the vibration of the Si−O−Ti bond in the Ti-containing silica materials.[36] Therefore, it can be inferred that the postsynthesis water treatment probably leads to a promotion in the Si−O−Ti bond formation. However, as the 965 cm^{-1} band may be attributed to other vibrations besides that of the Si−O−Ti bond in Ti−MCM-41, the state of Ti was further investigated by means of

UV−vis absorption spectroscopy. The results are shown in Figure 4. TiO$_2$ (anatase) shows a strong absorption in the range 200−350 nm. For the Ti−MCM-41 samples with a Si/Ti of 20, there is a strong absorption at 220 nm, which indicates that the Ti in these samples is present in a tetrahedral coordination. When the Si/Ti ratio decreased to 10, the UV absorption peak shifted to 250 nm. It is interesting to note that, in the normally prepared Ti−MCM-41 (Si/Ti = 10), there is a shoulder around 280 nm. This shoulder is absent, or rather weak, in the water-treated sample. This indicates that the water treatment promotes the Ti dispersion in the silica matrix.
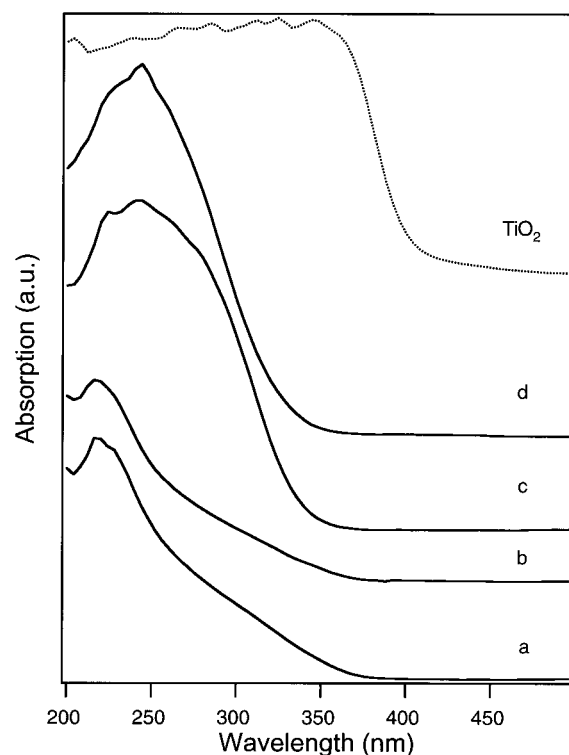
In the case of Si−MCM-48, there is a significant increase in XRD intensity and also the unit cell constant a_0 increased from 74 to 88 Å (Figure 5). Furthermore, the peaks with 2θ around 4−5° are very well resolved. Beside the peaks from (211) and (220), other reflections corresponding to (321), (400), (420), (332), (422), (431), (611), and (543) are also clearly seen. This is in contrast to the normally prepared Si−MCM-48 and indicates that the postsynthesis water treatment significantly improves the quality of Si−MCM-48 samples.

3.3. Mechanism of Postsynthesis Hydrothermal Restructuring. One significant difference between the uncalcined Si−MCM-41 obtained by a normal synthesis and a water treatment is the extent of the unit cell shrinkage during calcination. It was found that the water-treated sample showed much less shrinkage upon calcination. For example, the shrinkage of a_0 was 11.6% for the sample synthesized at 150 °C in its mother liquor for 72 h, while it was only 5.2% for the sample synthesized at 150 °C for 48 h and then treated in water at 150 °C for 24 h and calcined at 550 °C in air for 9 h. It is reasonable to suggest that the less shrinkage of the unit cell for the water-treated sample is as a result of better wall polymerization. To substantiate this speculation, we employed the ^{29}Si MAS NMR. It can be seen from Figure 6 that the Q$_4$ (Si(OSi)$_4$) to Q$_3$ (Si(OSi)$_3$(OH)) ratio of the water-treated uncalcined Si−MCM-41 is higher than that of the normally prepared one. The high portion of Q$_4$ in the water-treated Si−MCM-41 sample is an indication of a high degree of polymerization of the silicate wall or a better local atomic arrangement. For the Si−MCM-41 sample treated in water for 7 days, the ratio of Q$_4$/Q$_3$ increased further, indicating that the extent of polymerization depends on the treatment time. It is interesting to note that even after calcination, the Q$_4$/Q$_3$ ratio of water-treated Si−MCM-41 is still slightly higher than that of the normally prepared sample. Perhaps the high degree of polymerization is as a result of the further agglomeration of isolated small Si−MCM-41 particles by the condensation of silanol groups toward a better local atomic arrangement. The observation of the crystallite size increment after the water treatment is also supportive of this conclusion. This possibly can account for the enhancement of the long-distance order in Si−MCM-41 by the postsynthesis water treatment.

The pH of the solution would play a crucial role in the improvement of the quality of Si−MCM-41. In a typical synthesis under our conditions, the pH of the initial synthesis gel mixture was 11.2; it raised to 11.6 after 1 day synthesis at 150 °C. When the mother liquor was replaced with water, the pH of the resulting mixture was in the range 8−10 depending upon the amount water added and the previous sample synthesis conditions. It has been known that a low pH is favorable for the condensation of silanol groups. The returning of the synthesis gel to a pH lower than 10 favors the condensation of silanols and the redeposition of silicate anions.[37] Previous results indeed indicated that the product quality was greatly improved by
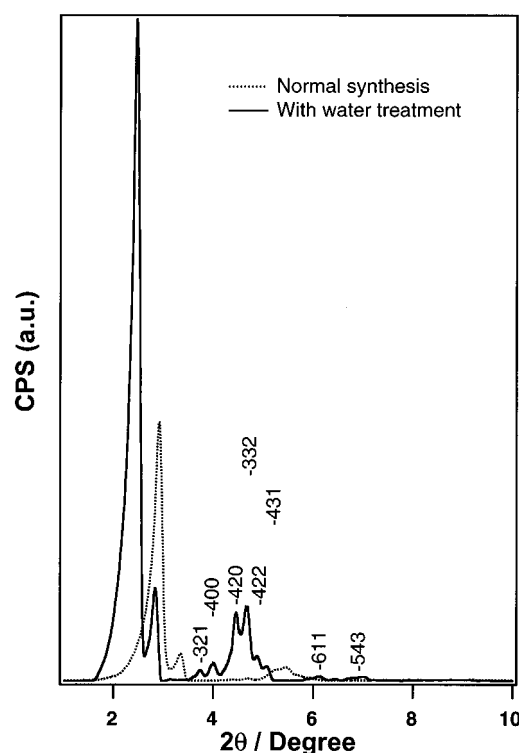
TABLE 2: Effect of a Water Treatment (120 °C, 24 h) on the Characteristics of Al−MCM-41 and Ti−MCM-41

sample	water treatment	unit cell a_0 (Å)	BET surface area (m^2/g)	primary pore diameter (Å)	XRD intensity of (100) face ($\times 10^3$, au)
Al−MCM-41 (Si/Al = 20)	no	40.1	1098	33	23
	yes	41.3	1065	34	36
Ti−MCM-41 (Si/Ti = 20)	no	39.1	962	32	21
	yes	41.9	1053	34	33
Ti−MCM-41 (Si/Ti = 10)	no	37.6	793	30	1.5
	yes	39.8	931	32	2.5

Figure 4. UV absorption spectra of Ti−MCM-41: (a) and (c) normally synthesized; (b) and (d) water treated for 24 h; (a) and (b), Si/Ti = 20; (c) and (d), Si/Ti = 10.
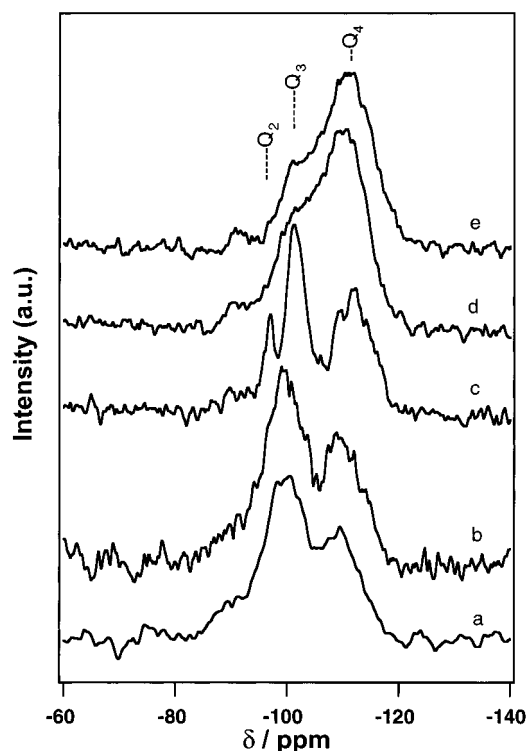

Figure 5. Influence of a postsynthesis water treatment (120 °C, 24 h) on the structure of Si−MCM-48.

repeated pH adjustments during synthesis.[21,22] Possibly the as-synthesized material with defective anionic sites and terminal silanol groups restructured toward a higher polymerization to form more Si(OSi)$_4$ bonds at a lower pH. The promoted condensation of silanols leads to a higher order of local atomic arrangement. Hence, it is inferred that the lowering of the pH by the replacement of the mother liquor with water is responsible for the better polymerization of the silicate wall.

3.4. Superior Thermal and Hydrothermal Stability of the Water-Treated Si−MCM-41. The Si−MCM-41 sample prepared at a low temperature exhibited a poor stability because of the low degree of polymerization of the pore wall.[3] Therefore, in the present study, we demonstrate the superior stability of the water-treated Si−MCM-41 by investigating the two samples synthesized at 165 °C; one was normally synthesized for 48 h, and the other was water treated for an additional 24 h after the normal synthesis for 24 h. When these samples were heated in air at 900 °C for 6 h, no structure destruction was observed. The unit cell contraction was negligible when the calcination temperature increased from 550 to 800 °C. However, when the temperature reached 900 °C, both samples suffered from a significant pore shrinkage. The structure was partially destroyed when the sample was calcined at 1000 °C as evidenced by the
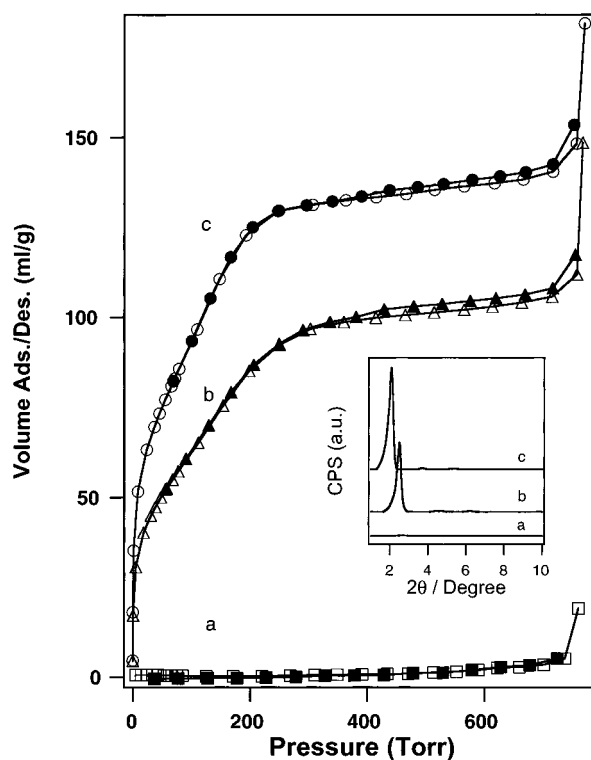
attenuation of their XRD intensities. However, the water-treated Si−MCM-41 possessed a higher thermal stability than the normally prepared sample (Figure 7 inset). The N$_2$ adsorption isotherms from different Si−MCM-41 samples calcined at 1000 °C for 6 h (Figure 7) demonstrate that the Si−MCM-41 samples synthesized from fumed silica still possess porous structure, whereas the Si−MCM-41 from TEOS becomes completely nonporous. Clearly, the fumed silica is a better silica source for the preparation of a highly stable Si−MCM-41. In addition, it can also be seen that the amount of N$_2$ adsorbed is larger for the water-treated Si−MCM-41 than that for the normally prepared sample after calcination at 1000 °C. This is an another indication of the higher thermal stability of water-treated sample.

The hydrothermal stability of the Si−MCM-41 was greatly enhanced when the sample was subjected to a postsynthesis water treatment. The XRD patterns of the water-treated and nontreated Si−MCM-41 samples that are heated in boiling water for 6 h are given in Figure 8 (inset). It reveals that the structure of the water-treated sample is largely maintained, whereas that of the normally prepared sample is greatly destroyed. It is believed that the structure destruction in water is caused by the hydrolysis of Si−O−Si bonds.[8] If the wall is thin and less polymerized, it is easy to collapse by hydrolysis. As a result of the collapse and dissolution of some of the pore walls in water,
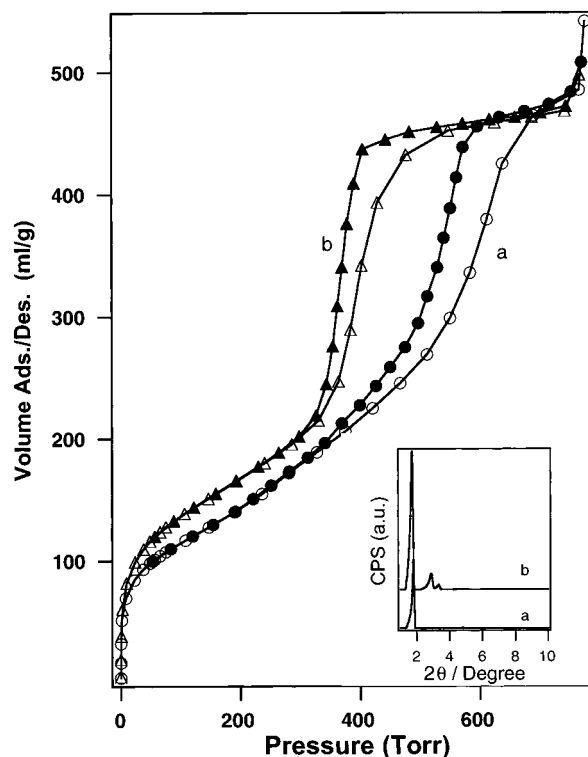
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Figure 6. ^{29}Si MAS NMR spectra of various Si−MCM-41s: (a) normally synthesized for 48 h, uncalcined; (b) water treated for 24 h, uncalcined; (c) water treated for 7 days, uncalcined; (d) sample a, calcined; (e) sample b, calcined. Si−MCM-41 synthesis and treatment temperature was 150 °C.

Figure 8. N$_2$ adsorption isotherms and XRD patterns (inset) of (a) normally synthesized and (b) water-treated Si−MCM-41 samples after heating in boiling water for 6 h: open symbols, adsorption; filled symbols, desorption.

for 6 h, as the N$_2$ adsorption−desorption isotherm of the water-treated Si−MCM-41 after boiling in water is almost identical to that of the original sample. These results clearly indicate that the water-treated sample is hydrothermally more stable compared to the untreated counterpart. The higher hydrothermal stability of the water-treated sample can largely be attributed to the better polymerized silicate wall, which is more resistant to hydrolysis.

More recently, the use of nonionic triblock coploymers as a template has been reported to be a new avenue for the preparation of highly stable mesoporous silica.[38−39] Unlike the ordinary ionic template method, the above method offered the mesoporous silica with pore sizes from 50 to 300 Å and wall thickness of 31−64 Å.[38] The unusually thick silica wall and large pore size makes the mesoporous silica extremely stable in boiling water. However, so far only the preparation of pure siliceous materials has been reported. In this method, the synthesis reaction is carried out in a strongly acidic media (pH < 1). Some of metals will only exist in the cationic form other than their corresponding oxo species under such an acidic condition. Consequently, the synthesis of metal (like Al) containing mesoporous materials, which are more important in catalysis application than the pure siliceous material, will be difficult.

4. Conclusions

Fumed silica was found to be a better silica source than TEOS and colloidal silica for the preparation of a high-quality Si−MCM-41. The quality of Si−MCM-41 was further improved by the postsynthesis water treatment. The BET surface area and the pore size of the water-treated Si−MCM-41 were larger than those of normally prepared samples. With the normal preparation, the best product quality was achieved at about 2−3 days synthesis; the structure deteriorated significantly if the synthesis

Figure 7. N$_2$ adsorption isotherms and XRD patterns (inset) for different Si−MCM-41 samples after calcination in air at 1000 °C for 6 h. Normally synthesized from (a) TEOS and (b) fumed silica; (c) water-treated sample b. Sample synthesis temperature was 165 °C: open symbols, adsorption; filled symbols, desorption.

new larger pores are generated. This is the case of normally prepared Si−MCM-41. In contrast, the water-treated Si−MCM-41 maintains its original structure after heating in boiling water

time was prolonged further. However, a long treatment time in water did not lead to significant quality deterioration, but the pore size was enlarged. The stability, especially the hydrothermal stability, was found to be enhanced by the postsynthesis water treatment. Heating in boiling water for 6 h caused little structure damage for the water-treated Si–MCM-41, whereas the structure of normally prepared Si–MCM-41 was greatly destroyed. The improvement of product quality by a water treatment was attributed to a high long-distance order and a well local atomic arrangement of the silicate wall, resulting from the lowering of pH by replacing the mother liquor with water. The interesting feature of the postsynthesis water treatment in the catalytic application of M41S materials was that the quality of other nonsiliceous MCM-41 materials such as Ti–MCM-41 and Al–MCM-41 also improved. The postsynthesis water treatment method was found to provide an easy and mild way to prepare high-quality M41S molecular sieves with the pore size controllable by altering either the treatment time or the temperature.

Supporting Information Available: Figure 1S: XRD spectra of calcined Si–MCM-41 synthesized at 150 °C in the mother liquor for (a) 24 h, (b) 48 h, (c) 72 h, (e) 120 h, and water treated for (d) 24 h and (f) 72 hrs after normal synthesis for 48 h. Figure 2S: XRD spectra of calcined Si–MCM-41 synthesized at 165 °C in the mother liquor for (a) 24 h, (b) 48 h, (c) 72 h, (e) 120 h, and water treated for (d) 24 h and (f) 72 h after normal synthesis for 48 h. Figure 3S: Effect of water treatment on the structure of Si–M CM-41 prepared from (a) TEOS and (b) colloidal silica. Figure 4S: Influence of water treatment on the XRD patterns of Ti–M CM-41 and Al–MCM-41. This material is available free of charge via the Internet at http://pubs.acs.org.

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