

Improvement of Hydrothermal Stability of Mesoporous Silica Using Salts: Reinvestigation for Time-Dependent Effects

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Recently, we reported on the improvement of hydrothermal stability of mesoporous silica using salts solutions (Ryoo, R.; Jun, S. *J. Phys. Chem. B* **1997**, *101*, 317. Ryoo et al. *J. Phys. Chem.* **1996**, *100*, 17718). The salt effect has been reinvestigated here to solve problems of poor reproducibility. It turned out that the time-dependent effect was missing in the previous reports. The salt effect required approximately 10 days of treatment at 373 K to give its full effect. The time dependence was a critical factor for the improvement of the hydrothermal stability.

1. Introduction

Mesoporous silica molecular sieves have attracted much attention as catalyst supports, adsorbents, and hosts for large molecules, due to the large pore diameter compared with that of conventional microporous zeolites.^{1–5} It is reported that typical mesoporous silica molecular sieves such as those having the acronyms MCM-41 and MCM-48 exhibit excellent thermal stability during heating to 1173 K in dry air and 1073 K in air saturated with water vapor at room temperature.^{6,7} Despite excellent thermal stability, many practical applications of the mesoporous molecular sieves are severely inhibited by the weak stability in distilled water and aqueous solutions compared with those of zeolites A, Y, and ZSM-5.^{8–12} For example, titanium-containing MCM-41 is a very active catalyst for partial oxidation of many organic compounds with aqueous solutions of hydrogen peroxide.⁵ However, the structure of the TiMCM-41 is reported to collapse and the titanium is leached out of the silicate frameworks under the mild reaction conditions for phenol hydroxylation with H₂O₂.⁸ In addition, the structure of aluminum-containing MCM-41 is easily lost in aqueous solutions during treatments for ion exchange and catalyst preparation.⁹ Although the MCM-41 structure is stable as long as the surfactant is maintained after synthesis, the material can lose structure even in distilled water or air saturated with water vapor at room temperature once the surfactant is removed by calcination or solvent extraction.^{10–12} The improvement of the hydrothermal stability is one of the most important targets for ultimate commercialization of the mesoporous materials.

Several techniques have been proposed to increase the hydrothermal stability of the mesoporous molecular sieves, including synthesis of materials with thick pore walls,^{11,13} removal of silanol groups by silylation,^{14,15} and stabilization by salt effect.¹⁶ The wall-thickening approach appears to be the simplest one among these techniques, but no synthetic strategies have yet been found for systematic control of the wall thickness. The silylation technique^{14,15} is used to decrease the concentration of silanol groups on the pore wall by the reaction with silanes. The degree of the silylation may be controlled so that the increase in hydrophobicity of the pore walls leads to a systematic

enhancement of the hydrothermal stability. This kind of treatment is useful for hydrophobic applications but can be undesirable for hydrophilic applications. Besides, the resultant silane coat may be lost due to the thermal decomposition during applications where high heating is required subsequently. Compared to the silylation, the third method using salts causes no changes in the silanol group concentration of the calcined sample but nevertheless has been claimed to be effective for the improvement of the hydrothermal stability.¹⁶ However, more recent experiments to exploit the salt effect pointed out its poor reproducibility.¹⁷

The salt effect has been reinvestigated in the present work in order to solve the problem of poor reproducibility. Mesoporous silica molecular sieves were synthesized in the presence of salts under various experimental conditions. The hydrothermal stability and the structure of the silica materials were analyzed using a hydrothermal stability test in boiling water, X-ray diffraction (XRD), infrared (IR) spectroscopy, and scanning electron microscopy (SEM). These analyses indicated that the salt effect required approximately 10 days of treatment at 373 K to give its full effect. We report the result here since we found out that the time dependence was a very critical factor for the improvement of the hydrothermal stability.

2. Experimental Section

2.1. Synthesis of Mesoporous Silica. The chemicals used in the synthesis were HTACl (25 wt % aqueous solution, Aldrich), sodium silicate solution (9 wt % SiO₂, Na/Si = 0.5),^{16,18,19} tetraethyl orthosilicate (TEOS), amorphous silica (Aerosil 200, Dugussa), and the following salts: EDTANa₄ (Acros), adipic acid disodium salt (ADANa₂, Aldrich), NaOAc (Junsei), NaCl (Aldrich), and sodium nitrate (NaNO₃, Aldrich). Distilled water and salt were combined with the 25% HTACl solution to obtain a surfactant solution. To the surfactant solution, the sodium silicate solution was added drop by drop with vigorous magnetic stirring at room temperature. The resultant mixture had a molar composition of 5 SiO₂/1.25 Na₂O/1 HTACl/*x* salt/400 H₂O. The salt and the number of moles *x* were varied among different samples. Stirring was continued for 1 h after the addition of the sodium silicate solution was completed. The mixture, contained in a polypro-

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pylene bottle, was placed in an oven at 373 K for 1 day. Precipitate on the bottom of the bottle was filtered, washed with hot doubly distilled water, and dried in a vacuum oven at room temperature after the hydrothermal reaction for 1 day. These samples are denoted MS- x EDTA, MS- x ADA, and MS- x NaCl, following the salts and mole numbers (x) used.

A series of disordered mesoporous silica samples were prepared with 5 SiO₂/1.25 Na₂O/1 HTACl/5 EDTANa₄/400 H₂O by following the same mixing procedure and hydrothermal reaction for 1 day. The reaction mixtures were then cooled to room temperature, and the pH of the mixture was adjusted to 10 using acetic acid. The reaction bottles were placed again in the oven at 373 K for various periods ranging from 1 to 10 days. The pH of the reaction mixtures was adjusted again to 10, and the bottles were heated for 1 day. The pH adjustment and subsequent heating for 1 day was repeated once more. The precipitated products were filtered, washed, and dried in the same ways as described above. The product was calcined in air under static conditions. The calcination temperature was increased to 823 K over 5 h and maintained there for 2 h. These samples are referred to as KIT-1- t , where t means the hydrothermal reaction time in days given between the first two successive pH adjustments. The KIT-1- t samples were used for the investigation of the salt effect on the hydrothermal stability, as a function of the synthesis reaction time with salts.

A series of the hexagonal MCM-41 samples were prepared with starting materials having a molar composition of 4 SiO₂/1 Na₂O/1 HTACl/400 H₂O, following the same procedure used for the KIT-1- t samples, except that EDTANa₄ for MCM-41 was added after the formation of the mesophase instead of to the initial surfactant solution. Since the mesophase formation is completed within 1 day of heating after the first pH adjustment, the reaction mixture was cooled to room temperature to add 8 mol of EDTANa₄ at this moment. Heating was continued afterward for 0–10 days depending on the sample. The remainder of the procedure, including the second pH adjustment, is the same as that for the disordered samples. The samples are designated as MCM-41-8EDTA- t , where t means the hydrothermal reaction time (in days) given between the salt addition and the second pH adjustment. MCM-41-3NaCl- t samples were also prepared using 3 mol of NaCl instead of 8 mol of EDTANa₄.

MCM-41 and disordered mesoporous silica were also synthesized at near salt-free conditions. To obtain such MCM-41, an aqueous solution of 0.9 HTAOH–0.1 HTACl surfactant was obtained by the anion exchange of HTACl. TEOS was added to the surfactant solution, giving a molar composition of 4 TEOS/HTAOH/Cl (OH/Cl = 0.9)/600 H₂O. The starting mixture was heated for 1 day at 373 K, allowing the resultant ethanol to escape from the reactor completely. The mixture was then placed in an autoclave and heated for 2 days at 393 K. For the synthesis of disordered silica, Aerosil 200 was mixed with the same HTAOH/Cl solution used for the MCM-41 sample. The resulting gel mixture, having a molar composition of 4 SiO₂/1 HTAOH/Cl/300 H₂O, was heated for 12 days at 373 K in a polypropylene bottle. The two samples are designated MCM-41-sf and DMS-sf, respectively. (sf means salt-free, although the synthesis with Cl was not exactly under salt-free conditions.)

2.2. Characterization Methods. Hydrothermal stability of the samples was investigated by following intensity and shape changes in XRD patterns after heating the calcined samples in doubly distilled water under reflux conditions at 373 K for 12 h, following procedures reported previously.^{10,16,18} XRD patterns were obtained with a Cu K α X-ray source (Rigaku Miniflex)

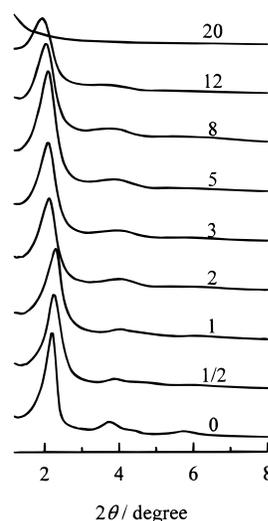


Figure 1. XRD patterns for the mesoporous silica series MS- x EDTA obtained by hydrothermal reaction at 373 K for 1 day from molar compositions of 5 SiO₂/1 HTACl/ x EDTANa₄/1.25 Na₂O/400 H₂O. The number x in the sample name denotes the EDTANa₄/HTACl molar ratios.

at room temperature. Magic-angle spinning (MAS) ²⁹Si NMR spectra were obtained at 296 K using a Bruker AM 300 instrument operating at 78.2 MHz with 30° pulses and 10 s relaxation delay. Samples were wetted with distilled water in order to increase the spin–lattice relaxation time.²⁰ The sample spinning rate for the NMR was 4 kHz. ¹H–²⁹Si cross-polarization (CP) MAS NMR spectra were recorded with a single contact pulse sequence, 3 ms contact time, 8 μ s ¹H 90° pulse, and 3 s relaxation delay. IR spectra were obtained with an FTIR instrument (Bruker Equinox 55). SEM images were obtained using a Philips SEM-535M instrument.

3. Results

Figure 1 shows XRD patterns for the MS- x EDTA samples, which were synthesized by the hydrothermal reaction for 1 day at 373 K from the starting molar composition of 5 SiO₂/1 HTACl/ x EDTANa₄/1.25 Na₂O/400 H₂O, with x varied over 0–20. When the mole number x of the EDTA salt was less than 2, the synthesized mesophases such as MS-0EDTA and MS-1EDTA showed an XRD pattern consisting of (100), (110), (200), and (210) diffraction for the hexagonal array of typical MCM-41 materials.^{1,2} As x was increased into the range 2–12, three broad XRD peaks were centered at $2\theta = 2.2^\circ$ (strong), 4.1° (weak), and 6.0° (very weak), respectively. The XRD lines, which are similar to those for lamellar mesophases, were in fact due to the disordered channel structure with a very uniform cross-sectional diameter.¹⁸ Thus, as the concentration of the salt increased, the structure of the synthesized mesoporous silica transformed from a hexagonal packing of one-dimensional channels to a three-dimensionally disordered network of short “wormhole-like” mesoporous channels. However, the use of more salt than $x = 12$ resulted in the formation of completely amorphous silica materials exhibiting no XRD lines. Results with other organic and inorganic salts such as ADANa₂, NaOAc, NaCl, and NaNO₃ instead of EDTANa₄ were also similar, except that the suitable range of x for the formation of the disordered mesophase depended on salts. The various salt ranges are presented in Figure 2.

Figure 3 shows XRD patterns for the MCM-41-sf, MCM-41-8EDTA- t , and MCM-41-3NaCl- t samples, which were measured after calcination and also after subsequent heating in

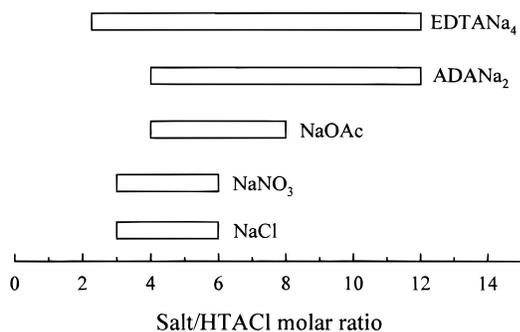


Figure 2. Schematic diagram presenting suitable ranges of the salts/HTACl ratio (x) for the formation of a disordered mesoporous molecular sieve, which has been determined by the shape of the XRD pattern. All samples have been obtained by the hydrothermal reaction for 1 day at 373 K with molar compositions of 5 SiO₂/1 HTACl/ x salt/1.25 Na₂O/400 H₂O.

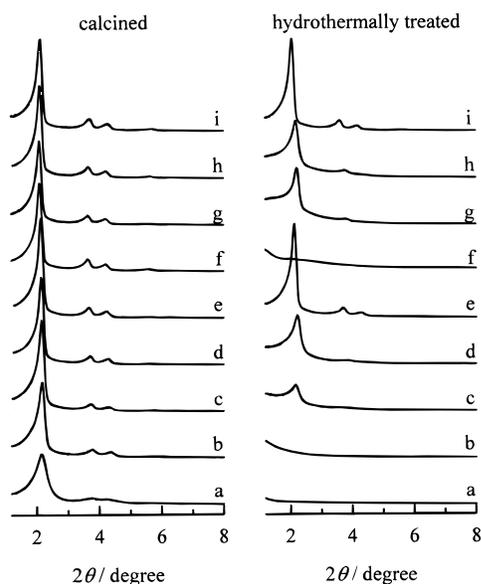


Figure 3. XRD patterns of MCM-41 samples after calcination and subsequent heating in boiling water for 12 h: (a) MCM-41-sf; (b) MCM-41-8EDTA-0; (c) MCM-41-8EDTA-1; (d) MCM-41-8EDTA-5; (e) MCM-41-8EDTA-10; (f) MCM-41-3NaCl-0; (g) MCM-41-3NaCl-1; (h) MCM-41-3NaCl-5; (i) MCM-41-3NaCl-10. Each number preceding the salt name indicates the mole number of the salt. The italic number following the salt name means the length of the “salting” period (in days) defined in section 2. sf means synthesis at near salt-free conditions.

boiling water for 12 h. The MCM-41-sf sample was synthesized at near salt-free conditions containing only a small amount of Cl⁻. The MCM-41-8EDTA- t and MCM-41-3NaCl- t samples were synthesized by allowing t days between the salt addition (8 mol of EDTANa₄ and 3 mol of NaCl, respectively) and the second pH adjustment, as described in the hydrothermal synthesis procedure in the Experimental Section. The time t refers to the “salting” period hereafter. All the calcined MCM-41 samples exhibited similarly resolved XRD peaks characteristic of the hexagonal phase.^{1,2} However, subsequent heating in boiling water caused a remarkable difference between various samples. The XRD patterns indicate that the structures of the MCM-41-sf, MCM-41-8EDTA-0, and MCM-41-3NaCl-0 samples were completely lost by boiling water. The structure of the MCM-41-sf sample disappeared within 6 h in boiling water. Contrary to the weak hydrothermal stability of the samples synthesized with no salt addition or no “salting” period, the hydrothermal stability increased remarkably when increasing

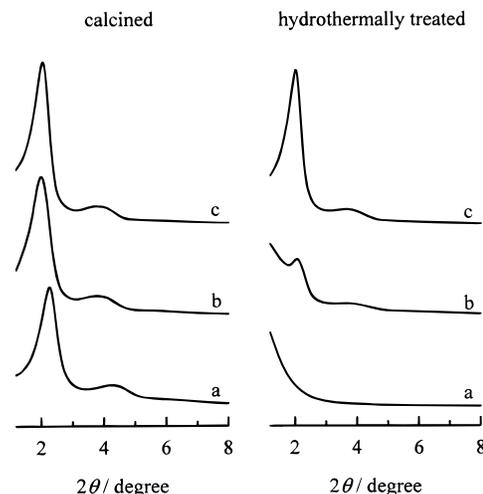


Figure 4. XRD patterns of the disordered mesoporous silica KIT-1 after calcination and subsequent heating in boiling water for 12 h: (a) DMS-sf; (b) KIT-1-1; (c) KIT-1-10. Sample notations are similar to those in Figure 3.

the “salting” period to 10 days after the addition of 8 mol of EDTANa₄ or 3 NaCl. The MCM-41 samples with a 10 day “salting” period indicated no sign of structure loss in boiling water for 12 h.

The effect of “salting” for KIT-1- t is described by the XRD patterns shown in Figure 4, following the same way presented for MCM-41- $nsalt-t$ in Figure 3. Here, the “salting” period t for KIT-1 is defined as the number of heating days between the first two successive pH adjustments during the hydrothermal synthesis. The results for KIT-1 were very similar to those for MCM-41. The DMS-sf sample, which was synthesized to have a disordered structure at near salt-free conditions, lost the structure completely within 6 h of boiling in distilled water. Compared to the structure loss of the present disordered sample, the XRD patterns for the KIT-1- t samples showed a progressive increase in hydrothermal stability when increasing the “salting” period to 10 days. The KIT-1-10 sample, which was “salted” for 10 days, showed high XRD intensity even after heating in boiling water for 48 h.

4. Discussion

4.1. Mesoporous Channel Branching. The effect of salts presented in Figures 1 and 2 is similar to the micelle branching and disordering observed in aqueous solutions containing surfactant.^{21,22} Let us consider the salt effect for a cationic surfactant solution containing spherical micelles. An increase of the salt concentration causes the constituent ions to screen out the electrostatic interactions in the headgroup region. Initially, the screening effect leads to a change from the spherical micelles to elongated one-dimensional micelles.^{23–27} The further addition of salts is known to induce cross-linking of the elongated or “worm-like” micelles, leading to a solution of entangled branched micelles and, upon further increase of salts, to a multiconnected network of micelles.^{23–27} The transition of micelles from linear to branched is very similar to the transition of the surfactant-silica mesophases from hexagonal MCM-41 to disordered KIT-1 by salts. The KIT-1 mesophase consists of disordered micellar networks which have a uniform cross-sectional diameter.¹⁸ When the salt concentration is exceedingly high, the resultant mesophase is further disordered, causing a broad distribution of the cross-sectional diameters. The disordered silica, obtained by the surfactant removal from this

mesophase has, therefore, a pore size distribution over 1–4 nm, similar to that of MSU-1.⁴

Figure 2 shows that the disordering effect depends very much on anions, as well as the salt concentration. NaNO₃ and NaCl are more effective than NaOAc. The effect of these anions agrees with the ability of binding to the surfactant molecules, which increases according to the Hofmeister series, i.e., CH₃COO⁻ < NO₃⁻ < Cl⁻.^{28,29} From the series, it is reasonable that NaNO₃ and NaCl are highly effective for screening out the electrostatic interaction, and the weakly hydrated CH₃COO⁻ salt needs relatively high concentrations for the same degree of the structural disordering effect. If the structural changes are controlled only by the screening effect, the sodium salts of the multivalent anions ADA²⁻ and EDTA,⁴⁻ causing much stronger ionic strength, are expected to cause more effective structure disordering under the same molar concentrations compared with the sodium salts of the monovalent anions. However, the results in Figure 2 do not agree with the ionic strength. The effect of salts may not be simply due to the ionic screening effect but also related to some other interactions between the organic moiety of the surfactant and the organic anions.

The structure of the silicate–surfactant assembly is controlled by the initial composition of the starting synthesis mixture. The disordered KIT-1 mesophase is obtained with salts, whereas the hexagonal MCM-41 mesophase is formed in the absence of salts or in low concentration. Our result in Figure 4 shows that the disordered structure was not affected significantly by the length of the “salting” period between 1 and 10 days. The present synthesis has been achieved under strongly basic conditions, where the formation of the mesophase can be energetically controlled by the reaction equilibrium.¹⁹ Under such conditions, the formation of the mesophase seems to occur very rapidly and not to be affected by the subsequent increase of the “salting” period.

4.2. Framework Reconstruction. The results in Figures 3 and 4 show that the addition of salts to the synthesis mixtures has led to a dramatic improvement in the hydrothermal stability of the synthesized mesoporous silica. The stabilization effect by salts is a slow, kinetically controlled process occurring over the 1–10 day “salting” period, which is in contrast to the rapid, energetically controlled effect for structure disordering. Recently, we have reported that KIT-1 in the pure silica form can be heated in boiling distilled water (under reflux condition) for 48 h without loss of the structure.¹⁸ However, the high stability is not obtained without sufficiently long “salting” treatments under suitable salt concentration, as shown by parts a and b of Figure 4. Figure 4a is the XRD pattern for a disordered silica sample synthesized at near salt-free conditions. The structure of the material is constructed with disordered silica mesopores similar to those of KIT-1,¹⁸ but nevertheless, the structure is completely lost during 12 h in boiling water. The KIT-1 sample in Figure 4b also shows similar loss of structure in boiling water, confirming that a sufficiently long “salting” period is essential for improvement of the hydrothermal stability. From these results, it is evident that the high hydrothermal stability of KIT-1 is due to the salt effect, rather than directly related to the structural disorder. If a suitable amount of salt is added to synthesis reaction mixtures after the formation of silicate–surfactant assemblies is completed instead of adding the salts to the initial reaction mixtures, MCM-41 and MCM-48 materials with good hydrothermal stability can be obtained.^{16,30}

In a previous report on the improvement of hydrothermal stability of MCM-41,¹⁶ we speculated that the salt effect could be related to an increase in the degree of silica cross-linking.

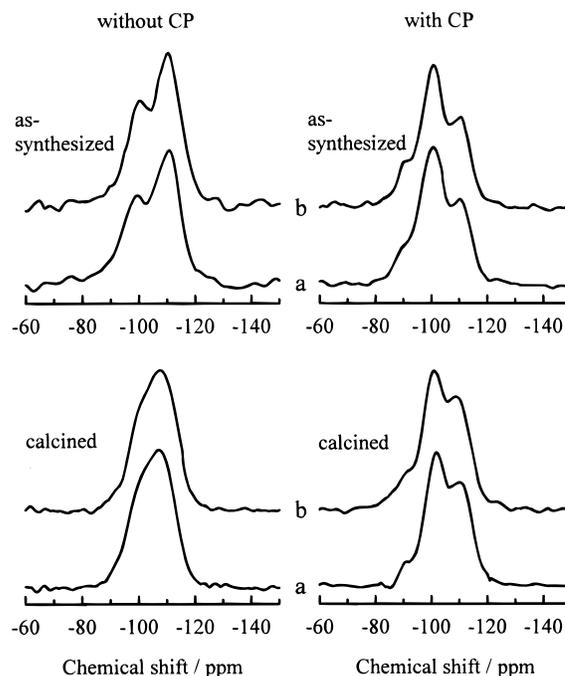


Figure 5. MAS ²⁹Si NMR spectra obtained with and without cross polarization for the disordered mesoporous silica samples after calcination: (a) KIT-1-1; (b) KIT-1-10.

We have therefore, in this work, investigated if any changes have occurred in the MAS ²⁹Si NMR spectrum for the KIT-1 samples presented in Figure 4. The MAS ²⁹Si NMR spectra measured with and without cross polarization are given in Figure 5. The NMR spectra show that the degrees of silica cross-linking in the frameworks are approximately the same despite their clearly different hydrothermal stability. Thus, the cross-linking degree did not change during the “salting” periods. It seems that the same degree of silica cross-linking was reached by the same final pH of the synthesis mixture. Pore wall thickness has been measured by the difference between the lattice constant from XRD and the BJH pore diameter from the N₂ adsorption analysis.^{11,13} However, this measurement has indicated no significant changes (2.05 ± 0.02 nm) that can be attributed to the different “salting” periods either.

Compared with no significant effects on the ²⁹Si NMR and pore diameter, a small difference has appeared in the FTIR spectrum after the “salting” treatments. The FTIR spectra in Figure 6 compare the three disordered samples presented in Figures 4a–c. Since other regions show no distinct differences, we focus on the spectral region between 400 and 700 cm⁻¹, where two peaks may be assigned to the framework vibrations: one band around 460 cm⁻¹ and another at 560–580 cm⁻¹. The intense 460 cm⁻¹ peak may be assigned to the Si–O bending mode similar to that observed in many SiO₂ polymorphs.³¹ The weak 560–580 cm⁻¹ peak is located in about the same position as the peaks which can be assigned to the stretching mode of a double ring unit in ordered, or at least locally ordered, silicates.^{31–33} In the present results for as-synthesized samples containing the surfactant, the two peaks are more clearly resolved when the salt content in the synthesis mixture is minimized as in Figure 6a (DMS-sf) or the length of the “salting” period is decreased as in Figure 6b (KIT-1-1) than when the “salting” period is 10 days as in Figure 6c (KIT-1-10). The peak resolution changes to the opposite order after calcination. The 560 cm⁻¹ peak of KIT-1-1 and DMS-sf shows about a 10 cm⁻¹ shift to low frequency upon calcination, while the peak of the “salted” sample KIT-1-10 remains almost

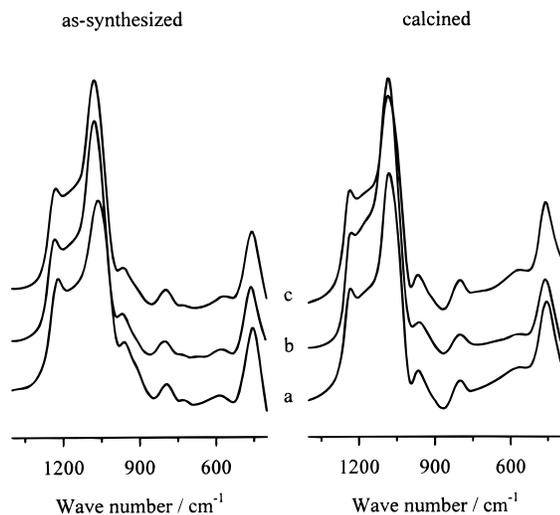


Figure 6. FTIR spectra for the disordered mesoporous silica samples: (a) DMS-sf; (b) KIT-1-1; (c) KIT-1-10.

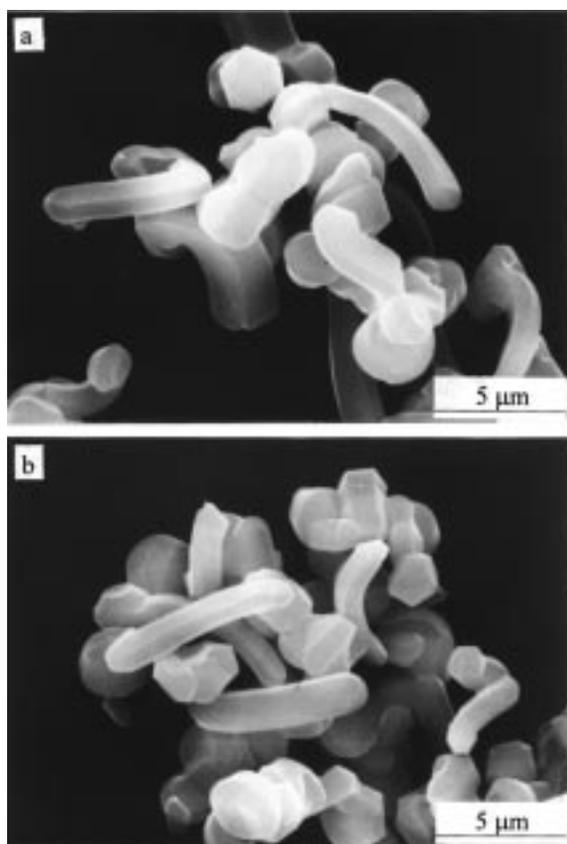


Figure 7. SEM images for an SBA-3 sample (a) and the sample after “salting” treatment for 10 days under a basic condition (b). A sample synthesis procedure is described in the last paragraph of section 4.

unchanged. Although accurate structural information is difficult to obtain from the IR spectroscopic data under this circumstance, it may be stated that properly “salted” samples exhibit comparatively small changes due to calcination that would lead to strain in the silica framework. From these results, the “salted” sample seems to have more stable frameworks, having more ordered local structure.

Does the framework change by salts occur through a local reconstruction process of the frameworks, maintaining the morphology of the particles unchanged, or through a particle dissolution and re-formation process? To answer this question,

we have carried out the following experiment. a hexagonal surfactant–silica mesophase with the acronym SBA-3 was synthesized in acidic medium using TEOS, HTACL, HCl, and distilled water and filtered at room temperature. The synthesis procedure for the SBA-3 sample was similar to those reported by Huo et al.^{3,34} and Yang et al.³⁵ previously. The SBA-3 mesophase thus obtained exhibited rope-like morphologies with the hexagonal cross-section shown in Figure 7a. The XRD pattern of the SBA-3 mesophase was similar to that of MCM-41.^{3,34} Subsequently, the SBA-3 mesophase, containing the surfactant, was placed in an aqueous solution containing NaOAc, NaOH, and HTACL. The amounts of the chemicals added to the solution were controlled so that the resultant mixture had a molar composition of 4 SiO₂/1 HTACL/1 NaOAc/400 H₂O. The pH of the mixture was adjusted to 10 by the subsequent addition of approximately 1 mol of NaOH. Three moles of NaCl were added to the mixture after it was heated for 1 day at 373 K. The mixture was continuously heated for 10 more days, for “salting”, until the mesophase was filtered. Whereas the original SBA-3 sample used in this experiment exhibited weak hydrothermal stability similar to that of the “unsalted” MCM-41, the “salted” and subsequently calcined sample showed no loss of the hexagonal XRD pattern after heating in boiling water for 12 h. As shown in Figure 7b, the morphology of the mesophase did not change during the “salting” experiment. The preservation of the morphology clarifies that the stabilization effect by salts occurs through a local reconstruction process within the silica framework.

5. Conclusions

The addition of salts to the synthesis mixture of the surfactant–silica mesostructures causes two kinds of effects. The first effect is the branching of micelles, which causes a transition from the hexagonal mesophase to a disordered network. The formation of the disordered mesophase is controlled energetically during an early stage of the hydrothermal synthesis following the initial reactant mixing. The second effect causes a slow local reconstruction of the silica frameworks, without exhibiting morphological changes. The framework reconstruction process takes places slowly over 10 days under the present experimental conditions. If the salt concentration, salt addition time, and salt contact time are properly controlled as reported by the present authors, the salt effects may be used for a remarkable improvement of the hydrothermal stability of various mesoporous silica molecular sieves such as KIT-1, MCM-41, and MCM-48. The stabilized materials are expected to be suitable for various applications requiring aqueous conditions such as ion exchangers, catalyst supports, adsorbents, and heterogeneous catalysts.

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References and Notes

- (1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- (2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- (3) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.
- (4) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.
- (5) Corma, A. *Chem. Rev.* **1997**, *97*, 2373 and references therein.
- (6) Chen, C.-Y.; Li, H.-X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17.

- (7) Kim, J. M.; Kwak, J. H.; Jun, S.; Ryoo, R. *J. Phys. Chem.* **1995**, *99*, 16742.
- (8) Rhee, C. H.; Lee, J. S. *Catal. Lett.* **1996**, *40*, 261.
- (9) Ryoo, R.; Ko, C. H.; Kim, J. M.; Howe, R. *Catal. Lett.* **1996**, *37*, 29.
- (10) Kim, J. M.; Ryoo, R. *Bull. Korean Chem. Soc.* **1996**, *17*, 66.
- (11) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.
- (12) Zhao, X. S.; Audsley, F.; Lu, G. Q. *J. Phys. Chem. B* **1998**, *102*, 4143.
- (13) Coustel, N.; Renzo, F. D.; Fajula, F. *J. Chem. Soc., Chem. Commun.* **1994**, 967.
- (14) Koyano, K. A.; Tatsumi, T.; Tanaka, Y.; Nakata, S. *J. Phys. Chem. B* **1997**, *101*, 9436.
- (15) Zhao, X. S.; Lu, G. Q. *J. Phys. Chem. B* **1998**, *102*, 1556.
- (16) Ryoo, R.; Jun, S. *J. Phys. Chem. B* **1997**, *101*, 317.
- (17) Personal communication with Prof. T. Tatsumi at University of Tokyo.
- (18) Ryoo, R.; Kim, J. M.; Ko, C. H.; Shin, C. H. *J. Phys. Chem.* **1996**, *100*, 17718.
- (19) Ryoo, R.; Kim, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 711.
- (20) Kim, M. J.; Ryoo, R. *Chem. Mater.*, in press.
- (21) Imae, T.; Kohsaka, T. *J. Phys. Chem.* **1992**, *96*, 10030.
- (22) Cassidy, M. A.; Warr, G. G. *J. Phys. Chem.* **1996**, *100*, 3237.
- (23) Lequeux, F.; Candau, S. J. In *Structure and Flow in Surfactant Solutions*; Herb, S. A., Prudhomme, R. K., Eds.; American Chemical Society: Washington, DC, 1994. Lequeux, F.; Candau, S. J. In *ACS Symposium Series 578*; American Chemical Society: Washington, DC, 1994; Chapter 3.
- (24) Lin, J. *Langmuir* **1996**, *12*, 1729.
- (25) May, S.; Bohbot, Y.; Ben-Shaul, A. *J. Phys. Chem. B* **1997**, *101*, 2256.
- (26) Mendes, E.; Narayanan, J.; Oda, R.; Kern, F.; Candau, S. J. *J. Phys. Chem. B* **1997**, *101*, 8648.
- (27) Bijma, K.; Blandamer, M. J.; Engberts, J. B. F. N. *Langmuir* **1998**, *14*, 79.
- (28) Collins, K. M.; Washabaugh, M. W. *Q. Rev. Biophys.* **1985**, *18*, 323.
- (29) Narayanan, J.; Manohar, C.; Kern, F.; Candau, S. J. *Langmuir* **1997**, *13*, 5235.
- (30) Kim, J. M.; Kim, S. K.; Ryoo, R. *Chem. Commun.* **1998**, 259.
- (31) Flanigen, E. M. In *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; American Chemical Society: Washington, DC, 1976. Flanigen, E. M. In *ACS Monograph 171*; American Chemical Society: Washington, DC, 1976; Chapter 2.
- (32) Coudurier, G.; Naccache, C.; Vedrine, J. C. *J. Chem. Soc., Chem. Commun.* **1982**, 1413.
- (33) Jansen, J. C.; van der Gaag, F. J.; van Bekkum, H. *Zeolites* **1984**, *4*, 369.
- (34) Huo, Q.; Margolese, D. I.; Diesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.
- (35) Yang, H.; Coombs, N.; Ozin, G. A. *Nature* **1997**, *386*, 692.