

# Hydrothermal stability of MCM-48 improved by post-synthesis restructuring in salt solution

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## Abstract

The hydrothermal stability of the mesoporous silica molecular sieves MCM-48 has been found to increase if the as-synthesized materials containing surfactant are heated in an aqueous solution of salts. Although the optimum treatment conditions depended on details of the synthesis procedures, this post-synthesis technique led to a significant improvement in the hydrothermal stability of various MCM-48 materials that were synthesized using cationic surfactants alone or cationic-neutral surfactant mixtures. These results were concluded as due to the restructuring effects of the pore walls by magic angle spinning <sup>29</sup>Si NMR spectroscopy, nitrogen adsorption and scanning electron microscopy. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The MCM-48 silica is a mesoporous molecular sieve constructed by the cubic Ia3d packing of an enantiomeric pair of three-dimensional channel systems [1,2]. In this structure, cylindrical tubes, typically 3 nm in the cross-sectional diameter, are three-way branched and interconnected only within the same channel system. The pore walls are typically 1 nm thick and constructed by a disordered network of silica units. The regular array of building blocks has been found to form single

crystals despite the disordered atomic arrangement [3]. The MCM-48 structure has recently been solved using the single-crystal electron diffraction [4]. More recently, a synthesis procedure using mixtures of cationic surfactant and non-ionic surfactant has been developed to obtain MCM-48 in high yield, high purity and with various pore diameters [5,6]. In addition, the MCM-48 synthesis procedure uses rapid shaking for reactants mixing, which is suitable for large-scale synthesis. The convenient synthesis procedure allows MCM-48 to be readily available as a template for various nanostructured materials, such as carbon and platinum [7,8]. Ryoo et al. reported the first successful synthesis of ordered mesoporous carbon molecular sieves using sucrose as a carbon source and MCM-48 as the template [7]. The mesoporous

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carbon, obtained after removal of the silica template with NaOH or HF, exhibited three Bragg lines in the X-ray powder diffraction (XRD) pattern. Ordered mesoporous Pt materials exhibiting similarly XRD lines were also synthesized using the MCM-48 template [8]. There have been a large number of other studies of synthesis, modification, characterization, adsorption and catalytic applications of MCM-48. These works were recently reviewed in the literature [9–11].

The MCM-48 silica attracts much attention as a prospective new material for template synthesis, adsorption and catalysis as mentioned above. However, conventional MCM-48 materials, synthesized without special treatments, easily lose their cubic structure in boiling water for a short period of time [12]. This lack of hydrothermal stability is a considerable drawback, inhibiting practical applications of MCM-48, similar to the case of its more widely studied hexagonal analogue, MCM-41. In the case of MCM-41, several methods have been proposed for the improvement of the hydrothermal stability. Inorganic or organic salts were added to the synthesis gel or during the hydrothermal synthesis reaction [13–15]. The pore-wall thickness was increased by careful choice of the synthesis conditions or via secondary synthesis [16]. Aluminum incorporation to silica frameworks led to an improvement of the hydrothermal stability [17]. The hydrothermal stability was also improved by post-synthesis hydrothermal restructuring of the as-synthesized MCM-41 in water [18].

Compared with these extensive efforts to improve hydrothermal stability of MCM-41, the improvement of the hydrothermal stability was studied very little for MCM-48. Kim et al. reported that the addition of salts during hydrothermal synthesis of MCM-48 resulted in a remarkable improvement of the hydrothermal stability, similar to the salt effect for MCM-41 [3]. However, the use of salts during the hydrothermal synthesis is not convenient for MCM-48 because the formation of the MCM-48 mesophase requires narrow, specific synthesis conditions. That is, the MCM-48 mesophase in the conventional syntheses is obtained as an intermediate between the transitions from a hexagonal or disordered mesophase

to lamellar mesophases, making the salt-addition timing very difficult. The addition of salts during the course of the reaction can thus alter the reaction pathway to a different mesophase. The present work was therefore undertaken in order to develop a post-synthesis treatment technique that is suitable for the improvement of the hydrothermal stability of MCM-48 independently of the synthesis procedures.

## 2. Experimental

### 2.1. Synthesis of MCM-48

Three kinds of MCM-48 silica sample were obtained as synthesized, following different synthesis procedures reported in the literature [1–3,5,6]. The first procedure used tetraethylorthosilicate (TEOS, Acros 98%) as the silica source and cetyltrimethylammonium bromide (CTABr, Acros 99%) as the surfactant [1,2]. The molar composition of the starting mixture was 1.5 SiO<sub>2</sub>:1 CTABr:0.38 Na<sub>2</sub>O:154 H<sub>2</sub>O. This mixture was heated for 4 d at 373 K in an autoclave under static conditions. The resulting MCM-48 product was filtered, washed with hot distilled water, and dried at 373 K. In the second procedure, MCM-48 was synthesized with a sodium silicate solution (20 wt.% aqueous solution, Na/Si = 0.5), CTABr and ethanol [3]. The starting composition was 1.4 SiO<sub>2</sub>:1 CTABr:0.35 Na<sub>2</sub>O:5.0 EtOH:140 H<sub>2</sub>O. The MCM-48 mesophase was hydrothermally crystallized from this mixture under static conditions, for 4 d at 373 K or for 27 h at 413 K. The third synthesis method used a surfactant mixture of CTABr and tetraoxyethylene dodecyl ether [C<sub>12</sub>H<sub>25</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>4</sub>H, Hannong Chemicals] [5,6]. The silica source was the same sodium silicate solution used in the second procedure. The starting composition was 5 SiO<sub>2</sub>:0.85 CTABr:0.15 C<sub>12</sub>H<sub>25</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>4</sub>H:1.25 Na<sub>2</sub>O:400 H<sub>2</sub>O. The starting mixture was first heated at 373 K for 60 h, using a polypropylene bottle without autoclave. After cooled to room temperature, an amount of acetic acid that could neutralize 60% of the total Na content was added to this mixture with vigorous stirring. The MCM-48 product was finally

filtered after an additional heating period of 2 d at 373 K.

### 2.2. Post-synthesis treatments in salt solution

The MCM-48 samples containing the surfactants as synthesized were added to an aqueous solution of EDTANa<sub>4</sub> (Acros, 99%) or NaCl, in the ratio of 1 g MCM-48 to 25 g solution. The concentration of the salt solution was varied from 0 to 6 wt.%. The pH of the EDTANa<sub>4</sub> solution was approximately 10. In the case of the NaCl solution, the pH was adjusted to 10 by the addition of a few drops of concentrated EDTANa<sub>4</sub> solution. The MCM-48 samples in the salt solutions were heated in an oven for the desired periods of time (2–20 d) at 373 K. The MCM-48 samples after these “salting” treatments were filtered and washed with hot distilled water before cooling. The samples were then dried in an oven at 373 K, washed with an ethanol–HCl mixture to remove as much surfactant as possible, and finally calcined in air under static conditions at 813 K. The details of the washing and calcination conditions are the same as used for MCM-41 in our previous studies [19].

### 2.3. Hydrothermal stability test

0.1 g of calcined MCM-48 was boiled for 12 h in 100 ml of distilled water, using a Pyrex flask equipped with reflux condenser. XRD pattern was obtained after this boiled sample was subsequently filtered and dried in an oven at 413 K. Loss in the XRD peak intensity, as compared with that of the same sample before the boiling treatment, was used to judge the hydrothermal stability as in our previous works on MCM-41 [12–14].

### 2.4. Characterization

XRD patterns were obtained at room temperature, using a Rigaku Miniflex instrument (30 kV, 15 mA, CuK<sub>α</sub> X-ray source). All samples were scanned under the same conditions ( $2\theta = 1.2$ – $10^\circ$ ). Magic angle spinning (MAS) <sup>29</sup>Si NMR spectra were taken with a Bruker AM300 instrument operating at 59.6 MHz. The relaxation delay was

given as 5 s. Samples were spun at 3.5 kHz. All samples were completely wet with distilled water before taking the NMR spectra, in order to decrease the spin-lattice relaxation time. Scanning electron micrographs (SEM) were obtained on a Philips SEM-535M microscope operating at an acceleration voltage of 20 kV. N<sub>2</sub> adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2010 instrument. The pore-size distributions were analyzed with the N<sub>2</sub> adsorption branch, using the Barrett–Joyner–Halenda (BJH) method with the calibration as described in Ref. [20].

## 3. Results

Fig. 1 shows the effects of the post-synthesis salt treatment for an MCM-48 sample obtained by the second synthesis procedure, i.e., the procedure using sodium silicate, ethanol and CTABr. The lowermost XRD patterns shown on the left side in Fig. 1(a) and (b) are the same one that was obtained after the MCM-48 silica was heated in water (containing no salt except for the addition of a small amount of EDTANa<sub>4</sub> for the adjustment of pH to 10) at 373 K for 12 d and subsequently calcined. This XRD pattern was very similar to a result (not shown here) obtained after the sample was directly calcined, i.e., calcined without the treatment in water. The other XRD patterns shown on the left side in Fig. 1 were obtained in the same way as for the lowermost one, except that 0.32–2.56 wt.% NaCl or 2.8–5.6 wt.% EDTANa<sub>4</sub> solutions were used instead of water. Compared with the treatment in water or the direct calcination, the treatments in the salt solutions led to a significant increase in the XRD intensity of the subsequently calcined samples. The “salted” samples also showed increases in the peak resolution and  $d_{110}$  spacing. As far as the XRD patterns after calcination were concerned, the salt effects appeared to be independent of the salt concentration in the given experimental ranges. However, upon subsequent treatments in boiling water, the MCM-48 samples exhibited different XRD intensities depending on the salt concentration. For a systematic investigation, all the XRD patterns were

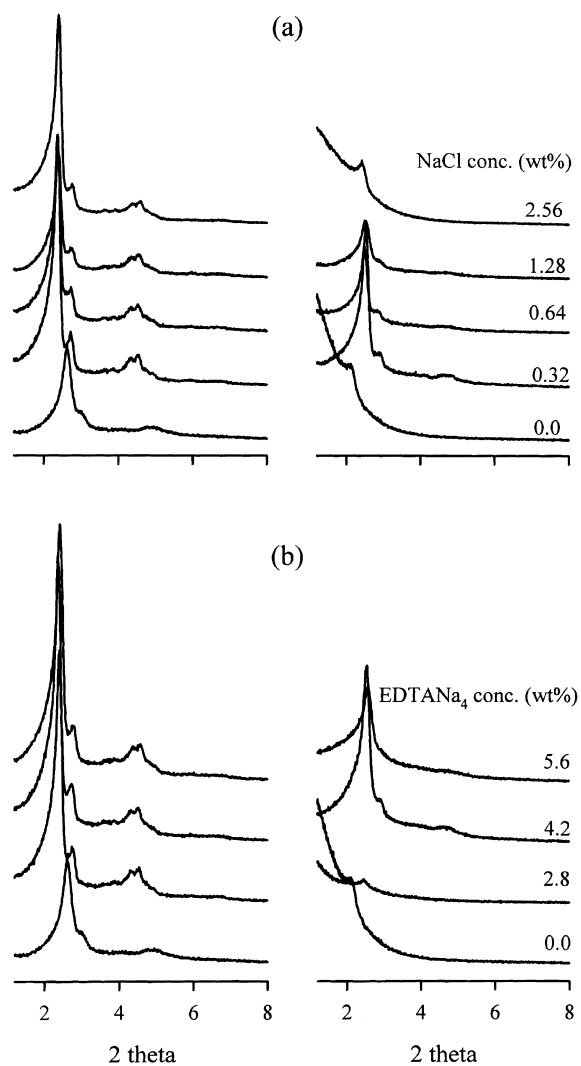


Fig. 1. XRD patterns of MCM-48 synthesized using sodium silicate, ethanol and CTABr. The as-synthesized MCM-48 sample was treated for 12 d at 373 K in (a) NaCl or EDTANa<sub>4</sub> (b) solution. The pH of the salt solution was adjusted to 10. The amount of the salt solution was fixed as 25 ml/g MCM-48. Left: calcined after salting for 12 d. Right: boiled in distilled water for 12 h after calcination.

obtained under the same measurement conditions after boiled in distilled water for 12 h under the same refluxing conditions. The hydrothermal stability of the MCM-48 samples was then judged from the diffraction intensity. This investigation gave the results shown on the right side of Fig. 1, which indicates that the hydrothermal stability

increased until the concentration reached to 0.32 wt.% NaCl or 4.2 wt.% EDTANa<sub>4</sub>. However, further increase of the salt concentration caused the hydrothermal stability to decrease.

The salting effect for the improvement of the hydrothermal stability depended not only on the salt concentration but also on the volume of the salt solution used per gram of MCM-48 sample. The amount of the solution and the salt concentration had to be optimized simultaneously, in order to achieve the maximum hydrothermal stability. Fig. 2 displays the salting effects depending on the amount of the salt solution, where the concentration and the amount of the NaCl solution were inverse-proportionally changed so that the total amount of NaCl contained in the solution remained constant. The salting experiment except for this change was conducted in the same way as for Fig. 1, using the same MCM-48 sample. The result in Fig. 2 shows that small amounts of concentrated salt solutions are preferred to a large volume of dilute solutions containing the same

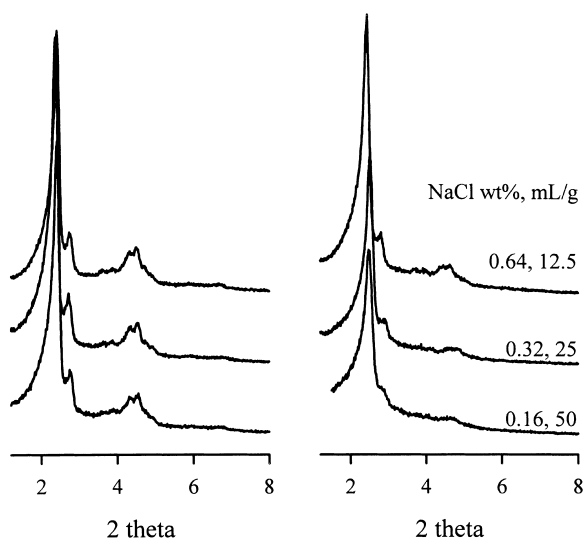


Fig. 2. XRD patterns of MCM-48 (the same sample used in Fig. 1) after salting for 12 d in NaCl solution at 373 K. The concentration and the amount of the NaCl solution were inverse-proportionally changed so that the total amount of NaCl in the solution did not change. Numbers given to XRD patterns denote the NaCl concentration and solution-to-sample ratio (ml/g).

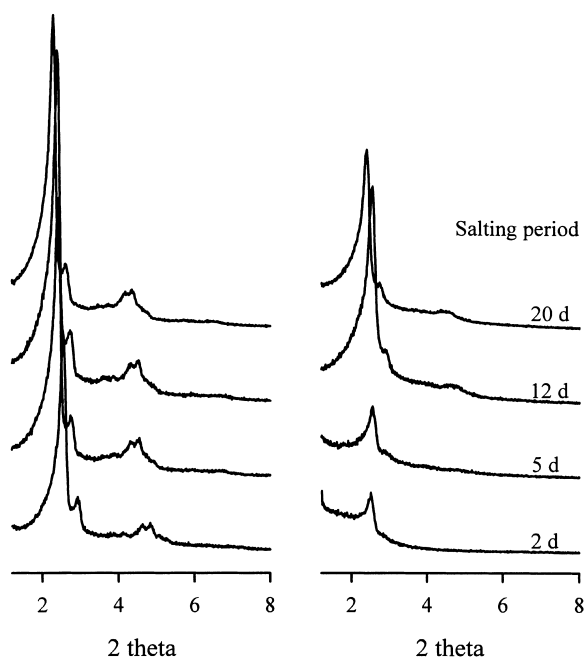


Fig. 3. XRD patterns of MCM-48 (the same sample used in Figs. 1 and 2) after salting for various lengths of period, using 12.5 ml of 0.64 wt.% NaCl aqueous solution per gram MCM-48 at 373 K. Numbers given to XRD patterns denote the duration of the salting period.

total amount of salts. The advantage of the small volume is reasonable, in that the loss of the surfactant and silica by leaching can be minimized.

The salting effect depended also on the length of the salting period as shown in Fig. 3. The XRD patterns were obtained with various lengths of the salting period (used in Figs. 1 and 2). As this result shows, the XRD pattern of the calcined sample continuously increased in the peak intensity until the salting period increased to about 12 d. The (1 0 0) peak position also shifted to a larger lattice spacing during this period. Further, the result for the hydrothermal stability indicates that at least a 12-d “salting” period is required to bring about the full effect for the improvement of the hydrothermal stability under these experimental conditions.

Fig. 4 shows the salting effect for two MCM-48 samples obtained using the other synthesis procedures. The sample in Fig. 4(a) was synthesized by the first procedure described in Section 2.1, using

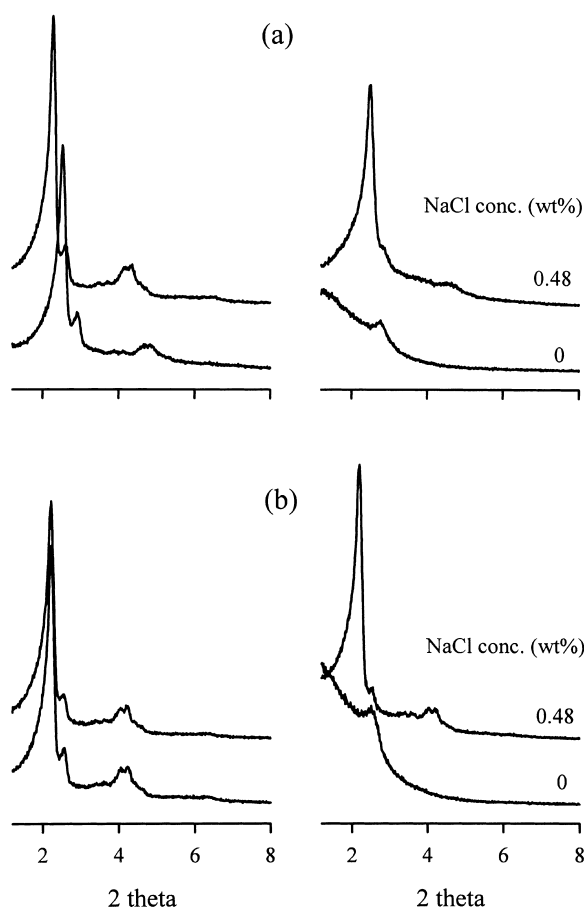


Fig. 4. XRD patterns of MCM-48: (a) synthesized using TEOS as a silica source and CTABr as a surfactant and (b) synthesized using sodium silicate and a mixture of CTABr with tetraoxyethylene dodecyl ether. Left: calcined after treatment with water or 0.48 wt.% NaCl solution. Right: boiled after calcination as in Fig. 1.

TEOS as the silica source and CTABr as the surfactant. The sample in Fig. 4(b) was obtained using sodium silicate and a mixture of CTABr with tetraoxyethylene dodecyl ether. As these results show, the present post-synthesis salting technique can be generally used for the improvement of the hydrothermal stability of MCM-48, in principle, regardless of the synthesis methods. However, the details of the salting conditions should be individually optimized depending on the synthesis conditions. In the case of properly salted samples, the XRD pattern exhibited no significant changes

due to structure loss even after boiling in water for 12 h.

## 4. Discussion

### 4.1. Restructuring process

Normally, if the silica forms of calcined MCM-41 or MCM-48 are subjected to pH 10 in an aqueous solution at 373 K, the structural order becomes completely lost within an hour. The thin pore walls, about 1 nm thick, are destroyed by the base-catalyzed silica hydrolysis. Such a rapid loss of the structure is difficult to prevent for calcined MCM-48 in the high-pH solution, even if salts are added to the solution. In the case of the as-synthesized materials, however, the structure containing the surfactant is very stable under the high-pH conditions. The structural order is maintained even after 20 d as shown in Fig. 3. This is because the pore walls are supported by the surfactant micelles filling the pores. Although no apparent changes in the structural order can be detected in the XRD pattern during this period, it is reasonable that the pore walls would experience the silica hydrolysis similar to the case of the calcined samples [12,21]. Under this situation, the pore walls must be maintained by compensating the silica hydrolysis with the reverse reaction, i.e., the silica condensation.

In the high-pH conditions, the silica frameworks can undergo the local reconstruction through continuous hydrolysis and condensation. Fig. 5 shows magic angle  $^{29}\text{Si}$  NMR spectra taken from the as-synthesized MCM-48 samples after various salting periods as given in Fig. 3. The NMR spectrum taken after 2 d of the salting treatment shows a decrease in the  $Q^3$  band intensity as compared with before the treatment. However, this relatively initial change during the salting period does not seem to be closely related to the improvement of the hydrothermal stability since the improvement requires a much longer period of treatment. It may be suggested that such an initial decrease in the  $Q^3/Q^4$  band ratio can occur when the condensation–hydrolysis equilibrium is suddenly shifted to the condensation side

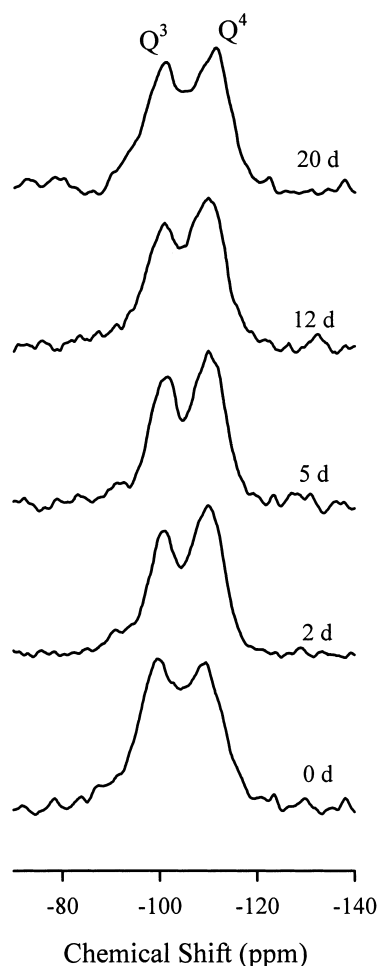


Fig. 5. MAS  $^{29}\text{Si}$  NMR spectra of MCM-48 after salting as in Fig. 3. Numbers given to NMR spectra denote the salting periods.

under the somewhat low pH conditions for the salting treatment compared with the high-pH conditions in the hydrothermal synthesis mixture. A more significant change that can be consequent to the improvement of the hydrothermal stability is the NMR line broadening which becomes conspicuous after 12 d of the salting period. Based on these data, it is reasonable that the improvement of the hydrothermal stability is a result of relaxation of the local framework structure to a more disordered state, through the condensation–hydrolysis dynamic processes. The increase in the d value indicated in Fig. 3 seems to occur in par-

allel with the framework relaxation. Here, the salt is believed to provide ions that can neutralize the positive charge of the surfactant's head group and also the negative charge of the silica framework, between the pore wall and the surfactant micelle. This role of salt, resultantly weakening or moderating the wall-surfactant interaction, as suggested in previous studies on MCM-41 [22], is believed to be an important factor that drives the framework restructuring process. If this is the case, the optimum salt concentration will be changed by the affinity of the individual salt or constituting ions with the head-group region, depending on various factors such as the hydrophilic property of the ions, the ionic size and charges.

Fig. 6 shows SEM images of the MCM-48 samples, which were synthesized with sodium silicate, ethanol and CTABr. As this figure shows, the single crystal morphologies of the as-synthesized material were maintained even after they were salted for 12 d in 0.64 wt.% NaCl solution at 373 K. From the SEM investigation, we can conclude that the improved hydrothermal stability is the result of a local restructuring process that leads to the lattice expansion without changing the morphologies. Any re-synthesis or re-crystallization processes can be excluded since such processes should lead to changes in the morphologies, whereas the MCM-48 crystal morphologies can be obtained only in narrow synthesis conditions.

The hydrothermal stability of the mesoporous silica is known to increase normally with the increase in the pore wall thickness. It is therefore interesting to investigate whether the salting treatment is involved with the increase in the wall thickness. Such an investigation can be performed more easily for MCM-41 than MCM-48. While both the materials exhibit very similar salting effects (see Section 4.2), the straightforward channel structure of MCM-41 allows the wall thickness to be assessed by subtracting the pore diameter determined from the N<sub>2</sub> adsorption isotherm from the lattice spacing. On this ground, the investigation was carried out for MCM-41 samples treated in 6.5 wt.% NaCl solution for 12 d. This investigation showed that the pore-wall thickness decreased from 1.3 to 1.2 nm, instead of increasing. The decrease of the wall thickness agrees with the

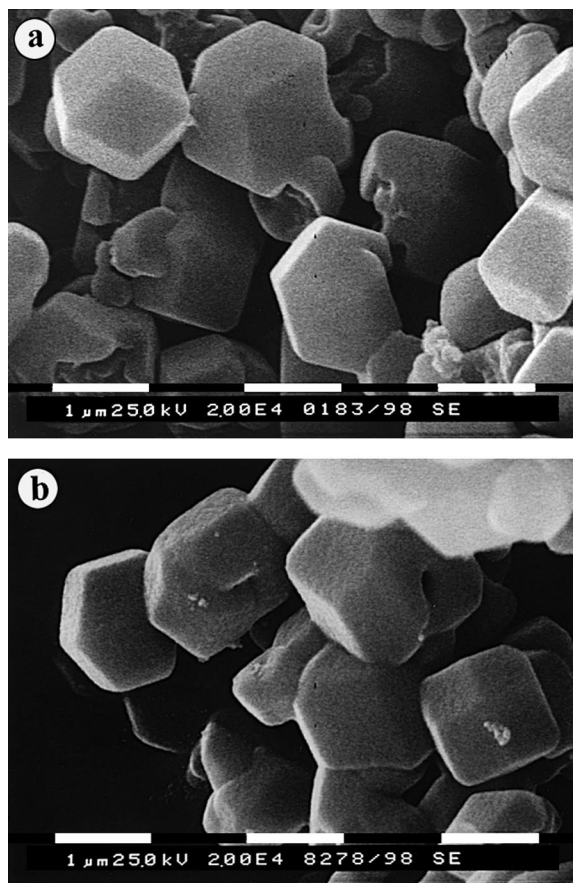


Fig. 6. SEM images of MCM-48 synthesized with sodium silicate, ethanol and CTABr: (a) before salting and (b) after salting as in Fig. 3.

SEM and XRD results, which indicated that the lattice expansion occurred without re-crystallization.

#### 4.2. Application of the post-synthesis "salting" technique to other silica

The MCM-41 silica is synthesized via an ionic templating mechanism like MCM-48. In this case, the post-synthesis salting technique is also effective for the improvement of the hydrothermal stability of MCM-41. Fig. 7 shows XRD patterns of MCM-41 synthesized using sodium silicate as a silica source and CTACl as the surfactant. As shown in Fig. 7, the salting effect for this MCM-41

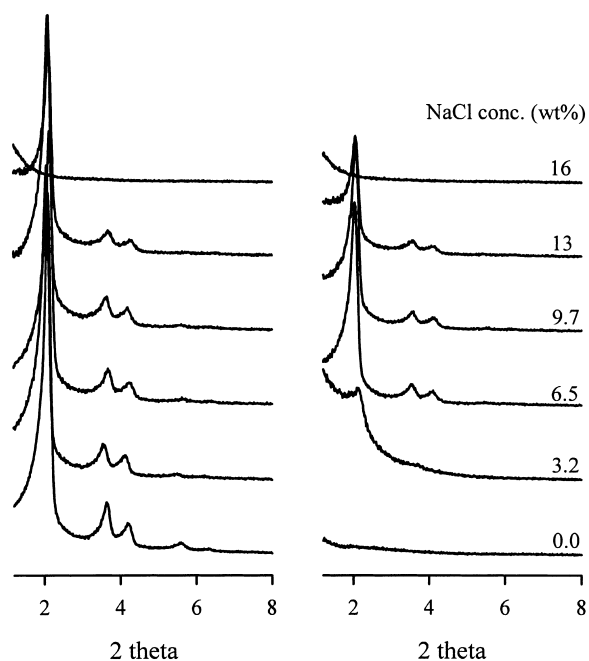


Fig. 7. XRD patterns of MCM-41 synthesized using sodium silicate and CTACl. The MCM-41 samples were treated as in Fig. 1.

sample was very similar to the data given for MCM-48 in Fig. 1 except for the difference (6.5 wt.% NaCl for MCM-41 and 0.32 wt.% NaCl for MCM-48) in the optimum salt concentration. We repeated the salting experiment with another MCM-41 sample, which was synthesized with dodecyltrimethylammonium bromide [ $C_{12}H_{25}N(CH_3)_3Br$ ] instead of the CTACl surfactant. The optimum NaCl concentration for this small-pore MCM-41 was 3.2 wt.%.

Recently, Bagshaw reported that the post-synthesis treatment of the MSU-1 mesoporous silica, which was synthesized using non-ionic surfactant, resulted in the improvement of the structural order and the stabilization of the silica framework due to the enhanced condensation [23,24]. We performed similar experiments with MSU-1 using distilled water, confirming the previous results. These results suggest that the hydrothermal stability can also increase. However, our test for the hydrothermal stability performed as described in the experimental section showed that the MSU-1

sample completely lost the XRD pattern after boiled in distilled water for 12 h. Furthermore, when salts were used, the structure of the as-synthesized MSU-1 was lost during the salting treatment at 373 K.

## 5. Conclusions

The results reported in this paper show that the hydrothermal stability of the mesoporous molecular sieves MCM-48 can be significantly improved by treating the as-synthesized materials in an aqueous solution of salts at 373 K. The salting treatment requires more than 12 d under the present experimental conditions. The long time requirement is probably due to the salting effect occurring so slowly as to cause fully the pore-wall restructuring. The restructuring process may be speeded up at a high temperature and higher pH.

The post-synthesis salting technique can be applied for MCM-48 samples that are obtained following various synthesis procedures. It can also be used for MCM-41 materials obtained following the same type of ionic templating mechanism. The optimum salting conditions depend on the details of the synthesis conditions. We expect that the post-synthesis technique would be useful for various applications of these materials especially where the improvement of the hydrothermal stability is essential.

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## References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.



- [3] J.M. Kim, S.K. Kim, R. Ryoo, *Chem. Commun.* (1998) 259.
- [4] A. Carlsson, M. Kaneda, Y. Sakamoto, O. Terasaki, R. Ryoo, S.H. Joo, *J. Electron Microsc.* 48 (1999) 795.
- [5] R. Ryoo, S.H. Joo, J.M. Kim, *J. Phys. Chem. B* 103 (1999) 7435.
- [6] M. Kruk, M. Jaroniec, R. Ryoo, S.H. Joo, *Chem. Mater.* 12 (2000) 1414.
- [7] R. Ryoo, S.H. Joo, S. Jun, *J. Phys. Chem. B* 103 (1999) 7743.
- [8] R. Ryoo, C.H. Ko, IUPAC Workshop on Advanced Materials: Nanostructured Systems, Hong Kong, July 14–18, 1999.
- [9] M.S. Morey, A. Davidson, G.D. Stucky, *J. Porous Mater.* 5 (1998) 195.
- [10] K. Moller, T. Bein, *Chem. Mater.* 10 (1998) 2950.
- [11] M. Kruk, M. Jaroniec, R. Ryoo, J.M. Kim, *Chem. Mater.* 11 (1999) 2568.
- [12] J.M. Kim, R. Ryoo, *Bull. Korean Chem. Soc.* 17 (1996) 66.
- [13] R. Ryoo, S. Jun, *J. Phys. Chem. B* 101 (1997) 317.
- [14] J.M. Kim, S. Jun, R. Ryoo, *J. Phys. Chem. B* 103 (1999) 6200.
- [15] D. Das, C.-M. Tsai, S. Cheng, *Chem. Commun.* (1999) 473.
- [16] R. Mokaya, *J. Phys. Chem. B* 103 (1999) 10204.
- [17] S.-C. Shen, S. Kawi, *J. Phys. Chem. B* 103 (1999) 8870.
- [18] L.T. Chen, T. Horiuchi, T. Mori, K. Maeda, *J. Phys. Chem. B* 103 (1999) 1216.
- [19] R. Ryoo, S. Jun, J. M. Kim, M. J. Kim, *Chem. Commun.* (1997) 2225.
- [20] M. Kruk, M. Jaroniec, A. Sayari, *J. Phys. Chem. B* 103 (1999) 10670.
- [21] R. Ryoo, J.M. Kim, *J. Chem. Soc. Chem. Commun.* (1995) 711.
- [22] A.R. Badiei, S. Cantournet, M. Morin, L. Bonneviot, *Langmuir* 14 (1998) 7087.
- [23] S.A. Bagshaw, *Stud. Surf. Sci. Catal.* 117 (1998) 381.
- [24] S.A. Bagshaw, *Chem. Commun.* (1999) 1785.