Drying induced phase transformation of mesoporous silica

Ming-Chang Liu,[a] **Hwo-Shuenn Sheu**[b] **and Soofin Cheng*[a]**

[a] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan.*
E-mail: chem1031@ccms.ntu.edu.tw; Fax: +886-2-23636359
[b] *Research Division, Synchrotron Radiation Research Center, Hsinchu 300, Taiwan*

Solvent evaporation upon drying the precipitate was found to be the key factor for the phase transformation of cubic mesoporous silica SBA-1 to hexagonal SBA-3 studied by *in-situ* X-ray diffraction and ^{29}Si solid state NMR on the precipitates formed under various crystallisation conditions.

In- and *ex-situ* X-ray diffraction techniques were used to examine the factors affecting the phase transformation of mesoporous silica SBA-1 in the crystallisation process. In contrast to the reports in the literature, the acid concentration and crystallisation temperature were found to have little effect. Cubic SBA-1 structure was observed as the only crystalline phase formed in the acid reaction media. However, a phase transformation from cubic to hexagonal was observed upon drying the precipitates. To the best of our knowledge, this is the first time in the literature that phase transformation of mesostructure materials induced by drying the precipitates has been observed.

The discovery of the M41S family of mesoporous molecular sieves by the researchers in Mobil Co.[1] has stimulated the studies of cooperative assembly of inorganic cluster ions and surfactant species in liquid crystal-like arrays.[2–4] Materials of uniformly arranged pores with tunable pore diameter ranging between 1.5–10 nm, narrow pore size distribution and very high surface areas are technologically promising for applications in catalysis,[5–7] sensors and optoelectronic devices.[8,9] As far as these applications are concerned, 3D cubic phase mesoporous materials are favourable to those of 2D hexagonal phase because the three-dimensional inter-connected pores offer better pore accessibility than the one-dimensional cylindrical pores.

Cubic phase SBA-1 (*Pm3n*), was synthesized with surfactants of relatively large head group ($C_nH_{2n+1}(C_2H_5)_3N^+$, n = 12, 14, 16, 18) in strong acidic media.[2,3,10] In the reports dealing with SBA-1 synthesis, several researchers observed phase transformation from hexagonal (SBA-3, *P6m*) to cubic (SBA-1, *Pm3n*) at early stage of crystallisation.[11,12] Although the effective surfactant ion pair packing parameter, $g = V/a_0l$, is considered a useful molecular structure-directing index to characterise the geometry of the mesophase products,[4,13] the mechanism of surfactant-templated phase transformation reaction was still not well understood. This subject is of great importance for the purpose of synthesizing the desired mesostructure material.

SBA-1 was synthesized using cetyltriethyl ammonium bromide (CTEABr) as the surfactant and tetraethylorthosilicate (TEOS) as the silica source, and the procedures mentioned in ref. 12 were followed. The molar composition of the reaction mixture was TEOS:CTEABr:HCl:H_2O = 1:0.13:*x*:125, where *x* = 2–5. The reaction temperature was maintained at *ca.* 273–275 K, if not otherwise specified. In the *ex-situ* study, powder XRD patterns were recorded using a Scintag X1 instrument with a Cu Kα radiation (λ = 0.15414 nm). *In-situ* XRD studies of the synthesis gels were conducted at the Synchrotron Radiation Research Center, Hsinchu, Taiwan. The patterns were recorded in the transmission mode with λ = 0.132633 nm radiation (1.85 GeV and 200 mA).

The effect of acidity was examined by varying the amount of hydrochloric acid used. *Ex-situ* powder XRD patterns of the precipitates dried at 373 K overnight showed that cubic SBA-1 was the only crystalline phase observed on the precipitates synthesized under higher acidic conditions (HCl/TEOS 5). For those formed in lower acidic conditions (HCl/TEOS = 2–4), a hexagonal SBA-3 phase was observed in a short crystallisation period, while cubic SBA-1 would be obtained if the reaction was prolonged. These results are consistent with those reported in the literature.[11,12]

In order to investigate the phase transformation in the synthesis gel, *in-situ* XRD experiments were performed on the reaction mixture sealed in a Teflon container of 10 mm inner diameter and *ca.* 2 mm thickness with Kapton tapes. It was found that only cubic phase was formed when the HCl concentration was varied in the range of HCl/TEOS = 2–5. The crystallinity of the precipitate increased with the crystallisation period, as shown in Fig. 1. However, no hexagonal phase was detected even when the synthesis gel was in low acidic conditions. These results were contradictory to those observed on the dried precipitates. On the other hand, the HCl concentration would affect the rate of crystallisation. For the synthesis gel prepared with HCl/TEOS = 2, 3, 4, and 5, it took 7, 1.4, 0.7, and 0.6 h, respectively, for the resolvable cubic phase to appear.

The effect of reaction temperature was also examined by raising the temperature of the reaction mixture 10 K in 3 min, followed by *in-situ* pattern recording isothermally over 10 min.
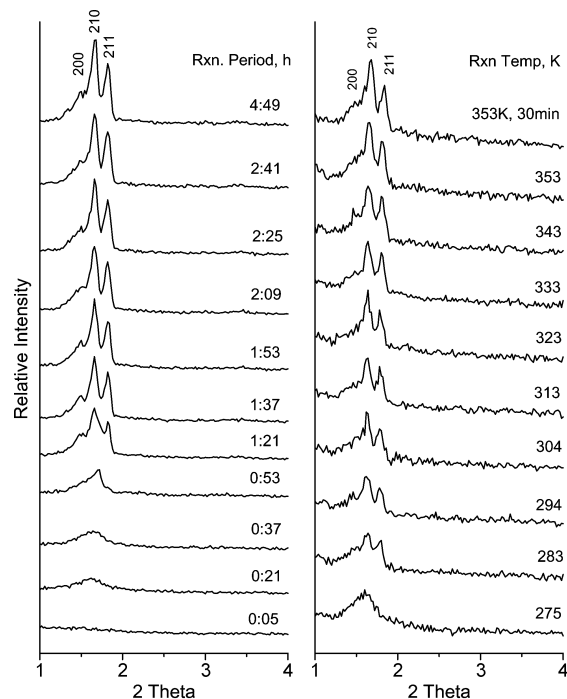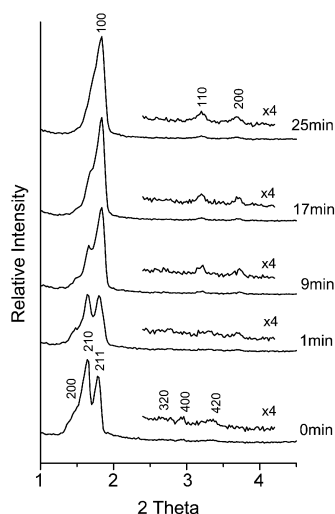

Fig. 1 *In-situ* XRD studies of SBA-1 gel prepared with TEOS:CTEABr:HCl:H_2O = 1:0.13:3:125 for different crystallisation periods and at various temperatures.

Fig. 2 *In-situ* XRD patterns of wet SBA-1 precipitate after exposing to air for different periods.

Fig. 1 shows that cubic SBA-1 was the only phase observed again when the synthesis gel was heated from 275 to 353 K, and the crystallinity was found to increase with the crystallisation temperature. These results demonstrate that the cubic SBA-1 precipitate is stable upon heating, and the reaction temperature is not an important factor for phase transformation.

The phase transformation from cubic to hexagonal occurred only when the wet precipitate crystallised for a short period (less than 2 h with HCl/TEOS = 3) was dried in open air. Fig. 2 shows that the 210 and 200 peaks of the cubic phase started shrinking just 1 min after the seal tape on the wet precipitate was removed. After 9 min, the 100 peak of the hexagonal phase has grown relatively strong and the 110 and 200 peaks can be clearly seen. The phase transformation apparently is somehow related to the solvent evaporation. However, for the precipitate crystallised for a long period of time such as 4 h with HCl/TEOS = 3, or with higher acid concentration, the cubic phase was retained even after the precipitates were dried. The differences between the stable and unstable cubic SBA-1 crystallites should be the extent of silica condensation. SEM photographs show that the stable SBA-1 crystallites have a spherical shape and highly isotropic morphology while those of unstable phase are irregular granules.

Since drying is the essential process in obtaining the solid materials, the present studies demonstrate that drying the precipitate can be an important factor in obtaining mesostructure materials of different phases. The cubic SBA-1 phase formed in the acidic media is a thermodynamic product of silica condensation around the spherical micelles of surfactant molecules. The extent of silica condensation was examined by ^{29}Si NMR. Fig. 3 compares the ^{29}Si NMR spectra of the precipitate prepared with HCl/TEOS = 3 and crystallisation for 1 h before and after drying. It can be seen that the Q_4/Q_2 and Q_3/Q_2 ratios in the wet precipitate were much higher than that of the dry sample. These results imply that condensation between the silanol groups is increased upon drying the precipitate. As the solvent was evaporated, surfactant is concentrated, which then favours the formation of rod-shape micelles instead of spherical micelles. Concomitantly, the mesoporous silica, which still contained large amount of silanol groups, probably reorganised around the rod-shape micelle templates and formed a hexagonal mesophase. This accounts for the phase transformation from cubic to hexagonal observed during the drying process. Previous reports,[11,12] which consider that the hexagonal mesophase was the intermediate phase in cubic SBA-1 formation, may be misleading due to the fact that all the structural analyses were done with the dried precipitates.

Recently, *in-situ* time-resolved small angle X-ray scattering was used to study the intermediate phases formed during the formation of mesostructured silica film from aqueous–alcohol
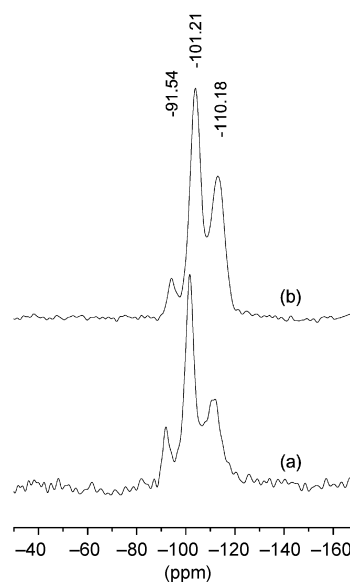
Fig. 3 ^{29}Si solid state NMR of mesoporous silica prepared with HCl/TEOS = 3 after 1 h crystallisation: (a) the wet precipitate of cubic SBA-1 (taken under static conditions), and (b) the dried precipitate in hexagonal phase (taken under 5k rpm MAS).

solution of CTMAB/TEOS.[14] Lamella and hexagonal phases were proposed to be the intermediate phases of the cubic phase. However, because of the presence of alcohol as the solvent, their system was more complicated and very different from ours. First, two-stage rapid evaporation (in seconds) of the solvents, primarily ethanol then water, occurred during the film formation. Second, the condensation of TEOS and the organisation of the silica precursor into ordered meso-structures proceeded concomitantly upon solvent evaporation. Third, the micelle phases of surfactant formed in aqueous–alcohol media are different from that in water. Moreover, because alcohol evaporated very rapidly, the meso-phases observed during the film formation were more like kinetic-controlled products. As to the phase transformation upon drying the wet precipitate in the present study, it involved changes between thermodynamically meta-stable phases.

Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **357**, 710.
2 A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299.
3 Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gler, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
4 Q. Huo, D. I. Margolese and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 1147.
5 C.-L. Tsai, B. Chou, S. Cheng and J.-F. Lee, *Appl. Catal.*, 2001, **208**, 279.
6 D. Das, J.-F. Lee and S. Cheng, *Chem. Commun.*, 2001, 2178.
7 M. Hsien, H.-T. Sheu, T. Lee, S. Cheng and J.-F. Lee, *J. Mol. Catal.*, 2002, **181**, 189.
8 P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides and G. D. Stucky, *Science*, 1998, **282**, 2244.
9 S. Baskaran, J. Liu, K. Domansky, N. Kohler, X. Li, C. Coyle, G. E. Fryxell, S. Thevuthasan and R. E. Williford, *Adv. Mater.*, 2000, **12**, 291.
10 Y. Sakamoto, M. Kaneda, O. Terasaki, D. Zhao, J. M. Kim, G. Stucky, H. J. Shin and R. Ryoo, *Nature*, 2000, **408**, 449.
11 M. J. Kim and R. Ryoo, *Chem. Mater.*, 1999, **11**, 487.
12 S. Che, S. Kamiya, O. Terasaki and T. Tatsumi, *J. Am. Chem. Soc.*, 2001, **123**, 12089.
13 S. T. Hyde, *Pure Appl. Chem*, 1992, **64**, 1617.
14 D. Grosso, F. Babonneau, G. J. de A. A. Soler-Illia, P. A. Albouy and H. Amenitsch, *Chem. Commun.*, 2002, 748.