

## Synthesis of Mesoporous Silica in Acidic Condition by Solvent Evaporation Method

Hyun-Seog Roh, Jong-San Chang and Sang-Eon Park<sup>†</sup>

Industrial Catalysis Research Lab., Korea Research Institute of Chemical Technology (KRICT),  
Taejon 305-343, Korea

(Received 17 November 1998 • accepted 6 April 1999)

**Abstract-** Both powder-type and film-type mesoporous silica materials have been prepared by using a sol-gel process in highly acidic, solvent-rich and mild conditions by solvent evaporation method. Powder mesoporous silica which has hexagonal arrays was well synthesized within only 10 minutes, and mesoporous film was formed on the glass plate within only several seconds by supramolecular interactions between the silicate species and surfactant-templates. In particular, the synthesis time was very short compared with that of hydrothermal synthesis owing to the solvent evaporation. This method has some characteristics different from the hydrothermal method such as the following. There is no precipitation because particles do not form in the solution before solvent evaporation, bulk powder is rigid, whereas that of hydrothermal synthesis is very soft, and mesoporous materials are synthesized in acidic condition. Solvent evaporation method for the synthesis of mesoporous materials is promising because the method is very simple and time-saving.

Key words : Mesoporous Silica, Solvent Evaporation Method, Supramolecular Interactions, Acidic Condition

### INTRODUCTION

Large pore-size molecular sieves are much in demand for reactions or separations involving large molecules [Estermann et al., 1991]. Since the MCM (Mobil's Composition of Matter) series was invented by Mobil Corporation scientists in 1992 [Kresge et al., 1992; Beck et al., 1992], surfactant-templated synthetic procedures have been extended to include a wide range of compositions, and a variety of conditions have been developed for exploiting the structure-directing functions of electrostatic, hydrogen-bonding, and van der Waals interactions associated with amphiphilic molecules [Huo et al., 1994a, b; Stucky et al., 1997; Sayari, 1996]. Mesoporous molecular sieves, of which the pore size could be tailored accurately in the range of 2-10 nm by preparation conditions or postsynthesis treatments, could encapsulate the heavier feeds which could not get into the micropores. One of the members of M41S called MCM-41 shows a hexagonal array of uniform mesopores which depends on the template and synthesis conditions employed. Usually MCM-41 is prepared hydrothermally at 100 °C for several days in the basic condition [Kresge et al., 1992; Beck et al., 1992; Stucky et al., 1997; Sayari, 1996; Ryoo et al., 1997a; Kim and Woo, 1997]. Recently, attention has been paid to the utilization of microwave heating technique in the field of mesoporous materials [Wu and Bein, 1996; Park et al., 1998a, b]. MCM-41 is obtained by microwave treatment of precursor gel at 100-120 °C for 1 h or less, a very short period of time compared with the hydrothermal method [Park et al., 1998a, b].

Stucky et al. presented four pathways to the synthesis of mesostructured surfactant-inorganic biphasic arrays [Stucky et al., 1997].

The first way involves the direct co-condensation of anionic inorganic species with a cationic surfactant ( $S^+I^-$ ). The base-synthesis of MCM-41 and MCM-48 forms prototypic examples. The second way involves cooperative condensation of cationic inorganic species with an anionic surfactant ( $S^-I^+$ ). The examples of this way are periodic tubular non-silica structures such as iron oxide, lead oxide, and aluminum oxide. The third and the fourth way involve condensation of ionic inorganic species in the presence of similarly charged surfactant molecules. These pathways are mediated by counterions of opposite charge to that of the surfactant head groups. In the case that the mediated ions are cations ( $S^-M^+I^-$ ), the formed materials are zinc oxide in the base condition. If the mediated ions are anions ( $S^+M^-I^+$ ), then the prepared materials are acid-synthesized M41S or zincphosphate [Huo et al., 1994a, b; Stucky et al., 1997].

Thin films of surfactant-templated mesoporous materials could find applications in membrane-based separations, selective catalysis and sensors. Above the CMC (critical micelle concentration) of a bulk silica-surfactant solution, films of mesophases with hexagonally packed one-dimensional channels can be formed at solid-liquid and liquid-vapour interfaces [Yang et al., 1996a, b]. Lu et al. reported film formation during the last few seconds of film deposition through surfactant enrichment by solvent evaporation to exceed CMC even though the initial surfactant concentration was under the CMC [Lu et al., 1997]. Ryoo et al. prepared mesoporous silica films and plates using azeotropic mixture of ethanol and n-hexane [Ryoo et al., 1997b]. Bruinsma et al. synthesized mesoporous silica in the form of spun fibers and spray-dried hollow spheres by solvent evaporation [Bruinsma et al., 1997]. Ogawa and Kikuchi prepared self-standing transparent films of silica-surfactant mesostructured materials using supramolecular assemblies of surfactants to template the reactions of inorganic species [Ogawa and Kikuchi, 1998].

<sup>†</sup>To whom correspondence should be addressed.

E-mail : separk@pado.kRICT.re.kr

In this study, mesoporous materials were prepared in acidic condition by solvent evaporation method which accelerates supramolecular interactions involving condensation of cationic inorganic species in the presence of similarly charged surfactant molecules which are mediated by counterions ( $\text{Cl}^-$  or  $\text{Br}^-$ ) of opposite charge to that of the surfactant head groups. Hexagonal arrayed powders were successfully synthesized in acidic and thermally mild conditions within 10 minutes. Mesoporous films were also formed on the glass plate in a similar condition but the formation time was about several seconds. Solvent evaporation method can be used as a promising tool for the preparation of mesoporous materials because of many advantages such as the following. Synthesis time is very short, the solvent which is employed can be recovered by evaporation, and the synthesis condition is mild.

## EXPERIMENTAL

### 1. Bulk Synthesis and Film Formation of Mesoporous Materials

The synthesis procedure of mesoporous powders and films is depicted in Fig. 1. TEOS (Tetraethylorthosilicate, Aldrich, 98 %) was employed as a silica source. Ethanol (Merck, 99 %), methanol (Merck, 99 %) and MEK (Methylethylketone, Aldrich, 99 %) were used as solvent. CTAB ( $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ ) was used as surfactant-temple. Precursor solutions were prepared by addition of cationic surfactant, CTAB, to polymeric silica sols. TEOS, solvent, distilled water and HCl (mol ratios: 1 : 3 : 8 :  $5 \times 10^{-2}$ ) were refluxed at 60 °C for 90 min. And then the sols were diluted with solvent at a ratio of 1 : 3. Finally, CTAB was added in quantities corresponding to the concentration range of 0.06-0.12 M. This solution was evacuated at 60 °C for the bulk synthesis. Films were deposited on the glass plate by dip-coating. Prepared powders were calcined at

550 °C for 6 hr. Mesoporous films were calcined at 400 °C for 10 min. The heating rate was controlled to 1 °C/min because the mesoporous structure should be protected from collapsing by the rapid change of temperature.

### 2. Characterization of Mesoporous Powders and Films

Synthesized mesoporous materials were characterized by FT-IR (Nicolet). Bulk powders were directly pelletized, and the mesoporous films were rubbed by knife to be pelletized after being mixed with dry KBr. In order to identify the mesostructure, the prepared mesoporous samples were analysed by X-ray diffraction (XRD). The unit used was an X-ray diffractometer (Rigaku 2155D6, Ni-filtered  $\text{CuK}\alpha$  radiation with  $\lambda = 1.5418 \text{ \AA}$ ). The specific surface areas and mesopore volumes were determined by nitrogen physisorption with the BET sorption analyser (Micromeritics ASAP 2400). The morphology of the samples was examined with an SEM (Scanning electron microscope, 20 kV, Jeol JEM-300). TGA profile was obtained by IGA (Intelligent gravimetric analyser, Hidden analytical) system.

## RESULTS AND DISCUSSION

By solvent evaporation method, both mesoporous powders and films were prepared and characterized. Powder samples ground by mortar and film samples rubbed by knife were mixed with dry KBr to be pelletized for FT-IR analysis. FT-IR spectra are shown in Fig. 2. In the case of bulk synthesis of powder, the intensities of two Si-O-Si asymmetric stretching vibration bands appearing at 1,230  $\text{cm}^{-1}$  and 1,080  $\text{cm}^{-1}$  were significantly changed upon calcination. While the peak at 1,230  $\text{cm}^{-1}$  was decreased after calcination, the peak at 1,080  $\text{cm}^{-1}$  was increased after calcination. The changes observed in the Si-O-Si region after calcination are due to irreversible silicate polymerization and reflect irreversible transformations in the silicate structure [Calabro et al., 1996]. So after calcination, the

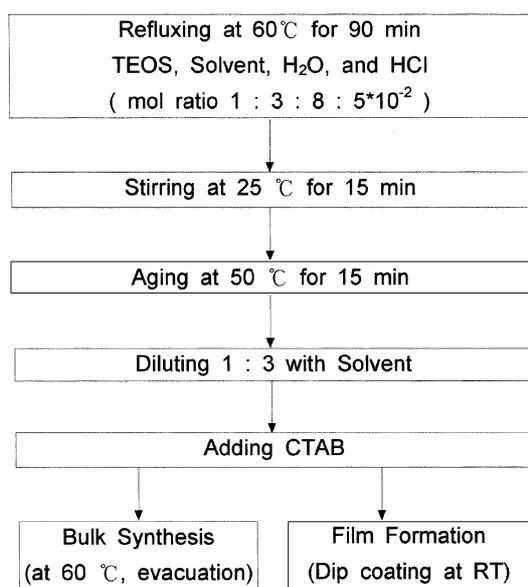


Fig. 1. A typical procedure for the synthesis of mesoporous silica by solvent evaporation method.

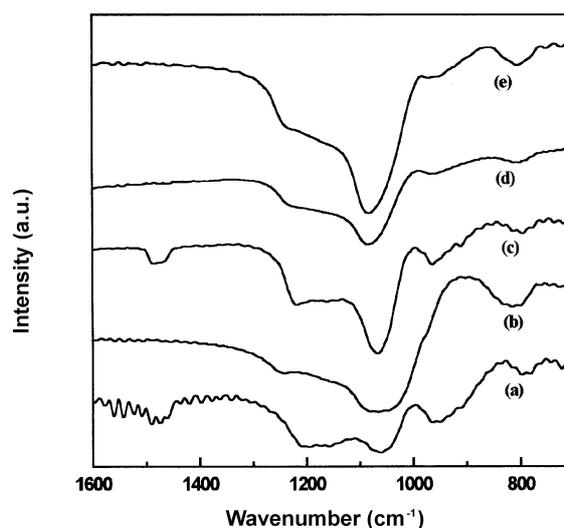


Fig. 2. FT-IR spectra of mesoporous silica; solvent: ethanol;  $C_0 = 0.10 \text{ M}$  (a) bulk, as-synthesized (b) bulk, calcined (c) film, as-synthesized (d) film, calcined (e) MCM-41, calcined.

spectrum of bulk synthesized powder became similar to that of MCM-41 reference, (e), which was prepared in the basic condition. In the case of film formation, there was no significant change in the peak intensity after calcination.

The XRD patterns of bulk powders are illustrated in Fig. 3. And those obtained on silicate/surfactant films grown at the air-water interface are shown in Fig. 4. In both cases ethanol was used as solvent. In Fig. 5, the XRD patterns of the samples with respect to various solvents are described. According to Fig. 3, in the bulk synthesis, mesophases are confirmed from the XRD patterns. As the initial surfactant concentration increased, the maximum peak intensity was found when the initial surfactant concentration was 0.10 M. The intensities of the cal-

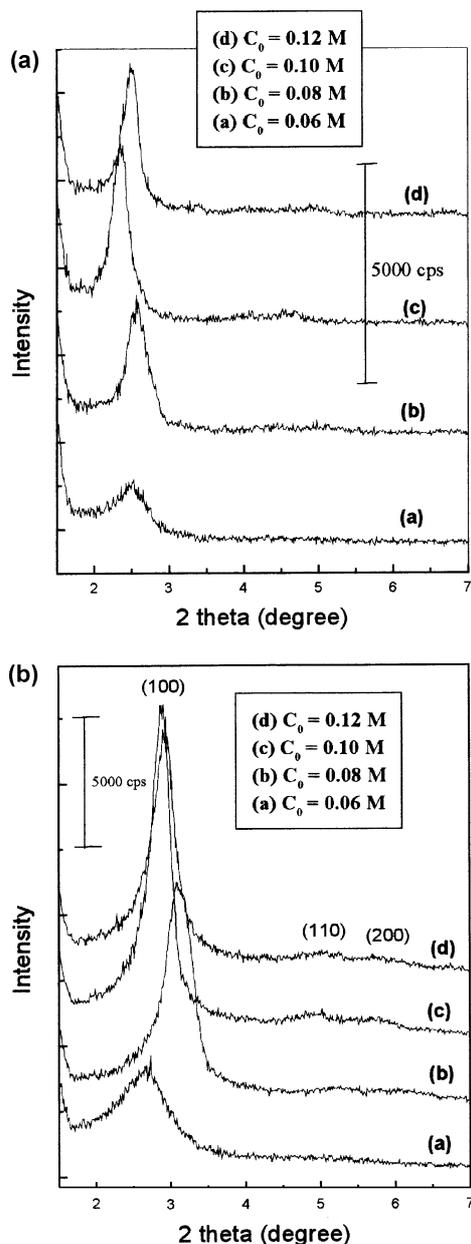


Fig. 3. XRD patterns of mesoporous silica with initial surfactant concentration; solvent: ethanol; bulk synthesis (a) as-synthesized (b) calcined.

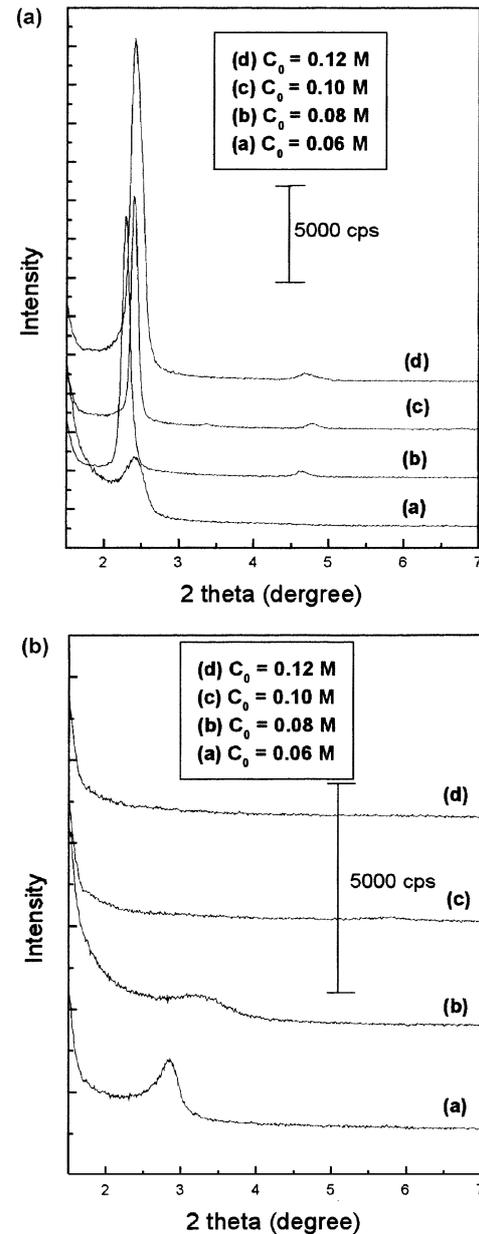


Fig. 4. XRD patterns of mesoporous silica with initial surfactant concentration; solvent: ethanol; film synthesis (a) as-synthesized (b) calcined.

cined samples were higher than those of the as-synthesized ones, and the powder patterns showed (100), (110) and (200) reflections corresponding to a hexagonal structure after calcination. (110) and (200) reflection patterns are apparent if the scales of intensities are magnified to about 5 times. The increase in peak intensity after calcination is due to condensations of mesophases. The d-spacing values of as-synthesized samples are about 40 Å, and the values are changed to about 30 Å after calcination. This results are due to the fact that there are condensations of mesophases in the calcination process. These results indicate that the structure is not so strong because mesophases are formed very rapidly. This result of calcination shrinkage is in good agreement with that of spun fibers

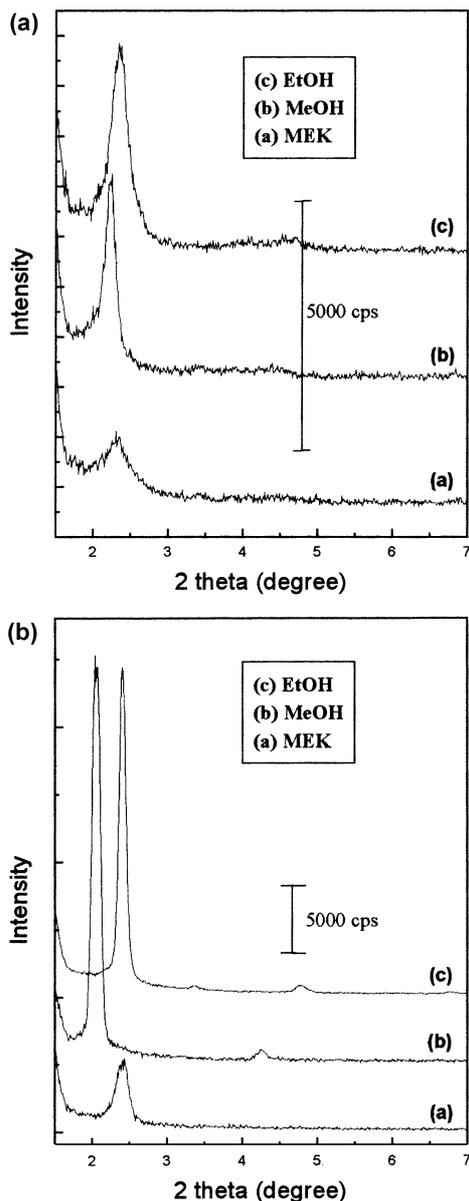


Fig. 5. XRD patterns of mesoporous silica with change of solvent;  $C_0=0.10$  M; as-synthesized (a) bulk synthesis (b) film synthesis.

synthesized by Bruinsma et al. According to the result of Bruinsma et al.,  $9 \text{ \AA}$  shrinkage was observed after calcination [Bruinsma et al., 1997]. The XRD patterns of the films are significantly different from those of bulk materials. As shown in Fig. 4(a), very sharp diffraction peaks with  $d$  values of about  $4 \text{ nm}$ , which accompanied second-order reflections, were observed in the XRD patterns of the as-synthesized products, indicating that the films possess periodic mesostructures over the initial concentration of  $0.08 \text{ M}$ . So, the structures were broken during the calcination process, as are shown in Fig. 4(b). If the initial surfactant concentration was  $0.06 \text{ M}$ , mesophases still existed after calcination. Thus, it is suspected that mesophases change to lamellar phases with increasing the initial surfactant concentration. And the change point is between  $0.08$  and  $0.10 \text{ M}$ . A-

May, 1999

According to Fig. 5, among three different solvents, alcohols such as methanol and ethanol effectively form bulk mesoporous materials, but MEK forms bulk materials of mesophases which have low quality. In the film formation, alcohols form lamellar phases.

Mesoporous powders have a BET surface area of about  $1,600 \text{ m}^2/\text{g}$  and a narrow pore-size distribution around  $16 \text{ \AA}$ , when  $C_0$  was  $0.10 \text{ M}$  and the solvent was ethanol. The high value of surface area is similar to that of hollow spheres produced by spray drying, which was prepared by Bruinsma et al. [Bruinsma et al., 1997]. Bruinsma et al. obtained the data of BET surface area with change of surfactant/silicate ratio, and the highest surface area ( $1,770 \text{ m}^2/\text{g}$ ) was achieved at the highest surfactant concentration (surfactant/silicate mole ratio= $0.28$ ) [Bruinsma et al., 1997]. The pore size distribution curve de-

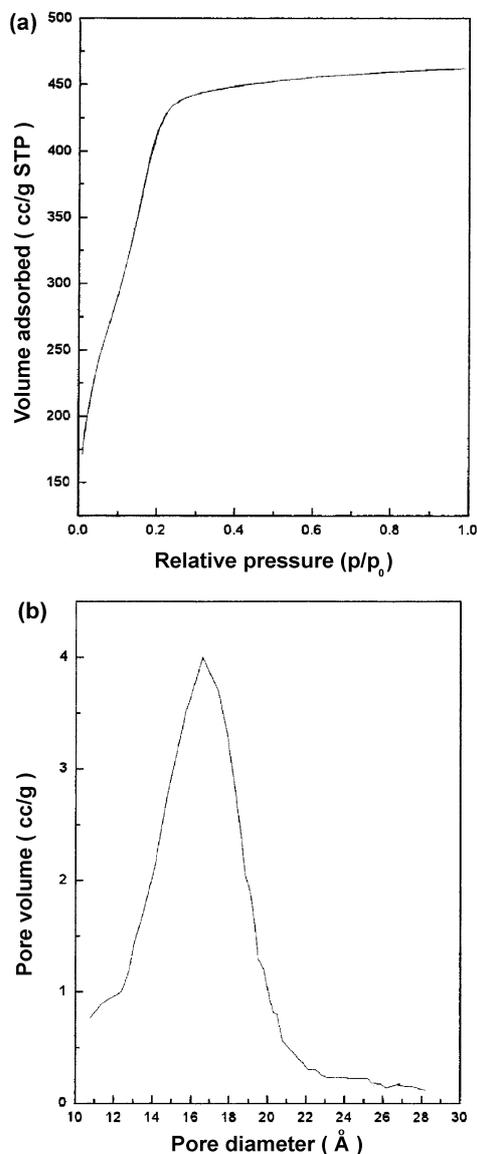


Fig. 6. BET data of mesoporous silica; solvent: ethanol;  $C_0=0.10 \text{ M}$ ; bulk synthesis (a)  $\text{N}_2$  adsorption-desorption isotherms; pretreated at  $300 \text{ }^\circ\text{C}$  (b) Pore size distribution curve obtained by the BJH analysis.

picted in Fig. 6 has been obtained using the BJH (Barrett-Joyner-Halenda) method with  $N_2$  adsorption isotherm. The adsorption-desorption isotherms show no hysteresis within the resolution of the equipment, indicating that the pores are unconfined. Similar results can be seen from the other groups' data [Ryoo et al., 1997; Bruinsma et al., 1997]. The wall thickness was 19 Å which was calculated as:  $2 \times d(100) / \sqrt{3}$  -pore size. The thickness is similar to that of hydrothermal synthesis. So, after calcination, the wall becomes rather stable.

Fig. 7 shows the SEM images obtained for the mesoporous silica materials. Fig. 7(a) was obtained from calcined powders of bulk synthesis when  $C_0$  was 0.10 M and ethanol was used as the solvent. Almost all particle sizes are over 10  $\mu\text{m}$ , and the bigger ones are over 200  $\mu\text{m}$ . The sizes are irregular and very large compared with those of hydrothermal synthesis. Calcined powders are very rigid compared with hydrothermally synthesized MCM-41. The reason that the particle size prepared by solvent evaporation is bigger is as follows. The condition of synthesis is not water-rich but solvent-rich, and there is no precipitation before evaporation. During solvent evaporation, rapid arrays of inorganic species and organic surfactants result in rapid precipitation of the particle which is very rigid. Fig. 7(b) was obtained from calcined mesoporous film when  $C_0$  was 0.06 M and the solvent was ethanol. The film depos-

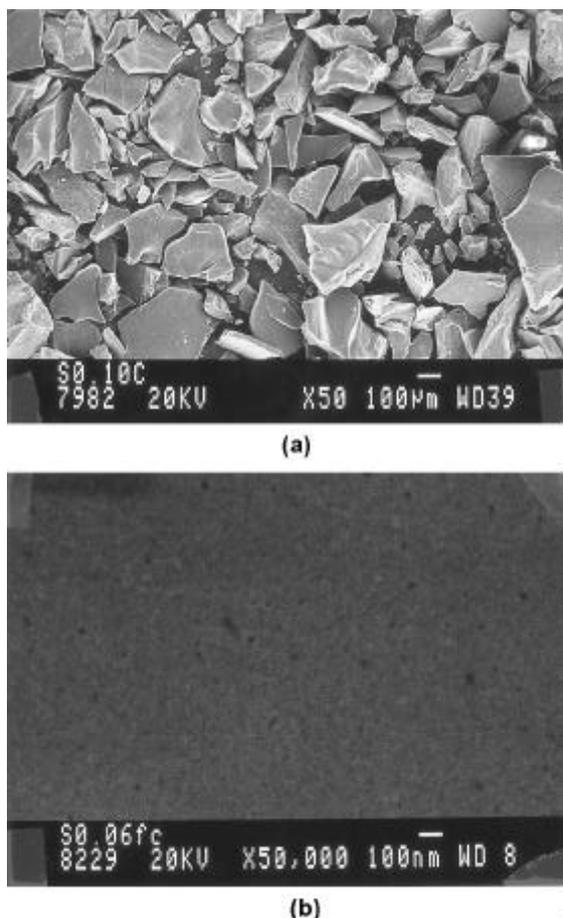


Fig. 7. SEM images of mesoporous silica ; solvent : ethanol (a)  $C_0=0.10$  M, bulk, calcined (b)  $C_0=0.06$  M, film, calcined.

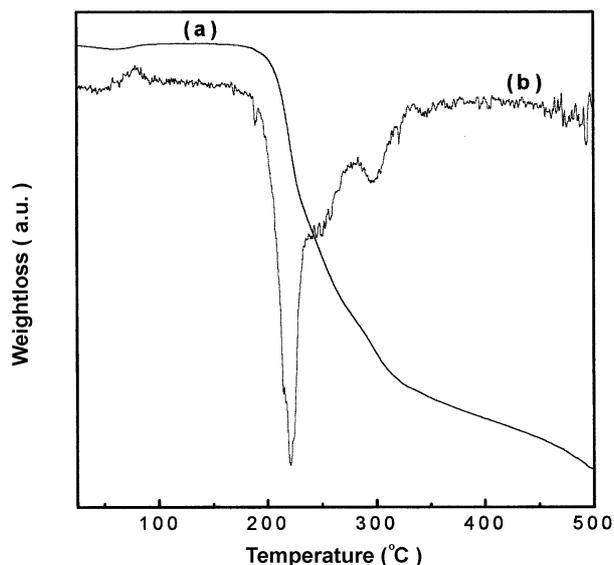


Fig. 8. Simultaneous thermal analysis of as-synthesized mesoporous silica, (a) TGA and (b) DTA ; solvent : ethanol ;  $C_0=0.10$  M ; bulk.

ited on the glass plate is transparent, which is like the result of Ryoo et al. [Ryoo et al., 1997b].

TGA and DTA of as-synthesized powder samples prepared with the condition that  $C_0$  was 0.10 M and ethanol was employed as solvent is illustrated in Fig. 8. This sample shows similar decomposition behavior with three distinct stages of weight loss. A first step up to 180 °C, a second on between 180 and 240 °C, and finally a third from 240 to 500 °C are clearly visible in the TGA diagram. The endothermic weight loss is due to the desorption of water. The second one, exothermic in nature, indicates the combustion and decomposition of the organic surfactants in air during the calcination. The third stage is related to water losses via condensation of silanol groups to form siloxane bonds and continuing loss of residual hydrocarbon. This result is similar to that of hydrothermally synthesized MCM-41, which is in good agreement with that of Stucky's group [Huo et al., 1994b].

According to the above results, it is assumed that the reaction of the micelle formation during the solvent evaporation proceeds as follows. At the refluxing step as is shown in Fig. 1, silicate oligomers are formed, and then CTAB is added to the solvent-rich solution where silicate oligomers are formed. As solvent evaporates, concentration of surfactant varies from initial surfactant concentration,  $C_0$  ( $\ll$  CMC) to  $C$  exceeding CMC. At CMC spherical micelle is formed, and above CMC rod-like micelle is made. It is confirmed that forced evacuation is necessary to form the mesopores of powders. But in the case of film formation, films were prepared at 1 atm, 20 °C without forced evacuation. So, it is suspected that solvent evaporation accelerates the interactions between inorganic silicates and organic surfactants. During the solvent evaporation, mesophases are formed by supramolecular self-assembly of organic-inorganic layer. Both in the bulk synthesis and the film formation, the solvent played an important role in the formation of mesophases. Without a solvent dilution step in the pro-

cedure mesophases did not appear. It is assumed that mesophase formation needs energy and energy is obtained by solvent evaporation. Furthermore, the energy of bulk synthesis is bigger than that of film formation. Bulk formation of powder needs forced evacuation in order to form mesophases by evaporating solvent, but in the case of film formation mesophases are formed without mechanical evacuation. The pathway to the synthesis of mesostructured surfactant-inorganic arrays involves condensation of cationic surfactant molecules with identically charged inorganic species because the preparation is done at acidic condition. This pathway is mediated by anionic ions of surfactant head groups ( $\text{Br}^-$ ) or chlorine anion from HCl solution ( $\text{S}^+\text{M}^-\text{T}^+$  where  $\text{M}^- = \text{Br}^-$  or  $\text{Cl}^-$ ).

The significant difference between bulk synthesis and film formation is attributed to the important difference in the preparation condition. The available time for the formation of mesophases is very short in the case of film formation (a few seconds), but is relatively long in the case of bulk synthesis (about 10 minutes). Short timescales significantly reduce the time available for aggregation, gelation, and aging compared with powder synthesis. Brinker et al. anticipated several consequences of the short timescale of the film deposition processes. There is little time available for reacting species to find low energy configurations, for the particles to order and for condensation reactions to occur. Thus the dominant aggregative process responsible for network formation may change from reaction-limited to transport-limited [Brinker et al., 1995; Nishida et al., 1995].

## CONCLUSIONS

The solvent evaporation method proved to be able to synthesize mesoporous materials both in bulk and film form. Mesoporous powders were successfully prepared with d-space value of (100)=30.6 Å, (110)=17.6 Å, (200)=15.6 Å and (100) intensity of 13,000 cps within 10 minutes. Mesoporous film was formed on the glass plate, and the phases were changed with respect to initial surfactant concentration,  $C_0$ . Enhancement in the rate of mesophase formation is ascribed to the driving force induced by the evaporation of solvent through controlling surfactant concentration exceeding CMC (Critical micelle concentration). Even if  $C_0$  is beyond the CMC, micelles are formed on account of the preferential evaporation of the solvent. So finally rodlike micelles are formed and then mesophases are formed. During evaporation, the role of solvent is to accelerate the supramolecular interactions between surfactant and silicate cation mediated with anion dissolved in the solvent. In the synthesis of powders, forced evacuation was indispensable to the formation of mesophases. The available time for the formation of mesophases is important. In bulk synthesis, the available time is sufficient to form the mesophases, but in the case of film formation, the available time is little for the particles to order. Non-covalent interactions, especially H-bonding, play an important role in the crystallization of mesoporous materials through the arrangement of surfactant-silicate assembly (e. g. alcoholic solvents such as methanol and ethanol).

## ACKNOWLEDGEMENT

This research was supported financially by the Ministry of Commerce, Industry and Energy (95-E-ID02-P-01) in Korea.

## REFERENCES

- Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. T., Chu, C. T.-W., Olson, D. H., Sheppard, E. W., McCullen, S. B., Higgins, J. B. and Schlenker, J. L., "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates," *J. Am. Chem. Soc.*, **114**, 10834 (1992).
- Brinker, C. J., Hurd, A. J., Schunk, P. R., Frye, G. C. and Ashley, C. S., "Review of Sol-Gel Thin Film Formation," *J. Non-Cryst. Solids*, **147**, **148**, 424 (1992).
- Bruinsma, P. J., Kim, A. Y., Liu, J. and Baskaran, S., "Mesoporous Silica Synthesized by Solvent Evaporation: Spun Fibers and Spray-Dried Hollow Spheres," *Chem. Mat.*, **9**, 2507 (1997).
- Calabro, D. C., Valyocsik, E. W. and Ryan, F. X., "In situ ATR/FTIR Study of Mesoporous Silicate Syntheses," *Microporous Mater.*, **7**, 243 (1996).
- Estermann, M., McCusker, L. B., Baerischer, C., Merroche, A. and Kessler, H., "A Synthetic Gallophosphate Molecular-Sieve with a 20-Tetrahedral-Atom Pore Opening," *Nature*, **352**, 320 (1991).
- Huo, Q., Margolese, D. I., Ciesla, U., Demuth, D. G., Feng, P., Gier, T. E., Sieger, P., Firouzi, A., Chmelka, B. F., Schuth, F. and Stucky, G. D., "Organization of Organic Molecules with Inorganic Molecular Species into Nanocomposite Biphase Arrays," *Chem. Mat.*, **6**, 1176 (1994a).
- Huo, Q., Margolese, D. I., Ciesla, U., Feng, P., Gier, T. E., Sieger, P., Leon, R., Petroff, P. M., Schuth, F. and Stucky, G. D., "Generalized Synthesis of Periodic Surfactant/Inorganic Composite Materials," *Nature*, **368**, 317 (1994b).
- Kim, C.-H. and Woo, S. I., "A Study on the Optimum Synthesis of Mesoporous Molecular Sieve, MCM-41," *HWAHAK KONG-HAK*, **35**, 135 (1997).
- Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C. and Beck, J. S., "Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism," *Nature*, **359**, 710 (1992).
- Lu, Y., Ganguli, R., Drewien, C. A., Anderson, M. T., Brinker, C. J., Gong, W., Guo, Y., Soyey, H., Dunn, B., Huang, M. H. and Zink, J. I., "Continuous Formation of Supported Cubic and Hexagonal Mesoporous Films by Sol-Gel Dip-Coating," *Nature*, **389**, 364 (1997).
- Nishida, F., McKiernan, J. M., Cunn, B., Zink, J. I., Brinker, C. J. and Hurd, A. J., "In Situ Fluorescence Probing of the Chemical Changes during Sol-Gel Thin Film Formation," *J. Am. Ceram. Soc.*, **78**, 1640 (1995).
- Ogawa, M. and Kikuchi, T., "Preparation of Self-Standing Transparent Films of Silica-Surfactant Mesostructured Materials and the Conversion to Porous Silica Films," *Adv. Mat.*, **10**, 1077 (1998).
- Park, S.-E., Kim, D. S., Chang, J.-S. and Kim, W. Y., "Photoluminescence Spectroscopic Monitoring in the Synthesis of Mesoporous Materials by Microwave-Induced Heating," *Stud. Surf.*

- Sci. Catal.*, **117**, 265 (1998a).
- Park, S.-E., Kim, D. S., Chang, J.-S. and Kim, W. Y., "Synthesis of MCM-41 Using Microwave Heating with Ethylene Glycol," *Catal. Today*, **44**, 301 (1998b).
- Ryoo, R., Ko, C. H. and Howe, R. F., "Imaging the Distribution of Framework Aluminum in Mesoporous Molecular Sieve MCM-41," *Chem. Mater.*, **9**, 1607 (1997a).
- Ryoo, R., Ko, C. H., Cho, S. J. and Kim, J. M., "Optically Transparent, Single-Crystal-Like Oriented Mesoporous Silica Films and Plates," *J. Phys. Chem. B*, **101**, 10610 (1997b).
- Sayari, A., "Catalysis by Crystalline Mesoporous Molecular-Sieves," *Chem. Mater.*, **8**, 1840 (1996).
- Stucky, G. D., Huo, Q., Firouzi, A., Chmelka, B. F., Schacht, S., Voigt-Martin, I. G. and Schuth, F., "Directed Synthesis of Organic/Inorganic Composite Structures," *Stud. Surf. Sci. Catal.*, **105**, 3 (1997).
- Wu, C.-G. and Bein, T., "Microwave Synthesis of Molecular Sieve MCM-41," *Chem. Commun.*, 925 (1996).
- Yang, H., Coombs, N., Sokolov, I. and Ozin, G. A., "Free-Standing and Oriented Mesoporous Silica Films Grown at the Air-Water Interface," *Nature*, **381**, 589 (1996a).
- Yang, H., Kuperman, A., Coombs, N., Mamiche-Afara, S. and Ozin, G. A., "Synthesis of Oriented Films of Mesoporous Silica on Mica," *Nature*, **379**, 703 (1996b).