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Investigation on the Drying Induced Phase Transformation of Mesoporous Silica; A Comprehensive Understanding toward Mesophase Determination

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Abstract: Phase transformation of mesoporous silica during the drying process is investigated. As-synthesized hexagonal *p6mm* obtained under the conditions used in this study is transformed to cubic *Ia*3*d* as drying proceeds, even at room temperature. Prolonged synthesis results in the formation of a well-ordered hexagonal mesophase, with almost no phase transformation. Drying at a higher temperature promotes the phase transformation of not only hexagonal to cubic, but also cubic to lamellar mesophases. Release of water is detected during drying, which is followed by the phase transformation of the mesophases. The phase transformations observed here proceed against the direction estimated on the basis of the state-of-the-art understanding. Here, considering the degree of silicate condensation and the amount of residual water in the as-synthesized mesoporous silica, a comprehensive explanation of mesophase determination is proposed including thermodynamic and kinetic aspects to account for the results observed here and those in the literature.

Introduction

Mesoporous silica is a series of materials that contain well-ordered and uniform-sized pores. It is generally synthesized in the presence of cationic or block-copolymer surfactant micelles in addition to a reactive source of silica. In 1990, Yanagisawa et al.[1] discovered a mesoporous material with a hexagonal mesophase; the material was synthesized using a long-chained, trimethyl quaternary ammonium cation and kanemite, a layered silicate compound. Two years later, Mobil researchers reported the M41s family of silicate mesoporous molecular sieves with an exceptionally large and uniform pore-structure.[2] Mesoporous silica has various types of mesophases because of the different interactions between silicate species and surfactant micelles as a template, and because of the shapes of the micelles. By changing the size and shape of the surfactant micelles, the structure and pore size of mesoporous silica can be individually controlled. Furthermore, the addition of a cosurfactant such as trimethylbenzene (TMB) can expand the pore size of the mesoporous silica. Due to the easily tunable pore size and ordered structure, mesoporous silica has attracted considerable interests toward many kinds of applications. The presence of ordered pores in the mesoporous range makes mesoporous silica a promising candidate not only for catalysts, adsorbents, and

separation membranes, as has already been demonstrated during the past decade, but also for hosts or molds for functional molecules and nanoparticles.

Various earlier works have elucidated the formation mechanism of mesoporous silica and its structure can now be controlled to some extent. As for the synthesis mechanism of mesoporous silica, an LCT (liquid-crystal templating) mechanism has been proposed, since its structure is similar to the lyotropic liquid-crystal phase of the surfactant.[3] But the fact that very low concentrations of surfactant also produce mesoporous silica seems to support the mechanism of cooperative organization of inorganic silica species and surfactant micelles.[4]

Packing Parameters. As the parameter that determines the structure of mesoporous silica, Huo et al. have proposed a packing parameter.[5] The packing parameter "*g*" is defined as $g = V/(a_0l)$, where *V* is the total volume of surfactant chains plus any cosolvent organic molecule between chains, a_0 is the effective headgroup area at the micelle surface, and *l* is the kinetic surfactant tail length or the curvature elastic energy. This *g* factor originates from geometric constraints in the self-assembly of hydrocarbon amphiphiles.[6] The curvature of the silicate wall is at last determined to optimize the charge balance between the silicate and surfactant micelles. Accordingly, the size, shape, and charge (pH of the solution) of a surfactant used

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for synthesis can be the phase-determining parameters from a *thermodynamic* point of view.

Charge-Density Matching. Along with the *g* parameter, a charge-density matching concept has also been proposed to account for the changes in mesophases.[7] When silicate is highly charged depending on pH of the solution, a high density of counter-charged surfactant is required to balance the charges. This high density is most effectively accomplished by a silicate structure having a low curvature at the silicate/surfactant interface. Thus, the surfactant headgroup area determines the overall composite structure. Because silicate is dehydrated and condensed to decrease the negative or positive charge density of the silicate network, this concept involves the effects of silicate condensation on the mesoporous silica phase. To maintain the charge-density balance at the interface, the surfactant must pack to form a high surface curvature by increasing the effective headgroup area, which results in a larger a_0 value, and, therefore, a smaller *g* value. Then, mesoporous silica having a higher surface curvature becomes more favorable as silicate condensation proceeds.

Phase Transformation. With regard to the *g* parameter and the concept of charge-density matching, most of the phase transformation observed previously[8−15] has been comprehensively understood.

Hexagonal *p6mm* to Lamellar. In situ XRD measurements have clarified that the hexagonal *p6mm* structure, which was synthesized using a 20-carbon surfactant at room temperature, transforms into a lamellar structure when heated in water.[8] This phenomenon has been explained with respect to the packing parameter. At room temperature, the *g* value is presumed to be 1/2 because of hexagonal *p6mm* periodicity. As the material is heated, however, the conformational disorder of the surfactant tail is enhanced, increasing the effective molecular volume and a corresponding increase in the *g* value. Phase transformation then proceeds from hexagonal to lamellar.

Very recently, the same mesophase transformation was observed using in situ scanning microcalorimetry to determine the thermal energetic process during synthesis.[9] To hydrothermally restructure the inorganic/organic composites, high temperature where a melting transition of the surfactant tails and reorganization of the surfactant occur is needed as an external force from the system of silicate/surfactant solution.

Lamellar to Hexagonal *p6mm*. Phase transformation from lamellar to hexagonal *p6mm* has also been reported.[8] When a lamellar phase synthesized using cethyltrimethylammonium (16-carbon quaternary ammonium surfactant) cations as well as TMB as a cosurfactant was heated under hydrothermal condi-

tions, a transformation to hexagonal *p6mm* was observed. This transformation has also been rationalized in terms of the packing parameter. TMB is known to cause swelling at the hydrophobic regions of liquid crystal structures. Because the TMB molecules associate with the hydrophobic surfactant tail, the *g* value is reduced due to the enhancement of the surfactant volume without increasing the headgroup area or the tail length. The swelled geometry results in composites with a lamellar structure, indicating a larger *g* value. When the composite is suspended in water for hydrothermal treatment, a large concentration gradient is formed initially because a significant amount of TMB exists in the hydrophobic region of the composite, and there is essentially no TMB in the aqueous phase. The solubility of TMB in the aqueous phase increases rapidly with increasing temperature, and the hydrothermal treatment then leads to the release of TMB from the composite into the aqueous phase. This change lowers the value of *g*, resulting in the transformation to the hexagonal *p6mm* mesophase.

The same transformation from lamellar to hexagonal *p6mm* has been reported in response to acidification of a strongly basic medium of silicate with a surfactant.[10] The transformation has been proposed to occur due to the reactivity of the silicate species, which increases with the increasing acidity of the reactant gel to further aggregate the uncondensed silicate.

Hexagonal *p6mm* to Cubic *Ia3d*. Landry et al.[11] have reported that hexagonal *p6mm* is changed into cubic *Ia3d*, the direction of which is opposite to the one expected by the packing parameters, by heating it to 150 °C. Hexagonal *p6mm* composites were synthesized using cethyltrimethylammonium cations (CTA$^+$), and an in situ XRD measurement was then performed. Some of the peaks that appear during the phase transformation can be indexed to a lamellar phase, whereas most of the peaks correspond to those of a cubic *Ia3d* structure. This transformation has been proposed to proceed via a cylinder-merging or cylinder-branching mechanism.

Hexagonal *p6mm* to Cubic *Pm3n*. Che et al.[12] have reported that cubic *Pm3n* mesoporous materials are synthesized by transformation of the once-formed hexagonal mesophase. The rate of transformation depends on the structure and amount of additive TMB isomers. Furthermore, using high-resolution TEM, they have found that the phase transformation is epitaxially promoted, meaning that the silica mesophase is topologically restructured along the cylinder axis of the hexagonal and that the newly generated cubic mesophase is grown on the hexagonal phase. To account for this transformation, they considered the charge-density matching mechanism. Polymerization of the silicate species occurs during the synthesis, causing the positive charge density of the silicate network to decrease. To maintain the charge-density matching at the interface, the surfactant packs to form micelles with a high surface curvature. Therefore, transformation to the *Pm3n* cubic phase is considered to occur.

Cubic *Pm3n* to Hexagonal *p6mm*. Liu et al.[13] have observed that a phase transformation occurs from cubic *Pm3n* to hexagonal *p6mm*, in the direction of which the packing concept could not be explained, during drying the precipitates. They explained this phase transformation based on the nature of the surfactant micelles. As the solvent evaporates, surfactant is concentrated, which then favors the formation of rod-shaped instead of spherical micelles. Concomitantly, the mesoporous silica is reorganized around the rod-shape micelle, forming a

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hexagonal mesophase. The cubic *Pm3n* is considered to be a thermodynamic product of silica around the spherical micelles. They indicated that silicate condensation also affects this transformation.

Recently, in situ time-resolved small-angle X-ray scattering was performed during the synthesis of mesoporous silica thin film in an aqueous/alcohol solvent.[14] Lamellar and hexagonal mesophases were found as intermediates to the final cubic *Pm3n* mesophase. At the air interface, lamellar mesophase was formed, with spherical micelles then being formed underneath the lamellar phase to organize the 3-D hexagonal mesophase. The hexagonal phase was subsequently rearranged into discontinuous cubic mesophase. This process progressed toward the substrate interface, with the whole process occurring within the water-rich period range. In their latest report,[15] humidity maintained during the drying process was hypothesized as being an important factor for the mesophase transformation. The water content is a critical parameter, and poorly ordered, 2-D hexagonal, and 3-D cubic final structures are obtained depending on the humidity, in agreement with the *g* laws of mesophases.

Thus far, phase transformation of mesoporous silica has been explained based only on the concept of packing parameters. As described, however, some phenomena cannot be explained by these conventional rules alone; therefore, there is an urgent need for a comprehensive explanation of the phase transformation of mesoporous silica. There have been much fewer investigations of the effects of the synthesis process on the formation of mesoporous silica. Some recent reports as shown above, however, have indicated that elements of the synthesis process, including the synthesis period, drying, stirring, and so on, influence the structure of mesoporous silica. It is therefore important to understand the effects of such process conditions on mesophase evolution. In the present study, we focused on the drying procedure of as-synthesized mesoporous silica, as drying is one of the most important factors in determining the structure of mesoporous silica. On the basis of our investigation, we provide a comprehensive overview of silicate condensation and drying, and discuss the influence of drying procedures on the structure of mesoporous silica.

Experimental Section

Materials. The following materials were used for the synthesis: tetraethyl orthosilicate (TEOS, >96.0%, Tokyo Kasei Kogyo (TCI)), 1- bromohexadecane (>96%, TCI), triethylamine (>99.0%, TCI), acetone, and nitric acid (35%, Wako). The chemicals mentioned here were used without further purification.

Synthesis of Mesoporous Silica. Cetyltriethylammonium bromide (CTEABr) was synthesized by the reaction of cetylbromide ($C_{16}H_{33}$-Br) with triethylamine ((C_2H_5)$_3$N); $C_{16}H_{33}$Br was added to (C_2H_5)$_3$N dissolved in acetone. The resultant mixture was stirred for 1 week in an Erlenmeyer flask. The product was separated by filtration and dried under vacuum for several hours at 60 °C. ^{13}C MAS NMR results suggested that $CTEA^+$ was successfully obtained.

Mesoporous silica was synthesized using CTEABr as the surfactant micelles and TEOS as a silica source in the presence of HNO_3 and water, in accordance with the literature.[12] The synthesis was performed as follows. The surfactant, distilled water, and HNO_3 were mixed to obtain a homogeneous solution, which was cooled to 0 °C prior to the addition of TEOS. Typically, 0.25 g of CTEABr, 0.83 g of HNO_3, and 10.3 g of distilled water were mixed and cooled for at least 1 h in an ice bath. After this cooling period, 1.0 g of TEOS precooled to 0 °C for at least 1 h in an ice bath was added to the reaction mixture, whereas

the mixture was being stirred. The final hydrogel composition was $1.0SiO_2$: $0.13CTEABr$: $0.96HNO_3$: $125H_2O$. The mixture was stirred for 10 min in the ice bath and then allowed to react at 0 °C under static conditions for a desired period of 3, 6, 12, or 24 h. The resultant white precipitates were then centrifuged to collect the as-synthesized mesoporous silica. The obtained samples were dried in air at room temperature on a glass plate and also under controlled conditions.

Characterization. Powder X-ray diffraction (XRD) patterns were recorded with an M03X-HF (MAC Science) using CuKα radiation (40 kV, 20 mA) at a rate of 0.15 deg/min over a range of 1.5−6.0 deg (2 theta). The samples were prepared on a glass plate.

A simultaneous powder XRD (RINT-ULTIMA+, Rigaku)-differential scanning calorimetry (DSC, DSC8230, Rigaku) was carried out with using CuKα (40 kV, 50 mA) radiation at a scanning rate of 1.0 deg/min over a range of 1.8−4.8 deg (2 theta). The heating rate of the DSC measurement was 1.5 K/min, and the measurement was performed in air. Thermogravimetry (TG)-differential thermal analysis (DTA) and mass spectroscopy (MS) were carried out using a TG8120 (Rigaku) equipped with M-QA200TS (ANELVA). Samples were put on an alumina holder. The heating rate was 5 K/min, and the measurement was performed in 10%O_2/He.

Results and Discussion

Drying at Room Temperature. The structures of mesoporous silica have previously been controlled primarily by changing the initial conditions of synthesis such as the surfactants, pH, or solution compositions. Still, little attention has been paid to the effects of the drying of obtained precipitates on the mesophase of silica. In the present study, we observed the influence of drying on as-synthesized mesophase. XRD patterns of the obtained samples after drying are summarized in Figure 1. The XRD measurements were carried out after centrifugation, which is described as "as-synthesized", and after drying for 1, 2, 3, 6, and 24 h at room temperature. The diffraction of the as-synthesized sample in Figure 1a was assigned to the hexagonal *p6mm* mesophase. The pattern was obviously changed, as drying proceeded even at room temperature for 1 h, indicating that the mesophase of silica is transformed during drying. The diffraction patterns after drying for 1 h shown in Figure 1a correspond to the cubic *Ia3d* mesophase. The main diffraction peak of the 2 h-drying sample sharpened slightly compared to the 1 h-drying sample. After this period, the XRD patterns were hardly changed. The same phenomenon was also observed on the samples synthesized for 6 h, as shown in Figure 1b.

In Figure 1c, the diffraction pattern for the as-synthesized sample indicates a highly ordered hexagonal *p6mm* mesophase, and those after drying indicate cubic *Ia3d*. However, the peak intensity of the cubic (220) plane was very small although the intensity of the main peak (211) remained high. The second peak became more intense with prolonged drying, indicating that a cubic *Ia3d* structure was gradually evolving. Such a slow transformation can be more clearly observed in Figure 1d; in this case, the hexagonal *p6mm* mesophase was maintained for a longer period. It can also be noted that all diffraction peaks in Figure 1d appear broader than those of the other samples, indicating that the sample has a disordered structure. These results obviously suggest that the as-synthesized mesophase is changed during drying, from the hexagonal *p6mm* mesophase transforming to cubic *Ia3d*. This phase transformation leads to a larger *g* value, which cannot be rationalized by the rule of charge-density matching.

Effects of Silica Condensation. In all cases, the samples dried for more than 3 h included the cubic *Ia3d* mesophase. As
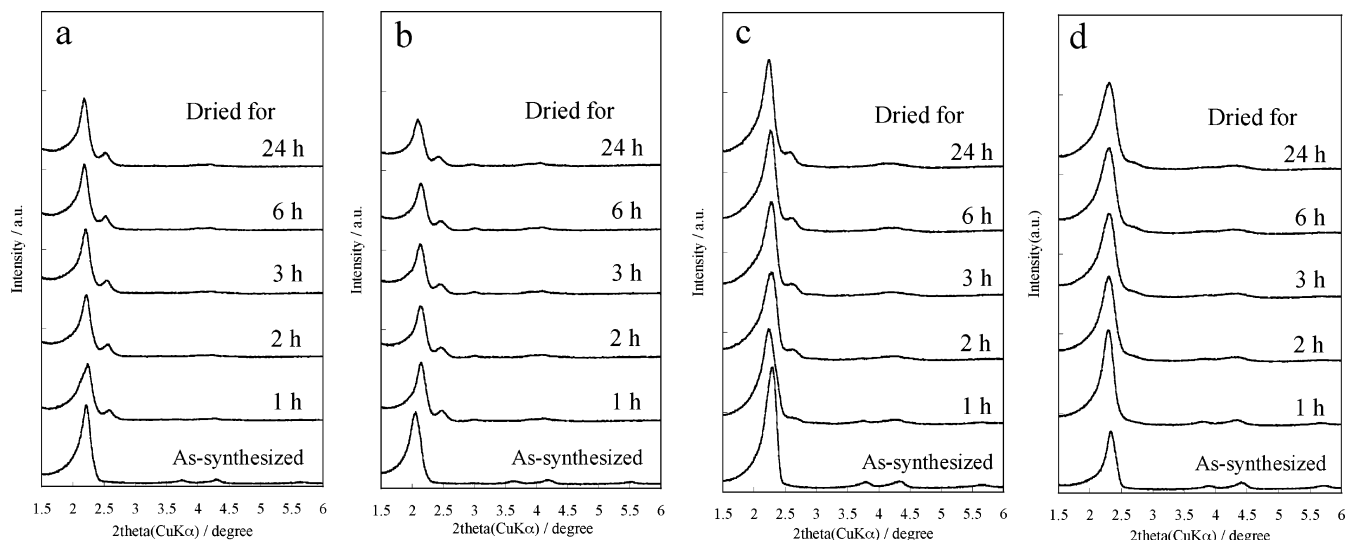
Figure 1. Mesophase transformation during drying of the samples synthesized at 0 °C for 3 h(a), 6 h(b), 12 h(c), and 24 h(d). The samples were dried at room temperature for each period noted in the figure.

discussed before, hexagonal mesophases synthesized for 3 and 6 h seem to transform smoothly into the cubic mesophase. On the other hand, the mesophase transformation in the sample synthesized for 12 h occurred over a longer period. These results indicate that the mesophase transformation strongly depends on the flexibility of the silicate network, as has been observed in the preparation of mesoporous silica film by a rapid evaporation method.[16] Considering the results for the mesoporous silica synthesized for 24 h, which consisted of a less-ordered cubic *Ia3d* mesophase, the silica wall appears to be too rigid to transform into another mesophase.

Drying at High Temperature. In the previous reports, mesophase transformation, or mesophase determination, has been considered thermodynamically by using the *g* parameter; but it is sometimes kinetically hindered by the limited mobility of surfactant micelles in the polymerized silicate network.[16] In such a case, a certain activation energy from the exterior to the interior system is required to overcome the kinetic barrier. Mesoporous silica sometimes changes its structure on drying at a higher temperature, showing that thermal energy promotes the phase transformation according to thermodynamic rules. Therefore, temperature variation in the procedures of synthesis and drying might lead to the different route of transformation from that observed at room temperature.

We investigated the effects of drying at high temperature, and the XRD patterns of the samples are illustrated in Figure 2, where Figure 2a shows the patterns of the samples dried at 60 °C and Figure 2b shows those of samples dried at 100 °C just after centrifugation. These two figures also show the effects of the synthesis period on the mesophase of silica. The diffraction pattern of the 3 h-synthesized sample has two broad peaks. Although it is difficult to determine its structure from these two broad peaks, they are similar to that of cubic *Ia3d* mesoporous silica. Accordingly, it can be inferred that this XRD pattern is derived from a partially disordered cubic *Ia3d* structure. The diffraction pattern of the 6 h-synthesized sample exhibits almost the same character, but a more disordered cubic structure. In contrast, the 12 h-synthesized sample shows sharp

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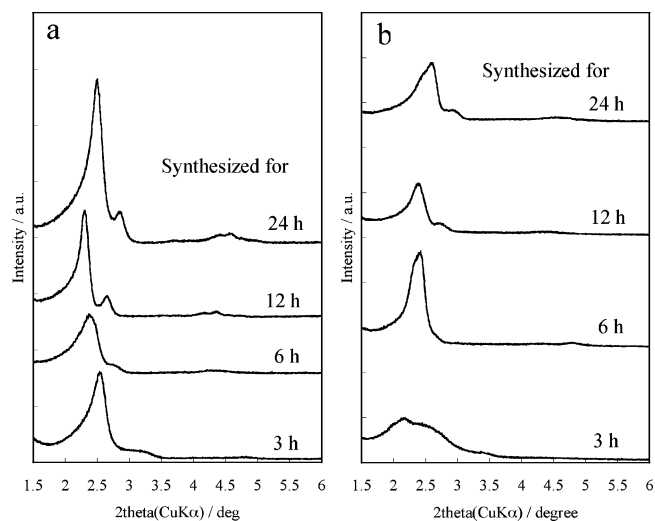
Figure 2. Effect of drying temperature on mesophase determination. The samples were synthesized at 0 °C for each period and then dried at 60 °C(a) or 100 °C(b) for 24 h.

peaks that are consistent with that of the cubic *Ia3d* mesophase. The 24 h-synthesized sample also has sharp peaks, indicating a highly ordered structure of cubic *Ia3d*.

In contrast, the diffraction patterns of the samples dried at 100 °C are totally different; the diffraction of the 3 h-synthesized sample shown in Figure 2b has one broad peak, indicating that the sample has an almost entirely disordered structure due to the silicate network being too weak to endure high temperatures. The pattern for the 6 h-synthesized sample has two peaks at 2.5 and 4.8 deg with a 1:2 lattice, which is characteristic of a lamellar mesophase. The sample synthesized for 6 h is expected to consist of a more rigid silicate network than that synthesized for 3 h. This result clarifies that, at high temperatures, mesoporous silica tends to transform into a lamellar mesophase, which has the largest *g* value. The appropriate flexibility of the silicate network allows mesoporous silica to transform from hexagonal *p6mm* to lamellar mesophase, presumably through an intermediate cubic *Ia3d* mesophase.

Drying at a high temperature of 100 °C after prolonged synthesis for more than 12 h resulted in the formation of two

Table 1. Mesophase Determined by Synthesis and Drying Conditions

drying period/h	drying temperature	synthesis period/h	3	6	12	24
0	as-synthesized		hexagonal	hexagonal	hexagonal	hexagonal
1	room temperature		cubic	cubic	hexagonal	hexagonal
2	room temperature		cubic	cubic	cubic	hexagonal + cubic
3	room temperature		cubic	cubic	cubic	hexagonal + cubic
6	room temperature		cubic	cubic	cubic	hexagonal + cubic
24	room temperature		cubic	cubic	cubic	hexagonal + cubic
24	room temperature + 100 °C		lamellar	lamellar	cubic	cubic(disordered)
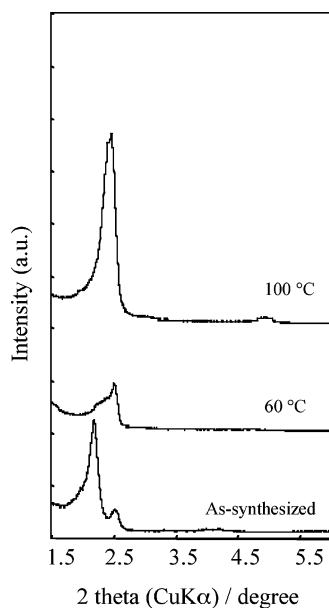
Figure 3. XRD patterns of the samples synthesized for 3 h and dried at room temperature for 24 h, and followed by drying at each temperature.

Figure 4. Mass spectra of the gaseous compounds released from the as-synthesized mesophase, which was kept at room temperature.

slightly broadened peaks that can be assigned to a partially disordered cubic *Ia3d* structure. In this case, similar phenomena would occur, but rather broader diffractions were observed compared to those shown in Figure 2a. These results indicate that a temperature of 100 °C is too high for these samples to maintain stable mesostructures.

Figure 3 shows the XRD patterns of the samples synthesized for 3 h and dried at 60 °C or 100 °C after initially drying at room temperature for 24 h. The XRD pattern of the 100 °C-dried sample has two sharp peaks whose *d* spacing are in the ratio 1:2, indicative of a lamellar mesophase. This figure indicates that mesoporous silica changes its structure to make its *g* value larger even after being dried at room temperature for 24 h. It should be noted that the sample dried at a higher temperature exhibits sharper diffractions, although the sample dried at a lower temperature appears to have mixed cubic and lamellar mesophases.

It is clear from Figures 2 and 3 that the mesophases are transformed because they have a hexagonal array before drying. The mesoporous silica dried at 60 °C has a cubic *Ia3d* mesophase. In contrast, the width of the X-ray diffraction peaks, which gives a measure of mesophase periodicity, depends largely on the synthesis period. In the case of drying at 100 °C, the mesophases show an apparently different dependence on the synthesis period: The sample synthesized for 3 h had a disordered structure, that synthesized for 6 h showed a lamellar mesophase, and those synthesized for 12 and 24 h had a cubic

Ia3d mesophase. The overall tendency for the samples is to transform their mesophases in the direction of a larger *g* value, with various dependencies on the synthesis period and drying temperature. All of the XRD patterns shown in Figure 2a are considered to show a cubic *Ia3d* mesophase, whereas the samples synthesized for 3 or 6 h exhibit a broad diffraction, meaning that their structures contain disordered mesophases. In contrast, the samples synthesized for a longer period showed a sharp diffraction, indicative of a highly ordered structure. This difference in the degree of mesophase periodicity is caused by the flexibility of the silicate network. As the synthesis is prolonged, silicate condensation proceeds, making the silicate network rigid. When the rigidity in the silicate network is not so high, the surfactant micelles destroy the silicate wall of the samples, leading to a relatively disordered structure.

The effect of drying at high temperatures on mesophase transformation is summarized in Table 1. The results of a 6 h-synthesis are almost the same as those of a 3 h-synthesis. The sample before drying has a cubic *Ia3d* mesophase, and that dried at 60 °C exhibits broad diffractions, while that dried at 100 °C shows a sharp XRD pattern derived from a lamellar structure.

The sample synthesized for 12 h before drying has a cubic *Ia3d* mesophase. Although the sample dried at 60 °C has a disordered structure, the XRD pattern of the sample dried at 100 °C demonstrates a cubic *Ia3d* mesophase. These results indicate that no phase transformation occurs on this sample. The silicate network in the sample synthesized for a longer period is more rigid than that synthesized for a shorter period because of the silicate condensation, as suggested by NMR studies.[16] These results therefore indicate that silicate condensation, which is directly correlated with the flexibility of the silicate network, is also a dominating factor in the phase transformation/determination of mesoporous silica. In the case of a 24 h-synthesis, all of the XRD patterns showed rather broad
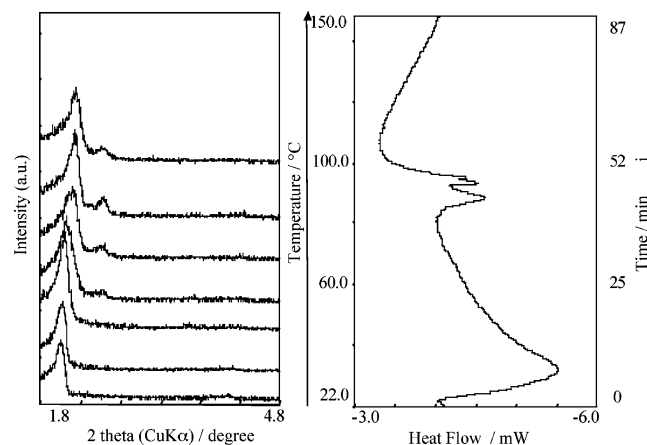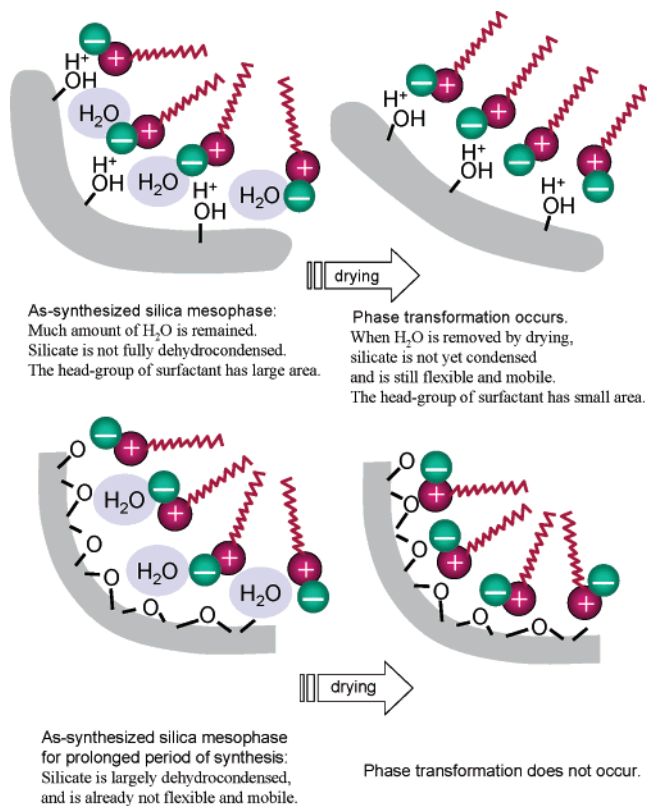
Figure 5. XRD-DSC in situ measurement for the mesophase during drying.
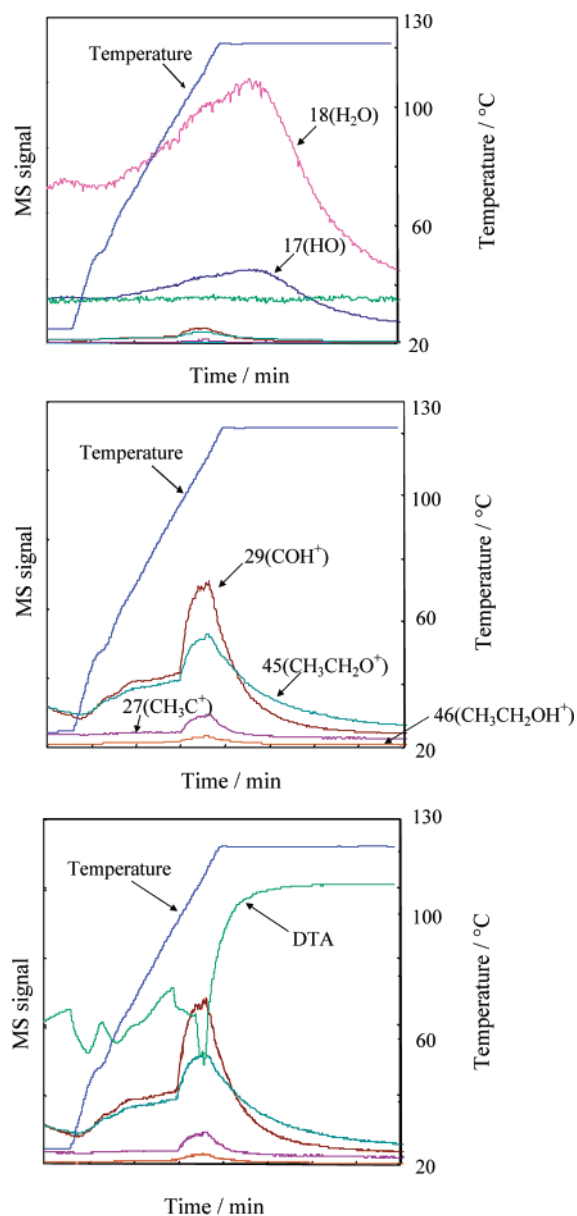
Figure 6. Mass spectra of the gaseous compounds released from the mesophase and DTA measurement for the mesophase during drying.
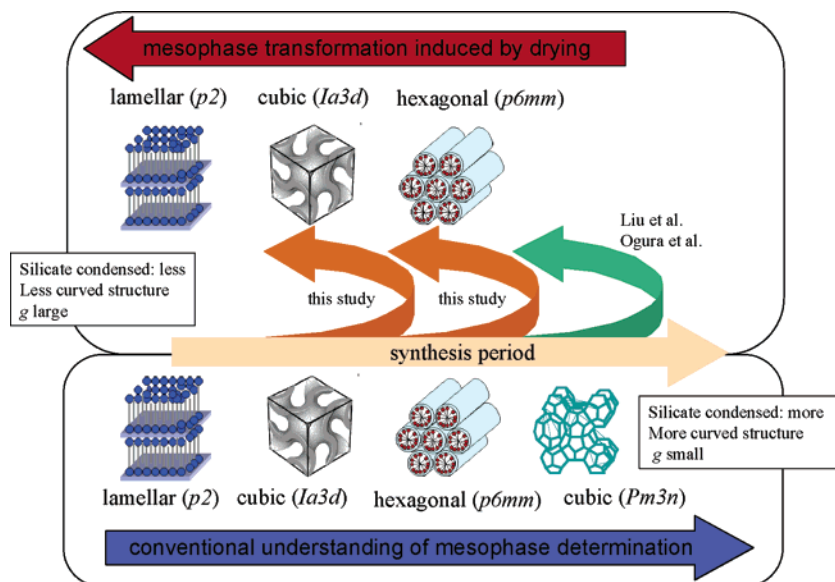

Figure 7. Illustration for the surfactant molecules and silicate in the determined mesophase.

deduced, along with a consideration of the silicate wall flexibility, that the samples cannot transform into an ordered structure.

In Situ Detection of Phase Transformation by XRD-DSC-MS and TG-DTA-MS. To elucidate the details of the phase transformation mechanism of mesoporous silica during drying, it is important to determine the compounds released from mesoporous silica during the drying process. In the present study, the as-synthesized sample was kept at room temperature in the TG chamber with flowing air, and released molecules were detected. The observed mass spectra are shown in Figure 4. These results clarify that H_2O molecules were released from mesoporous silica during drying at room temperature. Ethanol, which is generated by TEOS hydrolysis, was also released during drying. Judging from the mass spectra, the amount of evaporated ethanol is considered to be less than that of H_2O. Water evaporation can therefore be concluded as one of the driving forces for the phase transformation.

To determine the relationship between the phase transformation of mesoporous silica and the evaporation of water, an in situ XRD-DSC measurement was performed, as shown in Figure 5. Simultaneous detection of heat flow generated by water evaporation and mesophase diffraction provided some information regarding changes in the mesoporous silica structure. In the DSC results, two endothermic peaks were observed, one around 35 °C and the other around 95 °C. The first peak could be assigned to the heat flow from the evaporation of physisorbed water. The XRD patterns suggested that the hexagonal *p6mm* to cubic *Ia3d* phase transformation proceeded after the first endothermic peak. This result indicates that the phase transfor-

peaks, likely because the samples already had a relatively disordered structure before drying. Accordingly, it can be

Figure 8. Comprehensive insight into the phase transformation of silica mesophase.

mation of mesoporous silica is closely related to water evaporation.

When much water exists around TEOS, the main reaction would be condensation between hydroxyl groups, originating from the hydrolysis of TEOS. However, this reaction seems to be exothermic. It should also be noted that the second endothermic peak did not affect the structure of mesoporous silica. The evaporation temperature of ethanol is lower than that of water, so the possibility of vaporization of remaining ethanol in the mesoporous silica structure can likely be ignored. Therefore, as water evaporation proceeds, residual $-OH$ and $-OC_2H_5$ would react directly, thus causing the second endothermic peak.

The mass spectra obtained during TG measurement are shown in Figure 6. H_2O was primarily released from mesoporous silica at low temperature, while ethanol was primarily released around 100 °C. As described above, phase transformation occurs around 50 °C. No characteristic feature except the start of the release of H_2O could be observed around 50 °C from MS spectra. The endothermic peaks were detected around the same temperatures as observed in the DSC measurement. This result supports the hypothesis discussed above.

Proposed Comprehensive Mechanism of Phase Transformation. As described in the Introduction section, Liu et al. have discovered that cubic *Pm*3*n* mesoporous silica transforms into hexagonal *p6mm* mesoporous silica.[13] This transformation also proceeds toward a larger *g* value. They have explained that this phase transformation is well in accordance with the tendency of the micelles to change in shape from spherical to rod-type as the amount of solvent decreases. This phase transformation can actually be explained, however, using the packing parameter. It is possible that the phase transformation in this study occurs in the same manner as that observed by Liu et al., in that the *g* value directs to a large value. As described above, the phase transformation of mesoporous silica is closely related to water evaporation. But what favors the reconstruction of mesoporous silica with a larger *g* value? Totally from the perspective of phase transformation, two key factors are involved; one is the flexibility of silicate, and the other is the amount of H_2O molecules remaining in the silicate

mesophase. On the basis of these factors, a speculative illustration is proposed in Figure 7.

Mesoporous silica just after separation from the synthesis solution contains a large amount of H_2O. H_2O molecules should exist near the hydrophilic part of the surfactant, that is between the headgroup of the surfactant micelles and the silicate wall. The confinement of H_2O molecules in the hydrophilic region of the surfactants results in an enlargement of the effective headgroup area, leading to a reduced *g* value. As water evaporation proceeds, the H_2O molecules are taken away from the spacing area, causing a decrease in the effective headgroup area and thus a larger *g* value. The whole view of mesophase transformation is illustrated in Figure 8. According to our conventional understanding, the mesophase can be determined by the charge density of silicate against surfactant micelles, which is limited in shape by the conventional *g* parameter. As for each mesophase determination and transformation, the mobility of surfactant micelles is an important point, as has been suggested by Tolbert et al.[8] However, the transformation is sometimes hindered kinetically because the surfactant micelles are surrounded by silicate, and the flexible nature of silicate depends on the degree of silicate condensation; therefore, the reactivity of silicate is also required for the mesophase transformation, as has been suggested.[10-12] During the synthesis of mesoporous silica thin film, rapid solvent evaporation leads to a similar transformation, with silicate condensation being controlled by humidity,[14,15] or by the quenching of silicate species as they are synthesized.[16] In such a case, an energetic process is required to transform such a rigid structure.[9] Mesophase transformation is then induced by drying or heating at high temperatures. Force from an external system of silicate/surfactant aqueous solution affects the kinetically hindered transition, leading to a different route of mesophase transformation, which is sometimes in opposition to the direction suggested by the conventional packing rule. The critical criteria for transformation are silicate flexibility and the number of H_2O molecules involved at the hydrophilic headgroup area of surfactant for the confinement of surfactant micelles.

The results of the present study elucidate the effects of the drying process on the determination of silica mesophases. The

results obtained here provide us a comprehensive understanding of the effects of synthesis and drying procedures on the final structure of mesoporous silica based on packing parameters and charge-density matching rules with introducing kinetic hindrance caused by silicate condensation. These results will enable us to control the whole synthesis process to obtain desired silica mesophases.

Conclusions

Phase transformation of mesoporous silica during the drying process was found to proceed even at room temperature. As-synthesized hexagonal *p6mm* obtained under the conditions employed was transformed to cubic *Ia*3*d* as the drying period increased. Prolonged synthesis resulted in the formation of a well-ordered hexagonal *p6mm* mesophase; phase transformation was hardly observed. The flexibility of silicate, which correlates well with the degree of silicate condensation, plays an important role in determining the final mesophase. Drying at higher temperatures promotes the phase transformation not only from hexagonal *p6mm* to cubic *Ia*3*d*, but also from cubic *Ia*3*d* to a lamellar mesophase.

The direction of the phase transformation observed here, with the mesophase tending toward a larger *g* value, is in opposition to the one suggested by the packing-parameter rule. XRD-DSC and DTA-MS observations indicate that the phase transformation is closely related to water evaporation from the mesophase.

During drying, mesophase transformation was observed immediately after the release of water. The as-isolated mesoporous silica just after separation from the synthesis solution contains a large amount of water, which exists near the hydrophilic part of the surfactant. This arrangement causes a larger effective headgroup area, which in turn produces a smaller *g* value. As water evaporation proceeds, the H_2O molecules are taken away from the area, and a smaller effective headgroup area is attained, leading to a larger *g* value. This is the thermodynamic aspect of drying process. Water content in as-synthesized mesoporous silica, as well as the degree of silicate condensation, is an important factor in determining the direction of the phase transformation. Comprehensively, confinement of silicate and surfactant micelles should thermodynamically determine the final mesophase, but the final form of mesophase is also influenced by the flexibility of silicate based on kinetic factors.