Determination of Silica Mesophases by Controlling Silicate Condensation in Liquid Phase

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A different comprehension from the conventional packing rule is discussed on the formation of films of *Pm*3*n*: a 3-D cubic mesoporous silica phase, SBA-1, followed by the mesophase of *p*6*mm*: a 2-D hexagonal mesoporous silica, SBA-3, where the phase is determined by the degree of silicate condensation.

Since the discovery by Yanagisawa et al.[1] and Kresge et al.,[2] mesoporous silica has been widely investigated, and has been considered as a host material for electronic and optical devices, a low-k material, separation membranes, and so on. Furthermore, recent innovation in this field includes mesoporous materials, the wall of which is composed of not only silica but also other oxides such as TiO_2 and metal phosphates.[3] In addition, mesoporous carbon was fabricated by use of mesoporous silica as a replica.[4] The strict controls of the mesophases, the pore mouths opening and the dimensional direction of porous structures, are significantly important for their practical applications. Basic understanding concerning the formation mechanism of mesophase has been elucidated so far. One of the clear explanations for the determination of final mesophase is based on a g factor,[5] which shows a local packing effectiveness. This g factor is originated from geometric constraints in self-assembly of hydrocarbon amphiphiles,[6] and is demonstrated by the following equation: $g = V/(a_0L)$, where V, a_0, and L represent the total volume of surfactant and organic molecules if added, the effective head group area at the micelle surface, and the kinetic surfactant tail length or the curvature elastic energy, respectively. The curvature of silicate wall is at last determined to optimize a charge balance between silicate and surfactant molecules. Accordingly, the size, the shape, and the charge (pH of the solution) of a surfactant used for synthesis are the phase-determining parameters in a *thermodynamic* point of view. Many researches on phase selectivity and phase transition have been accounted for with the packing parameter.[7] In this study, we will report on a phase determination of mesoporous silica film by controlling silica condensation in a *kinetic* point of view. The phase selection observed in this study into *Pm*3*n*: a 3-D cubic or *p*6*mm*: a 2-D hexagonal was not dominated with the rule of the packing parameter, which indicates that a mesophase with a lower g value is preferable to form.

Preparation of mesoporous silica film was in accordance with the method reported by Ogawa, et al.;[8] that is, a rapid solvent evaporation method. Tetramethylorthosilicate (TMOS) as a silica source, hydrochloric acid (HCl) as an acid catalyst, and octadecyltrimethylammonium chloride (C_{18}TAC) as a surfactant were used for the syntheses. Typically, 3 g of TMOS was mixed with 1.26 g of distilled water and 150 µL of 0.1 M HCl aqueous solution, and stirred at 0 °C for 75 min. To this mixture, 10 mL of 0.25 M C_{18}TAC aqueous solution was poured while stirring for an adequate period. The final composition of the precursor solution was Si: $0.125C_{18}$TAC: 0.0008HCl: $29H_2O$. A drop of the precursor solution was spread on a glass substrate by a spin coater at the spinning rate of 3000 rpm, and then dried at 70 °C in a petri dish. Characterization of the obtained silica film was carried out by means of XRD using Cu Kα, and the silicate species before coating on the substrate was evaluated by ^{29}Si NMR spectroscopy.

Figure 1 shows the film products with various aging periods of silicate before the coating on the substrate. By using a drop soon after the mixing of the silicate solution with C_{18}TAC, a 3-D cubic SBA-1 (*Pm*3*n*) was formed after rapid drying at 70 °C. A slight prolonged period of aging, 20 min in this study, led to the formation of another phase together with SBA-1. Calcination revealed that the newly evolved phase is a 2-D hexagonal SBA-3 (*p*6*mm*). A further prolonged period resulted in SBA-3 in a single phase. Upon considerations of the g factor and a charge density matching theory, SBA-1 should be formed by phase transformation of SBA-3.[5,7a]

The solution was clear before coating, indicating that TMOS was almost fully hydrolyzed. Even after mixing with C_{18}TAC, the solution kept its clearness. The silicate species in the liquid phase was evaluated by ^{29}Si NMR, as summarized in Figure 2. As indicated, silicate species composed of a Q^2 unit at around −90 ppm was mainly observed before C_{18}TAC addition. It suggests that there exists a chain-like linear silicate species in the solution. Small amounts of Q^1 at −80 ppm as a chain-end group and Q^3 at −100 ppm as a chain-branching position, were also found by the cross polarization method. The chemical shift and the intensity hardly changed during the accumulation of

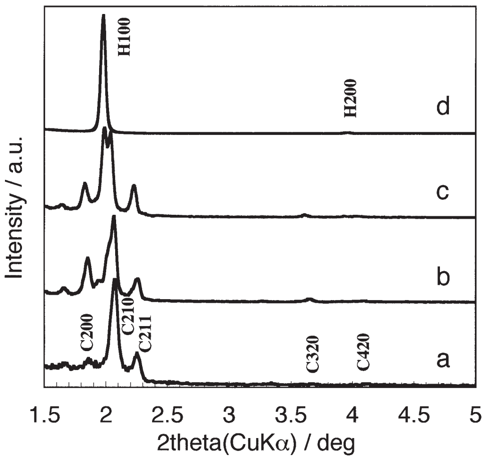

Figure 1. XRD patterns of mesoporous silica film on glass substrate. Silicate solution after mixing C_{18}TAC surfactant was stirred at 0 °C for (a) 10 min; (b) 20 min; (c) 40 min; and (d) 80 min, spun coated, and dried at 70 °C. **C**: cubic *Pm*3*n* SBA-1; **H**: hexagonal *p*6*mm* SBA-3.

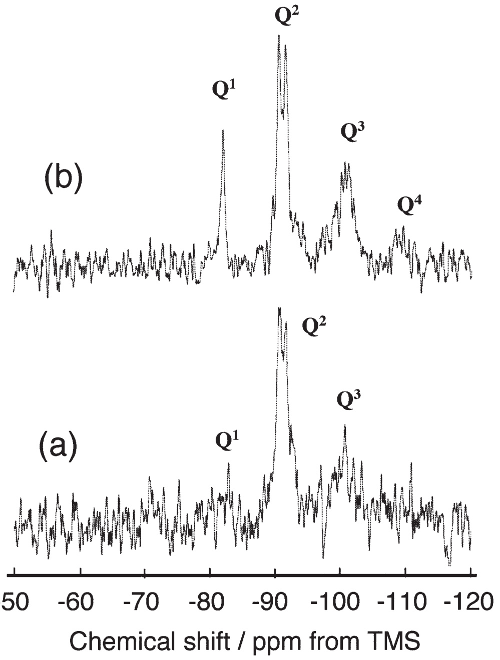

Figure 2. ^{29}Si NMR for the silicate aqueous solution (a) after stirring for 75 min at 0 °C; (b) after adding $C_{18}TAC$ and stirring for 80 min at 0 °C. Measurements were carried out at 53.45 MHz decoupled, and the sample temperature was kept at 15 °C with rotation 10 Hz, and the pulse width, repetition period, and accumulation were 13.5 μs, 1 s and 500 scans, respectively.

the NMR measurement. Then, $C_{18}TAC$ was mixed with the silicate solution. The spectrum for the silicate sample after mixing for 80 min showed Q^3 and Q^4 at around −100 and −110 ppm, respectively, along with the Q^2 unit and a Q^1 unit at −82 ppm. As accumulation increased, the relative intensities for Q^3 and Q^4 increased. Silicate structure with $C^{18}TAC$ facilitates condensation even in the clear liquid phase.

The formation and selection mechanism proposed here from these observation are illustrated in Figure 3a. Before the addition of the surfactant, a soluble silicate in the liquid phase kept a chain-like structure under the reaction conditions. Prolonged aging of silicate solution results in further polymerization of the silicate into a sheet-like structure. It is reasonable to consider that a sheet-like silicate shows less flexibility than a chain-like structure. The phase selection into SBA-1 or SBA-3 observed in this study is not accounted for by the rule of the charge density matching induced by condensation of silicate.[7a] In the conventional synthesis, the phase selection could be explained by the charge matching, as illustrated in Figure 3b: the silicate wall of SBA-3 shows a higher charge density than that of SBA-1, resulting in a smaller curvature of SBA-3. In contrast, a rapid evaporation of solvent results in formation of solidized (less flexible) silica which well reflects the former structure in the liquid. The structure is frozen (thermodynamically metastable) and further change is kinetically hindered. A more flexible structure facilitates to form a more curved structure. As a result, SBA-1 can be obtained before the silicate becomes more rigid. The *g* values of surfactant micelles for *Pm*3*n* cubic mesophase and *p*6*mm* hexagonal mesophase are 1/3 and 1/2, respectively;[5] namely, as for the products, SBA-3 has a larger *g* value than SBA-1. Therefore, the phase determination observed in this study into SBA-1 or SBA-3 is not dominated with the rule of the packing parameter, which indicates that a mesophase with a lower *g* value is preferably formed.

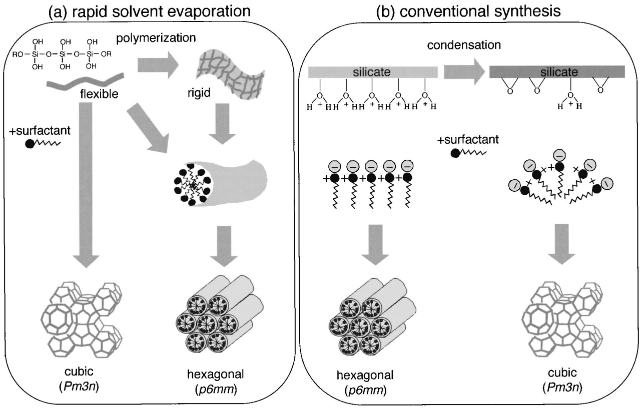

Figure 3. Formation of mesoporous silica SBA-1 (*Pm*3*n*) and SBA-3 (*p*6*mm*) by rapid solvent evaporation (a) and conventional synthetic (b) methods.

Well-ordered and organized structures might be attained during the following drying process, because normally higher chemical shifts of Q^3 and Q^4 were observed in the final products of hexagonal structures.[7b,7e] A phase transformation induced by drying will be discussed in the upcoming results which will appear in the nearest future.

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