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Synthesis of Thermally Stable and 2-D Hexagonal Super-Microporous Silica from Hydrated α -Sodium Disilicate

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Thermally stable and 2-D hexagonal super-microporous silicas were obtained utilizing hydrated α -sodium disilicate over a diverse range of surfactant/Si molar ratios. Silica-based mesostructured materials composed of hydrated α -sodium disilicate and hexadecyltrimethylammonium (C_{16} TMA) cations were acid-treated, resulting in the formation of 2-D hexagonal mesostructured silica(α)- n ($n = C_{16}$ TMA/Si molar ratio). Although the 2-D hexagonal structure of mesostructured silica(α)-0.2 collapsed at 900 °C, those of mesostructured silicas(α)-0.5, -0.7, and -1.0 were retained even after calcination at 1000 °C. The retention of the 2-D hexagonal structures was confirmed further by TEM. The higher thermal stability is ascribed to lower Na content in mesostructured silica(α)- n . Higher C_{16} TMA/Si molar ratios lowered the pH values in the reaction suspensions, and then interlayer Na ions in the silicates were further exchanged with hydrated protons. Because of the higher thermal stability, ordered super-microporous silicas can be formed in the present system. The condensation of the silicate frameworks proceeded with the rise of the calcination temperature, leading to a further decrease in pore size. The pore sizes of the products calcined at 1000 °C were 1.7–1.8 nm (BJH method), smaller than those reported for ordered mesoporous silicas prepared using C_{16} TMA cations.

Introduction

Since the beginning of the 1990s, a huge number of studies on surfactant-templated mesoporous materials has been reported. In the very initial stage, silica–organic mesostructured materials were prepared by the reaction of a layered polysilicate kanemite ($NaHSi_2O_5 \cdot 3H_2O$) with organoammonium cations,^{1,2} and calcination of those materials yielded porous silicas with tunable mesopores (denoted as KSW-1 at a later stage³). The reports on M41S mesoporous silicas by the Mobil group^{4,5} triggered extensive research on this type of materials.

Soluble silicate species such as TEOS and sodium silicates have mainly been used as the silica sources for synthesizing

mesoporous silica.^{4,5} However, mesoporous silica derived from kanemite is superior to those derived from soluble silicate species in thermal and hydrothermal stabilities⁶ as well as catalytic activities,⁷ and the formation mechanisms between them are different.⁸ Structurally different mesoporous silica, named KSW-2, can also be obtained from kanemite through another synthetic route.³ An intercalation compound composed of kanemite-derived individual silicate sheets and hexadecyltrimethylammonium (C_{16} TMA) cations⁹ is transformed into silica-based mesostructured materials containing fine 1-D squared mesopores by acid treatment.³ This reaction uses surfactant assemblies, but the periodic porous structures are not defined by the geometrical packing of C_{16} TMA molecules. The structure is only observed for the unique kanemite system. Therefore, the formation of mesoporous silicas from other layered polysilicates is quite interesting and should contribute to the development of mesoporous materials with designed local environments containing parent polysilicate structures.

Recently, we have succeeded in the synthesis of mesoporous silica from hydrated α -sodium disilicates, which has

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a different single-layered silicate structure.¹⁰ Compared to kanemite, hydrated α -sodium disilicate plays a role in making the volume occupied by the headgroup of C_{16} TMA cations larger. Therefore, the reaction of hydrated α -sodium disilicate with C_{16} TMA cations tends to form 2-D hexagonal mesostructured materials (named SSW-2 here) in a diverse range of the C_{16} TMA/Si molar ratio (C_{16} TMA/Si = 0.2–1.0), and a slightly disordered phase (named SSW-1) can be obtained at higher C_{16} TMA/Si molar ratios (≥ 2.0). However, the 2-D hexagonal mesostructures of SSW-2-type materials collapsed on calcination for template removal because the condensation degree in the silica network is low.

In the present study, the improvement of the structural stability can be accomplished by the acid treatment of the ordered SSW-2-type mesostructured silicas as in the case of FSM-16.¹¹ Then, thermally stable up to 1000 °C and 2-D hexagonal super-microporous silica (the pore size is in the range of 1–2 nm) was synthesized, although the wall thickness was thin and the condensation degree was relatively low.

From the viewpoint of potential applications such as precise molecular recognition, adsorption chemistry, drug delivery, and inclusion chemistry, the synthesis of ordered super-microporous silicas has strongly been demanded. There have already been several reports on the formation of ordered super-microporous silicas through silica–surfactant mesostructured materials.^{12–24} Lately, Iwamoto et al. reported that pore size has a major effect on the catalytic activity for the acetalization of cyclohexanone.²⁵ The report describes that the catalytic activity is maximized at around 1.9 nm in diameter. The improvement of thermal stability is also vital to the industrialization of mesoporous materials, and many groups have tried to prepare thermally stable mesoporous silicas. The techniques to increase the stability include the increase of wall thickness, high framework condensation, and a lowering of the Na content in the framework.^{6,26–35}

However, to the best of our knowledge, porous silica containing both these characteristics (super-microporosity and high thermal stability) with relatively thin walls has not been reported yet.

Experimental Procedures

Synthesis of Mesostructured Silica(α)-*n*. On the basis of our previous report,¹⁰ wet slurries of hydrated α -sodium disilicate were added to aqueous solutions (0.1 M) of hexadecyltrimethylammonium chloride (C_{16} TMACl) with the C_{16} TMA/Si molar ratios of 0.2, 0.5, 0.7, and 1.0. The suspensions were stirred at 70 °C for 3 h and then centrifuged. The precipitates were dispersed into distilled water, and the pH values of the suspensions were adjusted to 8.5 by adding 2 N HCl. After the stirring was continued at 70 °C for 3 h, the mixtures were then centrifuged, washed with distilled water, and dried at 80 °C for 24 h to form mesostructured silica(α)-*n* ($n = C_{16}$ TMA/Si) (SSW-2). A 2-D hexagonal mesostructured precursor for FSM-16 was also synthesized for comparison.¹¹

Comparison of Thermal Stability of Mesostructured Silica(α)-*n*. Mesostructured silica(α)-*n* and the mesostructured precursor for FSM-16 were calcined at 900, 1000, and 1100 °C for 6 h in an ambient air (heating rate: 5 °C min⁻¹). The temperature precision of a muffle furnace was calibrated using gold (melting point: 1064 °C), and the fluctuation of temperature was within ± 10 °C.

Characterization. Powder X-ray diffraction (XRD) patterns were recorded on Mac Science MXP3 (Cu K α) and M03XHF22 (Fe K α) diffractometers with a scanning speed of 2° min⁻¹. Solid-state ²⁹Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were measured by a JEOL CMX-400 spectrometer, using a resonance frequency of 79.4 MHz, a rotation speed of 5 kHz, an accumulation of 500–800 scans, a pulse delay of 100 s, and a pulse angle of 45°. Tetramethylsilane was used as a reference (0 ppm). Nitrogen adsorption–desorption isotherms were obtained by a BELSORP 28SA (Japan Bel Co.), and samples were outgassed at 120 °C under 10⁻² mmHg for 3 h prior to the measurements. Specific surface areas, pore volumes, and pore size distributions were calculated by the BET (Brunauer–Emmett–Teller) method,³⁶ the *t*-plot method, and the BJH (Barrett–Joyner–Halenda) method³⁷ using adsorption branches. Transmission electron microscopic (TEM) images were taken by a JEM-2010EX electron microscope (JEOL) at an accelerating voltage of 200 kV. Powdery samples were dispersed in acetone and mounted on Cu microgrids. The compositions were determined by ICP (inductively coupled plasma) spectrometry and CHN. ICP analysis was performed with an IRIS-AP spectrometer (Jarrell Ash), and samples were prepared by a melting method with lithium metaborate. CHN analysis was performed by using a PE-2400II instrument (Perkin-Elmer).

Results and Discussion

Synthesis of Mesostructured Silica(α)-*n* and Thermal Stability. The XRD patterns of mesostructured silica(α)-*n*

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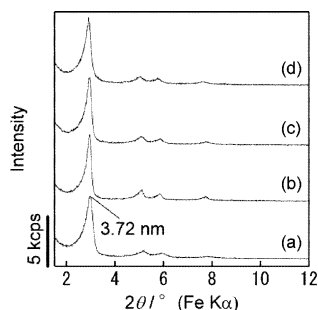


Figure 1. XRD patterns of mesostructured silica(α)- n ; n = (a) 0.2, (b) 0.5, (c) 0.7, and (d) 1.0.

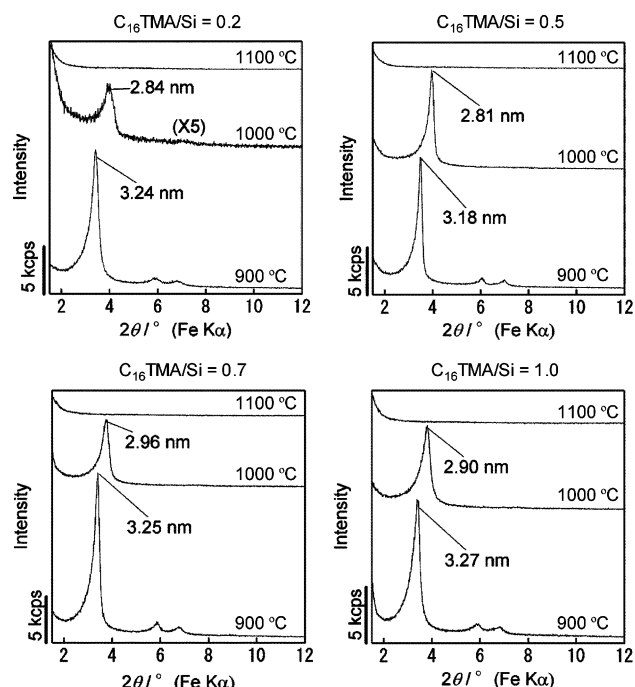


Figure 2. XRD patterns of mesostructured silica(α)- n calcined at 900, 1000, and 1100 °C; n = 0.2, 0.5, 0.7, and 1.0.

are shown in Figure 1. Four diffraction peaks characteristic of a 2-D hexagonal structure were observed for the pattern of each mesostructured silica(α)- n (n = 0.2, 0.5, 0.7, and 1.0). In these mesostructured silica(α)- n , the d_{100} values were in the range of 3.7–3.8 nm and the $Q^4/(Q^3 + Q^4)$ ratios were ca. 0.49 calculated from the ^{29}Si MAS NMR data (figures not shown). In all the mesostructured silica(α)- n , the ^{29}Si MAS NMR data revealed that the condensation degree in the silicate frameworks is quite similar. The d_{100} values of mesostructured silica(α)- n after acid treatment (3.7–3.8 nm) are smaller than those observed for mesostructured silica(α)- n before acid treatment (3.9–4.0 nm).¹⁰ These results imply that the silicate frameworks are condensed during the acid treatment.

The thermal stability of the acid-treated SSW-2-type materials was investigated. The XRD patterns of mesostructured silicas(α)- n calcined at 900, 1000, and 1100 °C are shown in Figure 2. In mesostructured silica(α)-0.2, four peaks characteristic of a 2-D hexagonal structure were preserved after calcination at 900 °C. Only one broad peak corresponding to the (100) plane and higher order diffractions was not observed at 1000 °C, indicating the deformation of the 2-D hexagonal structure. In mesostructured silicas(α)-0.5, -0.7,

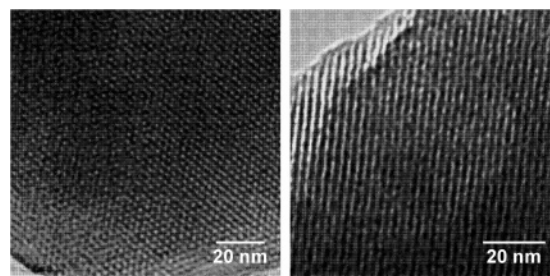


Figure 3. TEM images of the product obtained after calcination of mesostructured silica(α)-0.7 at 1000 °C.

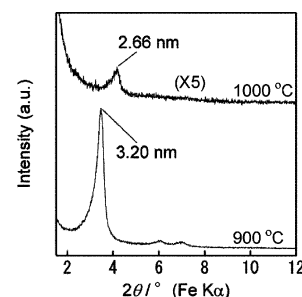


Figure 4. XRD patterns of FSM-16 calcined at 900 and 1000 °C.

and -1.0, four diffraction peaks characteristic of 2-D hexagonal structures were preserved at 900 °C. These diffraction peaks were still observed even after calcination at 1000 °C, although higher order diffraction peaks were barely detectable by high power XRD measurement (figure not shown), suggesting that the 2-D hexagonal structures were retained but that the structural integrity was lowered under the harsh conditions. The TEM images of mesostructured silica(α)-0.7 calcined at 1000 °C are shown in Figure 3. A highly ordered 2-D hexagonal structure, which accords with the sharpness of the diffraction peaks in Figure 2, was observed. The average distance between the pore centers is 3.3 nm, which nearly corresponds to the XRD result ($d_{100} \times (2/\sqrt{3}) = 3.4$ nm).

The thermal stability of the mesostructured precursor for FSM-16 was also investigated. The XRD patterns of the products calcined at 900 and 1000 °C are shown in Figure 4. Although four peaks characteristic of the 2-D hexagonal structure were preserved after calcination at 900 °C, only one broad peak corresponding to the (100) plane and no higher diffraction peaks were observed at 1000 °C, showing that the 2-D hexagonal structure almost collapsed at 1000 °C. Until now, several reports have been published with varying descriptions of the thermal stability of FSM-16. For instance, the mesostructure of FSM-16 was reported to be stable up to 800 °C under vacuum.^{7,38} FSM-16 in this paper has the same thermal stability up to 900 °C as reported by Inagaki.³⁹ The divergence of the thermal stability data would depend on the synthesis conditions.

From these results, it was confirmed that the structural stability of SSW-2-type mesostructured materials derived from hydrated α -sodium disilicate is improved by the acid treatment. Mesostructured silica(α)-0.2 was stable up to 900

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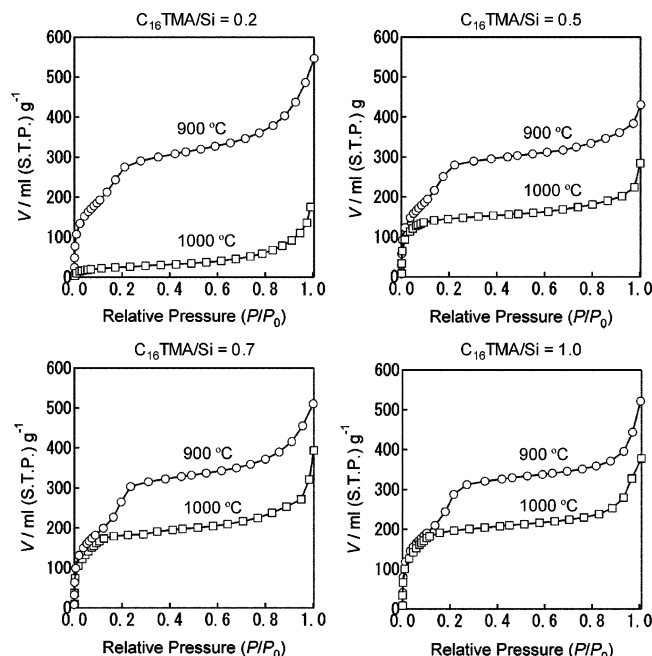


Figure 5. N_2 adsorption isotherms of mesostructured silica(α)- n calcined at 900 and 1000 °C; $n = 0.2, 0.5, 0.7$, and 1.0.

Table 1. Structural Properties of Mesostructured Silica(α)- n Calcined at 900 and 1000 °C Determined by XRD and N_2 Adsorption Data

n	calcination temperature/°C	BET specific surface area/ $m^2 g^{-1}$	pore volume/ $cm^3 g^{-1}$	pore size ^a /nm	wall thickness ^b /nm
0.2	900	860	0.39	2.2	1.5
	1000	92			^c
0.5	900	767	0.45	2.2	1.5
	1000	517	0.20	1.7	^c
0.7	900	891	0.44	2.3	1.6
	1000	705	0.23	1.8	^c
1.0	900	866	0.46	2.3	1.6
	1000	796	0.27	1.7	^c

^a Calculated from the BJH method. ^b Wall thickness = $2/\sqrt{3} - d_{100}$; pore size, d_{100} = XRD(100) interplanar spacing. ^c Not calculated because only one broad peak assignable to d_{100} appeared, and the 2-D hexagonal structure was not confirmed.

°C, whereas mesostructured silicas(α)-0.5, -0.7, and -1.0 were stable up to 1000 °C. The pore size of the resultants after calcination at 1000 °C was 1.7–1.8 nm, which is in the range of a super-micropore. The highly ordered 2-D hexagonal structure with super-micropores is preserved after calcination at 1000 °C. This is the superiority of the use of hydrated α -sodium disilicate, that is the ability to form 2-D hexagonal structures in the diverse range of $C_{16}TMA/Si$ molar ratios, which cannot be realized for another sodium disilicate such as kanemite.

Formation of Super-Microporous Silica via Condensation of Silanol Groups. The nitrogen adsorption–desorption isotherms of the products calcined at 900 and 1000 °C are shown in Figure 5. The porosities calculated from the adsorption data are summarized in Table 1. Type IV isotherms, which are typical for samples with uniform mesopores, were observed for all the mesostructured silica(α)- n calcined at 900 °C, whereas type I isotherms characteristic of adsorption in micropores or super-micropores were observed after calcination at 1000 °C.⁴⁰ The change of the isotherm type by the rise of the calcination temperature reveals that the

condensation of the silicate frameworks proceeded and then the pore size decreased. The pore sizes of the products calcined at 900 and 1000 °C were in the range of 2.2–2.3 and 1.7–1.8 nm, respectively. Although the pore sizes calculated by the BJH method³⁷ are considered to be underestimated,^{38,40,41} the BJH method is commonly used in many other reports for determining pore sizes of this range and most suitable to compare the present system with others. In this paper, therefore, the BJH method was used for comparison of the pore size with those using same surfactants in other reports.

It has been recognized that the control of pore size in the range of super-micropore is relatively difficult. Taking advantage of the high thermal stability of mesostructured silicas(α)-0.5, -0.7, and -1.0, 2-D hexagonal super-microporous silicas were formed via further condensation of the silicate frameworks in this paper. However, in other reports, mesostructured silicas formed with $C_{16}TMA$ did not lead to the formation of super-micropores after calcination even when they were calcined at 1000 °C.^{42–45} This is because hydrothermal treatment was performed to increase the condensation degree, and the number of silanol groups reduced. As a result, the condensation during calcination does not tend to occur. Moreover, the hydrothermal treatment can cause an increase of the pore size.^{42,46} For simultaneous achievement of two characters such as high thermal stability and super-microporosity, mesostructured silicas are needed to have sufficient thermal stability with the condensation degree as low as possible. The $Q^4/(Q^3 + Q^4)$ ratios are ca. 0.49 in mesostructured silicas(α)- n , and this condensation degree is lower than those reported for other mesostructured precursors that are stable up to 1000 °C. For example, the $Q^4/(Q^3 + Q^4)$ ratio for thermally stable mesostructured silica prepared by using fumed silica as a silica source is 0.77.⁴³ Consequently, the formation of super-micropores was only realized through the calcination of the well-designed precursor at 1000 °C in this study.

Na Content in Silicate Framework and Thermal Stability of Mesostructured Silica(α)- n . This section discusses why the thermal stabilities of mesostructured silicas(α)-0.5, -0.7, and -1.0 were improved. The following factors have mainly been considered to influence the thermal stability of mesostructured silica: wall thickness,^{26–30} framework condensation,^{6,31–33} and Na content.^{34,35}

The wall thicknesses calculated from XRD and nitrogen adsorption data were 1.5–1.6 nm in all the SSW-2-type materials calcined at 900 °C (Table 1). Because of the fact that the pore sizes from the BJH method are considered to be underestimated, the real wall thicknesses may be even thinner. However, the wall thicknesses are compared rela-

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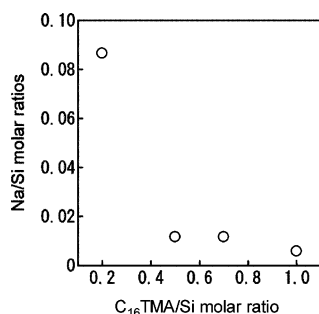


Figure 6. Na/Si molar ratio in mesostructured silica(α)- n with the starting C₁₆TMA/Si molar ratio.

tively by the same criterion in this paper, so that the argument can be reasonable. From these data, we can say that the difference of the thermal stability shown in Figure 3 does not result from the wall thicknesses and the condensation degrees in the silicate framework. The estimated wall thicknesses of 1.5–1.6 nm are thicker than that of mesoporous silica calcined at 550 °C (ca. 1 nm) because the framework condensation proceeds as the calcination temperature rises, which leads to the formation of thicker walls.

The Na content in mesostructured silica(α)- n is shown in Figure 6. The Na/Si molar ratio was 0.09 for mesostructured silica(α)-0.2 and ca. 0.01 for mesostructured silicas(α)-0.5, -0.7, and -1.0. The improvement of the thermal stability of mesostructured silica(α)- n is attributable to less Na content in the silicate frameworks. Pauly et al. investigated the hydrothermal stability of several MCM-41. They reported that the Na content in the silicate frameworks has an effect on hydrothermal stability and that less Na content in the frameworks leads to higher hydrothermal stability.³⁴ Mokaya also reported that the thermal stability of restructured Na-free MCM-41 is higher than that of restructured Na-containing MCM-41.³⁵ A similar trend is shown for the mesostructured silicas before acid treatment at pH 8.5 (Supporting Information, Figure S1), showing that not the acid treatment but the reaction conditions between hydrated α -sodium disilicate and C₁₆TMA resulted in the difference in the Na/Si molar ratio of mesostructured silica(α)- n .

Difference of Na Content in Mesostructured Silica(α)- n . The effects of varying the Na/Si molar ratio in mesostructured silicas(α)- n are clarified. C₁₆TMA cations and protons are able to ion exchange with Na ions in the synthetic process. The difference of the starting C₁₆TMA/Si molar ratios did not influence the C₁₆TMA/Si ratios in mesostructured silica(α)- n (C₁₆TMA/Si = ca. 0.17). Ion-exchange of Na ions with C₁₆TMA cations does not lead to the formation of mesostructured silica(α)- n with different Na contents. The pH values of the reaction suspensions are shown in Figure 7. The increase of the starting C₁₆TMA/Si molar ratios leads to the lowering of pH values because the relative amount of surfactant solution (pH ca. 5.5) over Si increased. The lower the pH of the solution is, the higher the concentration of protons is. Consequently, the ion exchange of Na ions with protons tends to occur in the solutions with higher C₁₆TMA/Si molar ratios. Therefore, the decrease in the Na/Si molar ratio can be caused by the ion exchange of Na ions with protons.

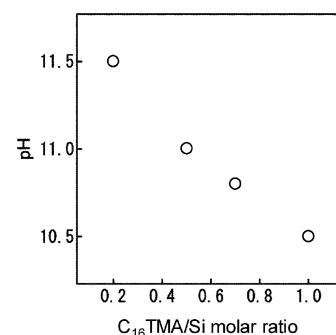


Figure 7. pH value in the reaction suspensions with the starting C₁₆TMA/Si ratio.

Control of the Na content was attempted in the synthetic stages preceding the formation of the mesostructure. Hydrated α -sodium disilicate in this paper (Na/H/Si = 1.2/0.8/2.0) is obtained as follows.¹⁰ One gram of α -Na₂Si₂O₅ was dispersed in 50 mL of water, and the mixture was stirred for 30 min. Here, by repeating this procedure 3 times, hydrated α -sodium disilicate with Na/H/Si of 0.9:1.1:2.0 was obtained. Using this as a silica source, mesostructured silica(α)-0.2 was synthesized. The idea is to synthesize mesostructured silica(α)- n with a lower Na content regardless of the starting C₁₆TMA/Si molar ratios. However, four peaks characteristic of a 2-D hexagonal structure were not observed in the XRD pattern. A diffraction peak derived from unreacted hydrated α -sodium disilicate was observed at around $2\theta = 11.6^\circ$ (Supporting Information, Figure S2). The control of Na in this stage of hydrated α -sodium disilicate synthesis does not lead to the formation of a 2-D hexagonal structure.

The control of Na content was also tried by the post acid treatment. After mesostructured silica(α)-0.2 was synthesized, the pH value of the reaction suspension was adjusted to 7.0 or 5.0, and the stirring was continued further for 3 h at 70 °C. The Na/Si molar ratio in the mesostructured materials was 0.08 for both of the resultants. These were stable up to 900 °C but not at 1000 °C as found for mesostructured silica(α)-0.2 (Supporting Information, Figure S3). Consequently, the Na content was not decreased by the posttreatment. The difficulty of ion exchange of Na ions with protons is due to the following two reasons. One is that Na ions exist within the silica walls and the other is that pores are filled with surfactants in this case.

On the basis of these results, we can say that it is important to control the Na content during the formation of silica–organic mesostructured materials to improve the thermal stability. The presence of Na ions within the silicate frameworks promotes the coarsening and densification of silica under hydrothermal conditions.^{34,47,48} Sodium ions trapped in the silicate frameworks cannot be eliminated by ion exchange easily, and therefore, it is important to prepare mesostructured silicas with a low Na content for retaining mesostructures of silica(α)- n . Although the same method was employed for the formation of FSM-16, the compatibility between the decline in the Na content and the retention of

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the 2-D hexagonal structure was impossible because the reaction of kanemite with low Na content and C₁₆TMA surfactant does not lead to the formation of a 2-D hexagonal phase (a lamellar mesophase is formed), and Na ions cannot be removed during acid treatment.

Uniqueness of the System using Hydrated α -Sodium Disilicate. The high thermal stability of mesostructured silicas(α)-0.5, -0.7, and -1.0 may be due to the partial retention of the silicate structure of hydrated α -sodium disilicate. Hydrated α -sodium disilicate can mainly form a 2-D hexagonal structure in the C₁₆TMA/Si molar ratios of 0.2–1.0,¹⁰ although the formation of the 2-D hexagonal structure without a byproduct is obtained from kanemite only in the C₁₆TMA/Si molar ratio of 0.2. Because the pH values of the reaction suspensions in mesostructured silicas(α)-0.5, -0.7, and -1.0 were lower than that in mesostructured silica(α)-0.2 and FSM-16, the silicate does not tend to dissolve during the synthesis of mesostructured silicas(α)-0.5, -0.7, and -1.0. Hydrated α -sodium disilicate has originally a crystalline structure,^{49,50} and its retention in mesostructured silica(α)- n may also contribute to the improvement of the thermal stability, although it is not sufficiently proved. The partial retention of the silicate structure is also suggested by the physical properties of the calcined products. No reports have described that a mesostructured material is stable up to 1000 °C despite the thin wall thickness (1.5–1.6 nm) and the low condensation degree in mesostructured silica(α)- n ($Q^4/(Q^3 + Q^4) = \text{ca. } 0.49$). Mokaya reported that the stability of mesostructured material is not simply due to their thicker walls but that it may also be related to the pore wall stabilization by recrystallization of the framework.⁴⁵

Conclusions

Mesostructured SSW-2-type silicas were synthesized by the reaction of hydrated α -sodium disilicate with alkyltri-

methyammonium cations. It was confirmed that the 2-D hexagonal structure was formed and that the structural stability was improved by the acid treatment. Mesostructured SSW-2-type silicas with low Na contents were thermally stable up to 1000 °C. The retention of the silicate frameworks in the mesostructured silicas may also contribute to the improvement of the thermal stability because the high thermal stability was realized despite a thin wall thickness (1.5–1.6 nm) and a low condensation degree ($Q^4/(Q^3 + Q^4) = \text{ca. } 0.49$). The pore size of the products calcined at 1000 °C is 1.7–1.8 nm. The range of super-micropore is distinctive, and the fascinating properties including selective adsorption, molecular recognition, a novel reaction vessel, interactions with biomolecules, host–guest interactions, and catalysis, which are unattainable by using mesopores, will be found. Because mesostructured silicas derived from hydrated α -sodium disilicate have a high thermal stability, they will be suitable for industrial and repeated uses. There is a possibility of retaining the silicate framework of hydrated α -sodium disilicate in mesostructured silica(α)- n at least partly; therefore, the improvement of the catalytic activity of mesoporous silica is also expected.

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Supporting Information Available: Figures S1 (Na content), S2 (XRD), and S3 (XRD). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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