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Catalysis Today 111 (2006) 379–384

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Synthesis of highly ordered mesoporous $P6_3/mmc$ and $p6mm$ phases by adding alcohols to the system for the SBA-1 synthesis

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Abstract

The influence of acidity, alkyl chain length of alcohols, synthesis temperature and time on the molecular sieve synthesis by adding alcohols to the system for the SBA-1 synthesis were studied. Upon increasing the concentration of alcohols ($C_mH_{2m+1}OH$) in the mixture of tetraethyl orthosilicate (TEOS), cetyltriethylammonium bromide (CTEABr), HCl and H_2O, highly ordered $P6_3/mmc$ and $p6mm$ phases were formed when $m = 2$ and $3 \leq m \leq 6$, respectively. The amount of HCl was an important factor for the phase-selection under acidic conditions.

Keywords: Mesoporous silica; SBA-1; Alcohol; Acidic conditions

1. Introduction

In recent years, new families of ordered mesoporous silica materials have initiated an intensive research effort toward applications in catalysis, adsorption, separation of bulky molecules and environmental pollution control [1–3]. The synthesis of mesoporous materials with controllable structures and a tunable pore size by suitable adjustment of the synthesis conditions is an area of great interest. Up to now, the main research efforts have been concentrated on the MCM-41-type structure that possesses a regular hexagonal array of uniform pores with diameters in the range of 2–10 nm [4,5]. A variety of mesoporous silicas with different structures have been obtained using cationic [6], anionic [7] and non-ionic [8] surfactants with uniform pore diameters and large surface areas. Addition of alcohols during the synthesis of mesoporous materials is an excellent method for synthesizing and controlling both the mesostructure and the morphology of mesoporous silicates. However, only few examples of the influence of alcohols on the synthesis of mesoporous materials have been reported. Lin et al. reported [9] that a marked improvement in the hexagonal order and the peculiar morphology of the synthesized MCM-41 was achieved by the addition of an optimal amount of alcohols to quaternary ammonium halides–silicate systems. It has also been reported that the increasing amount of alcohol in the synthesis mixture of mesoporous materials results in a mesophase transformation [10,11].

Synthesis of mesostructured materials at low temperature is a convenient approach. Huo et al. reported a novel mesoporous molecular sieves SBA-1 [12–15], which possesses a three-dimensional cubic structure (space group $Pm\bar{3}n$) with cage-type pores with open windows; it was prepared using cetyltriethylammonium bromide (CTEABr) [16,17] under strongly acidic synthesis conditions. Che et al. studied the effect of counter ion on mesophase formation, succeeding in the synthesis of highly ordered SBA-1 materials with 54 crystal facets [18–21]. Control of the product phase and morphology by modification of the typical conditions for the SBA-1 synthesis is of great interest. In the present contribution, we report the synthesis of ordered $P6_3/mmc$ and $p6mm$ phases by adding alcohols to the system for the SBA-1 synthesis. Furthermore, influence of acidity of the system, alkyl chain length of alcohols, and synthesis temperature and time were studied.

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doi:10.1016/j.cattod.2005.10.049

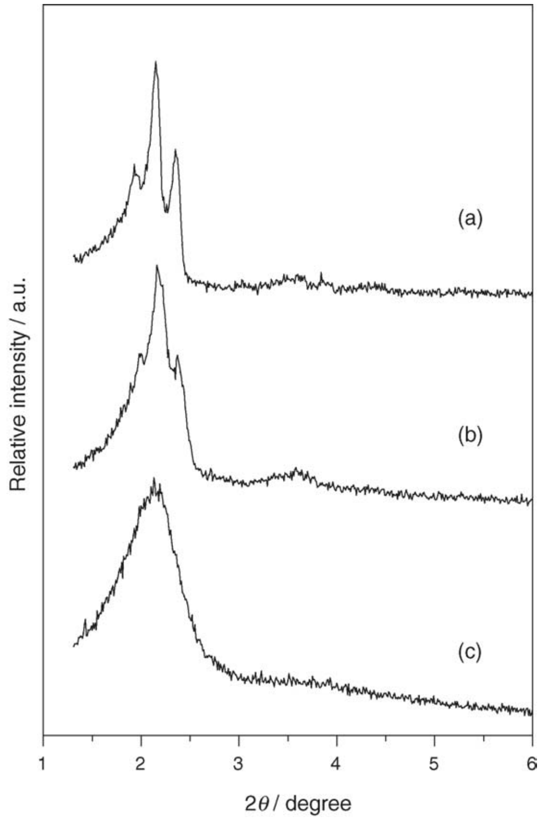

Fig. 1. XRD patterns of calcined samples synthesized with different amount of HCl at 0 °C for 24 h. Synthesis molar gel composition: TEOS–0.13CTEABr–*x*HCl–125H_2O, where (a) $x = 5.0$, (b) $x = 2.5$, and (c) $x = 1.25$.

2. Experimental

2.1. Synthesis of mesoporous materials

Mesoporous molecular sieves were synthesized using CTEABr as the surfactant and tetraethyl orthosilicate (TEOS) as the silica source. The surfactant (CTEABr) was synthesized by the reaction of 1-bromohexadecane with 1.5 equivalent of triethylamine in acetone under reflux for 7 d. The resulting crude product was purified by recrystallization from acetone. In a typical synthesis of mesoporous molecular sieves, 1.24 g of CTEABr was dissolved into the required amount of distilled water and alcohol. To this mixture, appropriate amount of hydrochloric acid (35%) was added. The solution thus obtained was cooled to 0 °C and stirred for 30 min. TEOS was precooled at 0 °C and then added to the solution under vigorous stirring. After stirring for 3 min, the mixture was allowed to react at 0 °C under static conditions for 24 h. The pH was lower than 2 in all the cases. The molar gel composition was TEOS–0.13CTEABr–$xC_mH_{2m+1}OH$–yHCl–125H_2O, where $0 \leq x < 10$, $1.25 \leq y \leq 5$, and $m = 1, 2, 3, 4, 5,$ and 6. The resultant white precipitate was filtered without washing and dried at 100 °C for several hours, followed by calcination at 600 °C to remove the template.

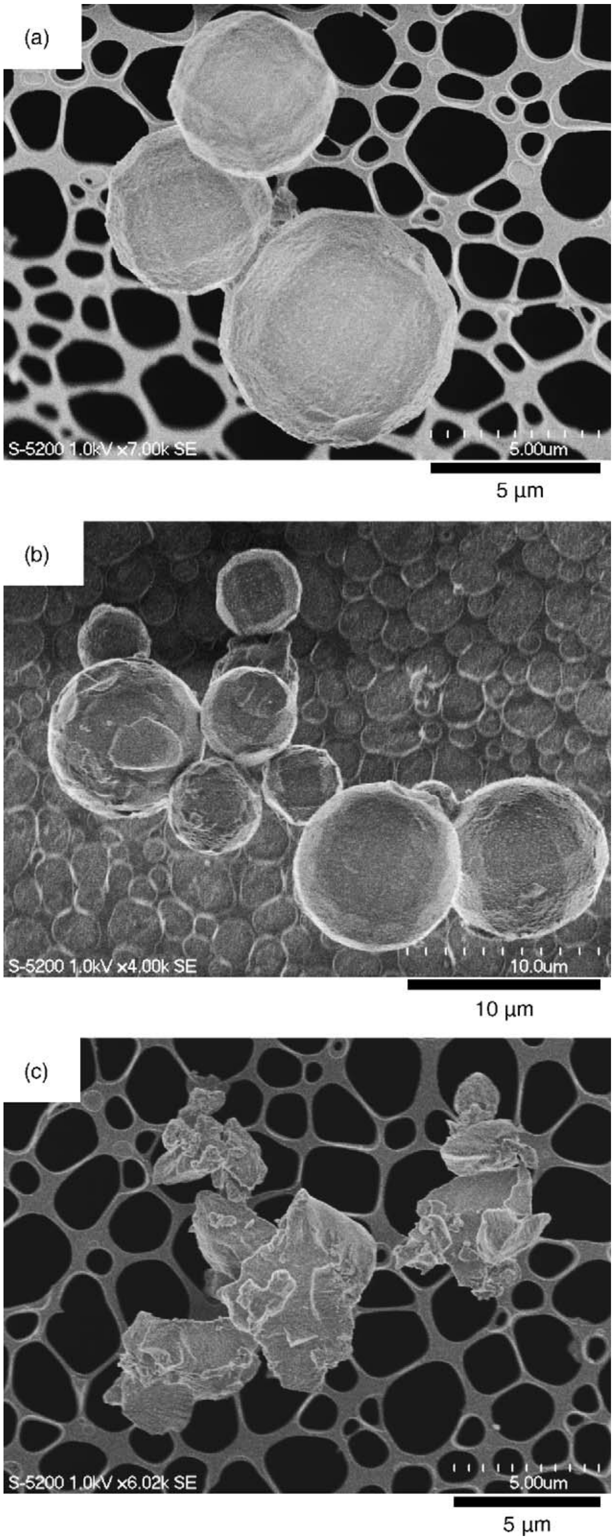

Fig. 2. FE-SEM images of the calcined SBA-1 samples synthesized with different amount of HCl at 0 °C for 24 h. Synthesis molar gel composition: TEOS–0.13CTEABr–*x*HCl–125H_2O, where (a) $x = 5.0$, (b) $x = 2.5$, and (c) $x = 1.25$.

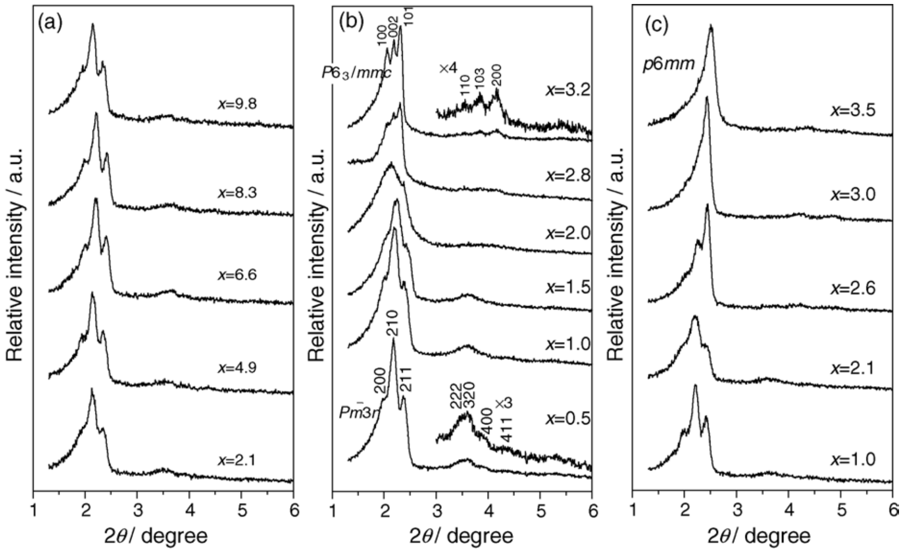

Fig. 3. XRD patterns of calcined samples synthesized by addition of (a) methanol, (b) ethanol, and (c) propanol to the system for the SBA-1 synthesis at 0 °C for 24 h. Synthesis molar gel composition: TEOS–0.13CTEABr–xC$_m$H$_{2m+1}$OH–yHCl–125H$_2$O, where (a) $m = 1$, $y = 5$, (b) $m = 2$, $y = 2.5$, and (c) $m = 3$, $y = 5$. Inset is expansion of region $2\theta = 3$–6°.

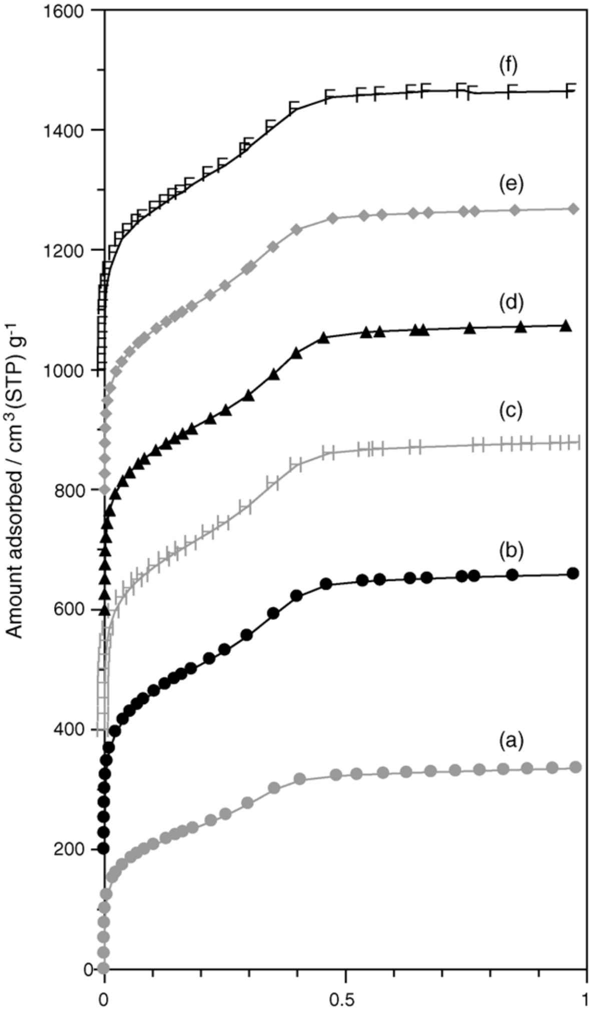

Fig. 4. Nitrogen adsorption isotherms for the samples in Fig. 2b. Synthesis molar gel composition: TEOS–0.13CTEABr–xC$_2$H$_5$OH–2.5HCl–125H$_2$O, where (a) $x = 0.5$, (b) $x = 1.0$, (c) $x = 1.5$, (d) $x = 2.0$, (e) $x = 2.8$, and (f) $x = 3.2$. The isotherms for the samples (b), (c), (d), (e), and (f) were offset vertically by 200, 400, 600, 800, and 1000 cm^3 (STP) g^{-1}, respectively.

Table 1
Properties of the samples in Fig. 4

Sample	S_{BET}[a] (m^2 g^{-1})	Pore diameter[b] (nm)	Pore volume[b] (cm^3 g^{-1})
a	1207	2.5	0.72
b	1245	2.6	0.71
c	1167	2.5	0.71
d	1122	2.7	0.70
e	1067	2.7	0.70
f	1051	2.6	0.71

[a] The BET surface areas based on N$_2$ adsorption isotherms.
[b] Values evaluated by the BJH method on N$_2$ adsorption isotherms.

2.2. *Characterization*

The powder X-ray diffraction patterns of prepared materials were collected on an MX Labo powder diffractometer using Cu Kα ($\lambda = 1.5418$ Å) radiation over the range of $2\theta = 1.5$–8°. Nitrogen adsorption and desorption isotherms were measured at −196 °C on a BELSORP 28SA gas adsorption instrument. The specific surface area was calculated using the BET method. The pore size distributions were obtained from the adsorption branch of isotherms using the BJH method. FE-SEM images were recorded on a Hitachi S4700 microscope.

3. Results and discussion

3.1. *Influence of acidity*

The synthesis in the absence of alcohols was examined first with the molar gel composition TEOS–0.13CTEABr–yHCl–125H$_2$O. Since the mesostructure formation usually depends on the concentration of acid, we changed the amount of HCl (expressed as y-value). In Fig. 1a, intense peaks of 200, 210 and 211 reflections are observed for the sample prepared with $y = 5.0$ ($H_2O/HCl = 25$), which is characteristic of the cubic $Pm\bar{3}n$ phase. With further decrease in the y-value, the resolutions of the lines decreased (Fig. 1b) and the lines were merged into a single and broad peak when $y = 1.25$ ($H_2O/HCl = 100$) as shown in Fig. 1c. Accordingly, the specific surface area and pore volume decreased from ($1324\ m^2\ g^{-1}$, $0.563\ cm^3\ g^{-1}$) to ($1016\ m^2\ g^{-1}$, $0.331\ cm^3\ g^{-1}$) as y-value changed from 5.0 to 1.25. The reduction in surface area and pore volume also indicated that a higher HCl amount was favorable to the synthesis of well-ordered cubic SBA-1 materials. The FE-SEM images of the samples in Fig. 1a–c are shown in Fig. 2a–c, respectively. Fig. 2a clearly shows the typical morphology of the SBA-1 with 54 crystal facets.

3.2. *Effect of alkyl chain length of alcohol*

Alcohols with different carbon chain length were added into the silicate–CTEABr–H_2O system, to investigate the effect of alcohol on the mesostructure. The typical gel composition was TEOS–0.13CTEABr–$xC_mH_{2m+1}OH$–yHCl–125H_2O.

The XRD patterns for the different silica mesophases synthesized by an increasing addition of methanol, ethanol and propanol to the system of SBA-1 synthesis are shown in Fig. 3. The typical diffraction patterns of SBA-1 cubic structure were observed for the samples synthesized in the presence of methanol when $y = 5.0$ ($H_2O/HCl = 25$) at 0 °C for 24 h. There was no effect of addition of different amounts of methanol on the structural order (Fig. 3a). The structural order was improved by addition of optimal amount of ethanol; however, the structural order of the cubic phase decreased with increasing concentration of ethanol when $y = 5.0$ (not shown). No collectable precipitate was formed with further increasing concentration of methanol or ethanol. It is interesting to note that the well-ordered 3d-hexagonal $P6_3/mmc$ mesostructure was formed upon increasing the addition of ethanol ($x = 3.2$) to the silicate–CTEABr–H_2O system when the synthesis was conducted with $y = 2.5$ ($H_2O/HCl = 50$) at 0 °C for 24 h. Three well-resolved peaks in the range of $2\theta = 2.0$–2.3° indexed to 100, 002 and 101 diffractions and the additional three weak peaks in the range of $2\theta = 3.7$–4.2° corresponding to 110, 103 and 200 diffractions, which are characteristic of 3d-hexagonal $P6_3/mmc$, with unit cell parameters $a = 73.4$ Å and $c = 119.5$ Å. The c/a ratio is 1.628, which is very close to the ideal c/a ratio of 1.633 for the hexagonal-packed system.

Nitrogen adsorption measurements of the samples in Fig. 3b gave similar type IV isotherms (Fig. 4). The properties derived from the isotherms are listed in Table 1. The specific surface area gradually decreased while the pore diameter slightly increased with increasing concentration of ethanol. FE-SEM images of the sample shown in Fig. 3b ($x = 3.2$) and Fig. 4f are shown in Fig. 5a–c, which exhibit 20 distinct crystal facets with one six-fold axis, matching well with the 3d-hexagonal $P6_3/mmc$ mesophase synthesized with H_2SO_4 [19].

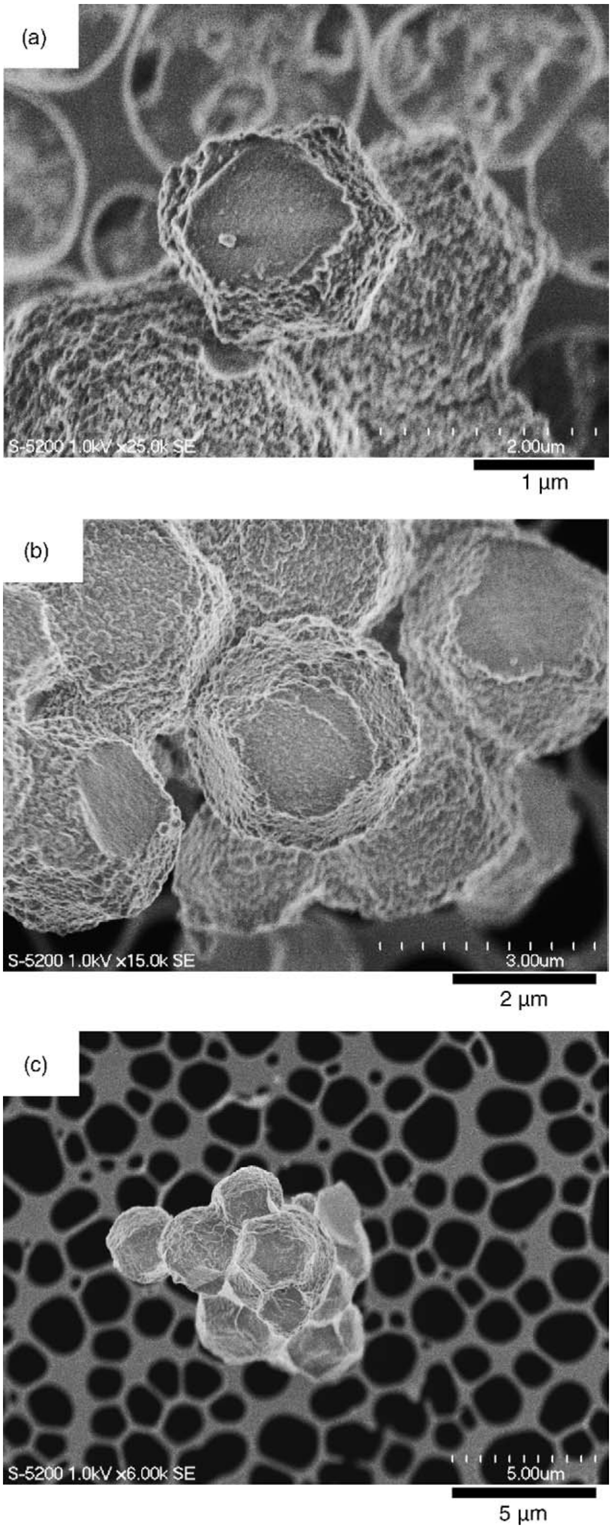

Fig. 5. FE-SEM images of a calcined sample obtained by adding ethanol to the system for the SBA-1 synthesis at 0 °C. Synthesis molar gel composition: TEOS–0.13CTEABr–3.2C_2H_5OH–2.5HCl–125H_2O. The images (a), (b), and (c) are different views of the same sample taken with different magnifications.

The X-ray diffractograms of mesoporous silica materials synthesized in the presence of butanol, pentanol and hexanol are shown in Fig. 6. The gel composition was TEOS–0.13CTEABr–$xC_mH_{2m+1}OH$–5.0HCl–125H_2O. Upon increas-

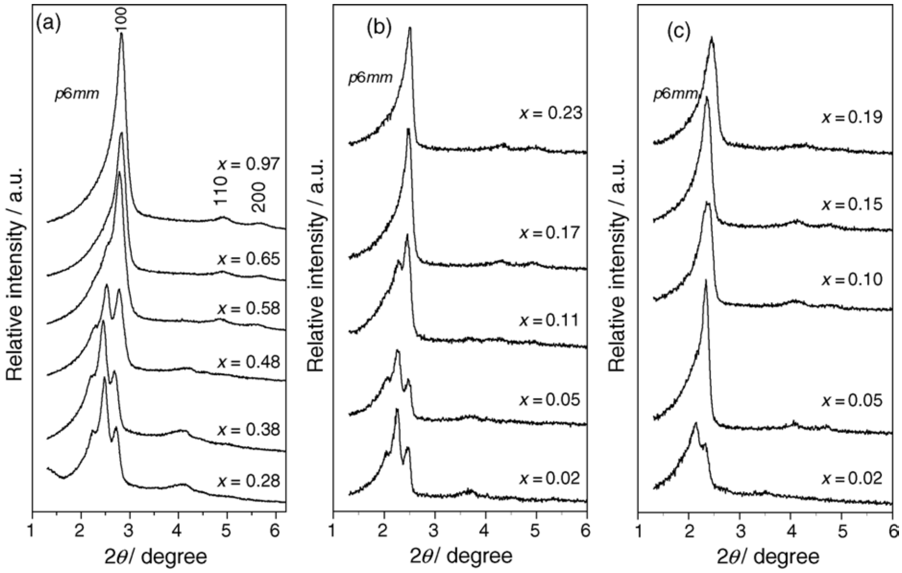

Fig. 6. XRD patterns of calcined samples synthesized by addition of (a) butanol, (b) pentanol, and (c) hexanol to the system for the SBA-1 synthesis at 0 °C for 24 h. Synthesis molar gel composition: TEOS–0.13CTEABr–$xC_mH_{2m+1}OH$–5HCl–125H_2O, where (a) $m = 4$, (b) $m = 5$, and (c) $m = 6$.

ing addition of relatively hydrophobic alcohol (propanol, butanol, pentanol, and hexanol) to the system for the SBA-1 synthesis, XRD reflections for the $Pm\bar{3}n$ phase disappeared and 2d-hexagonal (*p*6*mm*) diffraction pattern appeared. The clear 100 peak at $2\theta = 2.71^\circ$ as well as two weak peaks in the region between 4° and 6° attributable to the 1 1 0 and 2 0 0 reflections indicates that ordered SBA-3 was formed. The role of alcohol additives can be understood on the overall hydrophobicity of the silicate–CTEABr–$C_mH_{2m+1}OH$ system. When alcohol is added to the silicate–CTEABr–H_2O system, alcohol molecules may locate mainly inside the micelles. It is known that alcohols with medium carbon chain length may penetrate into the palisade region of the surfactant micelles resulting in a significant increase in the volume of the hydrophobic core to form surfactant molecular aggregates with a decreased surface curvature [22–24]. Therefore, addition of the relatively hydrophobic alcohol is considered to be favorable for the synthesis of hexagonal *p*6*mm* phase with higher *g* value.

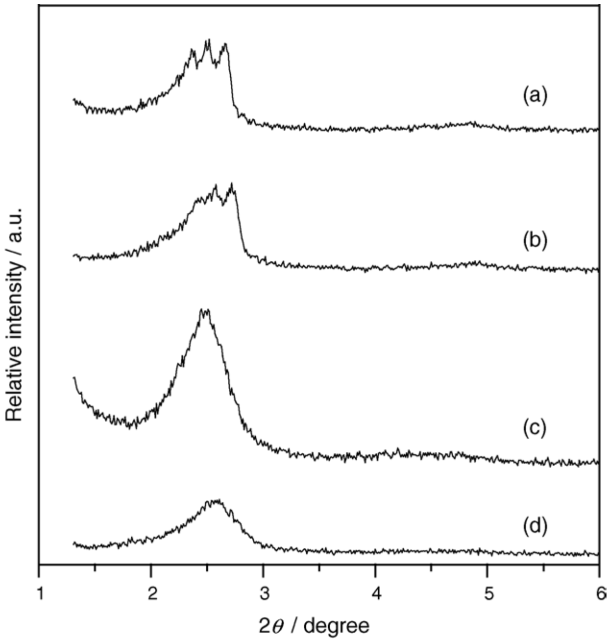

Fig. 7. XRD patterns of as-synthesized samples prepared at different temperatures: (a) 0 °C, (b) 30 °C, (c) 60 °C, and (d) 80 °C. Synthesis molar gel composition: TEOS–0.13CTEABr–3.2C_2H_5OH–2.5HCl–125H_2O.

3.3. Influence of temperature and time

The effect of temperature was investigated with the gel composition TEOS–0.13CTEABr–3.2C_2H_5OH–2.5HCl–125H_2O, from which the 3d-hexagonal $P6_3/mmc$ phase was

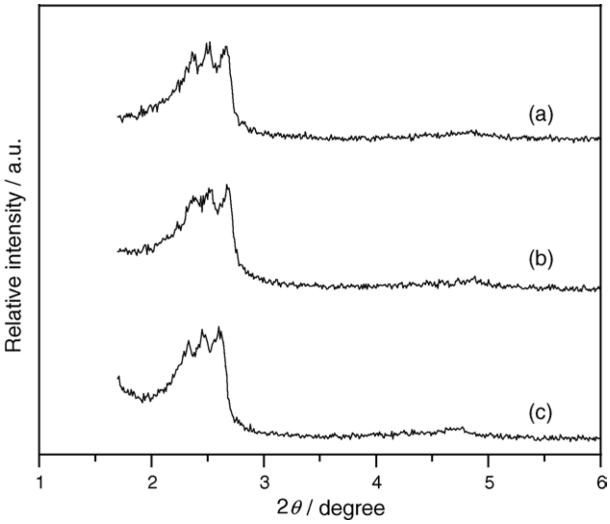

Fig. 8. XRD patterns of as-synthesized samples prepared by aging at 0 °C for (a) 24 h, (b) 48 h, and (c) 96 h. Synthesis molar gel composition: TEOS–0.13CTEABr–3.2C_2H_5OH–2.5HCl–125H_2O.

formed. XRD patterns of as-synthesized product are shown in Fig. 7. Temperatures below 30 °C were favorable for the formation of the well-ordered $P6_3/mmc$ phase (Fig. 7a and b). The structural order gradually decreased with increasing temperature (Fig. 7c and d). As shown in Fig. 8, the synthesis time in the range of 24–96 h produced no significant change in XRD patterns of the $P6_3/mmc$ phase.

4. Conclusions

Controlled synthesis of $P6_3/mmc$ and $p6mm$ phases of mesoporous silica has been carried out under acidic conditions by utilizing the effect of alcohols. The well-ordered 3d-hexagonal $P6_3/mmc$ phase was synthesized by careful addition of ethanol to the system for the SBA-1 synthesis, in which cetyltriethylammonium bromide (CTEABr) was used as a surfactant. Mesostructured 2d-hexagonal $p6mm$ phase was synthesized in the presence of relatively hydrophobic alcohol such as propanol, butanol, pentanol and hexanol. We demonstrated that with a proper control on the addition of alcohol to the system for the SBA-1 synthesis, two phases of mesoporous silica, 3d-hexagonal $P6_3/mmc$ and 2d-hexagonal $p6mm$, were synthesized.

Acknowledgement

P.S. thanks the Japan Society for the Promotion of Science for a postdoctoral fellowship.

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