SBA-15 합성에서의 실리카 원의 영향: 입자형태 및 세공형태의 변화에 관한 연구

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The effects of silica sources in synthesis of SBA-15: changes of morphology and pore shape

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Introduction

Mesoporous materials are of great interest in the materials fields because their physical properties (pore structure, pore shape, and pore size) as well as catalytic and adsorption characteristics can readly be tailored [1~3]. In recent years, a highly ordered large mesoporous silica SBA-15 was synthesized by using triblock copolymers as the structure-directing agents [3,4]. It is now evident that the morphology and texture of mesoporous silica are extremely important for application, and by use of synthesis method, mesoporous silica films, spheres, hollow spheres, and fibers have been synthesized for this purpose [4~7]. Also, there have been several reports that describe methods to control the shapes of smaller mesoporous particles [8].

In general, the pore and particle shape of mesoporous materials can be controled by addition of reagents and change of synthesis condition. Lin et al. [8] have synthesized hollow mesoporous silicate sphere with hierachically ordered structures by using butanol as a cosurfactant. Recently, Shio et al. [9] have described the synthesis of fine and rodlike mesoporous silica powder from completely dissolved aqueous solutions of sodium metasilicate and cationic surfactants. In this study, we report the synthesis of pure silica SBA-15 with different silica source. The synthesis of SBA-15 was carried out by a typical hydrothermal synthesis method with tetraethyl orthosilicate (TEOS). To study the effect of silica source in the synthesis of SBA-15, we used tetrabutyl orthosilicate (TBOS) as silica source. As a result, it is found that the change of morphology and pore shape can be accomplished by using different silica sources without change of typical synthesis condition of SBA-15.

Experimental

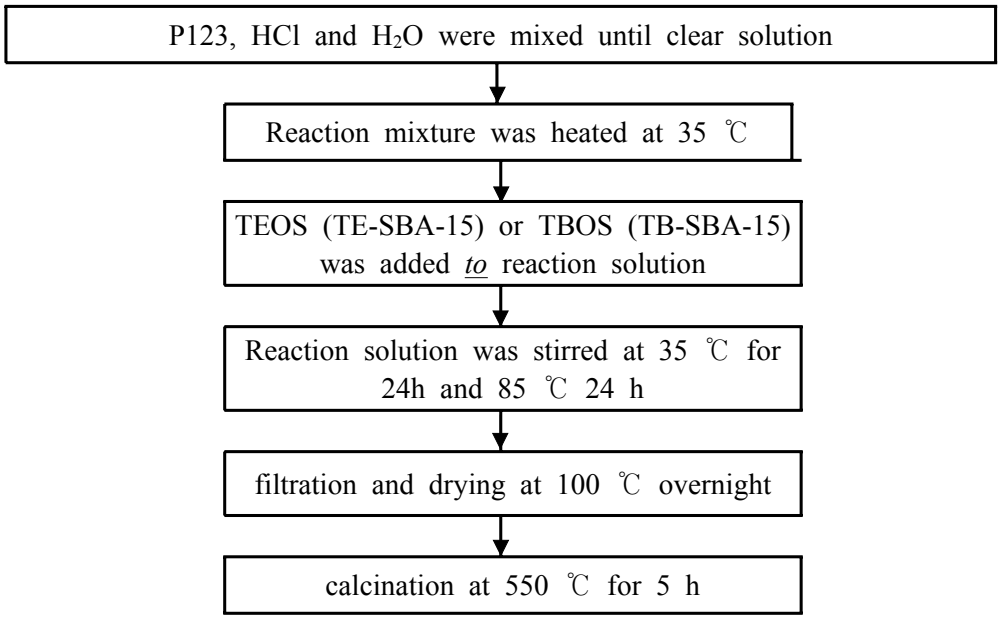
Synthesis

The mesoporous silica SBA-15 was prepared by using the typical hydrothermal synthesis method [3,4]. A template solution was prepared by combining aqueous HCl solution with poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer (BASF, Pluronic P123: $EO_{20}PO_{70}EO_{20}$). The resulting mixture was stirred for several hours until homogeneous solution. Tetraethyl orthosilicate (TEOS) and tetrabutyl orthosilicate (TBOS) as silica source was added to the template solution under vigorous stirring. The composition of the resultant gel was TEOS or TBOS : 0.017 P123 : 197.2 H_2O : 6.1 HCl. The gel obtained was stirred at 35 ℃ for 24 h. After this process, the resultant gel was heated to 85 ℃ for 24 h under stirring. All the hydrothermal

process was carried out in a mechanically stirred reactor equipped with a condenser and thermometer. The stirring speed was kept constant 300 rpm by using a speed regulator. After the hydrothermal process, the solid product was hot-filtered and dried in an oven at 100 ℃ overnight. The product was calcined in air at 550 ℃ for 5 h by using a muffle furnace.

Characterization

The phase identification of the solids was performed by using X-ray diffractometer (Rigaku, D/MAX-II A) equipped with an Ni-filtered monochromatic Cu K (=1.54056) radiation from a tube at 30 kV and 40 mA. The specific surface area and the average pore diameter were determined by nitrogen physisorption at the liquid nitrogen temperature using a Micrometrics ASAP 2010 automatic analyzer. The transmission electron microscopy (TEM, Jeol model JEM-2000EXII) and scanning electron microscopy (SEM, Jeol JSMT-200) were employed to observe the pore structure and morphology of the samples.



Scheme 1. Synthesis *procedure* of Si-SBA-15

Results and discussion

The SAXS pattern of the TE-SBA-15 sample synthesized in the present study is presented in Figure 1. The pattern for TE-SBA-15 sample consists of three distinguishable peaks, which can be indexed to (100), (110) and (200) diffraction lines, respectively, and these represent the characteristics of the hexagonal structure of TE-SBA-15 [3,4].

Figure 1 (b) shows the SAXS pattern of TB-SBA-15 which was prepared with TBOS as silica source. Here we can clearly observe one broad and strong diffraction peak. On the other hand, (110) and (200) peaks, which can be observed in the diffraction patterns of TE-SBA-15, disappeared. In general, the well ordered hexagonal mesoporous materials show distinguishable three or four diffraction patterns. However, the TB-SBA-15 shows only one broad and strong peak in SAXS analysis. It appears that TB-SBA-15 sample does not have hexagonal pore structure. The pore structure of TB-SBA-15 changed into disordered or wormholelike structure. TBOS hydrolyzed slowly compared with TEOS in the reaction mixture. Moreover, TBOS produced butyl alcohol during the

hydrolysis procedure in contrast to TEOS. The use of different silica source must have caused the change in the structure of SBA-15.

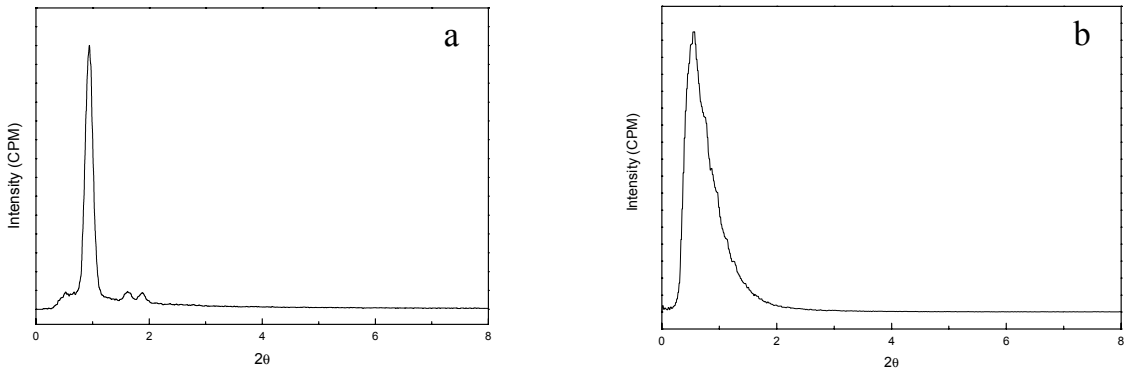


Figure 1. SAXS patterns of SBA-15 samples: (a) calcined TE-SBA-15, which was synthesized with TEOS; (b) calcined TB-SBA-15, which was synthesized with TBOS.

Figure 2 shows the isotherms and pore size distributions for the SBA-15 samples obtained at liquid nitrogen temperature using the Barrett-Joyner-Halenda (BJH) analysis [3,4]. Type IV isotherm, typical of mesoporous materials, is observed and as the relative pressure increases, each isotherm exhibits a sharp inflection, characteristic of capillary condensation within the mesopores [1]. This feature indicates that both samples possess a good mesoporosity. However, when the TBOS was used as silica source, the inflection point shifted to a high value of P/P_0 and the pore size was increased. These results indicate that the pore size of TB-SBA-15 is larger than that of TE-SBA-15.

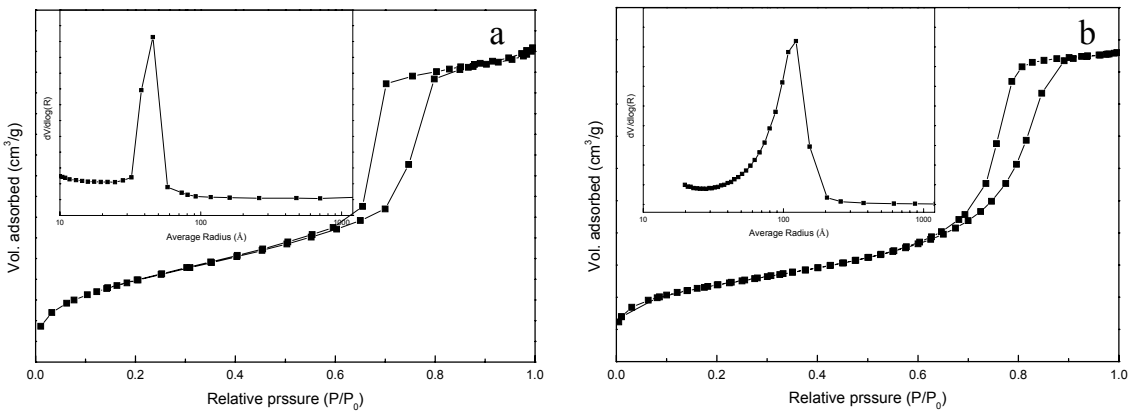


Figure 2. Isotherms and pore size distributions of SBA-15 samples: (a) calcined TE-SBA-15, which was synthesized with TEOS; (b) calcined TB-SBA-15, which was synthesized with TBOS.

The results of SEM and TEM imaging of SBA-15 are shown in Figure 3. The images of TB-SBA-15 clearly shows that the particle size was increased and the pore structure became a disordered phase.

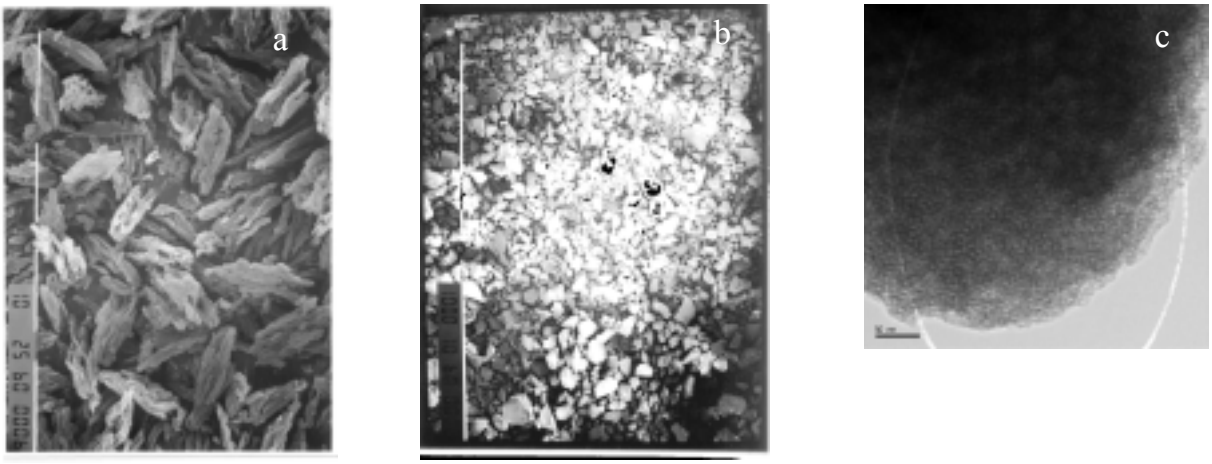


Figure 3. (a) SEM image of calcined TE-SBA-15, which was synthesized with TEOS; (b) SEM image of calcined TB-SBA-15, which was synthesized with TBOS (c) TEM image of calcined TB-SBA-15, which was synthesized with TBOS.

Conclusions

The synthesis of SBA-15 was carried out by the typical hydrothermal synthesis method with tetraethyl orthosilicate (TEOS) and tetrabutyl orthosilicate (TBOS), respectively. The SAXS patterns of the SBA-15 samples exhibited a well-defined (100) reflection. However, the TB-SBA-15 shows a different diffraction patterns. The isotherms and pore size distributions were of type IV and showed narrow distributions in the mesoporous region. However, when the TBOS was used as silica source, the inflection point shifted to a high value of P/P_0 and the pore size was increased. The SEM and TEM analysis showed distinguishable change. The pore structure of TB-SBA-15 changed into a disordered or wormholelike structure and the particle size was increased.

Acknowledgments

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