An Application Possibility of Self-Ordered Mesoporous Silicate for Surface Photo Voltage Type NO Gas Sensor (I): The Characterization of Nonionic Triblock Copolymer Templated Self-Ordered Mesoporous Silicates and Preparation Their Film for Device Application

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SUMMARY The mesoporous materials from the self-assembled organic-inorganic compound materials have great possibilities for a variety of applications. However, to make use of these kinds of materials effectively, they must be controlled. In this paper, we are succeeded in powder state pore size control and in significantly fabrication film state for device application use.

key words: mesoporous silicate powder, mesoporous silicate film, triblock copolymer, P123, F127

1. Introduction

The establishment of the template synthesis method progressed extendedly in porous material region in this decade. It is made by organic-inorganic compound materials that are constructed by organic self-assembled template materials and sol-gel synthesized inorganic materials. This innovative method is able to synthesize the highly uniform and orient mesoporous materials according to a self-assemble organic surfactant micelle structures e. g. hexagonal, cubic and lamella as shown in Fig. 1 [1]–[4]. After that, the calcination is carried out to remove organic template polymer from self-assembled ordered organic-inorganic compound materials to make mesopore.

In particular, MCM-41, which is synthesized by organic ionic surfactant template and has a hexagonal mesostructure, is one of the most energetic studied mesoporous materials [2], [5]–[10] for many applications [5]–[7]. For practical use of mesoporous materials, it is important to control the mesoporous especially the size of them and their morphology. However, MCM-41 type mesoporous silicate is restricted by ionic surfactant alkyl chain length of structure directing

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agent. So, It has a pore diameter from 3 nm to 5 nm [10]. Actually, there is a method to expand the mesopore beyond the restriction of alkyl chain length, which is introduced swelling agent into the micelle of ionic surfactant in synthesis process. But, in this method, the mesostructure is destroyed by swelling agent at the same time of expanding the mesopore. Recently, the new novel mesoporous materials were reported, which are synthesized by nonionic poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) type triblock copolymer as an organic structure directing agent and have a variety of pore diameter up to 7 nm without swelling agent by synthesis conditions and a sort of triblock copolymer [4]. The special features of our materials are uniform micropores, mesoporous, high surface area and bi-continuous structure. These potential properties can be systematically controlled by the template synthesis methods. They also exhibit good gas accessibility into both micropores and mesopores, and have many gas adsorption sites on their surface. Therefore, they will be good candidates for gas sensor device application.

In this paper, we report the characterization and a simple size control method in triblock copolymer templated mesoporous silicate powder SBA-15 and SBA-16, which are used triblock copolymer EO_{20} -PO₇₀-EO₂₀ (BASF Corporation: Pluronic P123, $M_{av} = 5750$) and EO_{100} -PO₆₅-EO₁₀₀ (BASF Corporation: Pluronic F127, $M_{av} = 12600$) as structure directing agent. And also, their triblock copolymer templated self-ordered mesoporous silicate films are exhibited for device application use.

2. Experimental

2.1 Synthesize Mesoporous Silicate

The triblock copolymer templated mesoporous silicates SBA-15 and SBA-16 were prepared as follow. P123 or F127 were dissolved in diluted Hydrochloric Acid (Wako Pure Chemical Industries, Ltd.: HCl Super Special Grade, M = 36.46) aqueous solution whilst stirring in different temperature T_s (Solution Temperature). Then silica precursor Tetraethyl Orthosilicate (Wako Pure Chemical Industries, Ltd.: TEOS Special Grade, M = 208.33) was added into the above solu-

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Fig. 1 Three kinds of self-assembled ionic surfactant micells. (a) Hexagonal structure, (b) Cubic structure, (c) Lammela structure.

tions whilst stirring at the T_s , a precipitated product was appeared. The mixture solutions with precipitated products were aged at 80 °C for 1 day. The precipitated products were filtered, washed by water, and air-dried at room temperature. Finally, calcination is carried out by slowly increasing the temperature from a room temperature to 500 °C in 8 hours and heating at 500 °C for 6 hours and decreasing the temperature from 500 °C to 100 °C in 8 hours and allowing to cool naturally from 100 °C to room temperature. The mole ratio of the chemicals were 1 TEOS: 0.0034 F127: 5.7 HCl: 193 H₂O for SBA-15 and 1 TEOS: 0.0034 F127: 5.7 HCl: 193 H₂O for SBA-16 [4].

2.2 Preparation Mesoporous Silicate Film

The mesoporous silicate film was synthesized by nonionic PEO-PPO-PEO triblock copolymer surfactant as the structure directing agent by the spin coating method [11], [12]. The precursor for the coating sol solution was prepared from two solutions. One is the polymer solution, which is dissolved in a P123 or a F127 type triblock copolymer into ethanol (Wako Pure Chemical Industries, Ltd.: EtOH Super Special Grade, M = 46.07) solution whilst stirring for about 2 hours at room temperature; the other is the silica solution, which consists of a mixed Tetraethyl Orthosilicate, EtOH, distilled water and Hydrochloric Acid whilst stirring for 1-2 hour from room temperature to 60 °C. The mole ratio of the chemicals is 1 TEOS: 0.014 P123: 15 H₂O: 0.16 HCl: 39 EtOH for the self-ordered hexagonal structure film and 1 TEOS: 0.0041 F127: 15 H₂O: 0.16 HCl: 40 EtOH for the self-ordered cubic structure film. After the above treatment, the ethanol solution and the silica solution are mixed. The mixed solution is stirred for a further 2 hours at room temperature and then the coating precursor solution is prepared. Next, the coating solution is used for film deposition on substrates by the spin coating method. This method is performed at a low-speed of 400 rpm for the initial 3 seconds and at a high-speed of 3000 rpm for the final 10 seconds. Finally, calcination is carried out by slowly increasing the temperature from a room temperature to 450 °C in 12 hours and heating at 450 °C for 24 hours and decreasing the temperature from 450 °C to 100 °C in 12 hours and allowing to cool naturally from 100 °C to room temperature. These processes result in homogeneous and transparent mesoporous silicate films.

3. Results and Discussions

3.1 The Characterization for Self-Ordered Mesoporous Silicate Powder

Figure 2 and Fig. 3 show the typical powder X-ray diffraction (Material Analysis and Characterization Science Co., Ltd.: XRD, M03XHF22) pattern of SBA-15 and SBA-16 mesoporous silicate, respectively. Six well resolved peaks are observed in each figure. These peaks have d spacing ratio of 1: $1/\sqrt{3}$: 1/2: $1/\sqrt{7}$: 1/3: $1/\sqrt{12}$ and can be indexed as (100), (110), (200), (210), (300) and (220) reflections corresponding to a hexagonal structure in Fig. 2 [4], and d spacing ratio of $1:1/\sqrt{2}: 1/2: 1/\sqrt{6}: 1/\sqrt{10}: 1/\sqrt{12}: 1/\sqrt{14}$ and can be index as (110), (200), (211), (310), (222) and (321) reflections corresponding to a cubic structure in Fig. 3 [4].

The transmission electron micrograph (HITACHI, Ltd.: TEM, HF-2000) images of SBA-15 and SBA-16 were exhibited in Figs. 4 and 5, respectively. In Fig. 4, the pore displayed a honeycomb like hexagonal structure and smartly arrayed themselves with same orientation. Also in Fig. 5, the pore laid out a square array and TEM images indicate the (110) surface (Figs. 5(a) and (b)) and the (111) surface (Figs. 5(c) and (d)) of cubic structure.

Figure 6 shows the nitrogen adsorption desorption isotherms (BEL JAPAN, INC: BELSORP 28SA) of the SBA-15 and the SBA-16. These measurements are carried out at 77 K liquid nitrogen temperature. The isotherms of the SBA-15 and the SBA-16 are a type IV physisorption curve each other, and exhibit a H_1 and a H_2 type hysteresis loop, respectively [4], [13], [14]. These hysteresis loops express particular hysteresis of the capillary condensation due to the structure of mesoporous silicate.



Fig. 2 The XRD pattern of the SBA-15.



Fig. 3 The XRD pattern of the SBA-16.



Fig. 4 The TEM images of SBA-15. (a) and (b) show honeycomb like hexagonal pores symetry. (c) exhibits orderly pore chanels alignment.



Fig. 5 The TEM images of SBA-16. (a) and (b) exhibit the (110) surface of cubic stracture. (c) and (d) also indicate the (111) surface of them.



Fig. 6 Nitrogen Adsorption Desorption (AD) isotherm for the SBA-15 (circle) and SBA-16 (square). These measurements are carried out at 77 K liquid nitrogen temperature. Close and open points mean the adsorption and desorption branch, respectively. The AD isotherm for the SBA-15 are shifted by 200 ml S. T. P. g⁻¹. Pore radius distributions for the SBA-15 and SBA-16 are also shown in inset as circle points with right side peak and square points with left side peak, respectively.

3.2 The Simple Pore Size Control Method in Powder State

Figure 7 shows the pore diameter size of the SBA-15 and the SBA-16 dependence on solution temperature T_s . The pore size is estimated using Dollimore-Heal (DH) method [9], [15] according to nitrogen desorption isotherm curve.

In hexagonal case (SBA-15), it is increased with increas-



Fig. 7 The pore size $(2R_p)$ dependence on solution temperature T_s for the SBA-15 (circle) and the SBA-16 (square). The solid line and the dotted line are fitted in with Eq. (1). The double logarithmic plot of the $2R_p$ versus reduced temperature for the SBA-15 (top one) and for the SBA-16 (bottom one), which is estimated critical micellization temperature (T_c) in aqueous solution as 13.75°C for the SBA-15 and 23.55°C for the SBA-16, are also shown in inset.

ing the T_s . The block copolymer that we use in this experiment consists of hydrophilic blocks EO and hydrophobic block PO. The micelle of this triblock copolymer in aqueous solution consists of a core and a shell formed by hydrophobic and hydrophilic part of the block copolymer, respectively [16]–[18]. Small angle neutron scattering experiment exhibit the dependence of the micelle core radius R_c upon temperature of aqueous solution [16], [17]. The empirical scaling relation Eq. (1) [17] between the R_c and temperature for EO_n-PO_m-EO_n triblock copolymer is revealed.

$$R_c \propto \left(T - T_c\right)^{0.2} \tag{1}$$

where T is the temperature of aqueous solution and T_{c} is the critical micellization temperature [17]. As increasing temperature, the aggregations number N_{p} of the block copolymer in the micelle [16], [17] and the hydrophobicity of EOblock in the block copolymer [16], [19] are grown. At the same time, the density of the core of micelle that is constructed hydrophobic part of the block copolymer is increased by the growth of them [16], [17] which is directly influence R_c . Therefore, R_c is increased during temperature raising. The T_c is a function of the number n, m of EO_n-PO_m-EO_n and the concentration of block copolymer. In our system, T_c for the P123 should be estimated as 13.75 °C according to the P123 concentration (= 4.91 mM) in our experiment [20], and T_c for the F127 should be estimated as 23.55 °C according to the F127 concentration (= 0.98 mM) in our experiment [20]. Figure 7 inset shows the plots of R_p (SBA-15) versus $T_r - T_r$ (P123) and R_{p} (SBA-16) versus $T_{s}-T_{c}$ (F127) in a double logarithmic axis. It exhibits linearity with 0.199 slope for SBA-15 and 0.123 slope for SBA-16. In the case of SBA-15, the T_s dependence curve is good agreement with $(T_{-}T_{-})^{0.2}$. On the other



Fig. 8 The scheme of the SBA-15 constraction process.

hand in the case of SBA-16, the T_{e} dependence curve is not good agreement with $(T_s - T_c)^{0.2}$, because of its complicated cubic structure. These results reveal that the pore size depends on the core size of micelle of P123 and F127 in the synthesis process which is determined by the solution temperature T_s as shown in Fig. 8 for construction scheme of SBA-15. Therefore, T_{c} is an effective parameter to control the pore size of mesoporous silicate synthesized from triblock copolymer EO_n-PO_m-EO_n. The pore size's change of the SBA-16 is very small because the T_c for the F127 is very high in our synthesis condition. However, there is a little deviation on this fitting. We think that one of the causes for this deviation is the influence of HCl and TEOS in synthesis solution, which influence T_c , EO-block dehydration effect and the aggregation degree of hydrophobic part of the block copolymer to make a micelle core.

3.3 The Characterization for Self-Ordered Mesoporous Silicate Film

Figure 9 and Fig. 10 show the XRD pattern and the TEM image of self ordered hexagonal and cubic structure film after calcination, respectively. In Fig. 9, The XRD patterns and TEM images indicate the ordered hexagonal pore structure in the self-ordered hexagonal structure film. The film has a highly oriented hexagonal structure and the pore channels are parallel to the substrate surface [12], [21]. Therefore, the self-ordered hexagonal structure film is estimated as a onedimensional hexagonal (1DH) structure. In Fig. 10, although it is difficult to infer exactly the structure in the self-ordered cubic film structure, the pores are in a three-dimensional cubic structure according to the TEM image. Also, from the powder results, SBA-16 powder has a cubic mesostructure as shown in Fig. 5. This SBA-16 powder and self-ordered cubic structure film use the same triblock copolymer F127 as the structure directing agent. Therefore, the self-ordered cubic structure film has a cubic structure with bi-continuous mesopore.

4. Conclusions

The pore sizes of the SBA-15 and the SBA-16 are systemati-



Fig. 9 (a) The XRD pattern of self-ordered 1 dimensional hexagonal film, which is synthesized by $EO_{20}PO_{70}EO_{20}$ (P123) triblock copolymer as the structure directing agent. (b) The TEM image of it.



Fig. 10 (a) The XRD pattern of self-ordered cubic structure film, which is synthesized by $EO_{100}PO_{65}EO_{100}$ (F127) triblock copolymer as the structure directing agent. (b) The TEM image of it.

cally controlled by the simple micelle control way directly related with assembled condition of the solution temperature T_s from 30 °C to 60 °C. The pore size R_p of mesoporous silicate is dependence on the solution temperature T_s in ~ $(T_s - T_c)^{0.2}$. we also are succeeded in fabrication of self-ordered one dimensional hexagonal and cubic structure mesoporous silicate films. They have great possibility for device application use of mesoporous materials. Next paper exhibits their device application possibility for surface photo voltage type NO gas sensor.

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