

# Synthesis of Zeolite Monolith with Hierarchical Micro/Macropores by Ice-Templating and Steam-Assisted Crystallization

Hajime Tamon\*, Takuya Akatsuka, Hiroki Mori, Noriaki Sano

Department of Chemical Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan  
 tamon@cheme.kyoto-u.ac.jp

Zeolite monolith was synthesized by ice-templating and steam-assisted crystallization (SAC) by using a structure-directing agent (SDA). The precursor silica gel was prepared by applying ice-templating to the hydrogels synthesized from colloidal silica. Sodium aluminate ( $\text{NaAlO}_2$ ) was supported in the precursor by impregnation to prepare zeolite monolith. Silicalite monolith or zeolite monolith with three-dimensionally interconnected macropores was synthesized by SAC of the precursor by using tetrapropylammonium hydroxide as SDA. The monolith had the continuous macropores, and the surface of these macropores was densely covered with zeolite crystals. The crystals were identified as MFI-type by XRD and had a well ordered microporous structure. Since the macropores, which were formed by ice-templating, were directly connected to the micropores of the synthesized zeolite crystals, the synthesized zeolite monolith had the hierarchical structure of macropores and micropores. The macroporous structure of monolith could be controlled by the freezing conditions because the macropore size became large with the decrease in freezing rate of hydrogels. The BET surface area and the degree of crystallinity of zeolite monolith were increased up to  $347 \text{ m}^2/\text{g}$  and 89 % by SAC. When the zeolite monolith was synthesized by changing the Si/Al ratio, the crystallization rate increased with the increase in Si/Al ratio, and the hydrophilic or hydrophobic property was also controlled by choosing the Si/Al ratio.

## 1. Introduction

Zeolites are widely used as catalysts, adsorbents, and ion exchangers. The mass transfer is one of the most important factors affecting the performance of microporous materials. The short diffusion length is needed to decrease the resistance of mass transfer. Zeolite is usually synthesized in the form of particles. Although extremely fine particles of zeolite are useful for the short diffusion length, the pressure drop is extremely large in the case where the particles are used in the packed bed (Hartmann M., 2004). Hence, the fabrication is important for the effective application of zeolite. Fiber or microhoneycomb morphology has recently attracted great attention from their low pressure drops and short diffusion lengths. However, it is extremely difficult to fabricate zeolite in honeycomb or fiber morphology without any binder.

Recently, porous materials with a hierarchical pore system have attracted considerable attention from the enhanced accessibility to their functional sites, which are distributed on the surface of their micro/mesopores (Soler-Illia et al., 2002). Such materials are usually prepared through sol-gel synthesis using special templates, such as fine polymer particles and microemulsions. Hence, it is extremely important to propose a novel methodology for preparing porous materials with hierarchical pore system.

The authors have proposed a novel template synthesis (ice-templating) using a unidirectional freezing of sols or hydrogels to synthesize porous fibers or microhoneycombs (Mukai et al., 2003). Ice-templating consists of sol-gel polycondensation, unidirectional freezing of hydrosols or hydrogels, and pore-protecting drying method, such as freeze drying. Therefore, highly porous cryogels with ordered morphology can be obtained. The authors have previously reported that silica cryogel microhoneycombs (Mukai et al., 2004a), titania cryogel fibers (Mukai et al., 2004b), carbon cryogel microhoneycombs (CMHs) (Nishihara et al., 2004), alumina-silica microhoneycombs (Nishihara et al., 2006) and titania-silica microhoneycomb

(Nishihara et al., 2010) can be obtained through the ice-templating method. Recently, the authors have applied ice-templating to the synthesis of silicalite monolith (Mori et al., 2011).

In this work, the zeolite monolith is synthesized by ice-templating and steam-assisted crystallization (SAC) (Matsukata et al., 2002) by using a structure-directing agent (SDA). The influence of freezing condition, SAC condition, and Si/Al ratio on morphology, crystallinity, nanostructure, and hydrophobicity of zeolite monolith is experimentally examined.

## 2. Experimental

### 2.1 Preparation of precursor monolith

The silica gel monolith used as the precursor of zeolite monolith was prepared by applying the ice templating method to a silica hydrogel. The silica hydrogel was synthesized from commercially available colloidal dispersion of silicon (IV) oxide (50 wt% in H<sub>2</sub>O, Alfa Aesar) by using an ion-exchange resin (Amberlite IR120B H AG, Organo Co.). The colloidal silica hydrogel was unidirectionally frozen by immersing the sample into a liquid nitrogen bath at various rates. Here the freezing temperature  $T_f$  was -196 °C, and the freezing rate  $v_f$  was changed from 15 cm/h to 70 cm/h to control the macroporous structure of silica gel. After the colloidal silica hydrogel was completely frozen, the sample was dried at 25 °C for 24 h, and then the silica gel monolith was obtained.

### 2.2 Preparation of zeolite monolith

The precursor silica gel was subsequently heated at 800 °C for 2 h in air atmosphere at a heating rate of 3 °C/min in order to give an alkali-proof property to the sample. After calcination, the precursor was impregnated with sodium aluminate (NaAlO<sub>2</sub>). Then the sample was soaked in the SDA solution and dried at 50 °C for 24 h. The SDA solution was prepared by diluting tetrapropyl ammonium hydroxide (TPAOH) solution (10 mass%, Wako Pure Chemicals Co.) with water. The obtained dry silica gel containing SDA was crystallized by SAC in an autoclave. The SDA concentration was 3.3 g-SDA/g-precursor. The crystallization temperature  $T_{SAC}$  was 130 °C, 150 °C or 180 °C, and the heating rate was 5 °C/min. The crystallization time  $t_{SAC}$  was varied from 3 to 24 h. The sample after crystallization was calcined at 600 °C for 4 h in air atmosphere at a heating rate of 10 °C/min. By the calcination, SDA was removed from crystallized samples, and finally the silicalite monolith or zeolite monolith was obtained.

### 2.3 Characterization

The morphology of the samples prepared was observed by a field emission scanning electron microscope (FE-SEM) (JEOL Japan Inc.; JSM-6700F), and the average size of silicalite-1 crystals was determined from the obtained SEM images. The crystal structure of silicalite monolith was investigated using a powder X-ray diffractometer (XRD) (Rigaku Co. Ltd.; RINT2100). The crystallinity of the sample was determined from the obtained XRD pattern, and the degree of crystallinity,  $X_c$ , is given by

$$X_c = I_c / (I_c + I_a) \times 100 (\%) \quad (1)$$

where  $I_c$  is the integrated intensity of crystalline peaks, and  $I_a$  is the integrated intensity of the amorphous halo. Zeolite synthesis was confirmed by a solid state nuclear magnetic resonance (NMR) spectrometer (Varian Inc.; VNMR-400).

Porous properties of cryogels were analyzed from N<sub>2</sub> adsorption-desorption isotherms measured at -196 °C using an adsorption apparatus (BEL Japan Inc.; BELSORP28). The BET surface area  $S_{BET}$  was calculated through the Brunauer-Emmett-Teller (BET) method, and mesopore size distribution and mesopore volume  $V_{mes}$  were calculated through the Dollimore-Heal method (Dollimore and Heal, 1964). The microporosity was evaluated by the  $t$ -plot method (Lippens and de Boer, 1965), and the micropore volume  $V_{mic}$  was calculated.

## 3. Results and discussion

### 3.1 Crystallization of precursor by SAC

Crack-free monoliths of precursor silica gel and silicalite can be synthesized by ice-templating and SAC. Figure 1 shows SEM images of cross section of silicalite monoliths synthesized under different freezing rates. Here the synthesis conditions of monoliths are as follows;  $T_f = -196$  °C,  $T_{SAC} = 130$  °C and  $t_{SAC} = 12$  h. The freezing rate  $v_f$  is changed as 15, 30, 50 and 70 cm/h. The continuous macroporous structure formed by ice-templating is observed in the crystallized samples as shown in Figure 1. It is experimentally confirmed that the channels run from one side to the opposite side of the sample by ink penetration tests, which were carried out using red ink dissolved in  $t$ -butanol, and that the monolith shows much lower pressure drop than that of the packed-bed of particles.

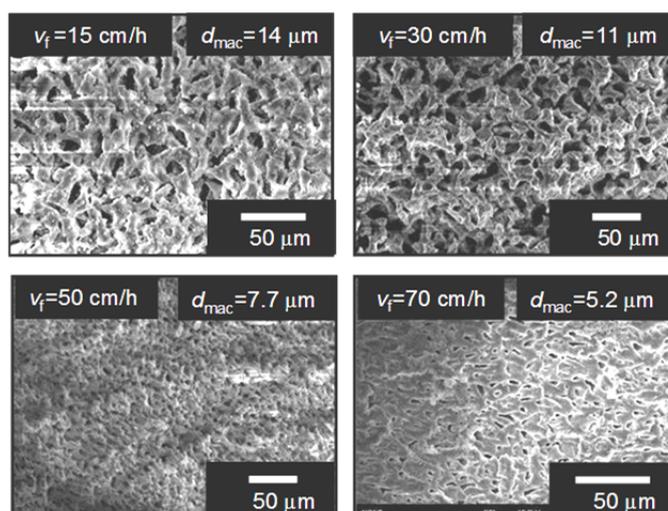


Figure 1: SEM images of cross section of silicalite monoliths synthesized under various freezing rates.

The crystal structure of precursor or silicalite monolith has been examined using a powder X-ray diffractometer (XRD). XRD patterns of the precursor silica gel and the samples after crystallization are shown in Figure 2. The samples of Figure 2 are the same as those shown in Figure 1. Only the broad halo centered at around  $2\theta = 23^\circ$  is observed in the XRD pattern of the precursor silica gel, and no crystalline phase is detected as shown in Figure 2 (a). In the sample after crystallization, sharp peaks are observed at around  $2\theta = 8^\circ$  and  $23^\circ$  as shown in Figure 2 (b). All of the observed diffraction peaks correspond to those of MFI-type zeolites. Since the synthesized samples contain no aluminum atom, the crystalline phase of the synthesized sample is identified as silicalite-1.

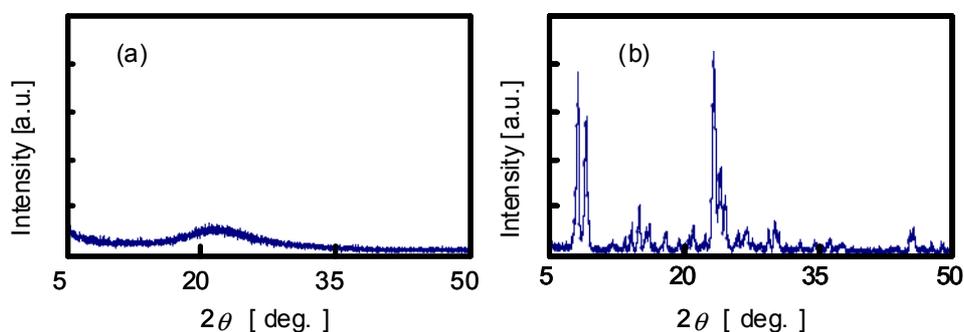


Figure 2: XRD patterns of precursor silica gel (a) and silicalite monolith after crystallization (b).

### 3.2 Control of macroporous structure of silicalite monolith

The authors have reported that the morphology of silica gel microhoneycombs depends on the unidirectional freezing conditions, and that the macropore size (channel size) and the wall thickness of SMHs can be controlled by the unidirectional freezing conditions and the silica concentration for synthesis of silica gels (Nishihara *et al.*, 2005). In the present work, the macropore size of silicalite is controlled by the unidirectional freezing rate. Figure 1 suggests that the average macropore size (channel size)  $d_{\text{mac}}$  of monolith changes as 5.2, 7.7, 11 and 14  $\mu\text{m}$  with the decrease in freezing rate  $v_f$ . Hence, the macropore size can be controlled by the freezing rate. The influence of freezing rate on macroporous structure is the same as the case of silica gel microhoneycomb synthesized by unidirectional freezing (Nishihara *et al.*, 2005).

### 3.3 Influence of SAC conditions on crystallinity of silicalite monolith

Figure 3 (a) shows the influence of SAC conditions on XRD patterns of silicalite monoliths synthesized for  $v_f = 40$  cm/h. It can be seen that the diffraction peaks become stronger with the increase in SAC temperature and SAC time. Figure 3 (b) shows the influence of SAC conditions on the degree of crystallinity of silicalite monolith. Here the degree of crystallinity is calculated from XRD patterns by using Equation (1). The degree of crystallinity increases with the increase in SAC temperature  $T_{\text{SAC}}$  and the SAC

time  $t_{\text{SAC}}$ , and reaches the values above 80 %. This result implies that the precursor silica gel is highly crystallized by the longer treatment than 12 h at high temperature. Hence, the XRD measurements of samples prepared suggest that silicalite monolith can be synthesized by ice-templating and SAC.

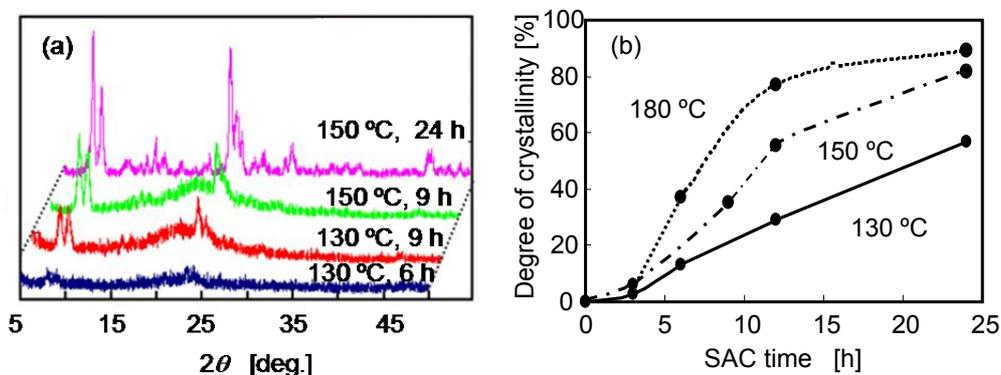


Figure 3: Influence of SAC temperature and SAC time on XRD patterns (a) and degree of crystallinity (b) of silicalite monoliths.

### 3.4 Influence of SAC conditions on porous property of silicalite monolith

Figure 4 shows the influence of SAC conditions on adsorption-desorption isotherms of nitrogen at  $-196\text{ }^{\circ}\text{C}$  on the precursor silica gel and the samples after crystallization. Here,  $p/p_0$  is relative pressure ( $p_0$  = saturated vapor pressure) and  $q$  is amount of  $\text{N}_2$  adsorbed. The isotherm on the precursor silica gel is classified into type IV in IUPAC classification, and this result indicates that the precursor silica gel is mesoporous. After the crystallization for 24 h, the isotherm changes into type I. This is because most part of the mesopores originally existed in the precursor silica gel disappears, and the crystallized sample becomes microporous. The isotherms suggest that the BET surface area  $S_{\text{BET}}$  and micropore volume  $V_{\text{mic}}$  of the precursor silica gel are  $118\text{ m}^2/\text{g}$  and  $0.01\text{ cm}^3/\text{g}$ . On the other hand,  $S_{\text{BET}}$  and  $V_{\text{mic}}$  of zeolite monolith increases up to  $347\text{ m}^2/\text{g}$  and  $0.17\text{ cm}^3/\text{g}$  after  $t_{\text{SAC}} = 24\text{ h}$ . Since the macropores are formed by ice-templating, the zeolite monolith has the hierarchical structure of macropores and micropores.

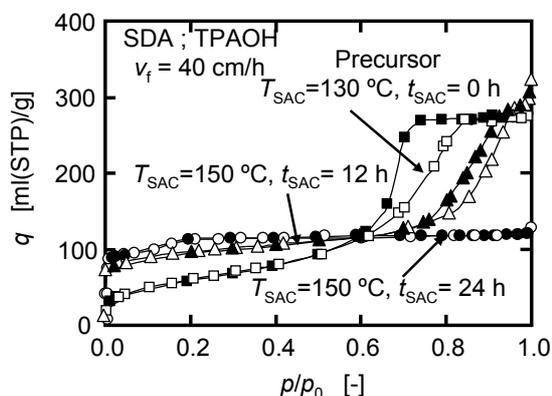


Figure 4: Influence of SAC conditions on adsorption-desorption isotherms of nitrogen at  $-196\text{ }^{\circ}\text{C}$  on zeolite monoliths (open symbols: adsorption, closed symbols: desorption).

### 3.5 Preparation of zeolite monolith by SAC

Figure 5 (a) shows SEM images of cross section of zeolite monolith synthesized for  $\text{Si}/\text{Al} = 50$ ,  $T_f = -196\text{ }^{\circ}\text{C}$ ,  $v_f = 40\text{ cm/h}$ ,  $T_{\text{SAC}} = 150\text{ }^{\circ}\text{C}$  and  $t_{\text{SAC}} = 120\text{ h}$ . From the SEM image, It is found that the zeolite monolith has three-dimensionally interconnected macropores as same as silicate monolith ( $\text{Si}/\text{Al} = \infty$ ) shown in Figure 1. The existence of aluminium in zeolite can be identified by NMR. The  $^{27}\text{Al}$  MAS NMR spectrum shown in Figure 5 (b) suggests that the sharp peak of 4-coordinated  $\text{Al}^{3+}$  is observed at chemical shift of  $\delta = 54\text{ ppm}$ . The result suggests that the sample has a framework structure composed of  $\text{AlO}_4$  tetrahedra.

Therefore, it can be concluded that not only silicalite monolith but also zeolite monolith can be synthesized by ice-templating and SAC.

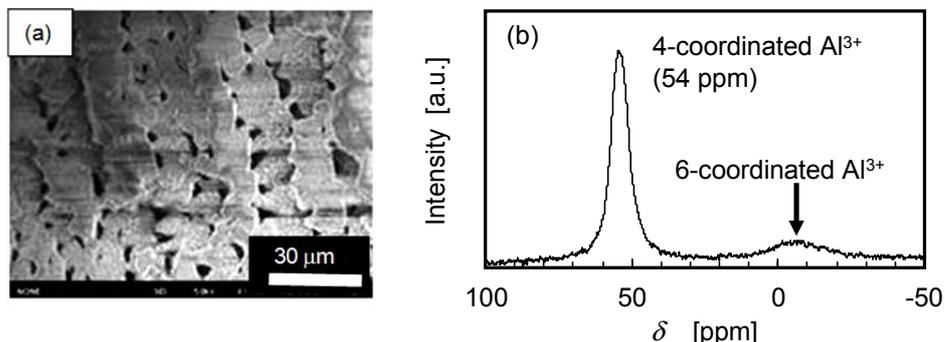


Figure 5: SEM image of cross section (a) and  $^{27}\text{Al}$  MAS NMR spectrum (b) of zeolite monolith synthesized for  $\text{Si}/\text{Al} = 50$ .

### 3.6 Influence of Si/Al ratio on crystallinity of zeolite monolith

The influence of Si/Al ratio of zeolite monolith on the degree of crystallinity is shown in Figure 6. This figure shows the relation between the degree of crystallinity and the SAC time in the case where zeolite monolith is synthesized for  $T_f = -196\text{ }^\circ\text{C}$ ,  $v_f = 40\text{ cm/h}$  and  $T_{\text{SAC}} = 150\text{ }^\circ\text{C}$ . As Si/Al ration decreases, the crystallization rate becomes slow. One can see that the degree of crystallinity of zeolite monolith synthesized for  $\text{Si}/\text{Al} = 20$  is below 60 % even at  $t_{\text{SAC}} = 120\text{ h}$ .

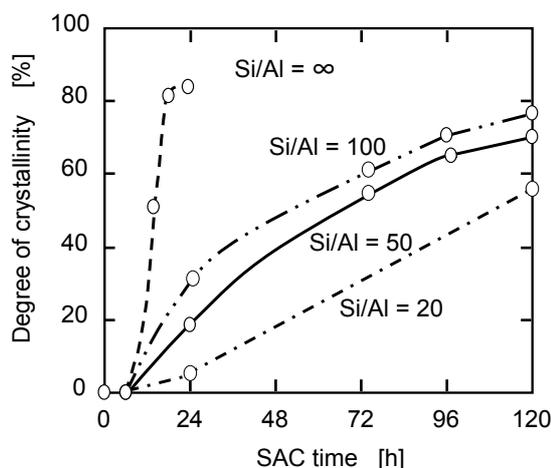


Figure 6: Influence of SAC time on degree of crystallinity of zeolite monoliths synthesized for various Si/Al ratios.

### 3.7 Influence of Si/Al ratio on hydrophilic property of zeolite monolith

Figure 7 shows adsorption isotherms of water vapor at  $25\text{ }^\circ\text{C}$  on zeolite monolith synthesized for  $\text{Si}/\text{Al} = \infty$ , 50 and 20. These samples have almost the same degree of crystallinity of 84 %. The amount of water vapor adsorbed increases with the decrease in Si/Al ratio (the increase in aluminium content). This result suggests that zeolite becomes hydrophilic as the Si/Al ratio decreases. Hence, the hydrophilic or hydrophobic property can be controlled by choosing the Si/Al ratio.

## 4. Conclusion

Zeolite monolith was synthesized from colloidal silica by ice-templating and steam-assisted crystallization (SAC) using a structure-directing agent (SDA). Since the macropores, which were formed by ice-templating, were directly connected to the micropores of the synthesized MFI-type crystals, the synthesized zeolite monolith had the hierarchical structure of macropores and micropores. The

macroporous structure of monolith can be controlled by the freezing conditions because the macropore size became large with the decrease in freezing rate of hydrogels. The BET surface area and the degree of crystallinity of zeolite monolith were increased up to 347 m<sup>2</sup>/g and 89 % by SAC. When the zeolite monolith was synthesized by changing Si/Al ratio, the crystallization rate decreased with the decrease in Si/Al ratio, and the hydrophilic or hydrophobic property was also controlled by choosing the Si/Al ratio.

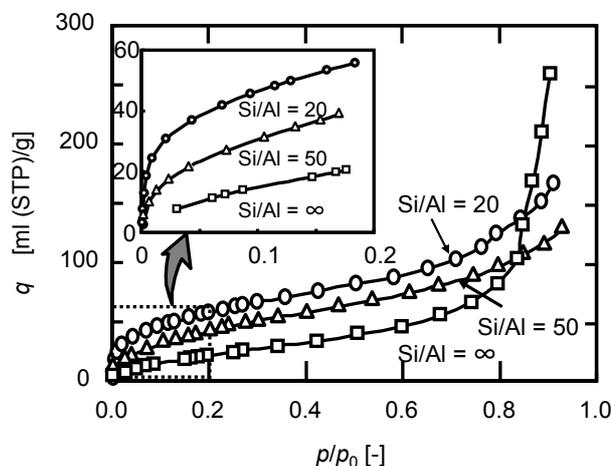


Figure 7: Influence of Si/Al ratio on adsorption isotherms of water vapor at 25°C on zeolite monoliths.

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