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Synthesis of Monolithic Zeolites with Macropores

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マクロ孔を有するゼオライト成形体の作製

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Monolithic polycrystalline zeolites with through-macropores were prepared by steam treatment of bimodal porous silica gel monolith in the presence of tetrapropylammonium hydroxide, where the bimodal porous silica gel was prepared by inducing phase separation during sol-gel process. The silica skeleton with mesopores was transformed into polycrystalline zeolites maintaining continuous macropore morphology and monolithic shape. In the zeolites, there are three different pores arranged hierarchically: through-macropores originally existed in the precursor silica gel, small macropores at interstitial of zeolite crystallites, and micropores in zeolite framework. [Received February 16, 2006; Accepted April 19, 2006]

Key-words : *Monolithic zeolite with through-macropores, Bimodal porous silica gel, Distinct trimodal pore structure*

1. Introduction

Zeolites are microporous crystals and have variety in micropore structures depending on their silicate framework.[1] Various kinds of zeolites have been synthesized mainly by hydrothermal process of silicate solution. Micropores of zeolites as well as their surface characteristics are efficient in selective catalysis, ion exchange, adsorption, separation and so on. Because of their small micropores, however, slow molecular diffusion in micropores sometimes becomes a large problem in practical usage. In order to improve molecular transportation in monolithic zeolites, much attention has been focused on the combination of large pores with micropores of zeolites. For example, various organic materials with pores have been used as templates of macropores in the zeolite synthesis.[2),3] Removal of the organic framework by combustion after crystallization of zeolites achieved the combination of macropores and zeolite micropores, although it has still been difficult to obtain a large monolith with a certain level of strength. It has been also reported that partial dissolution of zeolite with alkali solution gives mesopores in the zeolite.[4] Crystallization of silicalite-1 in macroporous silica gel was reported by Shikata et al.[5]

On the other hand, a new method of zeolite synthesis has been developed, where an amorphous silica-based gel is converted to zeolite by steam treatment in the presence of structure directing additive (SDA).[6),7] Tsuneki et al. succeeded to prepare monolithic aggregates of zeolite polycrystalline by steam treatment of silica-based gel.[8] Incidentally, we have reported the preparation of monolithic bimodal porous silica gel with both continuous macropores and mesopores from water glass.[9)-12] By treating the bimdodal porous silica with steam in appropriate conditions, the silica skeleton will be converted to zeolite without affecting macroporous morphology and shape of monolith. In this work, we prepared monolithic ZSM5 with MFI structure from the bimodal porous silica gel with maintaining continuous macropores by adopting steam treatment.

2. Experimental

A bimodal porous silica gel used as a precursor of monolithic zeolite was prepared from water glass (Japanease Industrial Standard, No. 3, Tokuyama Co.) in the presence of poly acrylic acid, as reported previously.[12] Poly acrylic acid with average molecular weight of 25000 (Wako Pure Chemicals Co.) was dissolved in nitric acid aqueous solution. Then, water glass diluted with water was slowly poured into the poly acrylic acid solution with vigorous stirring to be a homogeneous sol. The composition of the gel preparation was water glass: polyacrylic acid: water: nitric acid (60 mass% solution) = 60: 6.5: 97: 37 in weight ratio. The sol was geled in a sealed plastic container at 25°C. The obtained gel was washed with water for 3 days, and aged in ammonia solution with concentration of 0.01 mol dm^{-3} at 50°C for 3 days. After the gel had been dried at 50°C for 1 week, aluminum cation was introduced in the gel by impregnation before heating. The Si/Al ratio analyzed with ICP was 60. Finally, the gel was heated at 600°C for 2 h at heating rate of 100°C/h to be the precursor gel.

In the zeolite synthesis, the precursor gel was soaked in a SDA solution with tetrapropyl ammonium hydroxide (TPAOH), whose composition was TPAOH (10 mass% solution): H_2O:NaOH = 1.2: 1.2: 0.02 in weight ratio. Then, the gel was put in a pressured vessel, and heated with saturated water vapor at 150°C for 48 h for crystallization. For the purpose of micropore evaluation, the obtained material was ion-exchanged with ammonium cation, and heated at 500°C for 2 h.

Macropore structure of the obtained materials was evaluated with scanning electron microscope (SEM, SM200 Topcon) and Hg porosimetry (POREMASTER-60, Quantachrome). The nitrogen adsorption measurement was performed to observe micropore structure on an automated volumetric gas adsorption apparatus (ASAP2000, Micromeritics) after the sample had been pretreated under vacuum at 300°C for 1 h. X-ray diffraction patterns were recorded on M18XHF diffractometer (Mac Science). ^{27}Al magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra were obtained on DPX300 spectrometer (Bruker). The measurement details were reported elsewhere.[13]

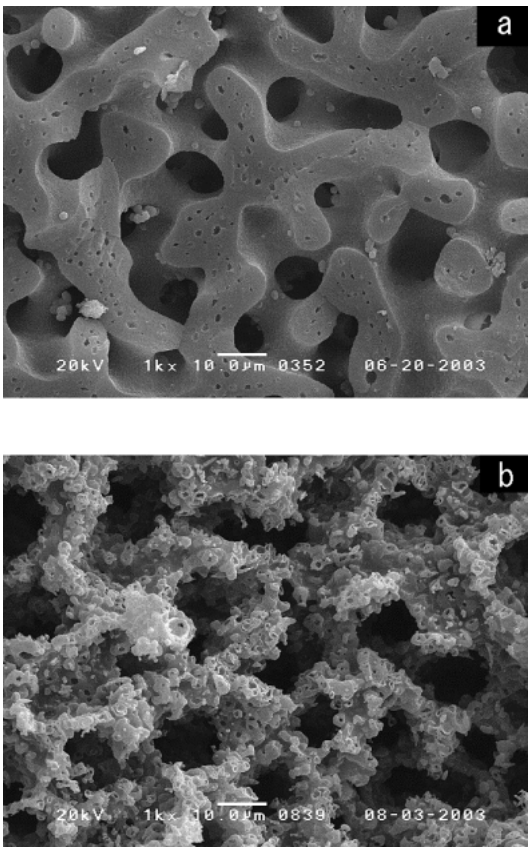

Fig. 1. SEM images of fractured surfaces of (a) precursor gel and (b) steam-treated sample.

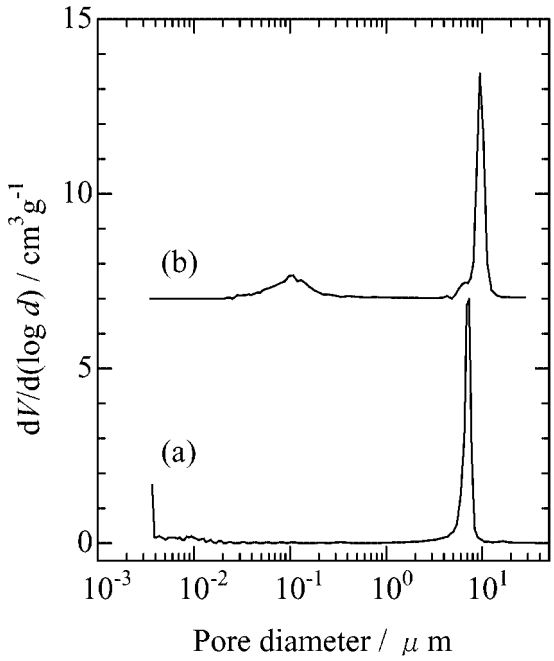

Fig. 2. Pore size distribution curves measured with Hg porosimetry for (a) precursor gel and (b) steam-treated sample.

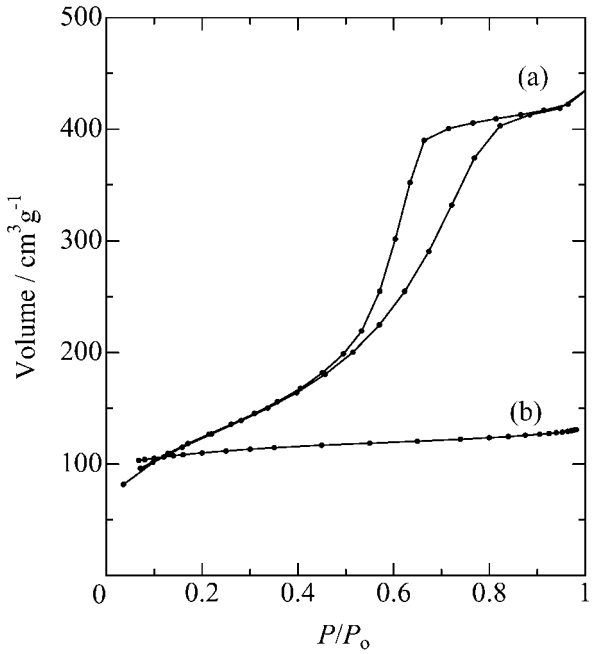

Fig. 3. Nitrogen adsorption isotherms of (a) precursor gel and (b) steam-treated sample.

3. Results and discussion

In the steaming treatment of bimodal porous silica gel, silica gel precursors did not crystallized under mild conditions at temperatures lower than 120°C, whereas they became slurry and lost the original monolithic body under severe conditions at temperatures higher than 180°C. The steam treatment at 150°C for 48 h was preferable to crystallize the bimodal porous silica gel without destroying the monolithic shape.

Figure 1 shows SEM images of precursor silica gel and the steam-treated sample. Three-dimensionally interconnected macropores with diameter of ca. 10 μm are observed in both samples. However, texture of the fractured surface of silica skeleton drastically changes during the steam treatment. The skeleton of silica before treatment has smooth surfaces, whereas that in the steam-treated sample seems to be aggregates of small particles with diameter of ca. 1 μm. Although such aggregates are sometimes fragile, the present material maintains a certain level of stiffness. This stiffness suggests that a small amount of amorphous silica remains at the interface of particles, although its presence is not detected by XRD and nitrogen adsorption as discussed below.

Figure 2 shows pore size distribution curves obtained with Hg porosimetry for the samples. Both samples show a sharp peak at ca. 8 μm, corresponding to the continuous macropores observed in SEM images (Fig. 1). In addition, presence of pores is suggested for the precursor silica gel at smaller size, <6 nm, although peak was not clear because of the limitation in measurement range in the apparatus. After the steam treatment, such mesopores seem to disappear, whereas the presence of small macropores with diameter of ca. 0.1 μm was recognized. This small macropores correspond to interstitials of particles observed in SEM image (Fig. 1(b)). **Figure 3** shows isotherms of nitrogen adsorption for both the samples. In the precursor silica gel, hysteresis loop classified into type IV in IUPAC classification was observed. The mesopore size calculated from the desorption branch was ca. 8 nm. After the steam treatment, the isotherm changes into type I. That is, mesopores originally existed in precursor silica gel disappear completely, and only micropores smaller than 2 nm are detected by the nitrogen adsorption. **Table 1** summarizes the structural features of the samples. The specific surface area varies

Table 1. Pore Structures of Samples

Sample	Pore volume / cm^3g^{-1}					BET SA
	Total	> 1 μm	> 50 nm	> 2 nm	micropores	/ m^2g^{-1}
Precursor	1.346	0.659	0.033	0.654	0	446
Zeolite	1.237	0.728	0.306	0.029	0.174	372

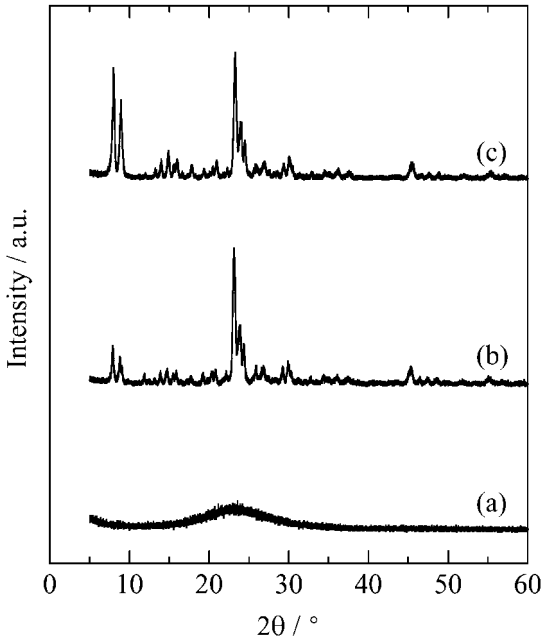

Fig. 4. XRD profiles of (a) precursor gel, (b) steam-treated sample and (c) steam-treated sample after removal of SDA.

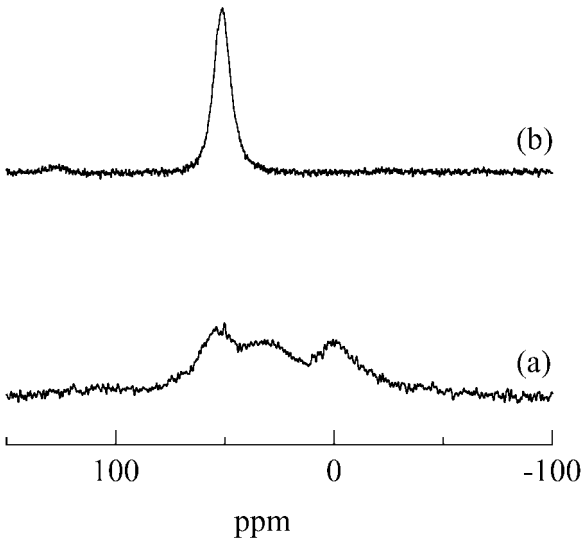

Fig. 5. ^{27}Al MAS NMR spectra of (a) precursor gel and (b) steam-treated sample.

from 446 $m^2 g^{-1}$ to 372 $m^2 g^{-1}$ during steam treatment. On the other hand, sum of all the pore volumes changes little during the treatment.

Figure 4 shows XRD profiles of the samples. The precursor silica gel was an amorphous and only a broad halo was observed centered at around 23 degree. After the steam treatment, sharp peaks were observed. These peaks are assigned to MFI-type zeolite. In the steamed samples, halo of amorphous silica gel disappeared, suggesting that amorphous phase was almost consumed. **Figure 5** shows the ^{27}Al MAS NMR spectra. After the steam treatment, only a peak was observed at ca. 50 ppm, assignable to 4-coordinated aluminum cation, while three broad peaks were observed in the precursor sample. This result strongly suggests that all the added aluminum cations are incorporated in the crystalline lattice of zeolites.

Thus, we succeeded to prepare monolithic polycrystalline zeolites with through-macropores. The zeolite has three different pores. The continuous macropores with size of ca. 8 μm, which originally existed in bimodal silica gel, retain after the crystallization to zeolite. The interstitials of crystallites become small macropores with size of ca. 0.1 μm. In the crystallites, there are micropores in zeolite framework. It is clear that the three different size pores are arranged hierarchically. The macropores can be pathways for rapid diffusion of molecules in both gas and liquid phases in practical use, and increase the efficiencies of zeolite. In addition, the large through-macropores can be a flow pathway as has been demonstrated.[14] Then, we expect different functionalities for three different pores, flow pathways for large through-macropores, diffusion pathways for macropores at interstitials of crystallites, and catalytic function for the surface in micropores in zeolite framework.

Various zeolites have been prepared by steaming treatment.[1] Most of them would be applicable to the present bimodal porous silica by changing the coexisting metal ion, SDA and steaming treatment conditions. This method would be attractive in preparing zeolite with improved molecular transportation.

4. Conclusion

Monolithic polycrystalline zeolites with continuous macropores were prepared by steam treatment of bimodal porous silica gel prepared by the phase separation method in the presence of tetrapropylammonium hydroxide. The 3-dimensionally bi-continuous morphology of macropores and silica skeleton in the precursor silica gel was retained after crystallization, and amorphous silica gel phase was converted into MFI zeolite without destroying monolithic body. In addition to the zeolite micropores and continuous macropores, there are third intermediate size pores at interstitials of crystallites, and the monolithic zeolite has hierarchical trimodal porous structures.

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