Synthesis of a Zeolite Column with a Monolithic Microhoneycomb Structure Using the Ice Template Method

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Introduction

Various porous materials are widely used as adsorbents and catalysts and are supporting our daily lives in many different ways. In such materials, active sites are usually dispersed throughout the whole volume of the material and provide the basic function(s) of the material.

Generally, the performance of such materials can be maximized by keeping the lengths of the diffusion paths, which lead substances from the outer surface of the material to the active sites within them, as short as possible. As porous materials are generally synthesized in the form of particles, the lengths of the diffusion paths in them can be shortened by simply reducing the size of the particle itself. However, small particles cause a severe resistance when fluids are passed through them, therefore this method does not always lead to the improvement of the total performance of the material. In fact, particles with fairly large sizes are usually used in industrial applications just only to avoid significant resistance to flows. This indicates that there are many cases that the performance of such materials can be further improved, if such materials can be synthesized to have a structure in which short diffusion paths and low resistance to fluid flows are compatible.

A monolithic microhoneycomb which has straight and aligned micrometer-sized channels within it may be an ideal structure, if the walls which form the channels are thin enough. It was thought to be difficult to obtain porous materials with such a structure through conventional synthesis methods, but recently we found that porous materials attainable through the sol-gel method can be molded into a monolithic microhoneycomb just by freezing their parent hydrosol or hydrogel unidirectionally. As ice crystals which grow within the precursor during freezing act as the template, we named this method the "Ice Template Method."

We also found that this method can also be applied to hydrogels including fine particles. The materials obtained through this process have a monolithic microhoneycomb structure and can be practically regarded as a monolithic column of the fine particles, in which the gel acts as the binder.

In this work we synthesized columns with a monolithic microhoneycomb structure from zeolites, a typical catalyst used in various petrochemical processes, using the ice template method, and checked their characteristics.

Experimental

Commercial sodium silicate solutions (Wako Pure Chemical Industries) were diluted with ion-exchanged and distilled water, and the SiO_2 concentration (C_s) in them were adjusted to a desired value set in the range 1.0 mol L^{-1} to 1.9 mol L^{-1}. Then the pH of the solutions was adjusted using an ion-exchange resin. To these solutions, high silica Y-type zeolite particles (HSZ, Tosoh, average particle size: 300 nm) were added. First, the particles were dispersed in the solutions using an ultrasonic homogenizer, and the resulting slurries were poured into polypropylene tubes (i.d.: 10 mm, L: 100 mm) and were aged for different periods. Next the tubes were dipped at a constant rate v, set in the range 6 cm h^{-1} to 20 cm h^{-1}, into a cold bath maintained at 77 K. After the tubes were completely frozen, they were taken out from the bath and thawed at 323 K. Then the water in the tubes was exchanged with *t*-butanol, and the samples were freeze-dried.

The morphology of the samples was directly observed using a scanning electron microscope (SEM). Next the samples were analyzed using an X-ray Diffractometer (XRD) to confirm whether the included zeolite particles maintained their structures after monolith synthesis. The porous properties of the samples were evaluated through nitrogen adsorption-desorption experiments. First, nitrogen adsorption-desorption isotherms of the samples were measured at 77 K. Next, BET surface areas of the samples were calculated using the BET method. The compression strengths (axial direction) of the monoliths were measured using a load cell. Finally, stainless steel columns in which the monoliths were fitted in were synthesized, and the pressure drop which occurs when air (293 K) was passed through the columns was measured. The dimension of the monoliths used in measurements was ϕ10 x 20.

Results and Discussion

Sample Morphology

In this work, samples including zeolite particles in the range of 0.2 g-zeolite (g-SiO_2)$^{-1}$ to 1.0 g-zeolite (g-SiO_2)$^{-1}$ were obtained. Figure 1 shows SEM images of cross sections of typical samples obtained in this work. The channels of the microhoneycombs were not as straight and as regularly ordered as those in the microhoneycombs obtained through the original ice template method. However, it was confirmed that fairly straight channels run from one side to the other side of the honeycomb through SEM observation and ink penetration tests.

Figure 2 shows the XRD patterns of typical samples. Peaks corresponding to the crystal structure of the included zeolite particles can be clearly identified, which indicates that the included particles maintained their nanostructure during freezing. Therefore, it is assumed that the particles maintain their unique functions.

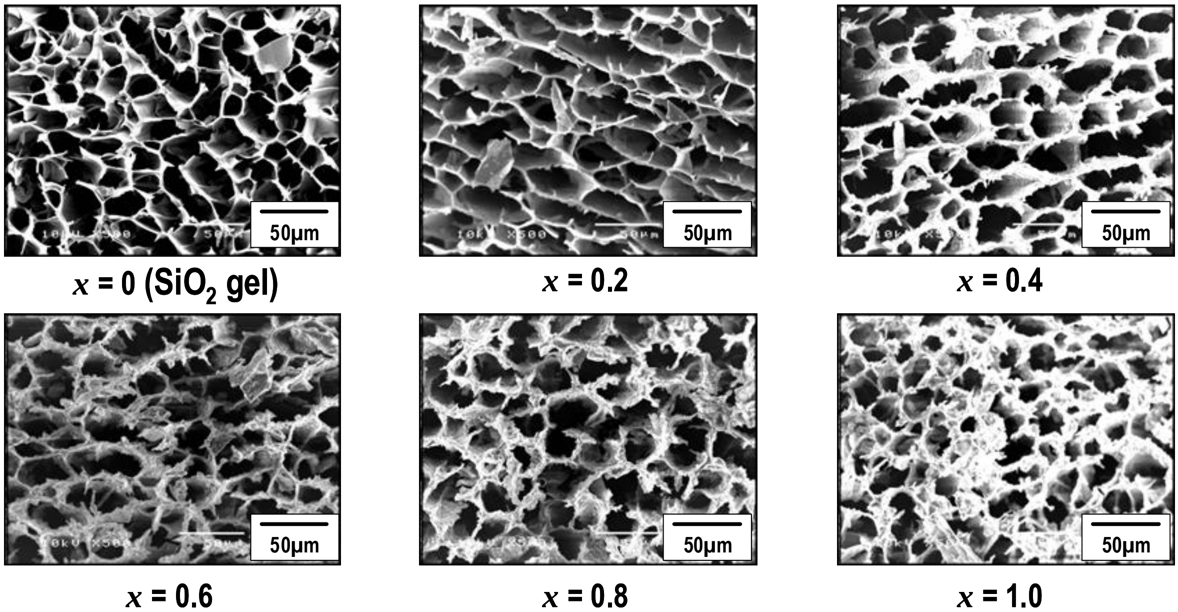

Fig. 1 Cross sectional SEM images of typical samples obtained in this work

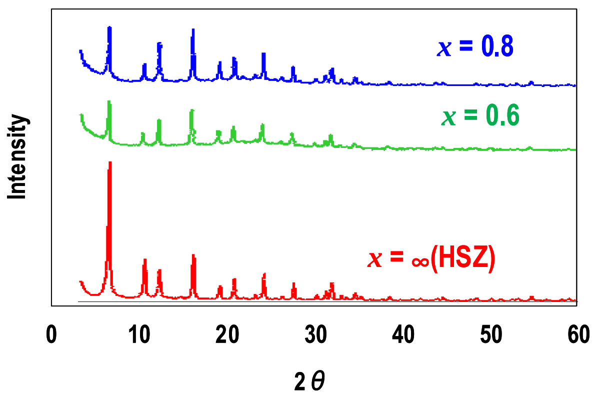

Fig. 2 XRD patterns of typical samples obtained in this work

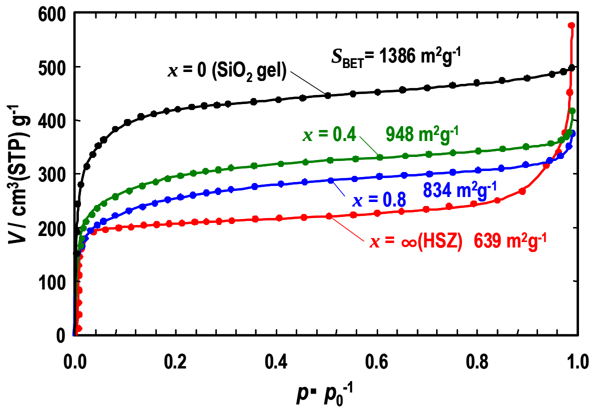

Fig. 3 N2 adsorption isotherms of typical samples obtained in this work

The porous properties of the samples were evaluated through nitrogen adsorption experiments. Figure 3 shows nitrogen adsorption isotherms of typical samples measured at 77 K. The BET surface areas (S_{BET}) are also listed in the figure. Silica gels prepared using the ice template method has developed micropores and possess fairly high BET surface areas. Zeolites are also microporous, but their isotherms indicate that they also have a slight amount of mesopores, with are thought to exist within or between the particles. Silica including zeolite samples show isotherms which correspond to the amounts of silica gel and zeolite included within them. Therefore, it is assumed that the pore inlets of the zeolite are not blocked by the silica gel matrix.

Next a typical sample was divided into 5 equal parts in the axial direction, and structural analysis of each part was conducted. Figure 4 shows SEM images and nitrogen adsorption isotherms measured at 77 K of the divided parts. A significant difference among the samples cannot be recognized, which indicates that the ice template method gives a fairly uniform sample.

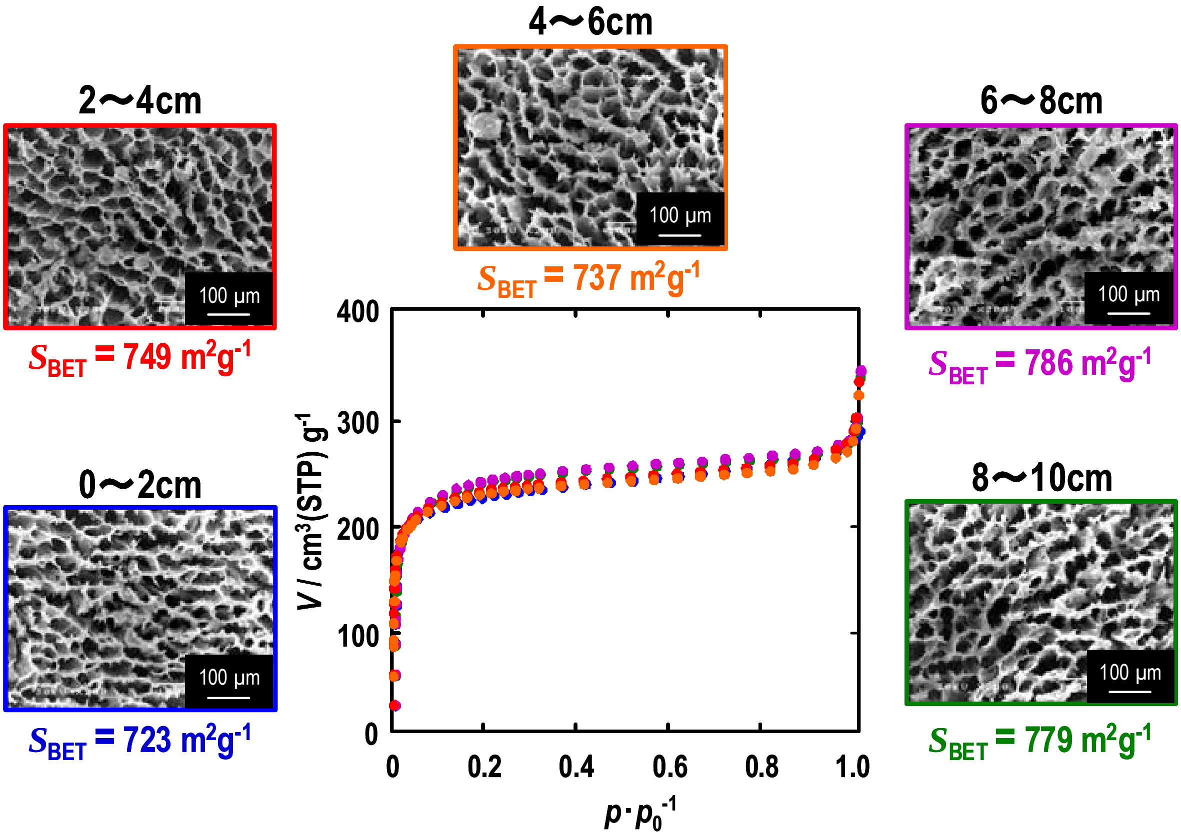

Fig. 4 SEM images and N2 adsorption isotherms of divided sections of a typical sample in the axial direction

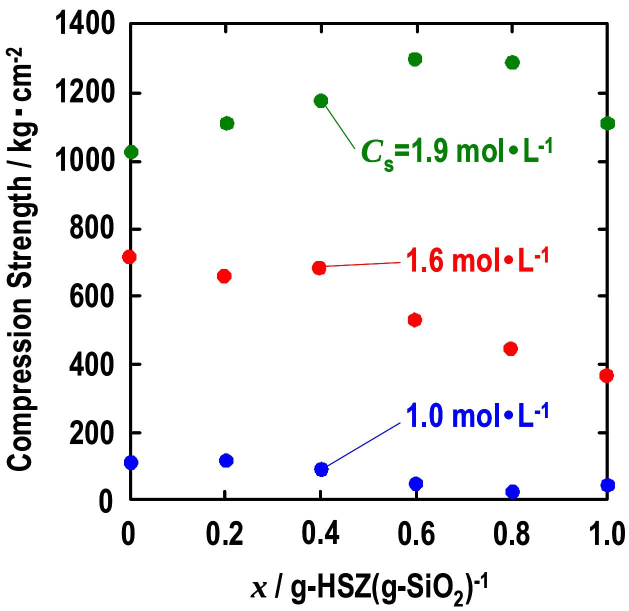

Fig. 5 Compression strengths of typical samples obtained in this work

Figure 5 shows the compression strengths of typical samples obtained in this work. As expected, the strength of samples synthesized using sodium silicate solutions with low C_s values was low, and the strength tended to decrease as the amount of zeolite particles was increased. However, moderate strengths can be achieved when C_s is increased, and the strength is hardly affected even when the amount of zeolite particles is significantly increased.

As it was confirmed that uniform zeolite monoliths with a microhoneycomb structure can be obtained through the ice template method, next we attempted to synthesize such monoliths directly in a stainless steel column. Figure 6 shows a

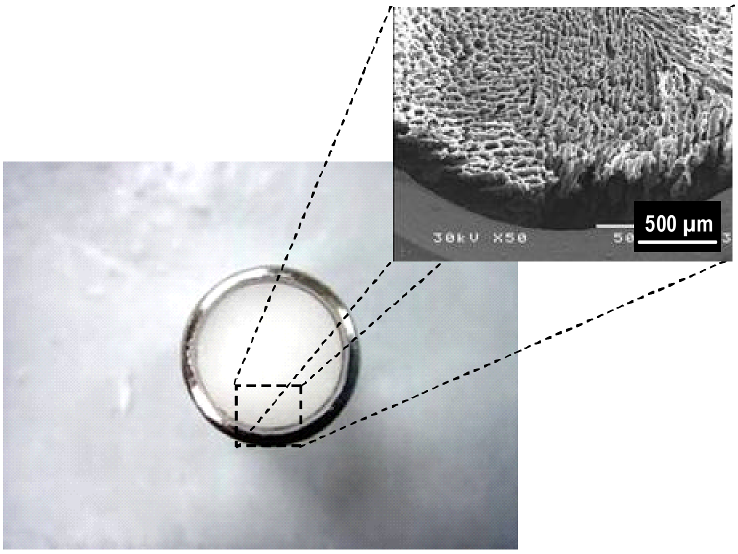

Fig. 6 Photograph and a SEM image of a typical column obtained in this work

photograph and an SEM micrograph of the cross section of a typical column. The existence of a slight gap between the monolith and the stainless steel column can be confirmed. However, the size of this gap is comparable to the sizes of the channels within the monolith, therefore this gap will probably not become a serious problem in most of the applications this monolith is expected to be used for.

Using these stainless steel columns, the pressure drop which occurs when air was passed through them was measured. All measurements were conducted at room temperature. Figure 7 shows the results, where the pressure drop is plotted against the flow rate of air. The pressure drop linearly increased with the increase in flow rate, but was extremely low even at high flow rates. The line in the same graph shows the predicted pressure drop of the column which was calculated using a multi-capillary model to represent the structure of the monolith. The measured values are slightly higher than the predicted values, which indicates that the channels in the monolith are basically straight and are fairly aligned, but slight irregularity which disturbs the flow also exists within them.

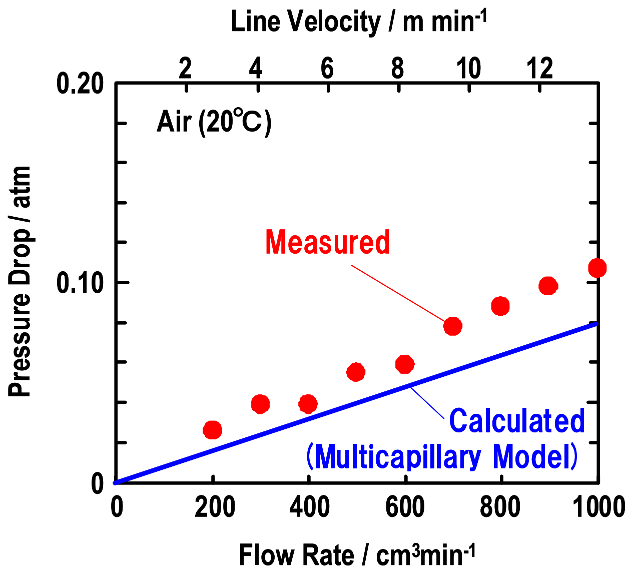

Fig. 7 Pressure drop which occurs in a typical column (x = 0.6, i.d. 10 mm, L 30 mm)

Conclusion

In this work, a zeolite monolith with a monolithic microhoneycomb structure was synthesized by applying the ice template method to a silica hydrogel including zeolite nanoparticles. The monolith was found to have a microhoneycomb structure and the included zeolite nanoparticles were found to be evenly distributed within it. The zeolite nanoparticles maintained their crystal structure, and there was no sign of pore blocking due to the inclusion in silica. As expected, the resistance to flows of the monoliths was extremely low. These monoliths can be used to provide a zeolite column in which short diffusion paths and low pressure drops are compatible.

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