

DEVELOPMENT OF A STRONG ACID ION EXCHANGE RESIN WITH A MONOLITHIC MICROHONEYCOMB STRUCTURE USING THE ICE TEMPLATING METHOD

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Summary

In this work, the synthesis of a strong acid ion exchange resin with a monolithic microhoneycomb structure was attempted using the ice templating method, a new micromolding method developed by the authors. The obtained monoliths were found to have μm -sized straight channels and the thickness of the walls which form the channels were also in the μm range. The monoliths showed strong acidity in esterification reactions which indicates that they can be used as an effective solid acid catalyst with an extremely low hydraulic resistance in various commercial reactions.

Keywords

Rational design of catalysts, Green CRE, Novel functional materials

Introduction

Ion exchange resins have been used for decades for water treatment and as catalysts. However, most resins swell or shrink during usage, which leads to the instability of activity. This problem can be avoided by decreasing the length of the diffusion paths within the resin. As most resins are synthesized as particles, shortening of diffusion paths can be achieved by simply decreasing their size. However, small particles cause a severe hydraulic resistance. Therefore, there are many cases in which large particles are used just to decrease resistance. In such cases, the accessibility to active sites within the resin is sacrificed.

Such problems may be avoided by changing the morphology of the resin. A monolithic microhoneycomb as shown in Fig. 1 is one example of an ideal morphology. As such monoliths have straight and aligned macropores, their hydraulic resistance can be minimized, and the resistance which actually occurs is thought to be hardly affected by the swelling of the resin. Moreover, as the walls which form the macropores are thin, the activity of the resin will also be hardly affected by swelling, as the diffusion paths within the resin are extremely short. Many advantages are expected from this morphology, but the problem is how to mold resins to have such a morphology.

Previously, we found that hydrogels which are obtained through sol-gel transition can be molded to have a microhoneycomb structure by simply freezing them “unidirectionally.” The needle shaped ice crystals which are formed within the hydrogel and which elongate during

freezing act as the template, and straight and aligned macropores are formed. By using this method, which we named the “Ice Templating Method,” we have succeeded in obtaining monolithic microhoneycombs of not only inorganic gels such as silica¹, silica-alumina, but also organic gels of resorcinol-formaldehyde (RF)².

Organic gels synthesized from resorcinol (R), sodium salts of benzaldehyde 2, 4 disulfonic acid (B) and formaldehyde (F) are known to have a high ion exchange ability, and also to show strong acidity when they are in the H^+ form. As the structure of this gel is quite similar to RF gels, we applied the ice templating method to this gel and attempted to synthesize a monolithic microhoneycomb.

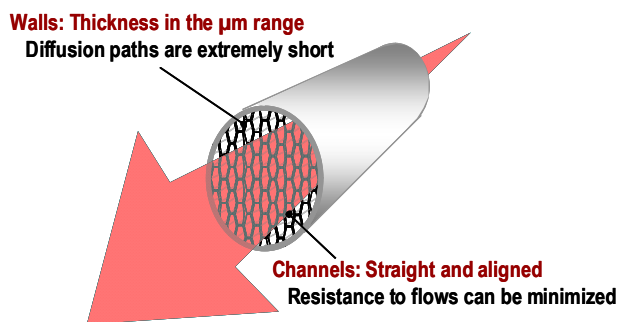


Fig. 1 Schematic of a Monolithic Microhoneycomb

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Experimental

Designated amounts of R, B and pure water (W) were mixed, and the resulting solution was heated to 373 K. Then the solution was cooled to room temperature and F was added. The solution was poured into polypropylene tubes and was aged. After the solution transformed to a gel, the tubes including the gel were dipped into a cold bath filled with liquid nitrogen at a constant rate. The completely frozen gels were thawed and freeze dried, and finally the monoliths were obtained.

The morphology of the samples was checked by direct observation using a scanning electron microscope (SEM). Fluid penetration tests were also conducted using a 0.1 mol/L NaOH solution. The ion exchange capacities of the samples were determined through titration experiments. Finally, the catalytic activities of the samples were evaluated using the esterification of ethanol with acetic acid as the model reaction. Reactions using H_2SO_4 as the catalyst were also conducted for comparison. Reactions were conducted at 333 K, and the molar ratios among acetic acid, ethanol and the H^+ in the catalyst were adjusted to be 1:1:0.001.

Results and Discussion

Fig. 2 shows a photograph and a cross sectional SEM image of a typical sample obtained in this work. As the overall shape of the samples reflect the shape of the vessel used for synthesis, cylindrical monoliths were obtained in this work. Through SEM observation and fluid penetration tests, the samples were confirmed to have a microhoneycomb structure, in which straight μm -sized channels extend from one side to the opposite side of the sample. The thicknesses of the walls which form the channels were in the range of 10 to 15 μm , which indicates that the diffusion paths within the sample are extremely short.

Fig. 3 shows a typical titration curve, in which a solution including a typical sample and NaCl was titrated using a 0.1 mol/L NaOH solution. It can be noticed that the pH rapidly increases when the equivalence point is about to be reached, a character which indicates that the sample is a strong acid resin.

Finally, the catalytic activities of the samples were evaluated. Fig. 4 summarizes the results. This esterification reaction proceeds without catalyst addition, but it is obvious that the reaction is accelerated with the addition of the monolith obtained in this work. It can also be noticed that the monoliths possess activities comparable to a homogeneous acid catalyst H_2SO_4 . From the obtained results, it can be concluded that this monolith can be used as an effective solid acid catalyst with an extremely low hydraulic resistance in various commercial reactions.

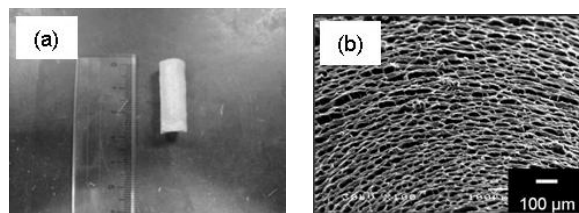


Fig. 2 (a) Photograph and (b) cross sectional SEM image of a typical sample obtained in this work

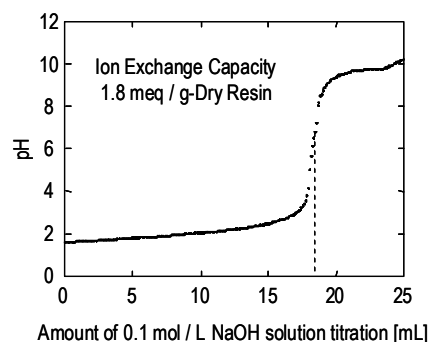


Fig. 3 Titration curve of a typical sample obtained in this work

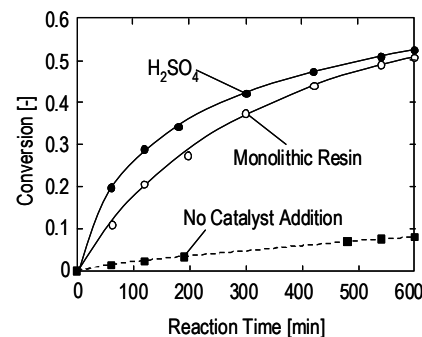


Fig. 4 Catalytic activities of a typical sample obtained in this work

References

- (1) Mukai, S. R.; Nishihara, H.; Tamon, H. Formation of Monolithic Silica Gel Microhoneycombs (SMHs) Using Pseudosteady State Growth of Microstructural Ice Crystals. *Chem Commun.* **2004**, 874
- (2) Mukai, S. R.; Nishihara, H.; Yoshida, T.; Taniguchi, K.; Tamon, H. Morphology of Resorcinol-Formaldehyde Gels Obtained through Ice-templating. *Carbon* **2005**, 43, 1563

Acknowledgements

This work was supported by the Industrial Technology Research Grant Program in 2006, 06B44702a from New Energy and Industrial Technology Development Organization (NEDO) of Japan and the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Scientific Research (B) 21360384.