CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci

DOI: 10.3303/CET1124019

Development of a Water Tolerant Solid Acid Catalyst with a Low Hydraulic Resistance Using the Ice Templating Method

Shin R. Mukai, Kazuhiro Murakami, Masatoshi Hashimoto and Yoshitaka Satoh

Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University
N13W8 Kita-ku, Sapporo 060-8628, Japan, smukai@eng.hokudai.ac.jp

A silica hydrogel including 12-molybdophosphoric acid was successfully molded into a monolithic microhoneycomb using the Ice Templating method, a new micromolding technique developed by the authors. The microhoneycombs were found to have straight and aligned micrometer-sized channels, which walls are porous and extremely thin. Therefore, such microhoneycombs do not cause a severe hydraulic resistance, even though the lengths of the diffusion paths within them are extremely short. This was confirmed by measuring the pressure drop which occurs when fluids were passed through them. The included acid was found to be uniformly distributed within the monolith and effectively immobilized. Moreover, the stability of the acid could be significantly enhanced by partially neutralizing the protons of it using $CsCO_3$. Such monoliths can be practically used as solid acids which only cause minimum hydraulic resistances in reactions which involve water.

1. Introduction

Methods to immobilize acidic species in order to obtain a solid acid catalyst which is not only water tolerant but also environmentally benign have been actively investigated. A typical approach is the immobilization of Keggin type heteropoly acids (HPAs) within a silica matrix (Izumi *et al.*, 1995a, Izumi, 1998). By adding them to the starting solution for silica synthesis, HPA molecules practically embed themselves through the formation of a silica network around them using their own catalysis. However, the silica matrix must be designed to be quite rigid in order to prevent leakage of the HPA molecules during usage. This means that only HPA molecules close to the outer surface of the silica-HPA complex can contribute to reactions. Therefore, such complexes are usually finely ground to small particles, in order to increase the area of their outer surface and increase their apparent activities. This not only leads to additional HPA leakage, but also limits the usage of such complexes, as they are likely to cause a severe hydraulic resistance.
The drawbacks of such complexes can be eliminated if they can be molded to have a morphology in which short diffusion paths and low hydraulic resistances are compatible. A microhoneycomb having straight and aligned micrometer-sized channels, the walls of

Please cite this article as: Mukai S., Murakami K., Hashimoto M. and Satoh Y., 2011, Development of a water tolerant solid acid catalyst with a low hydraulic resistance using the ice templating method, Chemical Engineering Transactions, 24, 109-114
DOI: 10.3303/CET1124019

which are fairly thin, is one example of an ideal morphology. However, it is difficult to mold silica to have such a morphology using conventional synthesis techniques.
Recently we found that silica can be molded into a microhoneycomb structure by freezing its parent hydrogel unidirectionally (Mukai *et al.*, 2003, 2004, Nishihara *et al.*, 2005). We named this method the Ice Templating method, as ice crystals act as the template. We also found that this method can be applied to silica hydrogels including HPAs. As microhoneycombs obtained through this method are expected to be used as solid acid catalysts, especially in reactions in which flow systems are involved, we verified how such microhoneycombs perform in flow systems in this work.

2. Experimental

Commercial sodium silicate solutions were diluted with ion-exchanged and distilled water, and their SiO_2 concentrations were adjusted to desired values. Then the pH of the solutions was adjusted using an ion-exchange resin. To these solutions, 12-Molybdophosphoric acid (PMo12) was added so that the amount of PMo12 in the resulting silica would be x g-HPA (g-SiO_2)$^{-1}$. x was varied in the range 0 to 1.6 g-HPA (g-SiO_2)$^{-1}$. The resulting solutions were poured into polypropylene tubes (*i.d.*: 10 mm, *L*: 120 mm) and were aged at 303 K. Next the tubes were dipped at a constant rate of 6 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. The resulting samples were released from the tubes and were freeze-dried. Part of the samples was further treated with controlled amounts of $CsCO_3$ to partially neutralize the protons of the included PMo12 to enhance their stability (Okuhara *et al.*, 1990, Izumi *et al.*, 1992, 1995b).
The morphology of the samples was directly observed using a scanning electron microscope (SEM). The hydraulic resistance of the samples was evaluated by measuring the pressure drop which occurs when ethanol was passed through the samples. The durability of the samples was evaluated by measuring the amount of PMo12 leakage when ethanol was passed through them at a constant rate. Finally, the catalytic activities of the samples were evaluated using the esterification of acetic acid with ethanol as a model reaction.

3. Results and Discussion

Figure 1 shows a photograph and a cross sectional SEM micrograph of a typical sample obtained in this work. The sample was uniformly bright yellow in color, the characteristic color of PMo12, suggesting that PMo12 is uniformly dispersed throughout the sample. The sample was confirmed to have a microhoneycomb structure, so the basic features of a microhoneycomb, low hydraulic resistance and short diffusion paths, can be expected. It was also confirmed that treatment with $CsCO_3$ doesn't affect the structure of the monoliths.
Figure 2 shows the pressure drop which occurs when ethanol was passed through the monoliths, where the pressure drop is shown as a function of linear velocity. The pressure drop that a monolithic silica microhoneycomb not including PMo12 causes is also shown for comparison. Microhoneycombs with a similar channel size were used in

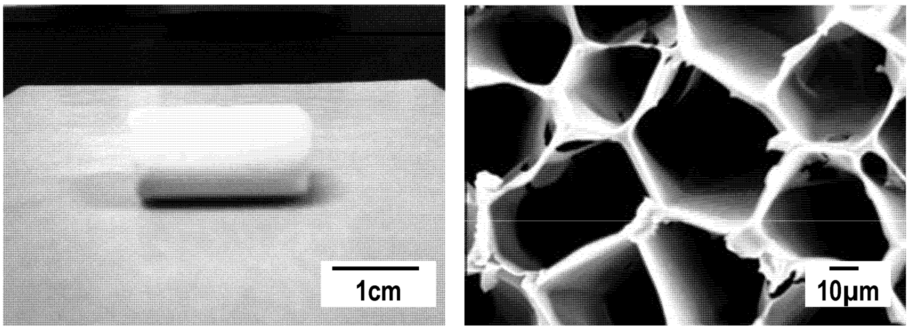

Figure 1: Photograph (left) and a cross-sectional SEM micrograph (right) of a typical monolithic silica microhoneycomb including PMo12 obtained in this work

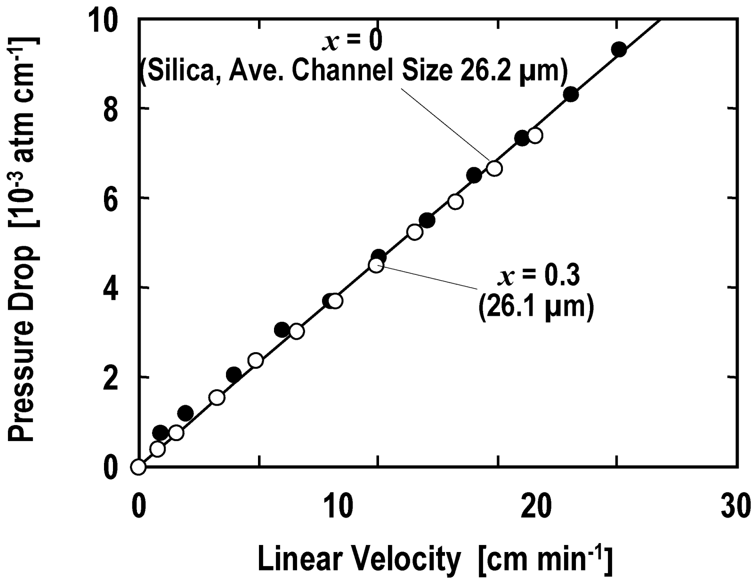

Figure 2: Hydraulic resistances of typical samples obtained in this work (fluid: ethanol (298 K))

this comparison. The pressure drop was found to be low, and was not affected by the inclusion of PMo12.

Figure 3 shows the results of durability tests, where the leakage ratio of PMo12 is plotted as a function of time on stream. A slight leakage, which is thought to be due to the PMo12 which exists on the outer surface of the walls of the as-prepared microhoneycombs, was observed in the beginning of treatment. However, this leakage terminated quite quickly, indicating that most of the PMo12 was effectively immobilized within the silica matrix. The total amount of leakage was found to be extremely low, especially when compared with silica including HPAs synthesized in the form of small particles. However, it was found that when water coexists within the

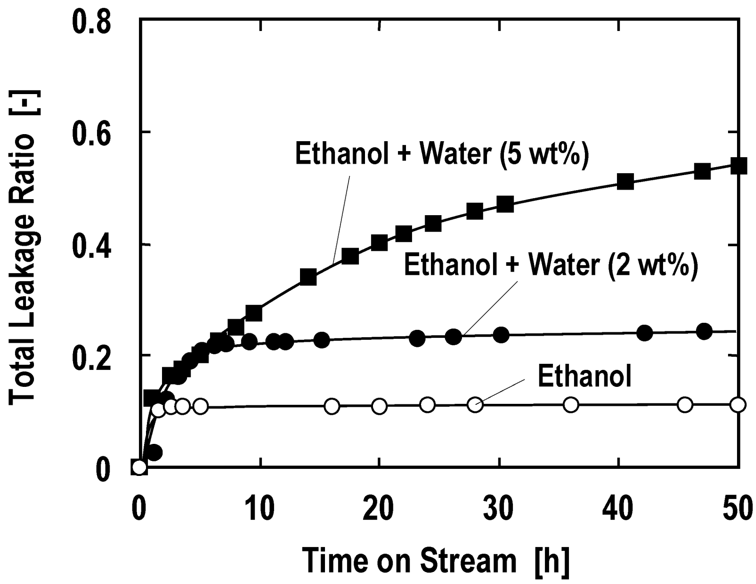

Figure 3: Durability of typical samples obtained in this work (amount of PMo12 inclusion: x = 0.8 g-HPA (g-SiO$_2$)$^{-1}$, treatment fluid: ethanol (333 K), flow rate: 0.056 mL min^{-1})

solution, the PMo12 included in the microhoneycombs becomes unstable and tends to leak out.

Next the catalytic activities of the samples were evaluated using the esterification of acetic acid with ethanol as a model reaction. As water is generated through this reaction, the PMo12 included in the samples is likely to become unstable and is thought to eventually leak out from the silica matrix. Therefore the included PMo12 must be stabilized before application to reactions.

It is well known that cesium salts and ammonium salts of HPAs are fairly stable and are insoluble in water. As the protons, the origin of acidity of HPAs, are neutralized in such salts, they cannot show catalytic activity in reactions which are accelerated by acids. However, Okuhara *et al.* (1990) showed that by partially neutralizing the protons, HPAs can be made insoluble while still maintaining acidity. Izumi *et al.* (1992, 1995b) have pointed out that such partially neutralized salts are very stable and can be applied to various reactions which involve water. Therefore we verified the possibility to stabilize the PMo12 included in silica through partial neutralization using $CsCO_3$.

HPA crystals are basically non-porous so their inner accessibility is quite limited. However, by exchanging their protons with cesium or ammonium cations, their surface area increases, indicating that their inner accessibility can be improved (Tatematsu *et al.*, 1984, Mizuno and Misono, 1987, Izumi, 1995a). This means that the acidity of HPA cesium or ammonium salts, and their inner accessibility are in a trade-off relationship. Studies to clarify the optimum degree of neutralization regarding this trade-off relationship have been conducted, and the optimum degree was reported to be about 5/6

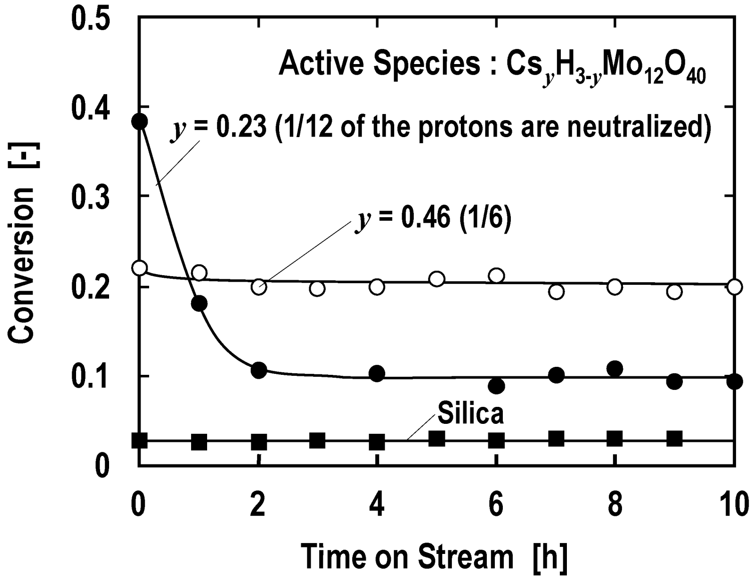

Figure 4: Catalytic activities of typical samples obtained in this work (amount of PMo12 inclusion: x = 0.8 g-HPA (g-SiO$_2$)$^{-1}$, reaction temperature: 333 K, residence time: 100 min)

(Okuhara *et al.*, 1990, Izumi *et al.*, 1995b). Considering the fact that PMo12 hardly leaked during treatment with ethanol, PMo12 is thought to be uniformly distributed and immobilized within the silica matrix of the microhoneycomb samples obtained in this work. Therefore only a stabilization effect is required from the cations, meaning that there is a high possibility that the degree of neutralization can be reduced while still obtaining stability in microhoneycomb samples.

Figure 4 shows the results of esterification experiments, where the conversion is plotted as a function of time on stream. When only 1/12 of the protons of PMo12 were neutralized, the microhoneycomb showed a high catalytic activity at the beginning, but this activity quickly dropped. This is thought to be due to the leakage of PMo12 which indicates that the stabilizing effect was insufficient. When 1/6 of the protons of PMo12 were neutralized, the initial conversion decreased but was fairly constant indicating that the leakage of PMo12 was prevented. As such samples can maintain a fairly high catalytic activity, it is assumed that they can be used as solid acid catalysts as alternatives to various liquid acids in various reactions.

4. Conclusions

In this work, a monolithic silica microhoneycomb in which PMo12 was immobilized was synthesized by applying the Ice Templating method to a silica hydrogel in which PMo12 was dispersed. Due to its unique morphology, the hydraulic resistance of the monolith was extremely low. PMo12 was effectively immobilized within the monolith, but was found to become unstable when it makes contact with water. This instability could be significantly improved by partially neutralizing a fraction of the protons of the included PMo12. Such monoliths showed a fairly high catalytic activity, indicating that they can be used as solid acid catalysts as alternatives to various liquid acids in various reactions.

References

Izumi Y., Ogawa M., Nohara W. and Urabe K., 1992, Acidic alkali metal salts and ammonium salts of Keggin-type heteropolyacids as efficient solid acid catalysts for liquid-phase Friedel-Crafts reactions, Chemistry Letters, 21, 1987-1990

Izumi Y., Ono M., Kitagawa M., Yoshida M. and Urabe K., 1995a, Silica-included heteropoly compounds as solid acid catalysts, Microporous Materials, 5, 255-262

Izumi Y., Ogawa M. and Urabe K., 1995b, Alkali metal salts and ammonium salts of Keggin-type heteropolyacids as solid acid catalysts for liquid-phase Friedel-Crafts reactions, Applied Catalysis A: General, 132, 127-140

Izumi Y., 1998, Recent advances in immobilization of heteropoly acids, Research on Chemical Intermediates, 24, 461-471

Mizuno N. and Misono M., 1987, Pore structure and surface area of $Cs_xH_{3-x}PM_{12}O_{40}$ (x = 0 – 3, M = W, Mo), Chemistry Letters, 16, 967-970

Mukai S. R., Nishihara H. and Tamon H., 2003, Porous properties of silica gels with controlled morphology synthesized by unidirectional freeze-gelation, Microporous and Mesoporous Materials, 63, 43-51

Mukai S. R., Nishihara H. and Tamon H., 2004, Formation of monolithic silica gel microhoneycombs (SMHs) using pseudosteady state growth of microstructural ice Crystals, Chemical Communications, 874-875

Nishihara H., Mukai S. R., Yamashita D. and Tamon H., 2005, Ordered Macroporous Silica by Ice-templating, Chemistry of Materials, 17, 683-689

Okuhara T., Nishimura T., Ohashi K. and Misono M., 1990, A pronounced catalytic activity of an acidic cesium salt of 12-tungstophosphoric acid for ester decomposition in solid–liquid system, Chemistry Letters, 19, 1201-1202

Tatematsu S., Hibi T., Okuhara T. and Misono M., 1984, Preparation process and catalytic activity of $Cs_xH_{3-x}PW_{12}O_{40}$, Chemistry Letters, 13, 865-868

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), 19360355 (2007), 21360384 (2009).