

## DEVELOPMENT OF A WATER TOLERANT SOLID ACID CATALYST WITH A LOW HYDRAULIC RESISTANCE USING THE ICE TEMPLATING METHOD

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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  $\text{CsCO}_3$ . Such monoliths can be practically used as solid acids which only cause minimum hydraulic resistances in reactions which involve water.

### 1. INTRODUCTION

There are several important liquid phase reactions which are catalyzed by acids such as esterification, acylation and hydrolysis. When such reactions are conducted at industrial scale, homogeneous acids such as sulfuric acid and hydrochloric acid are typically used as the catalyst. However, the usage of such highly soluble catalysts requires a catalyst separator after the reactor which is not only energy consuming, but which also generates a huge amount of chemical wastes. Such problems can be avoided by using a water tolerant solid acid catalyst instead. Presently, ion-exchange resins are commercially available for this purpose. However, as these resins lack thermal stability, the development of a new stable water tolerant solid acid catalyst which can be used at higher temperatures is desired.

One way to obtain such a solid acid is to physically immobilize an acidic species to a stable support. Many research groups have attempted the development of a solid acid catalyst based on this concept. A typical example is the immobilization of Keggin type heteropoly acids (which will be abbreviated to HPAs hereafter) 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 as shown in Fig. 1, which has straight and aligned micrometer-sized channels, the walls of 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.

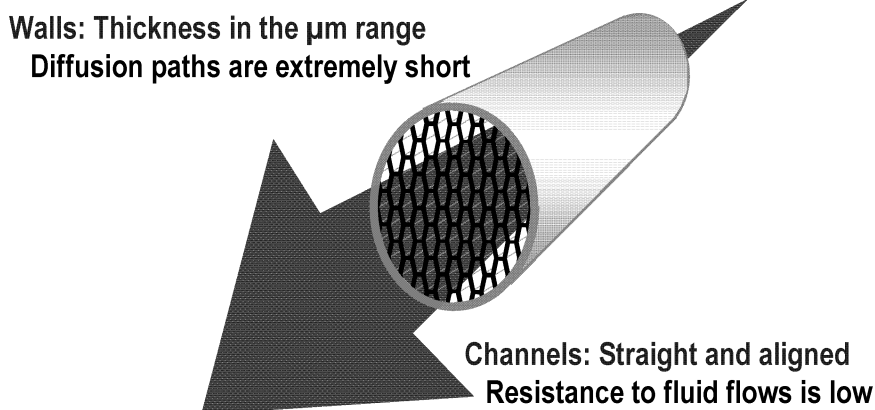


Fig. 1: Schematic of a monolithic microhoneycomb and its features

## 2. EXPERIMENTAL

Commercial sodium silicate solutions were diluted with ion-exchanged and distilled water, and their  $\text{SiO}_2$  concentrations were adjusted to the 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  $x \text{ g-HPA (g-SiO}_2\text{)}^{-1}$ .  $x$  was varied in the range 0 to  $1.6 \text{ g-HPA (g-SiO}_2\text{)}^{-1}$ . The resulting solutions were poured into polypropylene tubes (*i.d.*: 10 mm, *L*: 120 mm) and were aged at 303 K. After the solutions in the tubes transformed to hydrogels, the tubes were dipped at a constant rate of  $6 \text{ cm h}^{-1}$  into a cold bath maintained at 77 K. The completely frozen tubes 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  $\text{CsCO}_3$  to partially neutralize the protons of the included PMo12 to enhance its stability (Okuhara *et al.*, 1990, Izumi *et al.*, 1992, 1995b).

The morphology of the samples was checked using a scanning electron microscope (SEM). The hydraulic resistance of the samples was evaluated by measuring the pressure drop which occurs when ethanol (298 K) was passed through the samples using a digital manometer. The durability of the samples was evaluated by measuring the amount of PMo12 which leaks out from the silica matrix when the samples were treated with an excess amount of ethanol. Durability tests were conducted in a batch system (298 K) and also in a flow system (333 K). In durability tests conducted in a batch system, the ratio between the solvent volume and sample weight was fixed to  $1 \text{ L-solvent (g-sample)}^{-1}$ . In durability tests conducted in a flow system, the flow rate of the solvent was fixed to  $0.056 \text{ cm}^3 \text{ min}^{-1}$ . Tests using ethanol which include a slight amount of water were also conducted. Finally, the catalytic activities of the samples were evaluated using the esterification of acetic acid with ethanol as a model reaction. Reactions were conducted at 333 K in a flow system. A mixture of acetic acid and ethanol (molar ratio 1:1) was introduced to columns including the test samples at a flow rate fixed so that the residence time will be 100 min. The composition of the outlet flow was analysed using a gas chromatograph and the conversions were calculated

### 3. RESULTS AND DISCUSSION

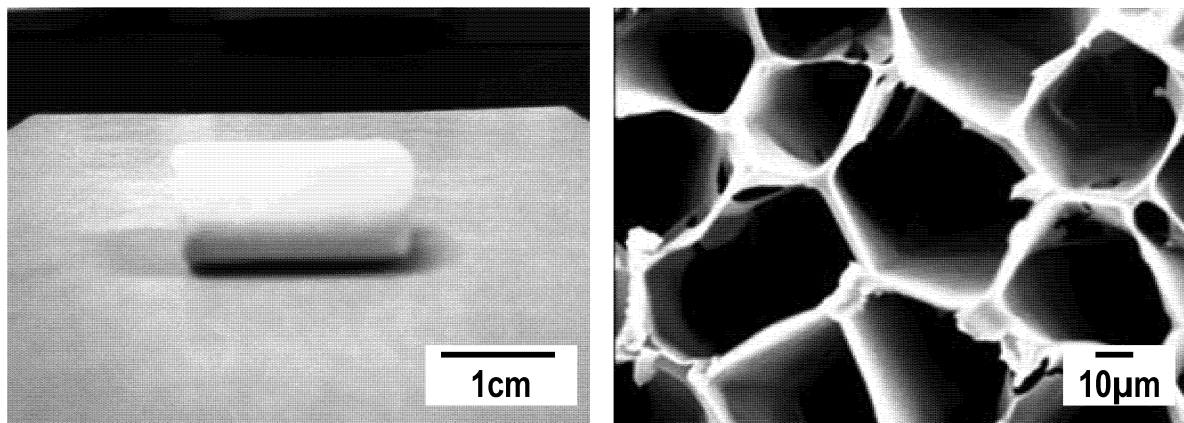


Fig. 2: Photograph (left) and a cross-sectional SEM micrograph (right) of a typical monolithic silica microhoneycomb including PMo12 obtained in this work

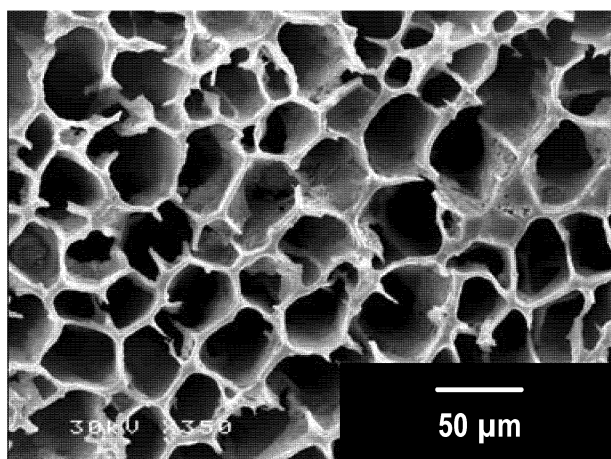


Fig. 3: Cross-sectional SEM micrograph of a typical monolithic silica microhoneycomb including PMo12 after treatment with  $\text{CsCO}_3$

In the synthesis of a monolithic silica microhoneycomb, first a silica hydrogel is prepared from a sodium silicate solution through sol-gel transformation. When solutions with the same silica concentration are used, the time required for a hydrogel to be formed mainly depends on its pH value. This pH value depends on the concentration of residual sodium cations. We typically use starting solutions with similar pH values, so the time required for gel formation is usually quite similar. However in this work, the gelation time of the silica sols prepared from sodium silicate solutions decreased with the increase in the amount of PMo12 loading, indicating that PMo12 accelerates the polycondensation of silica. The formed hydrogels had a bright yellow color, the characteristic color of PMo12. These hydrogels were then froze unidirectionally, and then freeze-dried.

Figure 2 shows a photograph and a cross sectional SEM micrograph of a typical sample. The sample was uniformly bright yellow in color, 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, a low hydraulic resistance and short diffusion paths, can be expected. It was also confirmed that treatment with  $\text{CsCO}_3$  doesn't affect the structure of the monoliths (Fig. 3).

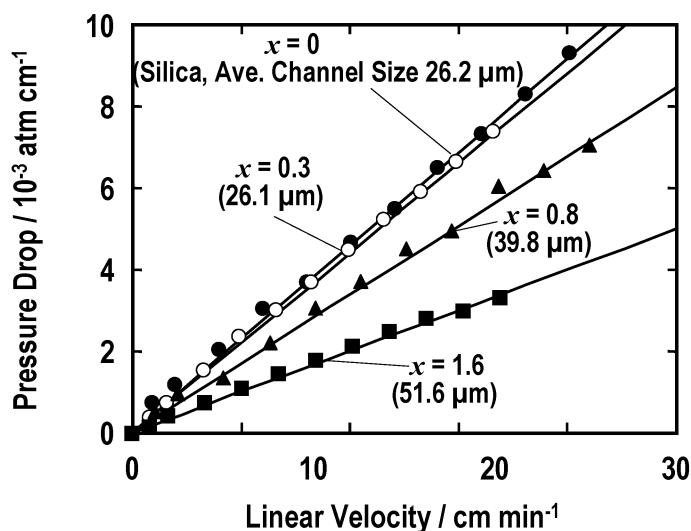


Fig. 4: Hydraulic resistance of typical samples obtained in this work (Fluid: Ethanol (298 K))

Next, we verified whether the monoliths possess the most expected feature considering its structure, a low hydraulic resistance. Figure 4 shows the pressure drop which occurs when ethanol was passed through typical monoliths obtained in this work, where the pressure drop is shown as a function of linear velocity. The average size of the channels in each monolith is also shown in the figure. Interestingly, the average channel size increased with the increase in the amount of PMo12 loading, and the pressure drop decreased accordingly. As all of the monoliths were synthesized using identical freezing conditions, this result indicates that the mobility of water in the precursor hydrogel during freezing was affected by PMo12, inclusion resulting in the difference in the size of the ice crystals which play the role of the template. The pressure drop that a monolithic silica microhoneycomb not including PMo12 causes is also shown for comparison. A microhoneycomb having an average channel size similar to that of a microhoneycomb including PMo12 at a ratio of 0.3 g-HPA (g-SiO<sub>2</sub>)<sup>-1</sup> was used in this comparison. The resistance that both microhoneycombs caused was quite similar, indicating that the resistance depends on the size of the channels, not on the amount of PMo12 loading.

The monoliths synthesized in this work are intended to be used in the liquid phase, so it has to be confirmed whether the included PMo12 doesn't leak out when it makes contact with liquids. First, tests were conducted in a batch system using ethanol as the treatment solution. Figure 5 summarizes the results, where the total leakage ratio is plotted as a function of the duration of solvent treatment. A slight leakage was detected at the beginning of treatment, regardless of the amount of the initial PMo12 loading, but this leakage terminated quite quickly. The total leakage ratio increased with the increase in PMo12 loading, but was low even when the amount of initial PMo12 loading was extremely high. It should be noted that in cases when samples were synthesized in the form of particles, over half of the included PMo12 leaks out when the amount of PMo12 loading is this high. The obtained monoliths are thought to be mainly used in flow systems. Therefore, we also conducted durability tests in a flow system using ethanol as the treatment solvent. A sample with a fairly high loading amount of 0.8 g-HPA (g-SiO<sub>2</sub>)<sup>-1</sup> was used in this test. The results are summarized in Figure 6, where the leakage ratio is plotted as a function of time on stream. As in the tests conducted in batch systems, slight leakage occurred at the beginning of treatment, but this leakage terminated quite quickly indicating that this leakage is due to the PMo12 existing on the outer surface of the channels. This test was much severer than those conducted using a batch system, as the treatment temperature was higher and the solvent which makes contact with the samples is constantly replaced, but the total amount of leakage was still low and was comparable to the values obtained in batch system tests. As the solubility of PMo12 in ethanol is extremely high, this result indicates that the PMo12

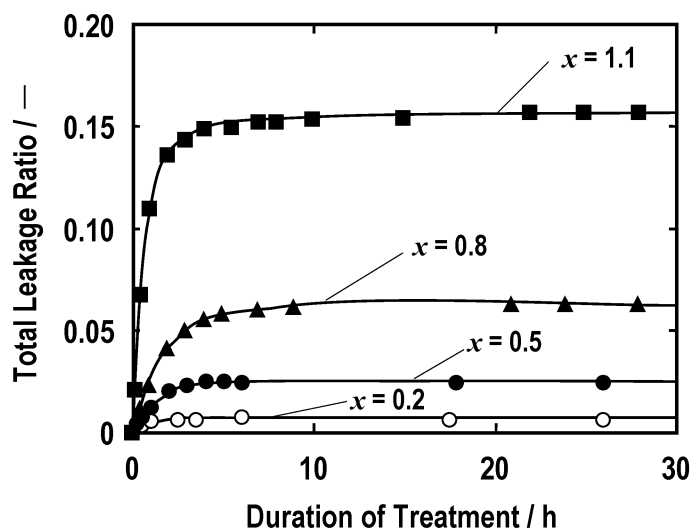


Fig. 5: Durability of typical samples obtained in this work evaluated in a batch system (treatment fluid: ethanol (298 K))

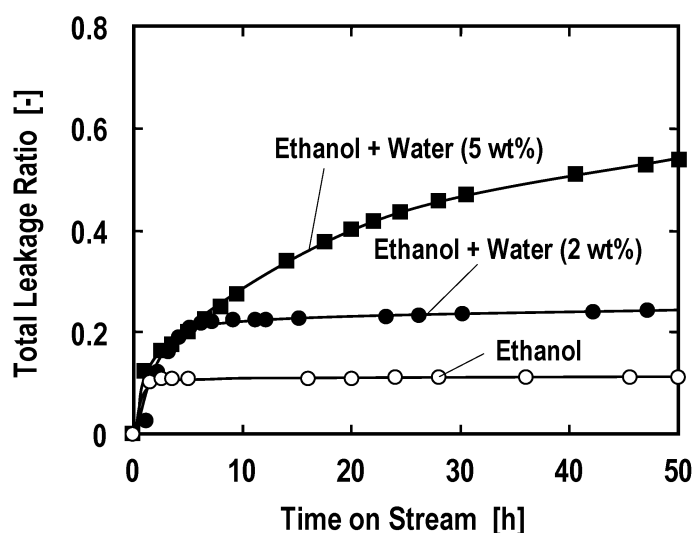


Fig. 6: Durability of typical samples obtained in this work evaluated in a flow system (amount of PMo12 inclusion:  $x = 0.8$  g-HPA (g-SiO<sub>2</sub>)<sup>-1</sup>, treatment fluid: ethanol (333 K), flow rate: 0.056 mL min<sup>-1</sup>)

molecules in the samples are physically entrapped within the silica matrix which form the walls of the channels of the monoliths.

Durability tests using ethanol which contain a small amount of water were also conducted. The results are also shown in Fig. 6. It was found that when water coexists in the solution, the PMo12 included in the microhoneycombs tends to gradually leak out. It is assumed that the water in the treatment solvent makes the included PMo12 unstable. This phenomena is observed when the concentration of PMo12 is low in a solution, indicating that the included PMo12 is highly dispersed within the silica matrix of the sample.

Finally, the catalytic activity of typical samples was evaluated using the esterification of acetic acid with ethanol as a model reaction. As water is generated through this reaction, the PMo12 in the samples is likely to become unstable and is thought to gradually leak out. Therefore the included PMo12 must be stabilized before usage.

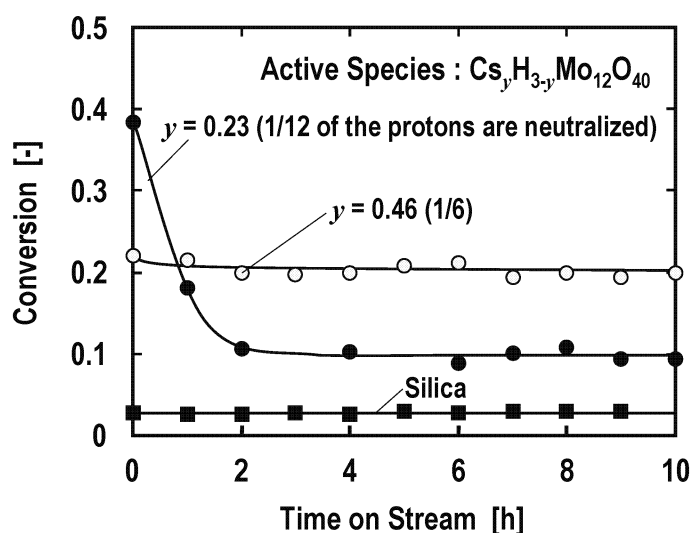


Fig. 7: Catalytic activities of typical samples obtained in this work (amount of PMo12 inclusion:  $x = 0.8$  g-HPA  $(\text{g-SiO}_2)^{-1}$ , reaction temperature: 333 K, residence time: 100 min)

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  $\text{CsCO}_3$ .

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 (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 7 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 neutralizing a fraction of the protons of the included PMo12 using cesium cations. 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.

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