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[Review Paper]

Synthesis of Monolithic Microhoneycombs Equipped with Unique Hierarchical Pore Systems Using Ice Templating

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Various porous materials with unique functions can be obtained through sol-gel synthesis. In many cases the performance of such materials can be significantly improved by controlling the morphology of them. Recently, we found that sol-gel derived materials can be molded into the form of monolithic microhoneycombs by freezing their parent hydrogel unidirectionally. In this process, the ice crystals which are formed within the hydrogel during freezing act as the template. The sizes of the monolith channels, the traces of the ice crystals, are in the micrometer range, therefore can be considered as macropores. The walls which form the channels have thicknesses around 1 μm , and have developed nanopores within them. Therefore, such monoliths are equipped with a unique hierarchical pore system in which short nanopores are directly connected to straight macropores. Due to this unique structure, such monoliths do not cause severe pressure drops when fluids are passed through them, even though the lengths of the diffusion paths within them are extremely short. This method can be applied to various hydrogels, either organic or inorganic, therefore monoliths having a wide variety of functions along with this unique structure can be easily obtained. This method can also be used to assemble fine particles into the form of a monolithic microhoneycomb by using a proper hydrogel as the binder.

Keywords

Ice templating method, Sol gel synthesis, Hydrogel, Hierarchical pore system, Monolithic microhoneycomb

1. Introduction

Various porous materials are widely used as adsorbents and catalysts and are supporting our daily lives in many different ways. In such materials, the active sites which provide the basic function(s) of the material are usually evenly dispersed throughout the whole volume of the material. Therefore, 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 distributed within them, as short as possible. Porous materials are generally synthesized in the form of particles, so 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 necessarily lead to the improvement of the performance of the material. In fact, particles with fairly large sizes are intentionally used in many industrial applications, only to avoid severe pressure drops. This indicates that there are many cases that the performance of such materials can be further improved, if such mate-

rials can be synthesized in a form in which short diffusion paths and low resistance to fluid flows are compatible.

The resistance which occurs when fluids are passed through the particles can be decreased by increasing the size and volume of the voids, or the “paths” which are formed between them. Keeping the paths as straight as possible is also thought to be effective to reduce resistance. Considering these facts, a monolithic microhoneycomb which has straight and aligned micrometer-sized channels within it is thought to be an ideal structure, if the walls which form the channels are thin enough. It is difficult to obtain porous materials with such a structure through conventional synthesis methods, but theoretically, such structures can be obtained through templating methods.

The introduction of micrometer-sized channels into monolithic functional materials has been attempted using phase-separated polymers^{1)~5)}, colloidal crystals^{6)~9)} and microemulsions as the template^{10),11)}. However, the introduced channels are not straight and it is generally difficult to synthesize monoliths with large dimensions. Moreover, micrometer-sized templates are generally extremely expensive and hard to remove.

The pioneering work of Mahler *et al.*¹²⁾ inspired us to use ice crystals as the template to introduce micrometer-

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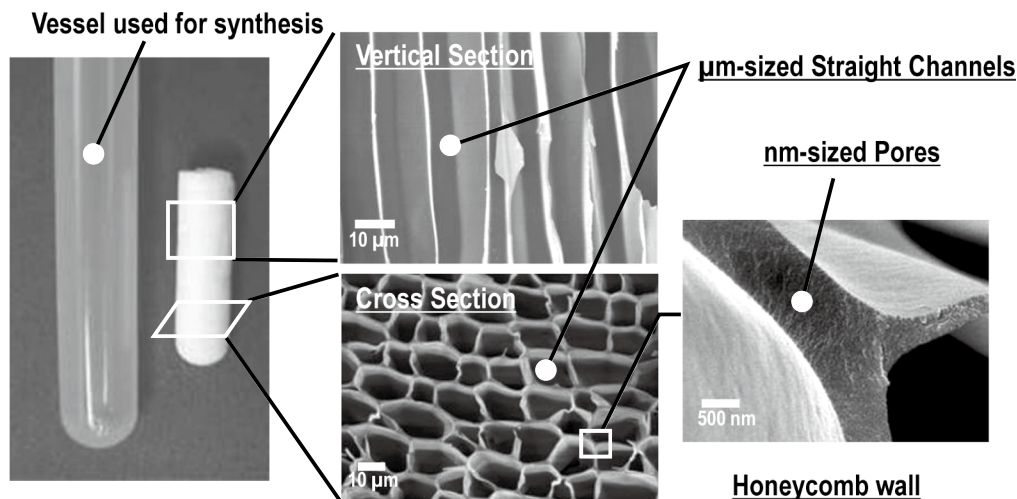


Fig. 1 A Typical Monolithic Silica Microhoneycomb Obtained through the Ice Templating Method

sized channels into porous materials. Ice crystals are extremely inexpensive, and as can be observed, for example, during the synthesis of ice cream, uniform micrometer-sized crystals can be generated at extremely large quantities through simple heat removal. Moreover, as can be witnessed in numerous food processing processes, such ice crystals can be easily removed through sublimation leaving traces of their original shape behind.

Mahler *et al.*¹²⁾ froze hydrogels “unidirectionally” and used the array of ice crystals which appeared within the hydrogel and which elongated in the freezing direction to divide the hydrogel into fibers with polygonal cross-sections. The hydrogel was divided as the hydrogel was too firm. In fact, thoroughly aged hydrogels were intentionally used in their work, as their main purpose was to obtain long and strong gel fibers. Therefore, we assumed that the monolithic hydrogel could be molded into the form of a microhoneycomb if the hydrogel used as the precursor was soft enough to withstand the intrusion of ice crystals and also firm enough to maintain a monolithic structure.

We actually verified this possibility using a monolithic silica hydrogel as the precursor, and succeeded in obtaining a monolithic silica microhoneycomb as shown in **Fig. 1**^{13)~15)}. As ice crystals acted as the template to mold the hydrogel to have this morphology, we named this method the “Ice Templating Method.” This article will describe the details of this method, and the features of the materials obtained through it.

2. The Ice Templating Method

The first step in the Ice Templating Method is to prepare the precursor hydrogel. In this preparation, the amount of impurities included in the hydrogel should be minimized, as such impurities are likely to disturb

the growth of ice crystals. Therefore when we synthesize silica microhoneycombs, we usually start from a sodium silicate solution and then remove the sodium cations using an ion exchange resin. The usage of this starting material is also preferable as it is extremely inexpensive, and also as the inclusion of solvents other than water can be avoided. The next step is to adjust the firmness of the hydrogel so that a microhoneycomb structure will appear during freezing¹⁶⁾. In the case of silica, this can be conducted by adjusting 2 factors, the time required for the precursor of the hydrogel to transform to a hydrogel, and the time allowed for the formed hydrogel to age.

The obtained hydrogel which has a proper firmness is then frozen unidirectionally by removing heat from a single direction. This can be achieved by simply dipping the hydrogel at a controlled rate into a cold bath which temperature is maintained below its freezing temperature. During this freezing process, an array of needle shaped ice crystals appears within the hydrogel and elongates in the freezing direction. This not only introduces the ice crystal templates into the hydrogel, but also causes the hydrogel to be condensed between the growing ice crystals, as the crystals can be formed only by extracting water from the hydrogel.

Such ice crystal templates can be removed by simply thawing and drying the completely frozen hydrogel. In this process, we use pore-protecting drying methods such as freeze drying and supercritical drying in order to ensure that the micro/mesopores do not collapse during drying.

A typical synthesis procedure will be explained in detail. First, a commercial sodium silicate solution (Wako, Japan) was diluted with distilled and deionized water giving a solution containing SiO_2 at a concentration of $1.9 \text{ mol} \cdot \text{L}^{-1}$. Then the pH of the solution was adjusted to 3 using an ion-exchange resin (Amberlite®

IR120B HAG, Organo, Japan). The obtained clear sol was poured into a polypropylene tube, which was 100 mm in length and 10 mm in diameter, and was kept at a constant temperature of 303 K. In about 3 h, the sol transformed to a hydrogel. This hydrogel was aged for an additional 1 h and then was unidirectionally frozen by dipping the tube including it into a cold bath maintained at 77 K at a constant rate of $6 \text{ cm} \cdot \text{h}^{-1}$. After the hydrogel was completely frozen, the tube was transferred to a cold bath maintained at 243 K and was kept in it for 2 h in order to strengthen the structure of the sample. Then the gel was released from the tube and was thawed at 323 K. The thawed sample was then immersed into 10 times its volume of *t*-butanol and was kept there for over 1 day in order to exchange the water included in its structure with *t*-butanol. This washing operation was repeated three times. Next, the wet sample was freeze-dried at 263 K, and finally a dry sample maintaining its wet-state nano/microstructures was finally obtained.

The main features of monolithic microhoneycombs obtained through the Ice Templating Method will be described using this silica microhoneycomb as an example (**Fig. 1**). The overall shape of samples obtained through this method depends on the shape of the vessel used for synthesis. We typically use a polypropylene tube, which is also shown in **Fig. 1**, so cylindrical monoliths are usually obtained. The micrographs of the cross section and vertical section of the silica monolith shows that the monolith has straight and aligned micrometer-sized channels. A high magnification micrograph of the channel wall tells us that the walls are formed by nanoparticles, and have developed nanometer-sized pores within them. This was also confirmed through adsorption experiments. Therefore a monolithic microhoneycomb which has a unique hierarchical pore system in which nanopores are directly connected to macropores can be easily obtained through this method.

Short diffusion paths and a low resistance to fluid flows are expected to be the most significant features of monolithic microhoneycombs obtained through this method. Short diffusion paths can be confirmed by observing the cross-sectional micrographs of the microhoneycombs, so next we evaluated the resistance the monoliths cause by measuring the pressure drop which occurs when air was passed through them.

A cylindrical monolithic silica microhoneycomb was prepared and was inserted into a stainless steel tube which inner diameter matched the outer diameter of the monolith. Air was passed through the monolith, and the pressure drop was measured using a digital manometer. The results are summarized in **Fig. 2**. The pressure drop of a capillary having an inner diameter equal to the average channel size of the microhoneycomb is also shown in the **Fig. 2**. As the structure of a monolithic microhoneycomb can be represented

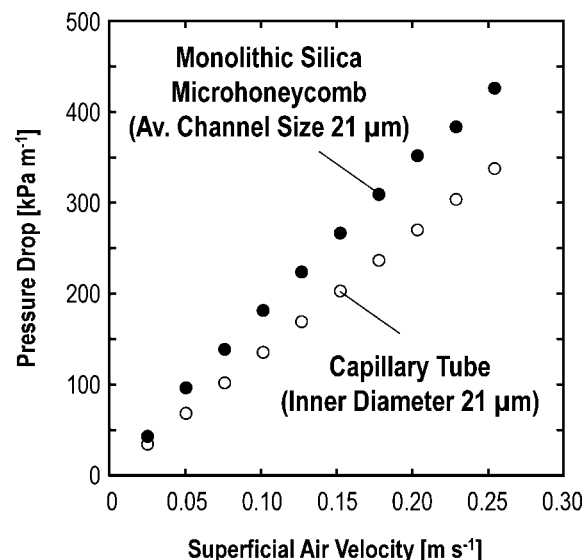


Fig. 2 Pressure Drop which Occurs when Air is Passed through a Monolithic Silica Microhoneycomb Measured at 298 K

by a bundle of capillaries, the pressure drop of a capillary shows the minimum values which a microhoneycomb can achieve. The actual pressure drop which occurs is only slightly higher than the minimum values, indicating that the resistance of the monolithic microhoneycomb is extremely low.

The low resistance can be confirmed by comparing the pressure drop which occurs in a monolithic microhoneycomb with that which occurs in a column packed with particles having the same diffusion path lengths. For example, here a microhoneycomb having channels which sizes are about $21 \mu\text{m}$ and walls which thicknesses are about $1 \mu\text{m}$ will be compared with that of a column packed with particles having diameters equal to the thickness of the walls of the microhoneycomb. Due to its high void fraction, the total volume of the honeycomb will become about 3 times that of the packed column, if the weights of the microhoneycomb and particles are the same. However, in return the pressure drop which occurs in a microhoneycomb will become negligibly small, lower than $1/1000$ of that of a packed column. This clearly shows that short diffusion paths and low hydraulic resistances are compatible in monolithic microhoneycombs.

3. Controlling Structural Parameters of the Monolithic Microhoneycomb

Monolithic microhoneycombs obtained through the Ice Templating Method were found to have an ideal structure, but in order to maximize their performances, the dimensions of the microhoneycombs must be tuned. This section describes how the structural parameters of a microhoneycomb can be controlled.

As previously mentioned, the firmness of the hydrogel used as the precursor must be properly adjusted in order to obtain a monolithic microhoneycomb. If the hydrogel is too soft, the ice crystals grow rather freely within the hydrogel, and the hydrogel will be molded into lamellar sheets. When the hydrogel becomes firm, the ice crystals will start to divide the hydrogel into fibers, and when the hydrogel becomes too firm, the hydrogel will be disintegrated into fine particles.

The sizes of the channels are determined by how freely the water molecules included in the hydrogel can move around when they are about to be frozen. If they can move rather freely, large ice crystals can be formed, so the sizes of the channels tend to increase. Therefore, the sizes of the channels can be controlled by adjusting the freezing rate; a higher freezing rate leads to smaller channels¹⁵⁾. From the same reason, the sizes of the channels tend to become small when the hydrophilicity of the hydrogel is high.

During unidirectional freezing, the level of the freezing front should be kept higher than the level of the refrigerant, in order to ensure heat removal from a single direction. As the freezing rate is limited by the heat removal rate, the freezing rate is not always equal to the dipping rate. Cold baths with lower temperatures are favorable for unidirectional freezing, as the heat of solidification of water is fairly high meaning that the range of the dipping rate will be limited when the temperature of the cold bath is high.

In order to verify the relationship between the actual freezing rate and the size of the channels of the resulting microhoneycomb, we prepared a series of silica hydrogels under the same conditions, and froze them at different dipping rates using cold baths with different temperatures. As the freezing front within the hydrogel could be clearly observed during freezing, its position can be constantly monitored so the actual freezing rate can be calculated. The relationship between the average channel size of each microhoneycomb and the actual freezing rate is shown in **Fig. 3**. This graph suggests that when the characters of the hydrogel are identical, the size of the channels is governed by the actual freezing rate, and decreases with the increase in the actual freezing rate.

Generally, a significant amount of micropores can be introduced within monolithic microhoneycombs when the Ice Templating Method is used for the production of them. In the case of silica, monolithic microhoneycombs having BET surface areas over $1000 \text{ m}^2 \cdot \text{g}^{-1}$ can be easily synthesized. Moreover, like typical silica gels, such micropores can be converted to mesopores by aging the microhoneycombs in a controlled atmosphere¹⁵⁾. As shown in **Fig. 4**, the sizes of the nanopores of the microhoneycomb can be adjusted in a wide range through such controlled aging.

As aging can be conducted after freezing, and the

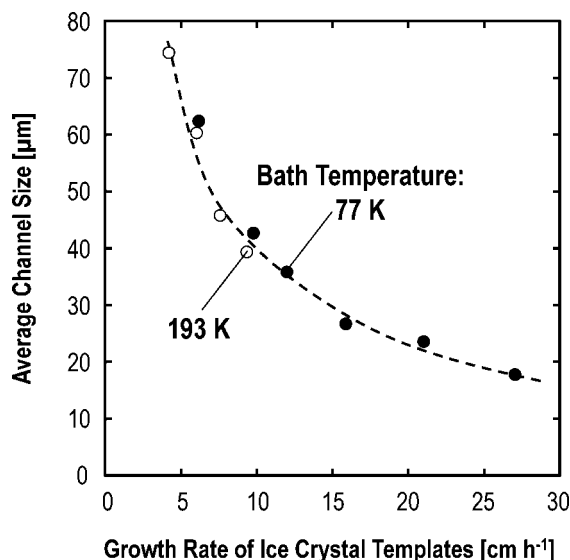
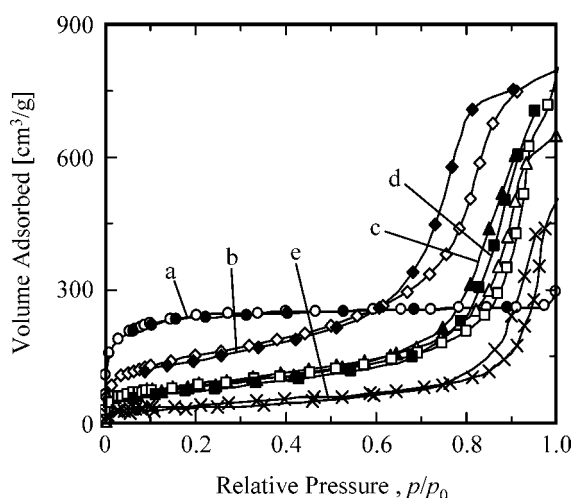


Fig. 3 Relationship between the Actual Growth Rate of the Ice Crystal Templates and the Average Channel Size of the Resulting Monolithic Microhoneycomb



(a) No treatment, (b) $C_N = 0.1 \text{ mol/L}$ and $T_{ht} = 298 \text{ K}$, (c) $C_N = 0.1 \text{ mol/L}$ and $T_{ht} = 323 \text{ K}$, (d) $C_N = 1.0 \text{ mol/L}$ and $T_{ht} = 323 \text{ K}$, (e) $C_N = 1.0 \text{ mol/L}$ and $T_{ht} = 363 \text{ K}$.

Fig. 4 Nitrogen Adsorption-desorption Isotherms of Monolithic Silica Microhoneycombs Hydrothermally Treated in $\text{NH}_3 \text{ aq.}$ of Different Concentrations of C_N at Different Temperatures of T_{ht}

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sizes of the channels are basically not affected through this process, the controlling of the channels (macropores) and nanopores (micro/mesopores) can be conducted independently. This means that it is extremely easy to tune the pore system of the microhoneycombs and maximize their performances.

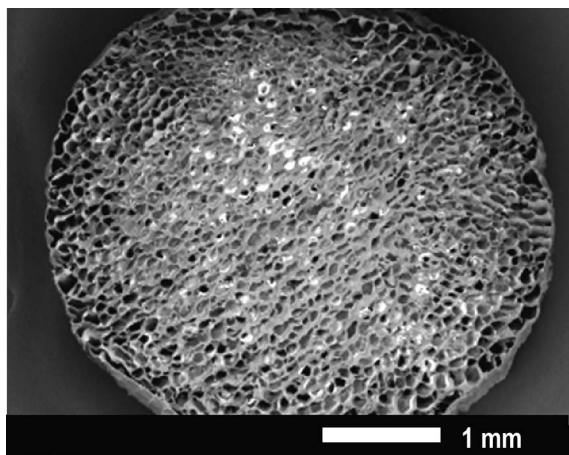


Fig. 5 Cross Sectional SEM Image of a Typical Monolithic RF Gel Microhoneycomb Obtained through the Ice Templating Method

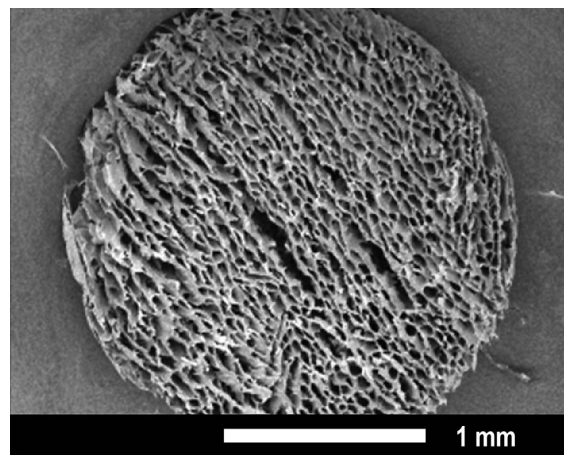


Fig. 6 Cross Sectional SEM Image of a Typical Monolithic Carbon Gel Microhoneycomb Obtained through the Carbonization of a Monolithic RF Gel Microhoneycomb

4. Applicability

The Ice Templating Method was originally developed using silica gels, an inorganic material which can be used for various purposes and which can be obtained from various inexpensive sources. Considering the principals of this method, it was assumed that it could generally be applied to materials which can be obtained through sol-gel synthesis. In order to prove this, we verified whether this method can be applied to organic gels.

We selected resorcinol-formaldehyde (RF) gels to represent organic gels, as they have a nanostructure similar to silica gels^{17),18)}. RF gels are synthesized from resorcinol and formaldehyde with the aid of a base catalyst. First, we directly applied the Ice Templating Method to a freshly prepared RF hydrogel, but found that the ice crystals grow rather randomly due to the catalyst which remained in the hydrogel. Therefore we thoroughly washed the RF hydrogel with pure water and froze it unidirectionally. **Figure 5** shows a cross sectional scanning electron microscope (SEM) image of the resulting monolith. A microhoneycomb structure can be confirmed which indicates that the Ice Templating Method can also be applied to organic gels. Due to the lower hydrophilicity of RF hydrogels, the sizes of the channels tended to be larger than those of silica microhoneycombs obtained under identical freezing conditions. Through adsorption experiments, it was confirmed that this microhoneycomb also possesses a hierarchical pore system.

RF gels can be carbonized and still maintain their unique nanostructure. Such carbonized gels are often referred to as "Carbon Gels." We also confirmed that this microhoneycomb can be converted to carbon and still maintain its unique pore system (**Fig. 6**).

We also confirmed the range of the size of hydrogels

that the Ice Templating Method can be applied to. It was found that if proper equipment can be utilized, monoliths with various dimensions can be easily synthesized. **Figure 7** shows 2 representative examples. One is a fairly long monolith with a small diameter, and the other is a short monolith with a fairly large diameter. The structure of such monoliths was found to be quite uniform throughout the whole sample.

We also found that the Ice Templating Method can be used to synthesize microhoneycombs in narrow passages. **Figure 8** shows a cross sectional SEM image of a silica microhoneycomb directly synthesized in a PTFE tube having a 350 μm inner diameter. The microhoneycomb basically has the same structure as those synthesized in larger vessels, indicating that microhoneycombs can be used where the hydraulic resistance of the material is likely to become a key issue, like in microchannels. However, it was also found that it is difficult to obtain a microhoneycomb structure when the material of the narrow tube easily conducts heat. As the ratio between the outer surface area and inner volume of a tube becomes large when the diameter of the tube is reduced, heat removal from the walls of the tube becomes significant when a tube made of a heat conducting material with a small diameter is used. Under such conditions, it will become difficult to grow ice crystals in parallel with the dipping direction.

5. Monolithic Microhoneycombs with Various Functions

It was shown that the Ice Templating Method can be applied to gels which represent inorganic and organic systems, silica and RF gels. Such gels are mainly used as adsorbents or adsorbent precursors. Therefore, next we attempted to develop monolithic microhoneycombs having unique functions.

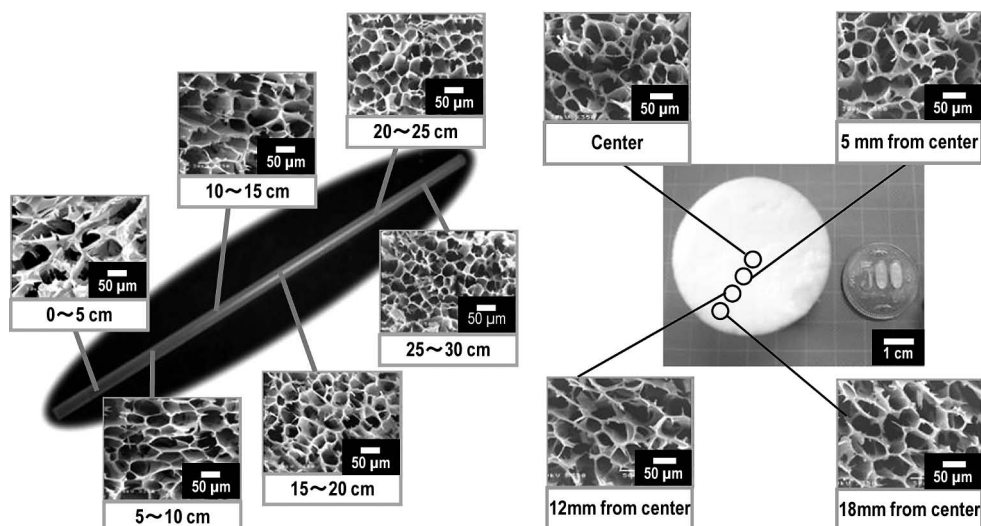


Fig. 7 Photographs and Cross Sectional SEM Images of 2 Representative Monolithic Silica Microhoneycombs: (left) diameter: 4 mm, length: 300 mm, (right) diameter: 50 mm, length: 50 mm

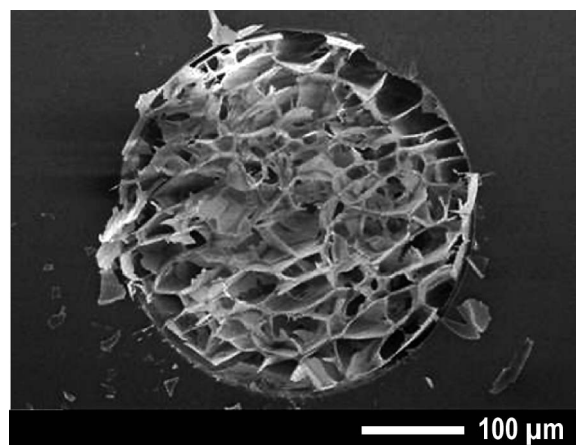


Fig. 8 Cross Sectional SEM Image of a Monolithic Silica Microhoneycomb Synthesized in a PTFE Tube

First we attempted to obtain a microhoneycomb which shows catalysis¹⁹⁾. A silica-alumina hydrogel was selected as the precursor. By using this hydrogel, the applicability of the Ice Templating Method to binary metal oxide systems can also be verified.

There are several routes to obtain silica-alumina hydrogels, but we adopted the cogelation method due to its compatibility with the Ice Templating Method. First a sodium silicate solution was prepared, and after adjusting the pH of it using an ion-exchange resin, aluminum nitrate, the aluminum source was added. After the solution transformed to a hydrogel, it was aged and the firmness of it was adjusted. The obtained hydrogel was thoroughly washed with pure water in order to reduce the amount of impurities which are thought to disturb the growth of ice crystals. Then it was frozen unidirectionally and dried.

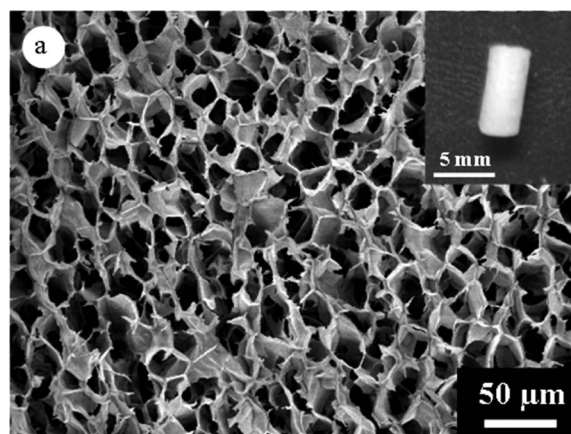


Fig. 9 Photograph and SEM Image of a Typical Monolithic Silica-alumina Microhoneycomb
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Figure 9 shows a typical silica-alumina monolith obtained through this procedure. The channels were not as ordered as those of silica microhoneycombs which was expected as the precursor hydrogel is not as homogeneous as silica hydrogels. However, the basic features of monolithic microhoneycombs, short diffusion paths and low resistance to fluid flows, were found to be maintained. It was also confirmed through ammonia temperature-programmed desorption (TPD) that this monolith has a significant amount of strong acid sites within its structure, indicating that such microhoneycombs can be used as catalysts with extremely low resistances to fluid flows.

Next we attempted to incorporate ion-exchange abilities into monolithic microhoneycombs²⁰⁾. Ion-exchangers are used in the liquid phase so reducing the

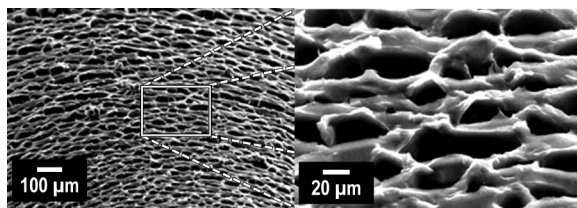


Fig. 10 Cross Sectional SEM Images of a Typical Monolithic Microhoneycomb Having Ion-exchange Abilities
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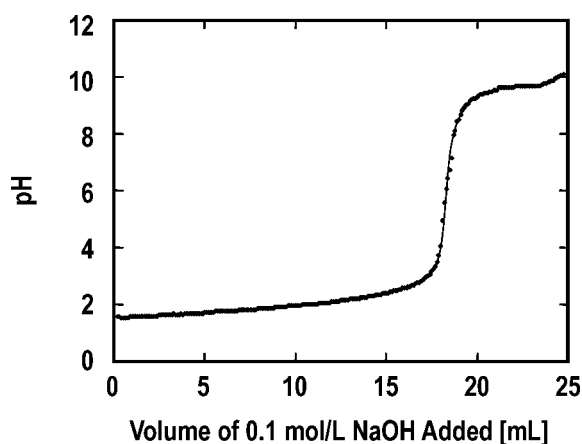


Fig. 11 Titration Curve of a Typical Monolithic Microhoneycomb Having Ion-exchange Abilities
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hydraulic resistance of them is thought to be extremely beneficial.

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. Designated amounts of R, B and pure water (W) were mixed, and the resulting solution was heated. Then the solution was cooled to room temperature and F was added. The solution was aged and the resulting hydrogel was frozen unidirectionally and finally dried.

Figure 10 shows cross sectional SEM images of a typical sample. A monolithic microhoneycomb structure can be confirmed. Figure 11 shows a typical titration curve, in which a solution including a typical monolith and NaCl was titrated using a $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution. It can be noticed that the monolith has a fairly high ion-exchange ability. Moreover, the pH rapidly increased when the equivalence point is about to be reached, a character which indicates that the sample is a strong acid resin. Therefore such mono-

liths can also be used as an effective solid acid catalyst with an extremely low hydraulic resistance in various liquid phase reactions.

We also attempted to widen the range of applicability of the Ice Templating Method by applying it to hydrogels including fine particles which have various functions²¹⁾. The hydrogel is expected to act as the binder to assemble fine particles to have a monolithic microhoneycomb structure.

Verifications were conducted using high silica Y-type zeolite as the model particle and silica as the model hydrogel which practically acts as the binder. A sodium silicate solution was prepared, and after the sodium cations within it was removed using an ion exchange resin, the zeolite particles were added and were dispersed using ultrasound. After aging, the resulting hydrogel including zeolite was frozen unidirectionally and dried.

Figure 12 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 Templating 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. Through X-ray diffraction (XRD) analysis, the included zeolites were found to maintain their nanostructure, and through adsorption experiments, it was confirmed that their pore inlets were not blocked by the silica binder.

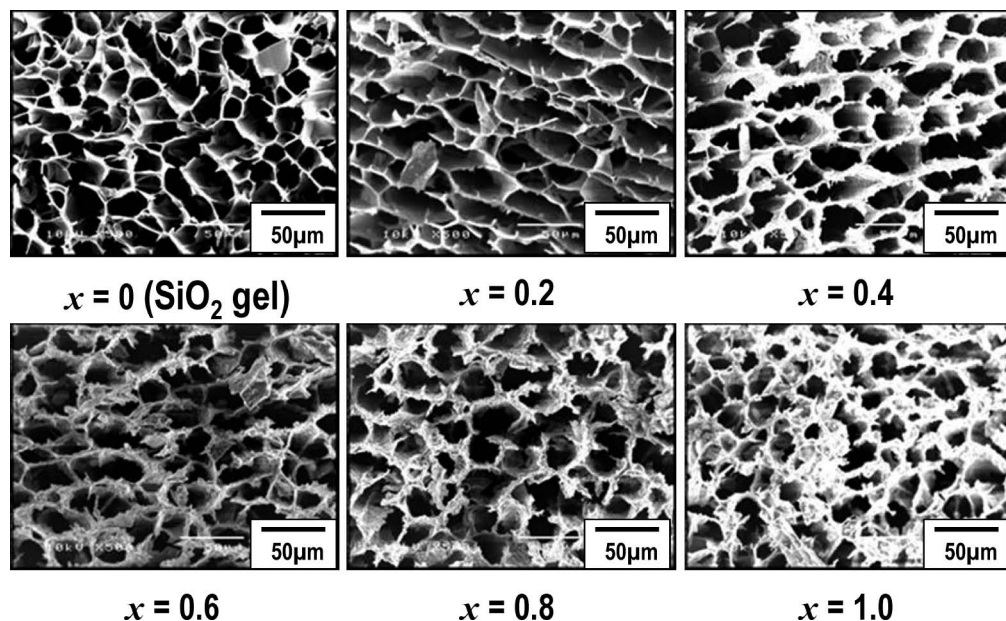
We also confirmed that titania particles and graphite particles can be molded into the form of a monolithic microhoneycomb using silica as the binder²¹⁾. These results show that by using the Ice Templating Method, monolithic microhoneycombs with a wide variety of functions can be obtained if a proper combination of fine particles and hydrogel binder can be found.

6. Conclusion

The Ice Templating Method is a very simple and versatile method for the synthesis of porous monolithic microhoneycombs. We intend to continuously extend the range of its applicability and also show practical usages in which the materials obtained through this method are thought to show significant advantages when compared with conventional materials. We hope to report the results in the near future.

Acknowledgments

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x : amount of zeolite inclusion [g-zeolite (g-SiO₂)⁻¹].

Fig. 12 Cross Sectional SEM Images of Typical Monolithic Silica Microhoneycombs Including High Silica Y-type Zeolite Particles

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要 旨

氷晶テンプレート法による細孔の階層構造を有するマイクロハニカム状モノリス体の作製

向井 紳

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ゾル-ゲル法を利用することで種々の機能を有する多孔質材料が得られるが、これら材料の機能はそのモルフォロジーを制御することでも向上させることが可能である。最近、我々は、ゾル-ゲル法で得られる材料の前駆体である湿潤ゲルを一方方向に凍結することにより、マイクロハニカム状のモノリス体に成型できることを見出した。このプロセスでは、凍結時に湿潤ゲル内に発生し、凍結方向に成長する氷晶がテンプレートの役割をし、材料が成型される。氷晶の痕跡である流路のサイズはマイクロメートルオーダーであり、マクロ孔として機能する。これら流路を形成する壁の厚さは1 μm 程度であり、その中には

ナノ細孔が発達している。よって、これらのモノリス体は短いナノ細孔が直状マクロ孔に直結している特異な細孔の階層構造を有する。この特異な構造のために、これらのモノリス体は材料内の拡散距離が非常に短いにもかかわらず、流体通過時の圧力損失が小さい。開発したこの手法は種々の有機系、無機系の湿潤ゲルに適用可能であるため、特異な構造に加え、種々の機能を有するモノリス体の製造が可能である。また、適当な湿潤ゲルを実質的なバインダーとして利用することにより、微粒子をマイクロハニカム状モノリス体に成型する手段として利用することも可能である。

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