Controlling the Morphology of Carbon Gels
Control de la morfología de los geles de carbón

S. R. Mukai*

Div. of Chem. Process Engineering, Graduate School of Engineering, Hokkaido University, N13W8 Kita-ku, Sapporo 060-8628, Japan
* Corresponding author: smukai@eng.hokudai.ac.jp

Abstract

Carbon gels are unique porous carbons, which are typically obtained through the carbonization of resorcinol-formaldehyde gels. This material is practically an aggregate of nanometer-sized carbon particles. Nanopores, mostly in the size range of mesopores, exist between the particles. Smaller pores, micropores being the majority, also exist within the particles. Therefore, this material has a hierarchical pore system in which short micropores are directly connected to mesopores.

The precursor of carbon gels can be obtained through sol-gel transition. Therefore there is a high possibility that the morphology of the resulting carbon can be easily controlled using various molding methods. We have actually challenged the controlling of the morphology of carbon gels, and have succeeded in obtaining them in the form of disks, microspheres and microhoneycombs. Details of such carbon gels will be reported.

Resumen

Los geles de carbón son materiales porosos únicos que se obtienen normalmente mediante la carbonización de geles de resorcinol-formaldehído. Este material es prácticamente un agregado de parículas de carbono nanométricas. Los nanoporos, mayoritariamente en el intervalo de tamaño de los mesoporos, existen entre las partículas. Los poros más pequeños, mayoritariamente microporos existen también dentro de las partículas. Por tanto, este material tiene un sitema jerárquico de poros en el que los cortos microporos están directamente conectados a los mesoporos.

El precursor de los geles de carbon se puede obtener a través de una transición soil-gel. Por tanto hay alta posibilidad de que la morfología del carbón resultante se pueda controlar fácilmente usando diferentes métodos de moldeo. De hecho, hemos afrontado el reto de controlar la morfología de los geles de carbón y hemos tenido éxito al obtenerlos en forma de discos, microesferas y micro panales de abejas. Los detalles de estos geles de carbón se presentarán en este trabajo.

1. Introduction

Carbon gels are unique porous carbons which were introduced in the late 1980s by Dr. Pekala and his coworkers[1-3]. Carbon gels are practically an aggregate of carbon nanoparticles. The voids formed between the nanoparticles are in the mesopore size-range, so this material is widely renowned as a mesoporous carbon. Moreover, micropores exist within the nanoparticles. Therefore it can be said that this material has a hierarchical pore system of micropores and mesopores[4-6].

Carbon gels are usually synthesized through the following method [1-3]: First resorcinol is mixed with formaldehyde, and with the aid of a base catalyst such as sodium carbonate, substituted resorcinols are formed. Through polycondensation, colloidal particles are formed, and these particles coagulate and form a 3 dimensional network of particles which

is called a resorcinol-formaldehyde (RF) hydrogel. Carbon gels can be obtained by drying and carbonizing this material. In the drying process, special drying methods such as supercritical drying are typically used in order to suppress shrinkage and maintain the unique structure of RF hydrogels. We showed that a more economical drying method, freeze drying, can be used in place of supercritical drying [7, 8]. Microwave drying can also be used in limited cases [9, 10].

It is also well known that carbon gels have a high nanostructure controllability [5, 6]. For example, the size of the mesopores of carbon gels depends on the size of the nanoparticles which consist it, and the size of such nanoparticles can be controlled by the catalyst concentration of the starting solution, which means that the size of the mesopores can also be controlled indirectly by adjusting this concentration. Moreover, the volume of micropores can be easily increased using conventional activation methods without hardly affecting the size and volume of mesopores. Therefore if a method to give carbon gels a desired morphology without affecting its porous properties can be established, unique porous carbons, the micro-, meso- and macro-scale structures of which can be independently controlled to best match their usages will be obtained. In this report, the attempts our group has made to obtain such carbons will be introduced.

2. Disks

As the precursor of carbon gels, RF gels, are usually obtained through sol-gel transition, we expected that it would be quite easy to mold them into a simple disk form without using any binders. To verify this possibility, first starting solutions with typical compositions were prepared, and then they were poured into teflon molds of different thicknesses. After sol-gel transition occurred, the resulting RF hydrogels were released from the molds, and were subsequently freeze-dried and carbonized yielding carbon gel disks [11].

Figure 1. Typical disks obtained in this work.
Figura 1. Discos típicos obtenidos en este trabajo.

Fig. 1 shows a photograph of typical disks obtained through this method. The disk on the left side is an RF hydrogel, the one in the middle an RF cryogel, and the one on the right, a carbon cryogel. Significant shrinkage occurred during drying and carbonization, but distorted disks or disks with cracks were hardly obtained, which indicates that shrinkage occurred fairly isotropically. Fig. 2 shows how the shrinkage ratio depends on the catalyst concentration. Isotropic

shrinkage can also be confirmed from this graph. Therefore it can be concluded that monolithic carbon gel disks can easily be obtained through this method.
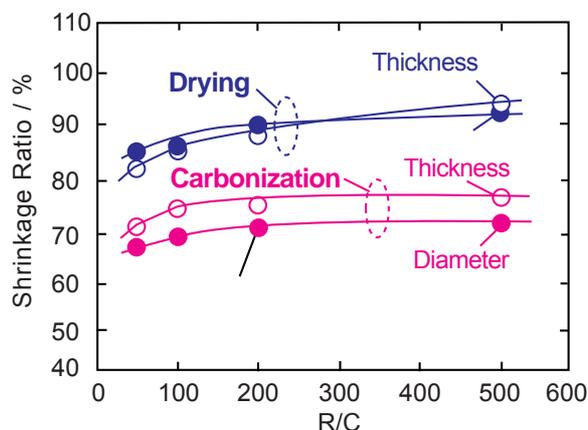
Figure 2. Shrinkage ratio of the obtained disks.
Figura 2. Relación de encogimiento de los discos obtenidos.

3. Microspheres

The next morphology to be explained about is microspheres. As the initial source of carbon gels is an aqueous solution, we assumed that they could be molded into microspheres through inverse emulsion polymerization. In order to verify this possibility, first a typical starting solution was prepared and was kept at a constant temperature T_{gel}, and just before the solution was about to transform to a gel, it was dispersed into a mixture of cyclohexane and SPAN80, a surfactant which was maintained at the same temperature T_{gel}. After agitating the resulting emulsion for 5 to 10 h, RF hydrogel microspheres were formed. Carbon gel microspheres were obtained by freeze drying and carbonizing these microspheres [12, 13].

Fig.3 shows SEM micrographs of typical microspheres obtained through this method. It can be seen that microspheres with diameters in the range of 5 to about 30 micrometers were obtained. The inner parts of the microspheres were found to be formed by nanoparticles, like typical carbon gels, but interestingly, macropores or large mesopores could not be found at the surface of the microspheres.

So next we analyzed the surface structure of the microspheres through the so-called molecular probe method. Fig. 4 shows the results where the micropore volume accessible to the probe molecule is plotted as a function of the minimum dimension of the probe molecule. It was confirmed that when T_{gel} was low and the carbonization temperature (T_{pyro}) was high, the surfaces of the microspheres tended to become microporous, and in certain cases, microspheres in which even carbon dioxide cannot penetrate into could be obtained. This indicates that microspheres having mesoporous inner parts and surfaces with unique properties can be obtained through this method. Therefore, this method not only enables the synthesis of carbon gel microspheres, but also allows the controlling of the nanostructure of the surface of the resulting microspheres.
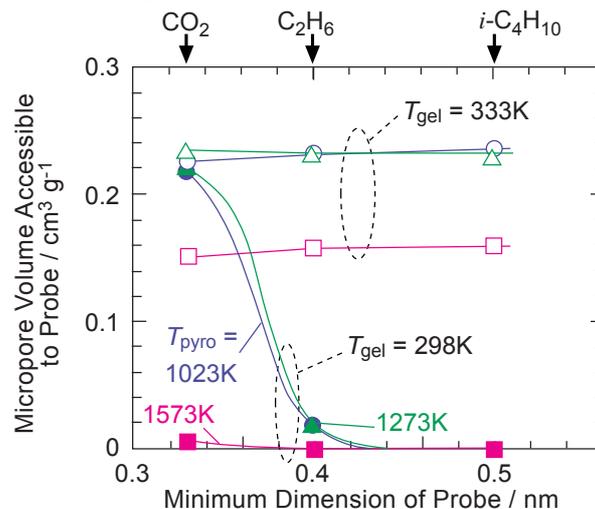
Figure 4. Estimation of inlet size of the surface pores of typical carbon gel microspheres.
Figura 4. Estimación del tamaño de entrada de los poros superficiales de microesferas típicas de geles de carbón.

4. Microhoneycombs

Porous carbons are usually synthesized in the form of particles, therefore the size of the particle determines the length of the diffusion paths within it. This means that the particle size must be small enough to ensure a high accessibilty to their inner parts. However as the voids formed between the particles provide paths or macropores to the material, the size of the particles also determines the resistance they cause when fluids are passed through them. So the particle size must be large to avoid significant resistance to flows. This means that a high accessibility to their inner part is a complete trade-off with a low resistance to flows. Indeed, there are many cases in which large particles are used just to avoid severe pressure drops. This dilemma can be avoided by changing the morphology of the material.

A microhoneycomb, which is a monolith having straight and aligned channels which sizes are in the micrometer range, and which channels are formed by nanoporous walls which thicknesses are also in the micrometer range is thought to be one example

a) Microspheres   b) Cross-Section   c) Surface
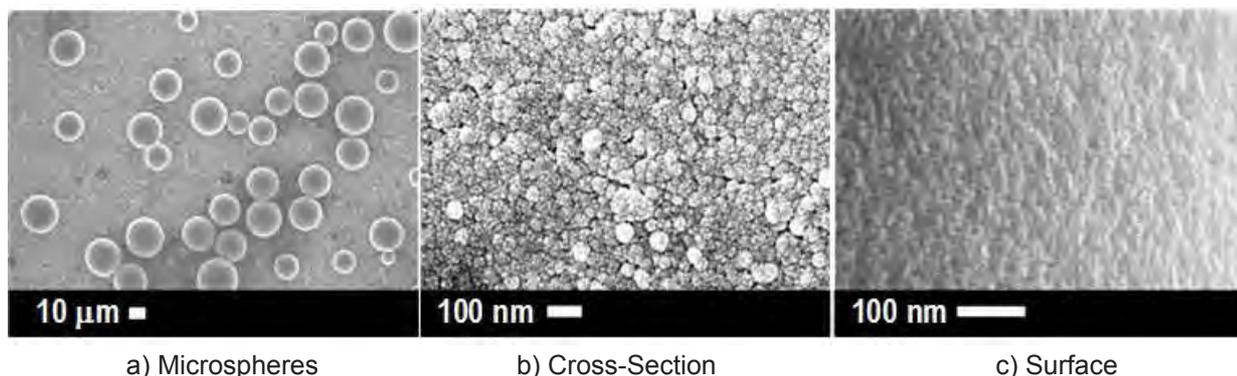
Figure 3. SEM micrograph of typical microsphere samples.
Figura 3. Microfotografía SEM de muestras de microesferas típicas.

of an ideal morphology. As the thickness of the walls is in the micrometer range, the diffusion paths within them are extremely short, and as the channels are straight and aligned, the resistance when fluids are passed through this monolith can be minimized. It was difficult, if not impossible to synthesize such microhoneycombs using conventional methods, but we found that such microhoneycombs can be synthesized through the sol-gel method using ice crystals as the template [14-16].

In the developed method, first a hydrogel precursor is prepared, and then this hydrogel is dipped at a constant rate into a cold bath which temperature was maintained below the freezing temperature of the gel. This freezing process is called unidirectional freezing. During this freezing process, an array of needle shaped ice crystals appears within the hydrogel and elongates in the freezing direction. This causes the hydrogel to be condensed between the growing ice crystals. So, a monolithic microhoneycomb as shown here could be obtained by thawing and drying the completely frozen material. As ice crystals act as the template in this method, we named it the ice templating method [14-16]. This method was originally developed using a silica hydrogel, but considering the similarity of hydrogels, we thought that this method will also be applicable to resorcinol-formaldehyde hydrogels.

We actually tested this possibility [17, 18]. First a typical starting solution was prepared, and through sol-gel polycondensation, rod type RF hydrogels were formed. As the catalyst was thought to disturb the growth of ice crystals, the hydrogels were thoroughly washed with distilled water. Then the samples were dipped at a constant rate into a cold bath. The obtained samples were aged, freeze-dried and carbonized yielding monolithic carbon gels.
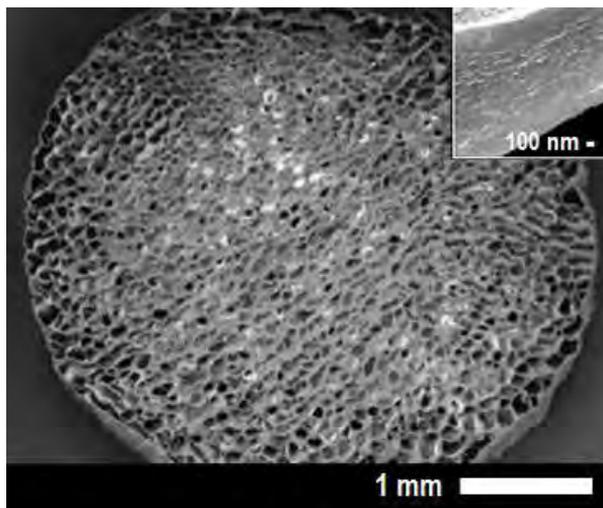
Figure 5. Cross sectional SEM image of a typical monolithic RF gel microhoneycomb.
Figura 5. Imagen SEM de la sección transversal de un típico gel RF monolítico en panal de abeja.

Figure 5 shows a SEM micrograph of the cross section of a typical sample obtained in this work. It can be noticed that the RF gel was successfully molded into the form of a microhoneycomb. Nanoparticles which are the origin of mesoporosity can be clearly distinguished in the enlarged micrograph of the honeycomb wall which indicates that the nanostructure of the gels is not altered by freezing. This was also confirmed through adsorption experiments. Therefore a mesoporous RF gel was

successfully obtained.
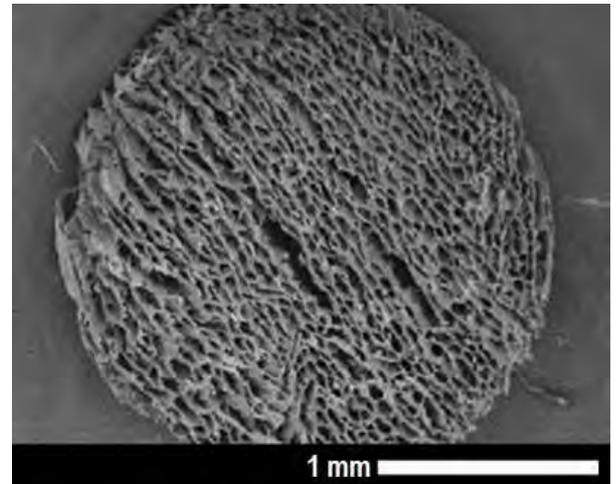
Figure 6. Cross sectional SEM image of a typical monolithic carbon gel microhoneycomb microhoneycomb.
Figura 6. Imagen SEM de la sección transversal de un típico gel monolítico de carbón en panal de abeja.

Next, we attempted to carbonize the RF gel microhoneycommb. Figure 6 shows a cross sectional SEM micrograph of a typical sample after carbonization. It can be noticed that although slight shrinkage occurs, the sample maintains its unique morphology. Therefore, it can be concluded that carbon gels having a unique microhoneycomb morphology can be obtained through ice templating.

5. Concluding Remarks

As was introduced in this article, we found that it is very easy to control the morphology of carbon gels. Therefore, not only the micro- and meso-structures, but also the macro-structure of this unique material can be tuned to best match its application. We are now investigating applications which can make full use of such carbon gels with controlled morphologies, and hope to report the results in the near future.

6. References

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