Synthesis of Monodisperse Carbon Beads with Developed Mesoporosity

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Introduction

Porous carbons and their composites are widely used as supporting materials for catalysts or as adsorbents in various chemical processes related to environmental protection or energy production.[1–4] In these chemical processes, the catalysts or adsorbents are generally packed in a fixed-bed reactor or a column. Fluidized beds are useful for improving the performance of catalysts since mass transfer at a solid-liquid or solid-gas interfaces is significantly enhanced as a result of fluidization.[5] To increase the mechanical strength of a packing material in a fixed bed or a fluidized bed, the packing should be shaped in the form of a bead. Furthermore, it is necessary to form the beads of a uniform size to facilitate process design, for example in the calculation of pressure drops or residence times of the reactants in reactors or columns.

Several methods have been proposed for the production of porous carbon structure with a controlled shape and particle size. Activated carbon beads are usually prepared by using an organic additive called a binder, for example coal-tar pitch or a phenolic resin, in the synthesis route. However, such binders often affect the porous properties and consequently, the adsorption characteristics of the resulting carbons.[6] Another approach is the replicate method, which involves the use of a porous silica template as a matrix that is impregnated with a carbon precursor.[7–9] By carbonization of the resulting composite, followed by removal of the silica matrix, porous carbon beads with a uniform particle size can be prepared. However, this method tends to be quite expensive, because monodisperse beads of the porous solid have to be used as the template.

Carbon gel is a unique form of porous carbon that has a developed and controllable mesoporosity, which can be synthesized by the sol-gel condensation of, for example, resorcinol with formaldehyde in a slightly basic aqueous solution followed by drying and carbonization in an inert atmosphere. Carbon aerogel can be prepared using supercritical drying in the drying process.[10] Many previously published articles reported that supercritical drying can minimize the shrinkage of the porous structure during drying, and a highly porous solid called as “aerogel” can be obtained using supercritical drying.[11–12] Although supercritical drying is widely used, this method requires expensive high-pressure equipment, and, consequently, its usage leads to a large increase in processing cost. From this point of view, we use more economical drying method, freeze-drying, instead of supercritical drying. Clay aerogels with extremely low-density have been synthesized using freeze-drying with the aim of controlling the formation of macropores.[13–15] In this article, a porous solid prepared by means of freeze-drying is referred as “cryogel,” and freeze-drying is used to obtain carbon cryogels with developed mesoporosity.

So far, the authors have reported the synthesis of spherical carbon cryogels through the inverse emulsion polymerization of a resorcinol-formaldehyde (RF) aqueous solution. However, this method does not provide monodisperse droplets of a RF solution, hence polydisperse carbon cryogel beads are

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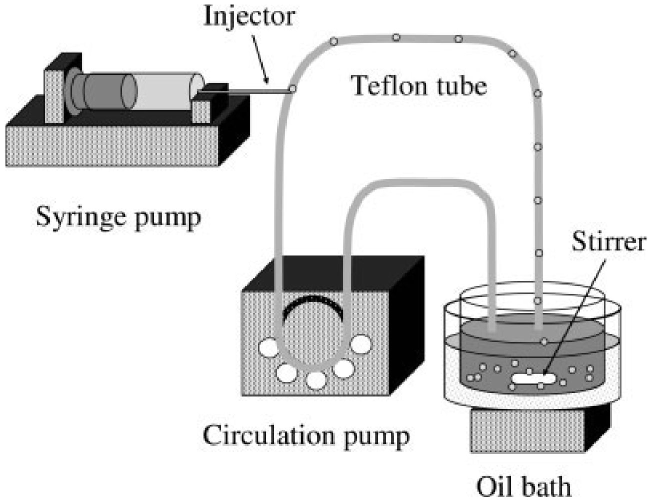

Figure 1. Apparatus used for the synthesis of m-CCMs.

formed.[16] In this study, a novel method is examined for preparing monodisperse droplets of a RF solution using oil which is insoluble to water. The key to this method is the sequential formation of droplets of the RF solution in the oil through the use of an injection apparatus. The monodisperse carbon cryogel microspheres that are obtained are referred to as m-CCMs.

Experimental

Initially, a resorcinol-formaldehyde (RF) solution was prepared in the same manner as previously reported.[16] Sodium carbonate was used as a basic catalyst for the sol-gel polycondensation, with water as the diluent. The concentration of sodium carbonate used for the preparation of the RF solution is an important parameter in controlling the time required for gelation and the mesoporosity of the m-CCMs that are obtained. The molar ratio of resorcinol to formaldehyde and the ratio of resorcinol to water were, respectively fixed at 0.5 mol/mol and 0.25 g/cm^3, respectively, while the molar ratio of resorcinol to sodium carbonate was fixed to 400 mol/mol. The prepared RF solution was kept at 298 K for 24 h to effect the sol-gel polycondensation. Although colloidal sol particles were formed in the RF solution after this reaction time, the gelation remained incomplete. The apparatus used for the synthesis of m-CCMs is illustrated in Figure 1. In this apparatus, a circulation pump and a syringe pump are used. The prepared RF solution was injected into a silicone oil (a nonsolvent for the RF solution) by the syringe pump at a constant injection rate of 0.025 cm^3/min, while the silicone oil was circulated at a constant flow rate, F_c, in the range 1.3–20 cm^3/min. The RF solution was constantly injected from an injector with a needle pore diameter of 0.41 mm, and monodisperse droplets of a RF solution were continually formed. The droplets of the RF solution spontaneously became spherical in the silicone oil and were cured at 363 K until the gelation was complete. By keeping the temperature of the oil phase at 363 K, the reaction rate of the RF solution was significantly enhanced and droplets of the RF solution injected into the oil phase were gelled within a few minutes. As a result, it was possible to prevent the aggregation of the droplets of the RF solution and, consequently, monodisperse RF hydrogel microspheres (m-RHMs) were obtained. These m-RHMs were washed with cyclohexane and ethanol, respectively, at least three times each to remove silicone oil sufficiently, and then immersed in *t*-butanol to exchange the solvent in the pores before freeze-drying. *t*-Butanol is a useful solvent for freeze-drying, because its volume change on freezing is much smaller than that of water, and its vapor pressure is much higher than that of water.[17] The beads were dried at 253 K under a reduced pressure and then carbonized in an inert atmosphere to obtain m-CCMs. The carbonization temperature was kept at 1273 K. Under these synthesis conditions, 10 g of m-CCMs could be obtained from 100 cm^3 of the RF solution.

The m-CCMs were examined by using an optical microscope and a scanning electron microscope. The particle-size distribution was measured by analyzing the images of the beads. On the basis of the measured particle-size distribution, the uniformity of the beads was evaluated from the coefficient of variation (CV). As expressed in Eq. 1, the CV can be obtained by dividing the standard deviation of the particle-size distribution by the mean diameter.

$$\mathrm{CV}\ [\%] = (\text{standard deviation})/(\text{mean diameter}) \times 100 \quad (1)$$

The porous properties of the m-CCMs were measured by nitrogen-gas adsorption experiments at 77 K. Mesoporosity was determined according to the IUPAC definition (mesopore: 2 nm $<$ pore dia. $<$ 50 nm). The pore-size distribution and mesopore volume were determined by applying the Dollimore-Heal method[18] to the desorption isotherms.

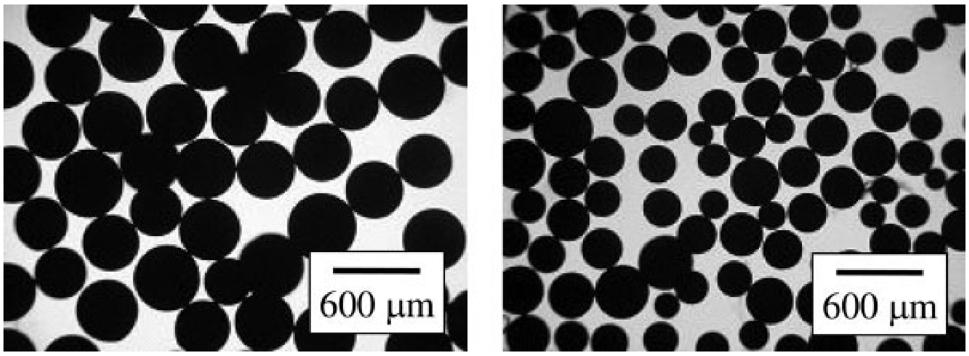

Figure 2. Images of m-CCMs (left), and CCMs (right).

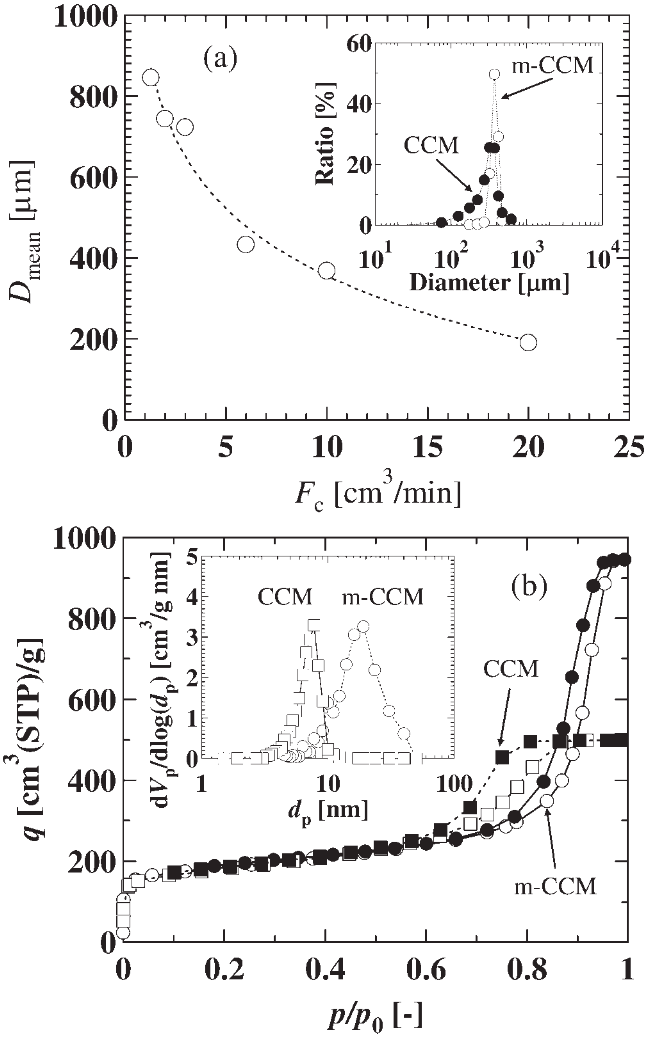

Figure 3. (a) Effect of circulation flow rate on mean diameter of m-CCM; the inset shows the particle size distributions, and (b) adsorption and desorption isotherms of nitrogen on m-CCM and CCM at 77 K.

The inset shows the mesopore size distributions obtained from the desorption branches.

Table 1. Physical properties of m-CCMs and CCMs

	F_c [cm^3/min]	CV [%]	V_{mes} [cm^3/g]	S_{BET}[a] [m^2/g]
m-CCM	1.3	10.2	0.86	699
	2.0	11.0	0.80	677
	10	12.7	1.28	667
CCM	–	56.2	0.63	654

[a] Brunauer–Emmett–Teller (BET) surface area. The apparent density of m-CCM is approximately 0.79 g/cm^3.

Results and Discussion

Figure 2 reproduces the images of m-CCMs and of carbon cryogel microspheres (CCMs) which were synthesized by the inverse emulsion polymerization method using a nonionic surfactant (SPAN 80) as an emulsifier. Note that the m-CCMs and CCMs were synthesized by using the same amounts of reactants. The particle-size distributions of the m-CCMs and CCMs are shown in Figure 3. As can be confirmed from Table 1, the CV value of the m-CCMs was less than 20% for all samples prepared in this work, whereas the CV value of the CCMs was more than 50%. This confirmed the uniformity of the particle sizes of the m-CCMs that were obtained. From the viewpoint of applying the m-CCMs as supporting materials for catalysts or as column-packing materials, it is important to be able to control the particle size of the m-CCMs. This was achieved by altering the rate of flow of the silicone oil from the circulation pump: as the flow rate of silicone oil increases, the size of the droplets of the injected RF solution become smaller, because droplets are detached more frequently from the tip of the injector. Larger droplets can be similarly produced by decreasing the flow rate. Consequently, as shown in Figure 3a, by changing the circulation flow rate of the circulation pump, it was possible to control the mean-particle dia. D_{mean}, of the m-CCMs in the range of 200 to 1,000 μm (Supplementary materials; Figure S1).

Figure 3b shows the adsorption and desorption isotherms of nitrogen on the CCMs, and the corresponding pore-size distribution. The isotherms exhibit a steep increase in the amount adsorbed at a high-relative pressure range, indicating the development of mesoporosity. A type-H2 hysteresis loop, which is characteristic of a porous solid formed from an interconnected network structure, also appears. As shown in Figure 3b and Table 1, m-CCMs possess a broader pore-size distribution, and a larger mesopore volume than do CCMs. This result can be explained as follows. During the inverse emulsion polymerization, dehydration of RHMs occurs, leading to shrinkage of the porous structure of the CCMs.[19] Because m-CCMs are synthesized without using surfactants, dehydration can be prevented. Consequently, it is possible to control the mesoporosity of the m-CCMs over a wider range than is the case with CCMs, for example, by changing the molar ratio of resorcinol to catalyst used in the preparation of the RF solution (Supplementary materials; Figures S2 and S3). On the basis of these results, m-CCMs are confirmed to have a developed mesoporosity, and are suitable for use as supporting materials for catalysts or adsorbents in various chemical processes.

Conclusions

In conclusion, our novel approach has enabled to synthesize m-CCMs without using any binder or template in the synthesis route. Because it is possible to scale-up the apparatus, this method could be used in the near future for the mass production of m-CCMs. The method could also be applied to the synthesis of monodisperse microspheres of other organic or inorganic substances.

Acknowledgments

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