

Adsorption Characteristics of Carbon Cryogel Microspheres

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Introduction

Carbon cryogels are mesoporous carbons prepared by sol-gel polycondensation of resorcinol (R) with formaldehyde (F) under slightly basic aqueous condition, followed by freeze drying and pyrolysis in an inert atmosphere. We have succeeded in preparing carbon cryogel microspheres (CC microspheres) by gelling resorcinol-formaldehyde (RF) solution using an emulsion, followed by freeze drying and pyrolysis. CC microspheres are expected to be used as adsorbents, column packing materials and catalyst supports. Here, we report the attractive adsorption characteristics of CC microspheres.

Experimental

RF solutions were prepared as the same way as previously reported [1,2]. The solutions were dispersed in cyclohexane containing 10 vol. % of surfactant (SPAN80) to obtain RF hydrogel microspheres, which were subsequently dried at -10 °C and pyrolyzed in an argon atmosphere at 750-1300 °C. The porous properties of CC microspheres were examined by gas adsorption methods using an automatic gas adsorption and desorption apparatus. The isotherms of nitrogen on CC microspheres were measured at -196 °C, and the isotherms of carbon dioxide, ethane, isobutane and water vapor were measured at 25 °C. The BET surface area and the mesopore volume were determined by respectively applying BET equations and Dollimore-Heal method to the desorption isotherms of nitrogen, and the micropore volume was determined by applying

Dubinin-Astakhov equations to the adsorption isotherms of carbon dioxide. Surface and cross sections of CC microspheres were observed by scanning electron microscopy (SEM).

Results and Discussion

SEM images of the surface and the cross section of CC microspheres are shown in Fig.1. Although numerous mesopores were observed between primary particles which form the inner part of CC microspheres, neither macropores nor large mesopores could be observed at the surface. Table 1 summarizes the synthetic conditions and the porous properties of CC microspheres. The values of R/C and R/W indicate the molar ratio of resorcinol to catalyst and the ratio of resorcinol to water, respectively. In our previous study, carbon cryogel columns have been prepared under the same R/C and R/W as listed in Table 1, and were confirmed to show high mesoporosity [1].

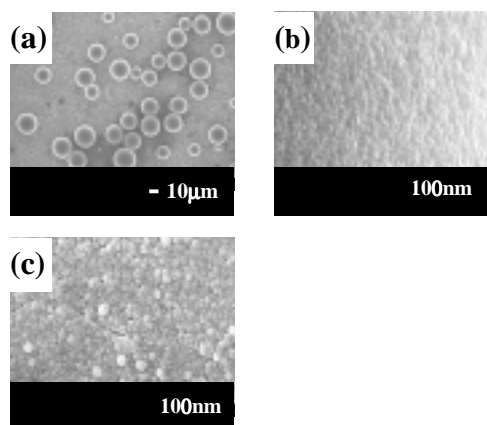


Fig.1. SEM images of CC microspheres; (a) microspheres, (b) surface and (c) cross section.

Table 1 Synthetic conditions and porous properties of CC microspheres

Gelling condition	R/C [-]	R/W [g/cm ³]	T _{gel} [°C]	T _{pyro} [°C]	S _{BET} [m ² /g]	V _{mes} [cm ³ /g]	V _{mic} [cm ³ /g]	
1	400	0.25	60	A	750	752	0.97	0.23
				B	1000	711	1.03	0.24
				C	1300	525	0.90	0.15
2	100	0.50	25	D	750	4.43	0.03	0.22
				E	1000	8.83	0.01	0.22
				F	1300	8.65	0.02	0.01

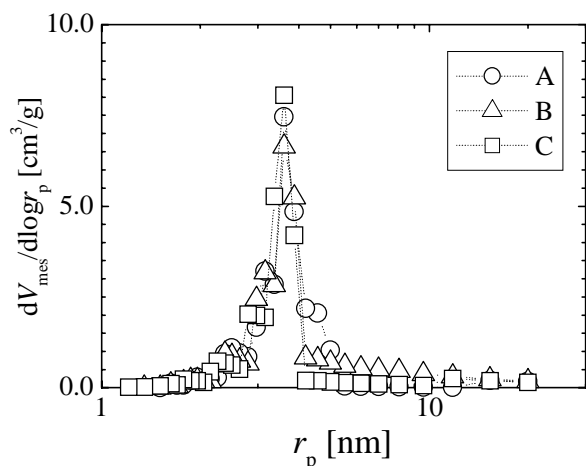


Fig.2. Mesopore size distributions of CC microspheres.

The samples prepared under condition 1 (A, B and C) have large mesopore volumes (≥ 0.90 cm³/g) and moderate micropore volumes (≤ 0.24 cm³/g). This apparent mesoporosity disappears in samples prepared under condition 2 (D, E and F). It should be noted that sample F hardly shows apparent microporosity. The mesopore size distributions of samples A, B and C are shown in Fig.2. One can see that they have similar sharp pore size distributions which have peak values at around 2 nm. Next, the sizes of the pores which exist at the surface of the microspheres were estimated. Figure 3 shows micropore volume distributions of CC microspheres measured by the molecular probe method. The sizes of the pores which exist at the surface of samples A, B and C were confirmed to be larger than the minimum molecular dimension of isobutane (5.0 Å). Interestingly, surface pore sizes of samples D and E are in the range of minimum molecular dimensions of carbon dioxide (3.3 Å) and ethane (4.0 Å), and that of sample F is smaller than the minimum molecular dimension of carbon dioxide.

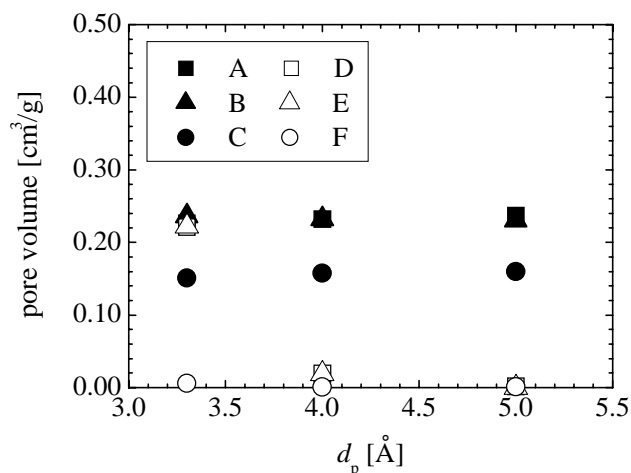


Fig.3. Pore volume distributions of CC microspheres.

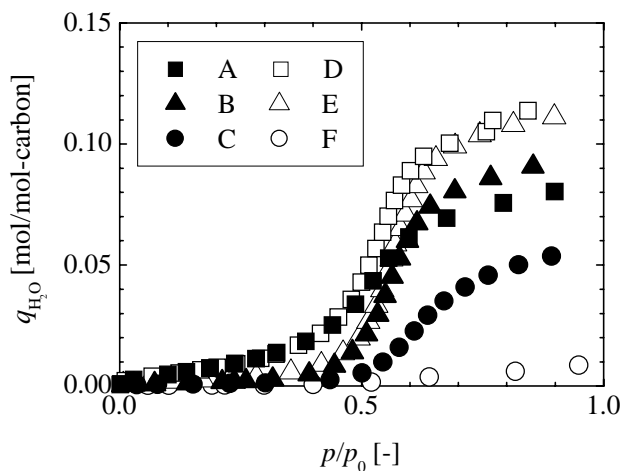


Fig.4. Adsorption isotherms of water vapor on CC microspheres.

Considering these results and the fact that mesopores could be observed even in the SEM images of the inner part of samples D, E and F, it is assumed that the microspheres have a dual structure, i.e. a mesoporous inner part covered by a microporous surface. Figure 4 shows adsorption isotherms of water vapor on CC microspheres. It can be seen that the amounts of water vapor adsorbed at low relative pressure, which

indicates the degree of hydrophobicity of the pore surface of CC microspheres, increases as increasing the pyrolysis temperature.

Conclusions

Carbon cryogel microspheres were successfully synthesized and their porous properties were evaluated by various gas adsorption experiments. By changing synthetic conditions of RF hydrogel microspheres, it is possible to prepare both mesoporous carbon microspheres and microspheres which surface pores are smaller than the minimum molecular dimension of ethane. It was also confirmed that the hydrophobicity of the pore surface of CC microspheres increases as increasing the pyrolysis temperature.

Nomenclature

T_{gel}	temperature RF solution is gelled [°C]
T_{pyro}	pyrolysis temperature [°C]
S_{BET}	BET surface area [m ² /g]
V_{mes}	mesopore volume [cm ³ /g]

V_{mic}	micropore volume [cm ³ /g]
r_p	pore radius [nm]
d_p	surface pore diameter [Å]
p/p_0	relative pressure [-]
$q_{\text{H}_2\text{O}}$	amount of water vapor adsorbed [mol/mol-carbon]

References

1. Tamon H, Ishizaka H, Yamamoto T and Suzuki T. Preparation of mesoporous carbon by freeze drying. Carbon 1999;37(12):2049-2055.
2. Tamon H, Ishizaka H, Yamamoto T and Suzuki T. Influence of freeze-drying conditions on the mesoporosity of organic gels as carbon precursors. Carbon 2000;38(7):1099-1105.

Acknowledgements

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