

Preparation of macroporous carbon foam using emulsion templating method

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Abstract A macroporous carbon foam (MCF) possessing three-dimensionally interconnected porous structure, that was composed of macropores, mesopores and micropores, could be synthesized by the oil-in-water (o/w) emulsion templating method using ultrasound. For the preparation of the o/w emulsion as a template of the macropores formed in the MCF, a resorcinol-formaldehyde (RF) solution and cyclohexane were used as an aqueous phase and an oil phase, respectively. We examined the effects of the viscosity of the RF solution, the mass ratio of cyclohexane with the RF solution as well as the concentration of a hydrophilic surfactant (Tween80) contained in the RF solution on the size distribution of the macropores. Consequently, the suitable viscosity of the RF solution to obtain a MCF with a narrow size distribution of the macropores was determined. It was revealed that the size of the macropores increased with the increase in the mass ratio of cyclohexane with the RF solution or with the decrease in the concentration of Tween80. It was possible to increase the porosity of the prepared MCF larger than 90% using a concentrated o/w emulsion as the template of the macropores.

Keywords Adsorbent · Emulsion templating method · Macroporous carbon foam · Pore size distribution · Ultrasound

1 Introduction

Recently, a porous solid with three-dimensionally (3D) interconnected porous structure, that is composed of macropores, mesopores and micropores, has attracted an increasing attention from the viewpoints of the large specific surface area as well as rapid mass transfer inside the porous structure (Yuan and Su 2006). Templating method has been extensively applied to produce such a porous solid. Among various templates, an oil-in-water (o/w) emulsion is a useful one to obtain a macroporous solid (Imhof and Pine 1998; Liu et al. 2007; Phadke et al. 2009; Towata et al. 2007; Yuan and Su 2006). In the “o/w emulsion templating method,” it is possible to obtain a unique macroporous solid by the removal of micrometer-sized oil droplets, that is used as a template, after solidification of an aqueous phase. The advantage of the method is the controllability of the macroporous structure by changing the emulsification conditions, since the oil droplets are highly deformable and can be easily removed without affecting the porous structure of the solid.

A macroporous carbon possessing 3D interconnected macroporous structure is expected to be applied to, for example, an adsorbent (Akolekar et al. 1998; Inagaki 2009), a thermal insulator (Gallego and Klett 2003), a catalyst support (Kim et al. 2010) and a gas diffusion layer for a proton exchange membrane fuel cell (Kim and Cunningham 2010). A resorcinol-formaldehyde (RF) aqueous solution is one of the most useful carbon precursors with controlled porous structure. Through the sol-gel polycondensation of a RF solution followed by drying and carbonization in an inert atmosphere, it is possible to obtain a porous carbon called as a carbon gel that possesses numerous mesopores and micropores (Yamamoto et al. 2001). Recently, Liu et al. (2007) reported the synthesis of a macroporous carbon foam (MCF) from an o/w emulsion using a RF solution and liquid paraffin

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as an aqueous phase and an oil phase, respectively. However, the conditions to prepare the MCF with 3D interconnected macroporous structure have not yet been clarified.

In this study, an attempt is made to prepare a MCF with 3D interconnected macroporous structure by the o/w emulsion templating method using ultrasound. For preparation of the o/w emulsion, a RF solution, cyclohexane and a hydrophilic surfactant (Tween80) are used as an aqueous phase, an oil phase and an emulsifier, respectively. Then, we examine the effects of the viscosity of a RF solution, the mass ratio of cyclohexane with the RF solution and the concentration of Tween80 on the size distribution of the macropores formed in the MCF.

2 Experimental

2.1 Preparation of MCFs

MCFs were synthesized in the following manner. For the preparation of a RF solution, resorcinol (*R*), formaldehyde (*F*) (37%; methanol stabilized), sodium carbonate as a catalyst (*C*) and distilled and ion-exchanged water (*W*) were used. All chemicals used were supplied from Wako Pure Chemical Industries, Ltd., Japan. The molar ratio of resorcinol to formaldehyde (*R/F*) and the ratio of resorcinol to water (*R/W*) were fixed as 0.5 [mol/mol] and 0.25 [g/cm³], respectively. The molar ratio of resorcinol to sodium carbonate (*R/C*) was either 25 or 400 [mol/mol]. The prepared RF solution was kept at 298 K to allow the sol-gel transition before starting the emulsification. A transient change in the viscosity of the RF solution during the sol-gel transition was measured at 298 K using an Ostwald viscometer.

Cyclohexane was dispersed in the RF solution, that contains Tween80, using an ultrasonic homogenizer (UH-600s, SMT Co., Ltd., Japan). The mass ratio of cyclohexane with the RF solution (M_{cyclo}/M_{RF}) was varied in the range of 0.50 to 3.0, whereas the concentration (C_s) of Tween80 in the RF solution was varied in the range of 0.10 to 1.0 wt.%. Ultrasound was irradiated intermittently for 10 minutes to prevent formation of large air bubbles in the emulsion (Towata et al. 2007). The effective intensity of the irradiated ultrasound to the emulsion was adjusted to 9 W. Thus prepared o/w emulsion was poured into a cylindrical glass tube (4.0 mm in inner diameter and 40.0 mm in length), and was kept at 298 K until the completion of the gelation of the RF solution. The samples were then cured at 333 K for 1 day to stiffen the structure. Subsequently, the samples were immersed in an excess amount of *t*-butanol for three times to exchange cyclohexane and water contained in the samples with *t*-butanol. The samples were frozen by liquid N₂ and then lyophilized in a vacuum for 1 day to remove

t-butanol from the samples. Finally, the dried samples were carbonized in a N₂ gas flow at 1273 K for 4 h to obtain MCFs.

2.2 Characterization of MCFs

The cross section of the MCF was observed using a scanning electron microscope (SEM, S-3400N, Hitachi, Ltd., Japan). The size distribution of the macropores was determined by analyzing the SEM image using an image processing software (ImageJ 1.38v). The average macropore size (d_m) was estimated by fitting the pore size distribution with the Gaussian function. Then, the coefficient of variation (CV) was estimated as the ratio between the standard deviation of the distribution and the average size of the macropores. The isotherms of N₂ on the MCF were measured at 77 K using an automatic adsorption and desorption apparatus (Belsorp-mini, Bel Japan Inc., Japan), and the porous properties of the MCF were determined based on the α_s analysis (Rouquerol et al. 1999). The mesopore size distribution was estimated by applying the Dollimore-Heal method to the desorption isotherm (Dollimore and Heal 1964). In the analysis, the IUPAC definitions of macropore (pore width > 50 nm), mesopore (2 nm < pore width < 50 nm) and micropore (pore width < 2 nm) were applied.

The apparent density (ρ_{app}) of the obtained samples was estimated from the weight and volume, while the skeletal density (ρ_s) was measured using a helium pycnometer (Accupyc 1330, Micromeritics Instrument Corp., GA, USA). Then, the total pore volume (V_t) and the porosity (ϕ) were calculated based on (1) and (2), respectively. The macropore volume (V_{mac}) was estimated based on (3).

$$V_t = \frac{1}{\rho_{app}} - \frac{1}{\rho_s} \quad (1)$$

$$\phi = \left(1 - \frac{\rho_{app}}{\rho_s} \right) \times 100 \quad (2)$$

$$V_{mac} = V_t - V_{mes} - V_{mic} \quad (3)$$

3 Results and discussion

3.1 Effect of viscosity of RF solution

As depicted in Fig. 1, the viscosity (μ_{RF}) of a RF solution increases with the progress of the sol-gel polycondensation. Finally, the RF solution loses its fluidity at the gelation time. Apparently, the gelation time increases with the increase in the ratio of *R/C*. This is because the reaction rate of the sol-gel polycondensation of the RF solution decreases with the decrease in the concentration of sodium carbonate (Yamamoto et al. 2002). If emulsification is conducted under

the condition that μ_{RF} is smaller than 1.6 [mPa·s], phase separation between cyclohexane and RF solution occurs during the subsequent curing period. Consequently, it is impossible to obtain a homogeneous o/w emulsion. This is because emulsified cyclohexane phase is not stable if the viscosity of the RF solution is not large enough. Judging from the appearance of the emulsified solution, the cyclohexane phase is stably dispersed in the RF solution if μ_{RF} is in the range of 1.6–2.2 [mPa·s]. Under this condition, as shown in Fig. 2(a), the macropores formed in the MCF is fairly uniform in size. On the other hand, if cyclohexane is emulsified with the RF solution under the condition that μ_{RF} is larger than 2.2 [mPa·s], the distribution of the macropores formed in the MCF tends to be broad as shown in Fig. 2(b). This is because μ_{RF} is too large to disperse cyclohexane homogeneously. Consequently, large droplets of cyclohexane can

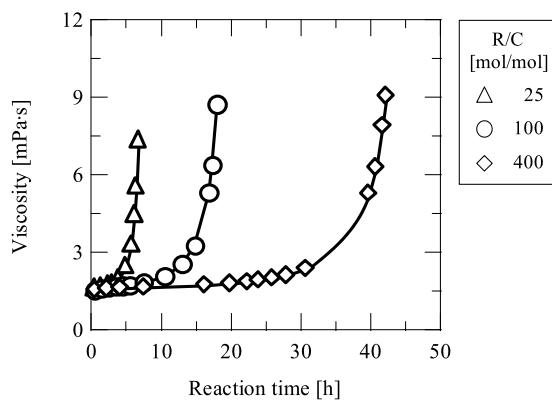


Fig. 1 Transient change in the viscosity of RF solutions prepared under the different R/C ratio

Fig. 2 (a) Cross section of MCFs prepared under the condition of different viscosity of the RF solution ($R/C = 25$ [mol/mol]) (a-1: $\mu_{RF} = 1.6$ [mPa·s], a-2: $\mu_{RF} = 2.2$ [mPa·s], a-3: $\mu_{RF} = 4.5$ [mPa·s]), scale bar: 20 μm . (b) Size distribution of the macropores of MCF prepared under the conditions of $M_{cyclo}/M_{RF} = 1.0$ [–] and $C_s = 0.1$ [wt. %], solid line: fitted curve with a Gaussian function

be observed in the RF solution even after the irradiation of ultrasound longer than 10 min. Thus, we confirm that the viscosity of a continuous phase strongly affects the stability of the o/w emulsion as well as the uniformity of the macropores in the MCFs prepared from the o/w emulsion.

3.2 Effect of mass ratio of cyclohexane with RF solution

If the volume fraction of a dispersed phase in an emulsion exceeds approximately 70%, the emulsion is called as “concentrated emulsion.” Wang et al. (2009) recently reported the synthesis of a monolithic epoxy resin with high porosity as well as 3D interconnected macropores using a concentrated emulsion as a template of the macropores. In the similar manner, with the aim of synthesizing a MCF with 3D interconnected macropores, we have examined the condition to prepare a concentrated emulsion of cyclohexane with the RF solution. Figure 3(a) shows the SEM images of the cross section of the MCFs prepared under the different mass ratio between cyclohexane and the RF solution (M_{cyclo}/M_{RF}). Interestingly, the macropores are interconnected with several adjacent macropores under the condition of the larger M_{cyclo}/M_{RF} ratio. Thus, a MCF possessing 3D interconnected macropores can be prepared as shown in the inset of Fig. 3(a-3). As shown in Fig. 3(b), it is also observed that, with the increase in the M_{cyclo}/M_{RF} ratio, the size of the macropores increases and the size distribution of the macropores tends to be broader.

Figure 4 shows adsorption and desorption isotherms of N_2 on the MCFs prepared under the different M_{cyclo}/M_{RF} ratio. The corresponding size distributions of the mesopores are also shown. The porous properties of the MCFs are summarized in Table 1. According to the IUPAC definition, the

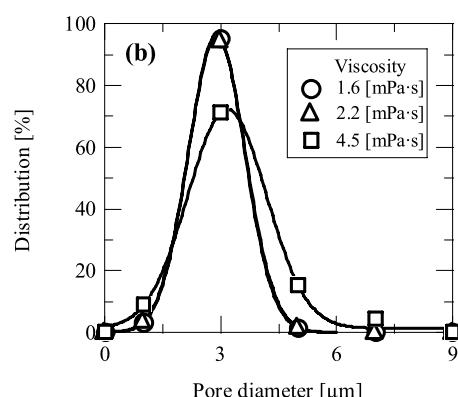
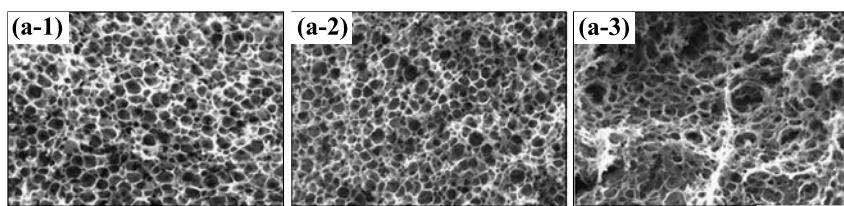


Fig. 3 (a) Cross section of MCFs prepared under the condition of a different mass ratio of cyclohexane with RF solution (a-1: MCF-1, a-2: MCF-2, a-3: MCF-3), scale bar: 20 μm . (b) Size distribution of the macropores of MCF prepared under the conditions of $R/C = 400$ [mol/mol], $\mu_{RF} = 1.7$ [mPa·s] and $C_s = 0.1$ [wt.%], solid line: fitted curve with a Gaussian function

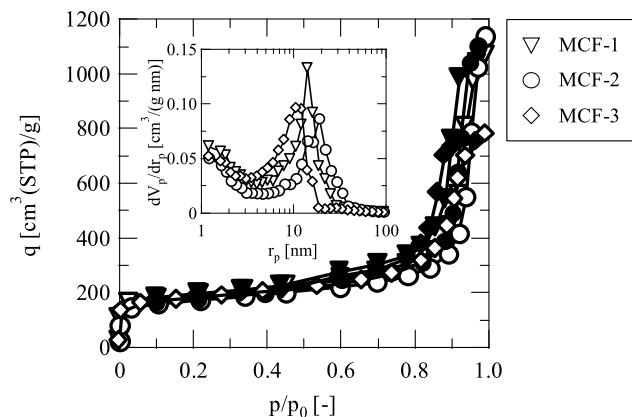
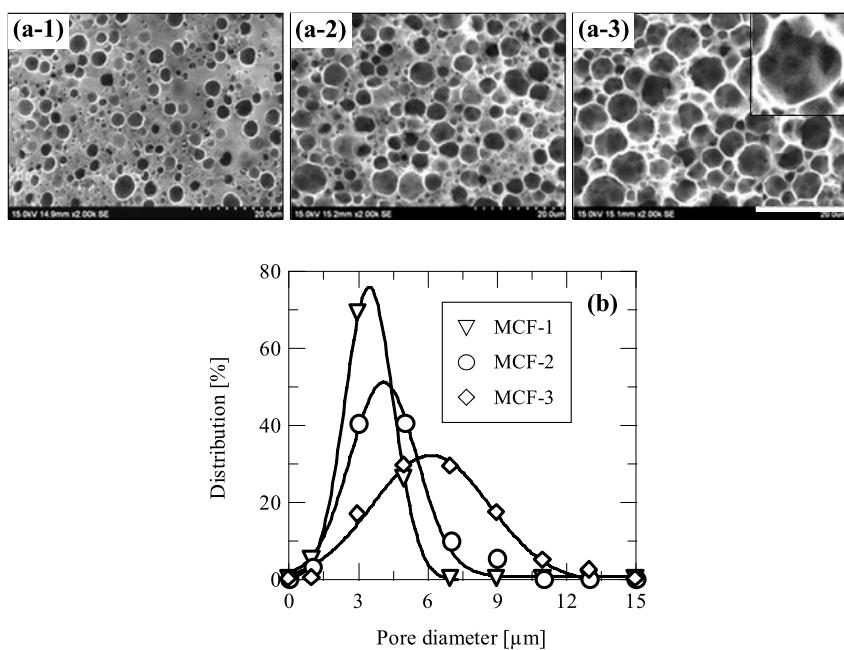


Fig. 4 Adsorption and desorption isotherms of N_2 on MCFs prepared under the condition of a different mass ratio of cyclohexane with RF solution, open symbols: adsorption, closed symbols: desorption, inset: mesopore size distribution

isotherms can be classified into type IV, that indicates the presence of numerous mesopores in addition to a certain amount of micropores. It should be noted that the size distribution of the mesopores or the volume of the micropores is almost unchanged by the $M_{\text{cyclo}}/M_{\text{RF}}$ ratio. This suggests that the size of the macropores can be changed independently from that of the mesopores or micropores. Since the MCF possesses not only macropores but also numerous mesopores as well as micropores, as summarized in Table 1, the porosity of the MCF was found to be much larger than that (less than 60%) of the monolithic epoxy resin (Wang et al. 2009).

3.3 Effect of concentration of surfactant in RF solution

Figure 5 shows the SEM images and the corresponding pore size distributions of the macropores formed in the MCFs prepared under the different concentration (C_s) of Tween80 in the RF solution. It is obvious that the larger C_s leads to the smaller size and the narrower distribution of the macropores. This tendency can be explained as follows. Since the concentration of Tween80 examined in this study is much larger than the critical micelle concentration (0.001 wt.%) (Samaha and Naggar 1988), most of Tween80 molecules are considered to adsorb on the interface formed between the RF solution phase and cyclohexane phase. Since the interfacial area that can be covered by the Tween80 molecules increases with the increase in the concentration (Abismail et al. 1999), it is assumed that the larger C_s results in the smaller droplet size. Consequently, the size of the macropores decreases as C_s increases.

Figure 6 shows adsorption and desorption isotherms of N_2 on MCFs prepared under the different values of C_s . The corresponding size distributions of the mesopores are also shown. The porous properties of the MCFs determined from the isotherms are summarized in Table 1. All isotherms can be classified into type IV that indicates the presence of both mesopores and micropores. It should be noted that the isotherms are almost unaffected by the change in the concentration of Tween80. As discussed in the previous section, this indicates that the volume of the mesopores or micropores is almost constant irrespective of the concentration of the surfactant that is used for preparing the o/w emulsion. Thus, by adjusting the concentration of the surfactant used in the emulsification process, it is also possible to change the

Table 1 Preparation conditions and porous properties of MCFs

Sample code	M_{cyclo}/M_{RF}	C_s [wt.%]	S_{BET} ^a [m^2/g]	S_{mes} ^b [m^2/g]	S_{mic} ^b [m^2/g]	V_{mes} ^c [cm^3/g]	V_{mic} ^c [cm^3/g]	V_{mac} ^d [cm^3/g]	ρ_{app} ^e [g/cm^3]	Φ ^f [%]	d_m ^g [μm]	CV ^h [%]
MCF-1	0.50	0.10	689	323	366	1.55	0.15	1.63	0.27	89.2	3.5	31
MCF-2	1.0	0.10	616	260	356	1.57	0.15	3.88	0.17	93.2	4.1	36
MCF-3	3.0	0.10	643	280	363	1.13	0.15	4.30	0.17	93.2	6.1	42
MCF-4	3.0	0.25	647	274	373	1.39	0.16	3.60	0.18	92.8	5.2	47
MCF-5	3.0	1.0	629	261	368	1.18	0.16	4.06	0.17	93.2	4.0	36

^aBET specific surface area (S_{BET}) estimated by applying the BET equation to the isotherms

^bSpecific surface area of mesopore (S_{mes}) and micropores (S_{mic}) determined based on the α_s analysis

^cVolume of mesopores (V_{mes}) and micropores (V_{mic}) determined based on the α_s analysis

^dVolume of macropores estimated using (1)–(3)

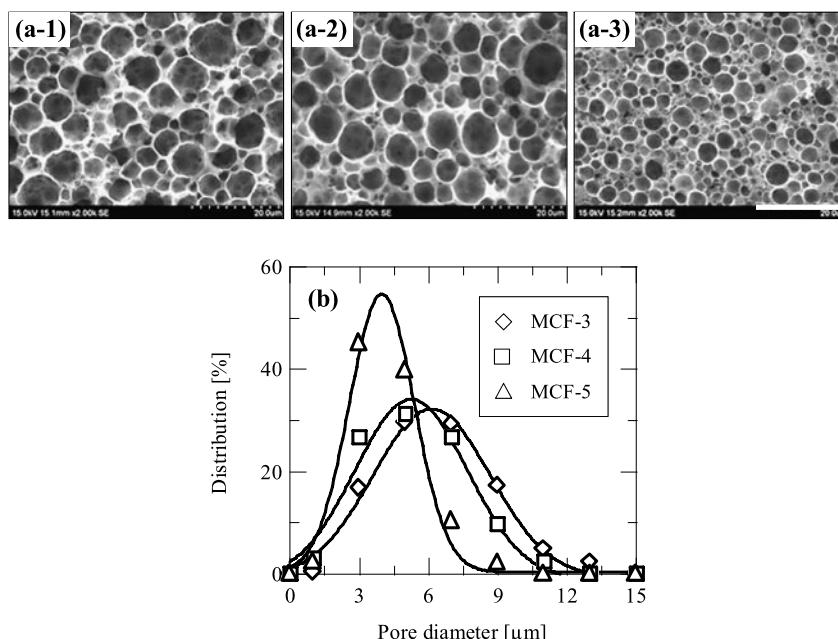
^eApparent density

^fPorosity

^gAverage size of macropores

^hCoefficient of variation

Fig. 5 (a) Cross section of MCFs prepared under the condition of different Tween80 concentration (**a-1**: MCF-3, **a-2**: MCF-4, **a-3**: MCF-5), scale bar: 20 μm . (b) Size distribution of the macropores of MCF prepared under the conditions of $R/C = 400$ [mol/mol], $\mu_{RF} = 1.7$ [mPa·s] and $M_{cyclo}/M_{RF} = 3.0$ [–], solid line: fitted curve with a Gaussian function



size of the macropores formed in the MCF independently from that of the mesopores or micropores.

4 Conclusion

A macroporous carbon foam (MCF) possessing 3-dimensionally interconnected macropores could be synthesized using a concentrated o/w emulsion as a template to form the macropores. In this study, the o/w emulsion was prepared from cyclohexane, a RF solution and Tween80 as an oil phase, an aqueous phase and an emulsifier, respectively.

We studied the effects of the viscosity of the RF solution, the mass ratio of cyclohexane with the RF solution as well as the concentration of Tween80 in the RF solution on the size distribution of the macropores. As a result, the following conclusions were obtained.

To prepare a MCF with a narrow size distribution of the macropores, it was necessary to adjust the viscosity of the RF solution in the suitable range. The average size of the macropores increased with the increase in the mass ratio between cyclohexane and the RF solution, or with the decrease in the concentration of Tween80 in the RF solution. It was found that the porosity of the MCF was larger than 90% due

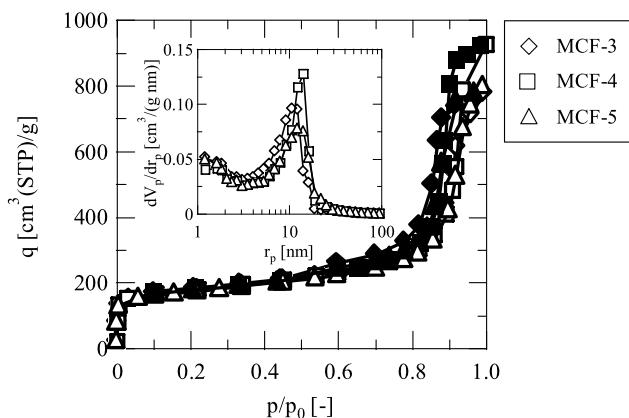


Fig. 6 Adsorption and desorption isotherms of N_2 on MCFs prepared under the condition of different Tween80 concentration, *open symbols*: adsorption, *closed symbols*: desorption, *inset*: mesopore size distribution

to the presence of numerous macropores. The performance of the MCF as an adsorbent will be examined in our subsequent study.

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