Control of the Mesoporosity of Carbon Cryogels

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Introduction

Resorcinol-formaldehyde (RF) cryogels are synthesized by sol-gel polycondensation of resorcinol (R) with formaldehyde (F) in a slightly basic aqueous solution followed by freeze drying. Carbon cryogels can be obtained by pyrolyzing such RF cryogels in an inert atmosphere. Carbon cryogels are confirmed to have high porosity, large BET surface area and large mesopore volume [1], therefore, they are expected to be used as adsorbents, column packing materials for hydrophobic chromatography, catalyst supports and materials for electric double layer capacitors. For these applications, controlled porous structures of the gels are required. In this work, the possibility of controlling the mesoporosity of carbon cryogels by changing the amounts of reactants and diluent used in sol-gel polycondensation was examined.

Experimental

Resorcinol-formaldehyde (RF) solution was prepared by the same method as previously reported [1]. The molar ratio of resorcinol to catalyst (R/C) and the ratio of resorcinol to water (R/W) were varied, while the molar ratio of resorcinol to formaldehyde (R/F) was fixed at 0.5. RF solutions were gelled by curing them at 25 °C for 2 days, at 50 °C for 1 day and at 90 °C for 3 days to obtain RF hydrogels. The solvent within the pores of RF hydrogels was exchanged with t-butanol. Thus obtained RF hydrogels were frozen and dried at –10 °C for 1 day to prepare RF cryogels. Finally, RF cryogels were pyrolyzed at 1000 °C in an inert atmosphere to obtain carbon cryogels. The porous structures of RF cryogels and carbon cryogels were examined by nitrogen adsorption measurements at 77 K and scanning electron microscopy (SEM).

Results and Discussion

Figure 1 shows the SEM images of cross sections of RF cryogels and carbon cryogels. The gels are composed of primary particles which sizes range from 10 to 60 nm. Mesopores are thought to be the voids formed between the particles. It was confirmed that RF cryogels maintain their mesoporosity during pyrolysis despite of shrinkage of the primary particles (Fig. 1(b)).
Figure 2 shows the mesopore size distributions of RF cryogels and carbon cryogels. The peak values obtained from these distributions, \( r_{\text{peak}} \), were plotted as a function of C/W (Fig. 3). Note that C/W approximately corresponds to the concentration of catalyst used in sol-gel polycondensation. It can be seen that \( r_{\text{peak}} \) decreases with the increase in C/W values. The \( r_{\text{peak}} \) values of RF cryogels and carbon cryogels can be related with C/W values by equations (1) and (2), respectively. As shown in Figs. 5 and 6, BET surface area (\( S_{\text{BET}} \)) and mesopore volume of carbon cryogels (\( V_{\text{mes}} \)) also highly depend on C/W values. These results imply that the concentration of catalyst used in sol-gel polycondensation is the key factor for controlling the mesoporosity of the resulting RF cryogels and carbon cryogels. In this work, the peak value of mesopore size distribution, BET surface area and mesopore volume of carbon cryogels were successfully controlled in the ranges of 1.4 to 7.0 nm, 400 to 750 m²/g and 0.1 to 1.3 cm³/g respectively.

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\begin{align*}
    r_{\text{peak}} &= 8.3e^{-220(C/W)} \quad (R^2 = 0.73) \quad (1) \\
    r_{\text{peak}} &= 8.7e^{-320(C/W)} \quad (R^2 = 0.93) \quad (2)
\end{align*}
\]
Fig. 6. Dependency of $V_{\text{mes}}$ of carbon cryogels on the value of C/W.

Conclusions

Carbon cryogels were prepared by varying the amounts of reactants and diluent used in sol-gel polycondensation. Among various parameters, it was found that mesoporosity of carbon cryogels strongly depends on the ratio of catalyst to water (C/W). It was confirmed that the peak value of mesopore size distribution, BET surface area and mesopore volume of carbon cryogels were successfully controlled by changing C/W values.

References


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