

PREPARATION OF POROUS CARBON FROM ORGANIC POLYMER/SILICA NANO COMPOSITE

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Introduction

It is well known that sol-gel process is an useful technique to prepare nano composite of organic and inorganic materials. For the production of nano composite by sol-gel process, tetraethoxy silane (TEOS) was often used as a silica precursor and the shape and size of silica obtained can be controlled by the sol-gel reaction conditions. If nano composite is prepared from carbon and silica by sol-gel method and then only silica framework is removed from the composite, one can expect the formation of a carbon whose pore structure reflects the silica framework. Here, using this method, we have prepared a porous carbon and investigated how the difference in sol-gel reaction conditions influences the pore structure of the resultant carbons. Furthermore, we have attempted to control the pore distribution of carbon by changing the sol-gel reaction conditions.

Experimental

Silica sol was prepared by stirring the mixture of tetraethoxy silane, ethyl alcohol, deionized water and HCl at 80 °C for 3 h. The molar ratios of ethyl alcohol and water to TEOS were 4 and 2, respectively. After cooling the mixture in an ice bath, furfuryl alcohol (FA) was added to the silica sol with FA / TEOS molar ratio to be 1. This mixture was poured into a teflon dish and then subjected to heat-treatment for 2 h at a given temperature up to 120 °C. During this treatment, both of the gelation of TEOS and the polymerization of FA took place. Then, the

polyfurfuryl alcohol (PFA) / silica gel film was further heat-treated at a rate of 2.5 °C/min to 800 °C and held there for 3 h to carbonize the polymer in the film. The resultant carbon / silica composite was washed with an excess amount of 46 % aqueous HF solution at room temperature to dissolve silica framework. As a result, carbon was obtained as an insoluble fraction. The surface area and the pore structure of the samples were investigated with an automatic volumetric sorption analyzer using N₂ as adsorbent at -196 °C. The surface area and the micropore volume were, respectively, determined from the BET equation and the Dubinin-Radushkevich equation. The mesopore volume was calculated by subtracting the micropore volume from the volume of N₂ adsorbed at a relative pressure of 0.95. The mesopore size distribution was determined using the BJH method.

Results and Discussion

The BET surface area and pore volume of the carbons obtained are shown in Table 1, which clearly indicates that they are highly porous. Since the surface area of PFA prepared at 800 °C without silica was almost zero, the mixing with silica endowed the resultant carbons with their porosity. It is noted that the composites have a dense structure and their surface areas are very small. This finding indicates that upon the HF treatment silica frameworks in the composites converted into the pores in the carbon, as we expected.

Table 1 revealed the effect of the sol-gel reaction conditions on carbon pore structure. The

BET surface area and micropore volume increases with decreasing the amount of HCl added. The gelation temperature appreciably influences mesopore volume. For the carbons prepared at the higher gelation temperature, their mesopore is highly developed. Figures 1 and 2 show the pore size distribution curves for these carbons. All the curves have a peak in the range of 2 - 6 nm, and their peak position and broadness change with the sol-gel reaction conditions. At low HCl/TEOS ratio, the pore size is about 2 nm and its distribution looks very sharp. However, the size and the broadness become larger with increasing HCl/TEOS ratio. The pore size also varies with the gelation temperature.

Conclusions

A nano composite of carbon and silica was prepared using sol-gel process. The removal of silica framework from such nano composite led to the formation of a carbon whose porosity consists of mesopore around 2 - 6 nm. It was found that the mesopore structure (pore size and distribution) of these carbons strongly depends on the sol-gel reaction conditions. In other words, this work opens up a possibility for the precise control of carbon mesopore structure by controlling the sol-gel process.

Table 1 Effect of sol-gel reaction conditions on carbon pore structure

Gelation temperature (°C)	HCl/TEOS molar ratio	BET surface area (m ² /g)	Micropore volume (cc/g)	Mesopore volume (cc/g)
25	0.1	860	0.27	0.35
25	0.01	1050	0.33	0.46
25	0.001	1650	0.46	0.41
60	0.01	580	0.21	0.53
120	0.01	1060	0.34	0.72

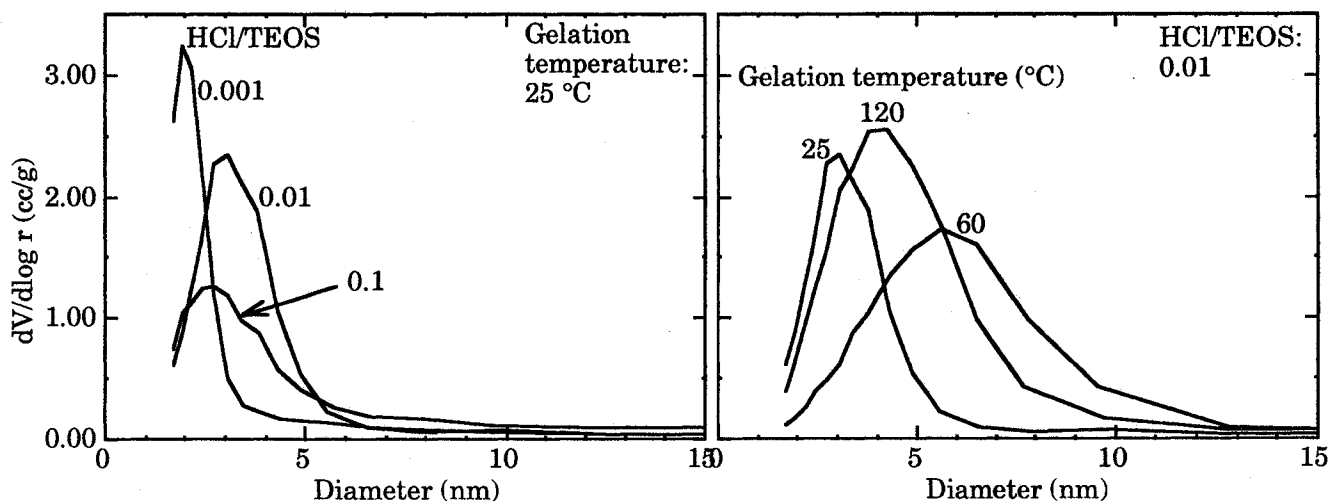


Figure 1 Pore size distribution curves for carbons prepared by sol-gel method with different HCl/TEOS ratios and gelation temperatures.