

PORE STRUCTURE AND ADSORPTIVE PROPERTIES OF CARBON AEROGELS DERIVED FROM VINYL-TYPE POLYMERS

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Introduction

Carbon aerogels are promising for the electrode materials of electric double layer capacitors because of high surface area, mesoporosity and electric conductivity [1,2]. Carbon aerogels derived from resolcinol-formaldehyde (RF) resins have been well studied [3-5]. Polycondensation of resolcinol with formaldehyde produces the surface functionalized nano-particles. The resolcinol-formaldehyde gels are formed due to the inter-connection of the particles. The structure consisting of inter-connected nano-particles maintains during supercritical drying and high-temperature heat-treatment. As a result, in the carbon aerogels, mesopores are formed between the particles. Thus, it is considered that the size and aggregation of the particles are of prime importance for controlling the pore structure of the carbon aerogels. If polymers are cross-linked in the solution with a reagent, it is expected that the formation mechanisms and structure of the gels will be changed and carbon aerogels with different pore structure will be obtained.

Halogenated vinyl-type polymers are chemically dehydrohalogenated with a strong base. Then, dehydrohalogenated polymers can be converted to the carbons with high yield as well as maintaining the precursor geometry since the thermal stability of the starting polymers are enhanced by the introduction of cross-links into the molecular chains via dehydrohalogenation. The present authors have obtained the carbon fibers and films by applying a combination of dehydrofluorination and high temperature heat-treatment to poly(vinylidene fluoride) (PVDF) [6,7]. In the present study, poly(vinyl chloride) (PVC) was used as starting materials and gels were prepared by dehydrochlorinating the PVC in the solutions. The dehydrochlorinated (DHC) gels were dried by using a supercritical drying with carbon dioxide and further heat-treated. The pore structure of the aerogels were characterized by using a nitrogen gas adsorption-desorption analysis. The relation between pore structure and processing conditions were studied.

Experimental

PVC with the inherent viscosity of 0.80 and 1.24 dl·g⁻¹ were used for the experiments. PVC was dissolved in dimethylformamide (DMF) at 60°C and the DMF solutions of PVC were cooled down to room temperature. One of the strongest organic base, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), was mixed with the solutions. The concentration of PVC to the mixture, *[PVC]*, and the number ratio of DBU/(vinylchloride monomer unit), *(DBU/VC)*, were varied. The mixtures were poured into the glass tubes and gelled by three-step curing at 30, 50 and 70°C. The duration of each curing step was 24 hr. After the curing, the DHC gels were removed from the glass tubes and rinsed in DMF. The supercritical drying of the DHC gels was carried out as shown below. The DHC gels were placed in the pressure vessel and liquefied carbon dioxide was introduced up to the pressure of 98MPa by using a plunger pump. The DHC gels were flushed with liquefied carbon dioxide at 25°C. After the DMF in the DHC gels was completely exchanged with liquefied carbon dioxide, the temperature of the vessel was increased up to 50°C and kept for 30 min while maintaining the pressure in the vessel at 98 MPa. Then, the pressure was decreased slowly to atmospheric pressure while maintaining the temperature at 50°C. The vessel was cooled down to the room temperature and the dried gels, that is, the DHC aerogels, were removed. In order to prevent the fusion during carbonization, the DHC aerogels required stabilization prior to carbonization. For stabilization, the specimens were heat-treated at 100°C for 24hr and further heated up to the desired temperatures below 260°C in an air-circulating oven. The maximum temperature of heat-treatment applied to the specimens was referred to as stabilization temperature. Carbonization was carried out at several temperatures below 1300°C in a nitrogen atmosphere.

Bulk density was calculated by dividing the mass of specimens with the volume measured by using a moving caliper. Nitrogen gas adsorption-desorption isotherm was measured at 77K using an automatic gas adsorption apparatus (BELSORP-28). Pore size distributions were obtained by applying the DH-method to the desorption isotherms.

Results and Discussion

The influences of the compositions of the mixtures on the characters of the DHC gels and aerogels was studied for the PVC with inherent viscosity of 1.24. Since the concentration of saturated solution of this PVC was about 13 wt% at room temperature, the mixtures in which the concentration of PVC to DMF exceeded 13 wt% could not be prepared. As dehydrochlorination progressed, the color of the mixture changed from colorless to yellow, to brown and finally to black. For $[PVC]$ smaller than 2.5 wt% or (DBU/VC) smaller than 0.1, gelation did not occur and only black sols could be derived. During gelation, it was observed that the gels gradually shrank and DMF exuded from the gels. This behavior is called as syneresis. The size of the DHC gels depended on both $[PVC]$ and (DBU/VC) . For the same $[PVC]$, the size of the DHC gels decreased with increasing (DBU/VC) up to about 0.5, slightly increased in the range of 0.5-2.0 and decreased again above 2.0.

Although the DHC gels with large size could be obtained at low (DBU/VC) , they wrinkled or deflected during supercritical drying. The DHC gels prepared with $[PVC]$ of 2.5, 5.0 and 10 wt% maintained its macroscopic geometry during supercritical drying when (DBU/VC) were higher than 0.7, 0.5 and 0.5, respectively. The bulk density of the DHC aerogels had the minimum value at (DBU/VC) of about 2.0. Therefore, in order to obtain the highly porous materials, it was required that (DBU/VC) was adjusted to about 2.0. Adsorption of nitrogen gas on the DHC aerogels steeply increased at high relative pressure, indicating that mesopores are preferentially developed and its pore size distribution is narrow. As shown in Fig.1, peak of pore size distribution shifted to smaller radius with increasing $[PVC]$. For the DHC aerogels derived with (DBU/VC) of 1.0 and $[PVC]$ of 2.5, 5.0 and 10 wt%, peak radius were 4.5, 6.1 and 19 nm, respectively. It has been reported that the mesopore radius of RF aerogels can be controlled in the range of 2.5-9.2 nm by changing the mole ratio of resorcinol to Na_2CO_3 used as catalyst and the ratio of resorcinol to distilled water used as diluent [5]. Thus, the preparation method shown in the present study can give the organic aerogels including larger pores as compared with RF aerogels.

If the DHC aerogels were exposed to the carbonization atmosphere, they melted and showed a large mass loss at temperature region of 300-500°C. In order to maintain the precursor geometry and reduce the mass loss, the DHC aerogels were stabilized by heat-treatment in air at temperature region of 100-260°C. When the stabilization was carried out at temperatures lower than 200°C, the progress of stabilization reaction was insufficient and significant shrinkage took place during carbonization. As a result, the pores developed in the DHC aerogels diminished during carbonization. On the other hand, when the stabilization temperatures exceeded 220°C, the DHC aerogels showed large mass loss during stabilization due to the extensive oxidation. From the

view point of minimizing the mass loss and preventing the collapse of the pores, it is preferable that the stabilization is carried out up to about 200°C.

During carbonization, mass loss due to the decomposition started at about 300°C and the change of mass loss with increasing carbonization temperature above 700°C was small. The DHC aerogels derived with (DBU/VC) of 1.0 and $[PVC]$ of 2.5 wt% showed the relative mass loss of 55% during stabilization and carbonization at 1300°C. Concomitantly with mass loss, the volume of the aerogels was reduced during carbonization. As a result, pore size and pore volume were decreased by carbonization as shown in Fig.2. In addition to that mesopores formed in the the DHC aerogels were transferred to that of the carbon aerogels, micropores were developed by the decomposition during carbonization. The increment of micropore volume in PVC-based aerogels, however, were smaller than that of the RF aerogels [5].

To study the influences of the inherent viscosity of the starting materials on the porous structure of the carbon aerogels, the carbon aerogels were prepared from the PVC with inherent viscosity of 0.80. Pore size and pore volume were remarkably increased by the reduction of inherent viscosity as shown in Fig.3.

Conclusions

The organic aerogels were prepared from poly(vinylchloride) (PVC) using chemical dehydrochlorination with the strong organic base, followed by supercritical drying with carbon dioxide. The dehydrochlorinated aerogels could be converted to the carbon aerogels via stabilization and carbonization. The pore structure of aerogels could be controlled by changing the processing conditions, such as the concentration of PVC, the number ratio of a base to vinylchloride monomer unit and inherent viscosity of PVC.

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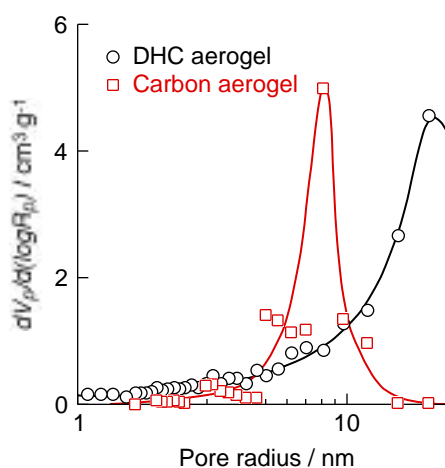


Fig.2 Pore size distributions of the DHC and carbon aerogels. (*DBU/VC*) and [*PVC*] were 1.0 and 2.5 wt%, respectively. The DHC aerogel was stabilized by heat-treatment up to 200°C in air. Carbonization temperature was 1300°C.

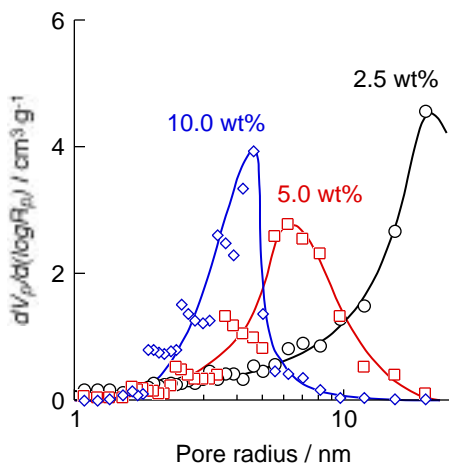


Fig.1 Pore size distributions of the dehydrochlorinated (DHC) aerogels. The number ratio of DBU/(vinylchloride monomer unit), (*DBU/VC*), were 1.0 for all specimens. The concentration of PVC in the mixture, [*PVC*], are shown in the figure.

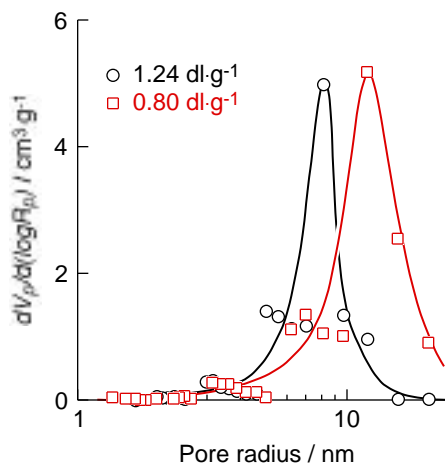


Fig.3 Pore size distributions of the carbon aerogels derived from PVC with inherent viscosity shown in the figure. (*DBU/VC*) and [*PVC*] were 1.0 and 2.5 wt%, respectively. The DHC aerogels were stabilized by heat-treatment up to 200°C in air. Carbonization temperature was 1300°C.