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Controllable fabrication of carbon aerogels

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Abstract: Nano-pore carbon aerogels were prepared by the sol-gel polymerization of resorcinol (1,3-dihydroxybenzene)($C_6H_4(OH)_2$) with formaldehyde (HCHO) in a slightly basic aqueous solution, followed by super-critical drying under liquid carbon dioxide as super-critical media and carbonization at 700 ℃ under N_2 gas atmosphere. The key of the work is to fabricate carbon aerogels with controllable nano-pore structure, which means extremely high surface area and sharp pore size distribution. Aiming to investigate the effects of preparation conditions on the gelation process, the bulk density, and the physical and chemical structure of the resultant carbon aerogels, the molar ratio of R/C (resorcinol to catalyst) and the amount of distilled water were varied, consequently two different sets of samples, with series of R/C ratio and RF/W (Resorcinol-Formaldehyde to water, or the content of reactant) ratio, were prepared. The result of N_2 adsorption/desorption experiment at 77 K shows that the pore sizes decreasing from 11.4 down to 2.2 nm with the increasing of the molar ratio of R/C from 100 to 400, and/or, the pore sizes decreasing from 3.8 down to 1.6 nm with the increasing of reactant content from 0.4 to 0.6.

Key words: resorcinol-formaldehyde aerogels; carbon aerogels; super-critical drying; N_2 adsorption/desorption

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1. Introduction

As carbon aerogels being promising materials in such applications as thermal and phonic insulators, adsorbents, capacitors, and fuel cell and catalyst support, it has seen an explosion of interest over the last few years, and many researches have fabricated by various processes [1-8]. Among them, Pekala et al. [2] first synthesized carbon aerogels via Resorcinol-Formaldehyde system aerogels. CF system and CF Cresol-Formaldehyde aerogels were successfully synthesized and characterized by Wencui L. *et al*. [3]. Czakkel O. *et al*. [4] investigated the influence of drying method on the structure and porosity of the RF aerogels and their carbonized derivatives. Berthon-Fabry S. *et al*. [5] investigated the multi-scale structure of the samples. Tamon H. *et al*. [6-7] synthesized the mesoporous carbon cryogels by freeze-drying with t-butanol. Reynolds G. A. M. *et al*. [8] synthesized the ordered macroporous RF and carbon aerogels with template-directed method. It is well known from the viewpoint of their applications that the control of nanoporous structure of RF and carbon aerogels is very important. Litter work has laid stress on this point. The objective of this work was to propose a controllable procedure of nanostructure aerogels by taking account of the synthesis recipe of the RF aerogels.

Based upon previous work[9] in which the molar ratio of R/F and the gelation process were

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investigated, in present work, the molar ratio of R/C and the content of reactants (resorcinol and formaldehyde) were mainly concerned. Furthermore, the bulk densities and the liner shrinkage of the RF aerogels were calculated. The thermal characterization of the RF aerogels was determined by Thermogravimetric Analyzer (TGA). The synthesised porous samples were characterized by N_2 adsorption/desorption analysis or Brunauer-Emmett-Teller (BET) method. The effects of recipe on the nanostructure and the porosity properties of the synthesized samples were investigated.

2. Experimental

2.1. Sample preparation

Resorcinol (99.5%) (R) with formaldehyde (37%) (F) both from Kishida, were mixed by stoichiometric R/F molar ratio of 1:2; catalyzed by sodium carbonate ($NaCO_3$) (C) with content of 0.1 or 1 mol·L^{-1} and R:C from 50 to 800; diluted by distilled water with different mass content of reactants from 10% to 60%. Two sets of RF hydrogels were prepared as shown in Table1 where the set number 1 followed after S stands for the samples prepared under different R/C ratio with constant RF contents, and the set number 2 does for the samples prepared under the different RF contents with constant R/C ratio.

The mixtures were stirred to obtain homogeneous solutions then were cast into glass molds and aging at 70 ℃ for 2-5 d. Since water and liquid CO_2 are immiscible, the solvent water embedded into the network structure of the gels should be exchanged with organic solvent of ethanol, in which both water and liquid CO_2 are miscible. The all monolith organic gels were rinsed by ethanol (10 times of sample in volume) for three times during 2 d; then transferred into a pressure vessel and processed under the super-critical drying by use of liquid CO_2 as super-critical media by applying the heating at 40 ℃ and the pressurizing at 8 MPa to the autoclave for 2 h in time duration. The organic aerogels were firstly obtained. The corresponding carbon derivatives were obtained by the pyrolyzing of the organic aerogels up to 973 K in N_2 flow (100 cm^3·min^{-1}). The heating rate was 1.0 K·min^{-1} and a soak time being 4 h. Carbon derivates were indicated by "C attached before the name of the aerogel" in the text.

2.2. TGA and adsorption/desorption analysis of aerogels and their carbon derivatives

The pylolytic chemical mechanism for the formation of RF aerogels was determined by TGA (Thermo plus TG8120 by RIGAKU Co. Ltd.). The powder sample was exposed to a high purity nitrogen atmosphere with fluid speed of 50 ml·min^{-1}, being heated up to 1273 K by a heating rate of 10 K·min^{-1} and being maintained at that temperature for 4 h.

A commercial adsorption apparatus (BELSORP 36SP by BEL JAPAN, INC) was used for the nitrogen adsorption/desorption experiment for the samples S-1_2, S-1_3, S-1_4, S-2_4, S-2_5, and S-2_6, and their carbon derivatives CS-1_2, CS-1_3, CS-1_4, CS-2_4, CS-2_5, and CS-2_6(See Table 1). The adsorption isotherms of nitrogen gas at 77 K, specific surface areas (S_{BET}), the pore size distributions of the aerogels and their carbonization derivatives were evaluated.

Table 1. Recipes of the samples, the bulk densities and liner shrinkage of the RF aerogels

Samples	S-1_1	S-1_2	S-1_3	S-1_4	S-1_5	S-2_1	S-2_2	S-2_3	S-2_4	S-2_5	S-2_6
R/F[-]			0.5						0.5		
R/C[-]	50	100	200	400	800				50		
RF contents			15%			10%	20%	30%	40%	50%	60%
Bulk density	ND	0.18	0.19	0.29	0.31	0.10	0.21	0.44	0.51	0.56	0.58
Liner shrinkage	27%	21%	14%	12%	7%	29.4%	25%	19.6%	17.6%	14.7%	12.1%

* ND: no experiment data; * * the unit of "Bulk density" is g·cm^{-3}.