Synthesis and characterization of carbon aerogels with acidizing process

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Keywords: Carbon aerogel, Acidizing process, Specific surface area, SEM

Abstract. Phloroglucinol–resorcinol–formaldehyde (PRF) carbon aerogels were synthesized using Na_2CO_3 as the catalyst. Acidizing process was introduced to the sol–gel reactions system. The results show that the acidizing process of trifluoroacetic acid acetone solution can decrease the shrinkage factor of carbon aerogel, increase absorption capacity and specific surface area. The SEM images of carbon aerogel with acidizing process possess closer network structure and excellent connectivity, the holes between the network are abundant. The XRD patterns show the acidizing process of trifluoroacetic acid acetone solution can enhance the graphitization degree of carbon aerogels.

Introduction

Carbon aerogels are novel porous carbon materials that have received considerable attention in the literature over the past decade or so[1,2]. These materials are very porous with interesting properties such as: low density, high surface area, continuous open porosity and electrical conductivity, can be obtained by sol–gel polycondensation of certain organic monomers such as resorcinol with formaldehyde. However, structure collapse of the obtained wet organic aerogels by sol-gel method was occurred due to the presence of the surface tension of solvent, which greatly affect the properties of carbon aerogels. Usually, this problem was solved by supercritical drying, but the high cost of this technology, complex process, and a certain dangerous nature, hinder the practical application of carbon aerogels. Therefore, researchers are exploring atmospheric drying instead of supercritical drying in order to optimize the preparation process [3].

In this paper, acidizing process was introduced to the sol–gel reactions system to enhance cross link intensity. Phloroglucinol–resorcinol–formaldehyde (PRF) caborn aerogels were synthesized using Na_2CO_3 as the catalyst, by aging, acidification, solvent exchange, atmospheric drying, high temperature carbonization process.

Experimental

Synthesis

Carbon aerogel samples were prepared by the sol-gel polymerization method. Resorcinol (R), Phloroglucinol (P), and formaldehyde (F) were dissolved in deionized water (W) and sodium carbonate as a catalyst (C). The molar ratios of reagents was set as P/R = 0.15; (P + R)/F = 0.5; (P + R)/C = 800, and R/W = 0.06. The monomer concentration of reactants (P +R +F) in solution was 45%. To ensure a homogeneous mixture, the reagents were shocked by ultrasonic oscillator in sealed glass moulds until gelification. This gel was heated in test tubes at 50 ^oC for 72 h and then 80 ^oC for 24 h and the PRF hydrogels were obtained. The obtained PRF hydrogels were treated by acidizing process, in this process the PRF hydrogels were submerged in 3% (volume fraction) trifluoroacetic acid solution for 72 h, and then aged PRF hydrogels with cross-linked netlike structure were obtained. Solvent

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exchange for acetone was carried out by changing solution after every 24 h for 3 times. Drying was carried out at ambient pressure. The dried PRF aerogels were carbonized at 900 ^{o}C for 3 h under a flowing high purity nitrogen atmosphere (100 mL/min).

Three carbon aerogel samples were generated: CA without acidizing process; PRF-acidizing-carb(1) with acidizing process by 3% (volume fraction) trifluoroacetic acid aqueous solution; PRF-acidizing-carb(2) with acidizing process by 3% (volume fraction) trifluoroacetic acid acetone solution.

Characterizations

The surface morphologies of carbon aerogels were observed by S-4800-I (Hitachi, Japan) scanning electron microscopy (SEM). Nitrogen adsorption and desorption were measured using ASAP 2420 surface area analyzer (Micromeritics, America). The samples were degassed at 350 ^{o}C overnight prior to the adsorption measurements. The specific surface areas were determined by BET method. And pore size distributions were calculated by the BJH method from adsorption branch of the isotherms. X-ray diffraction (XRD) patterns of carbon aerogels were obtained by UItima IV X-ray diffractometer (Rigaku, Japan).

Results and discussion

Condition of shrinkage

The samples obtained are regular cylindrical solids. The condition of shrinkage can be tested by diameter comparison of samples before and after carbonization. As shown in Table 1, the shrinkage condition of PRF-acidizing-carb(2) was improved greatly with acidizing process. This result indicate acidizing process of trifluoroacetic acid acetone solution (3%) improve the degree of crosslinking obviously, is advantageous to the formation of more stable network polymer and avoid structure collapse during carbonization.

Table 1 Diameter comparison of samples before and after carbonization

Samples	Diameier before carbonization/cm	Diameier after carbonization/cm	Shrinkage factor/%
PRF-acidizing-carb(1)	2.200	1.759	20.04
PRF-acidizing-carb(2)	2.137	1.903	15.63
CA	2.310	1.424	38.35

Physical characteristics

The pore structure of the carbon aerogels were investigated by low temperature nitrogen adsorption measurements. The N_2 adsorption/desorption isotherms and the pore size distribution (PSD) curves are shown in Fig. 1 and Fig. 2, respectively. The porosity data deduced from the isotherms are listed in Table 2.

These isotherms were the type IV indicating monolayer adsorption of possessing a capillary condensation phenomenon happening on the surface of carbon aerogels [4]. The hysteresis loops at relative pressures above 0.6 clearly show the presence of mesoporosity[5].The nitrogen adsorption capacity of PRF-acidizing-carb(2) is the highest, indicating the specific surface area of PRF-acidizing-carb(2) is the largest (697.65 $m^2 \cdot g^{-1}$).

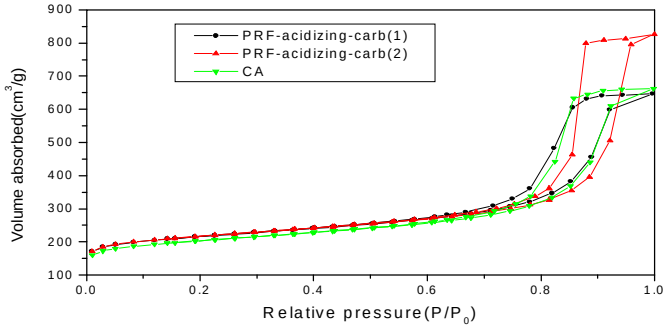


Fig. 1 – Low temperature nitrogen isotherms of carbon aerogels.●PRF-acidizing-carb(1), ▲PRF-acidizing-carb(2),▼CA.

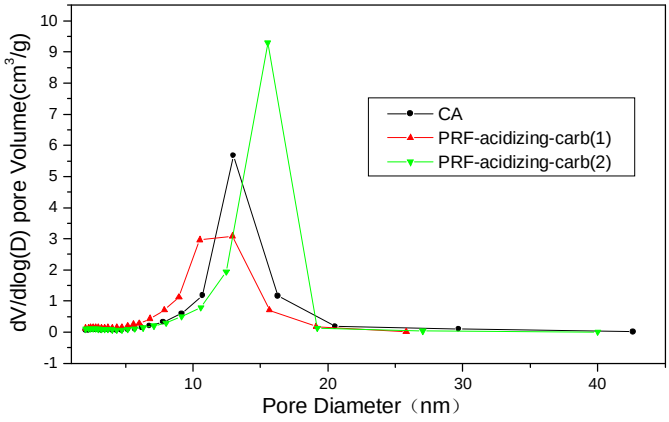


Fig. 2 – Mesopore size distribution from BJH method. ●CA, ▲PRF-acidizing-carb(1), ▼PRF-acidizing-carb(2).

The mesopore size distribution of three samples mainly focus on 10 nm-20 nm, PRF-acidizing-carb(2) display a narrow distribution at 15 nm. After acidizing process, the surface area of PRF-acidizing-carb(1) and PRF-acidizing-carb(2) are larger than CA, indicate acidizing process has positive effects on the formation of abundant network structures.

Table 2 Data reduced from low temperature nitrogen adsorption.

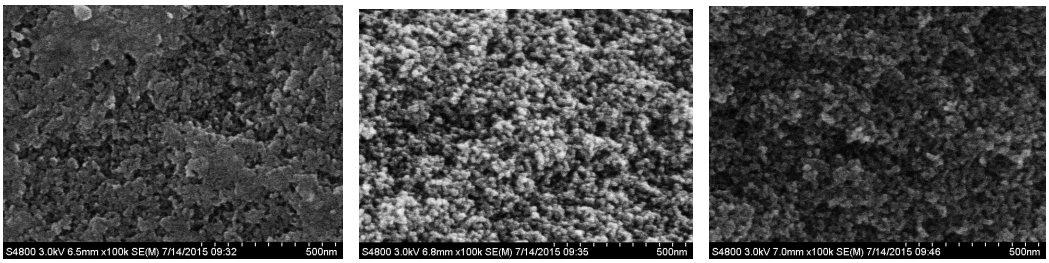
Samples	S_{BET} ($m^2 \cdot g^{-1}$)	V_{tot} ($cm^3 \cdot g^{-1}$)	R (nm)
PRF-acidizing-carb(1)	664.03	1.00	5.77
PRF-acidizing-carb(2)	697.65	1.28	7.33
CA	606.22	1.03	6.24

S_{BET}, specific surface area from BET model; V_{tot}, pore volume at p/p0→1; R, average pore size.

Structural characterization

SEM morphologies of carbon aerogels

SEM images of the surface morphology of three samples are depicted in Fig.1 (a)-(c). The clusters and holes of the sample without acidizing process are variant, made of slender network structure. The sample CA is typical disorder porous material. Compared with the sample CA, PRF-acidizing-carb(1) and PRF-acidizing-carb(2) possess closer network structure, the holes between the network are abundant, have excellent connectivity.



(a) (b) (c)

Fig. 3 SEM images of three samples. a: CA, b: PRF-acidizing-carb(1), and c: PRF-acidizing-carb(2).

XRD patterns of carbon aerogels

XRD patterns of carbon aerogels are characterized by two broadened bands located at 23.5° and 43.8° (2θ) ascribable to the (002) and (101) reflections of graphite, respectively (Fig. 4). These wide peaks are commonly observed in disordered carbons[6]. The peak at 23.5° (2θ) of PRF-acidizing-carb(2) is the sharpest, incidating the acidizing process of trifluoroacetic acid acetone solution can enhance the graphitization degree of carbon aerogels.

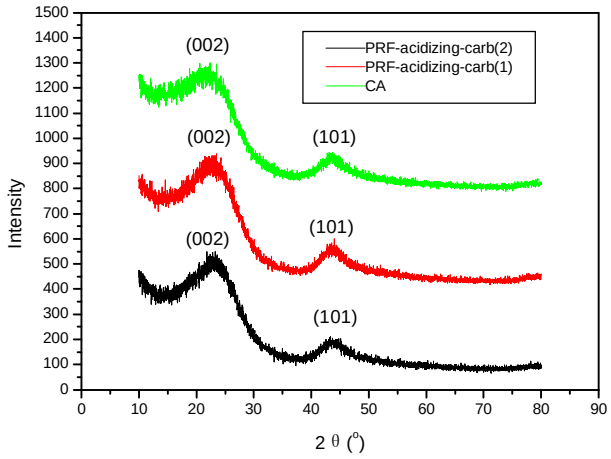


Fig. 4 XRD patterns of carbon aerogels

Conclusions

Carbon aerogel samples were prepared by the sol-gel polymerization method, resorcinol (R), phloroglucinol (P), and formaldehyde (F) were used as reactants. Acidizing process was introduced to the sol–gel reactions system.

The results show: (1) acidizing process of trifluoroacetic acid acetone solution decreased the shrinkage factor of carbon aerogel, increase absorption capacity and specific surface area; (2) the SEM images of carbon aerogel with acidizing process possess closer network structure and excellent connectivity, the holes between the network are abundant; (3) the XRD patterns show the acidizing process of trifluoroacetic acid acetone solution can enhance the graphitization degree of carbon aerogels.

Acknowledgements

This work was financially supported by Science-technology Support Plan Projects of Hebei Province (15291407D).

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