Synthesis of Nanoporous Carbon from Varied Carbon Precursor by Using Nanosized Silica oxide as Template

Zhihong Tang, Yan song*, Yongming tian, Lang Liu, Jingli Shi, Quangui Guo

Institute of Coal Chemistry, Chinese Academy of Sciences, China[*]

1. INTRODUCTION

Porous carbons are highly used in gas and liquid adsorption, energy storage, supercapacitors and catalyst support because of the high surface area and pore volume, inert nature in certain rigorous circumstance and easy for regeneration. The properties of the nanoporous carbons fundamentally rely on the raw materials and the treatment applied in the carbon preparation[1-4]. Template method has been proved to be an effective way to prepare nanoporous with controlled pore structure, for instance, carbons with controlled structures were prepared by using ordered mesoporous silica oxides, such as MCM-48 as template, and the process involving the filtering the pores by carbon precursor, and the synthesis process is extremely complicated[4,5]. The selection of nanosize particles as template not only can prepare porous carbons with controlled pore structure, but also can simplify the preparation procedure[6]. Phenol resin is a typical isotropic raw material to prepare porous carbons, which is often used in the preparation of porous carbons, and exhibit good adsorption ability. Mesophase pitch(MP) is considered a unique anisotropic carbon precursor to develop porous materials with high performances due to its excellent graphitizability, high carbonization yield and low inorganic content[6]. Polyacrlonitrile-based carbons have attracted much attention because of their higher adsorption ability and electrochemical performance arising from the rich nitrogen atoms contained in the matrix[1-3]. In this paper, porous carbons were prepared from three different polymers such as thermosetting phenol resin(TPR), mesophase pitch(MP) and polyacrlonitrile(PAN) by using nanosized silica oxide particles as template, and the pore structures of the as-prepared carbons are investigated.

* Corresponding author, Tel: +86-351-4250553; Fax: +86-351-4083952; E-mail: yansong1026@126.com

2. EXPERIMENTAL

2.1 Synthesis of mesoporous carbon

Nanosized silica oxide particles (particle size, ca. 10nm, surface area, $40m^2/g$, and skeletal density measured by Hg adsorption, $0.55g/cm^3$) were ultrasonically dispersed in ethanol solution of TPR. The mixture of SiO_2 and TPR was obtained after the solvent evaporation. The mixture(SiO_2/ TPR) was stabilized in air at 120℃ for 5 hours, followed by heat-treated in nitrogen at 700℃ for 1 hour to obtain SiO_2/C composite. The composite was then washed by excessive NaOH solution to remove the silica oxide particles, followed by washing with distilled water to neutral and drying at 110^oC for 48 hours to obtain MC. The samplewas labeled as STPR-n, in which n represented the mass ratio of silica oxide to TPR. The synthesis of MP and PAN based carbons was followed the above process in spite of the solvent was changed to pyridine and dimethylsulfoxide, respectively and the polymerization temperature changed to 270 and 300 ^oC, respectively. The samples were labeled as SMP-n, and SPAN-n, respectively, in which n represented the mass ratio of silica oxide to carbon precursor.

2.2 Characterization

Nitrogen adsorption-desorption isotherms were performed at 77K on a Micromeritics ASAP-2000 volumetric adsorption system. The specific surface area was calculated from the adsorption data in the relative pressure interval from 0.05-0.35 using the Brunauer-Emmett-Teller (BET) method. The Pore size distribution curve was gained from desorption branch by using Barrett-Joyner-Halenda (BJH) method. The total pore volume (V_{total}) was calculated at the relative pressure of 0.99. The micropore volume (V_{micro}) was determined by t-plot model, and the mesopore volume (V_{meso}) was calculated by the

difference of V_{total} and V_{micro}.

The weight changes of the raw materials were determined by thermogravimetric analysis (TGA, STA 409 PC). The sample was heated up to 900 ^{o}C at the rate of 5 ^{o}C/min in nitrogen.

3. RESULTS AND DISCUSSION

Table 1 summarized the primary parameters of as prepared carbons. The specific surface area, total pore volume, micropore volume and mesopore volume of STPR-3 were much higher than those of the other two samples. For TPR, there was higher weight loss after carbonization, which could be seen in Fig. 1, therefore, more small molecules were released in the matrix after carbonization, more pores formed, which led to the increase of the pore parameters.

Table 1 Properties of as-prepared carbon

Sample name	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	Ratio$_{meso}$ (%)
STPR-3	1003	2.99	0.14	2.85	95
SMP-3	610	2.23	0.09	2.14	96
SPAN-3	660	2.19	0.09	2.10	96

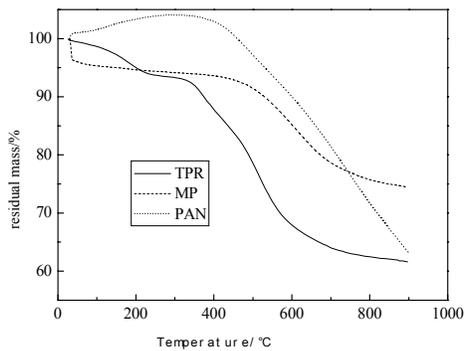Ratio$_{meso}$=(V_{total}-V_{micro})/$V_{total.}$

Fig. 1 TG curves of carbon precursors

Fig.2 displayed nitrogen adsorption-desorption isotherms of as prepared carbon. The

nitrogen adsorption capacity of STPR-3 was the highest of the three samples, which was in

accordance with the high surface area and pore volume. The obvious IV- type hysteresis

loops indicates the appearance of mesopores in the obtained carbons, which was observed in

the slit-shaped pores.

Fig. 3 showed BJH pore size distributions of as prepared carbon. There was a sharp peak

at about 10nm of the three samples, which indicated the abundant pores of about 10nm in the

carbons. Since the diameter of the particles used in the research was about 10nm, the

abundant pores of about 10nm should be attributed to the removal of the particles. However,

the number of pores of about 10nm was not the same of the samples. STPR-3 had the most

pores of about 10nm, and SMP-3 had the least pores of the same diameter among the three

samples. It reported that TPR had many hydroxyl groups (-OH)[9], which might cause more

silica oxide particles to disperse in ethanol, and in the end more pores with the same diameter
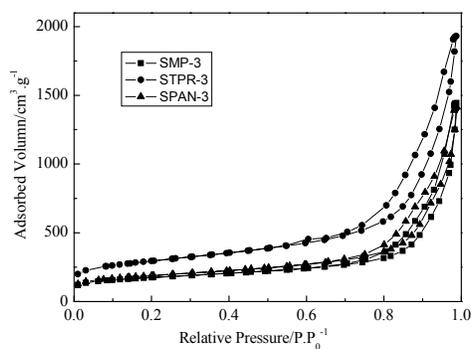

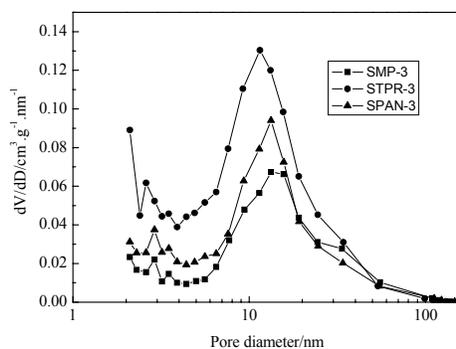Fig. 2 N_2 adsorption-desorption isotherms of as prepared carbons

Fig. 3 BJH pore size distribution curves of as prepared carbons

of the particles formed. PAN possessed polarity because that it contained abundant nitrogen

atoms, so the dispersion ability of silica particles in PAN/ dimethylsulfoxide solution was better

than that in MP/pyridine. Despite the pores of about 10nm, there were also some smaller

mesopores in the as prepared carbon, which should be introduced by the opening of the

closed pores after the template removal.

4. CONCLUSIONS

mesoporous carbons with uniform pore size were prepared from different carbon

precursor, and the carbons from TPR had the highest surface area and pore volume, reached

$1003m^2$/g and $2.99cm^3$/g, respectively. And the lowest surface area and pore volume of MP

derived carbon might be ascribed to the less small mesopores introduced by the

decomposition of the carbon precursor as well as the mesopore of about 10nm introduced by

the removal of the template.

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