

Effect of Surfactant on the Pore Structure of Mesoporous Carbons

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1. INTRODUCTION

Templating method has been widely used in the preparation of nanoporous carbons with controlled pore structure, large surface area and developed porosity. By impregnating or infiltrating of carbon precursors like furfuryl alcohol, phenol resin or sucrose into pores of the template framework, porous carbon is obtained after the subsequent removal of the inorganic template[1-6]. Using nanosized particles as template to prepare mesoporous carbon not only simplified the preparation process, but also could prepare MCs with controlled pore structure through selecting nanosized particles with proper size[1]. In such process, the dispersion capacity of nanosized particles was very important for the synthesis of nanoporous carbons with narrow pore size distribution. There were two ways including ultrasonic dispersion and the surface modification of nanosized particles to improve the dispersion capacity. However, the ultrasonic dispersion could only disperse nanosized particles in a limited extent, while the surface modification was proved to be more effective to solve the problem[8]. In this paper, Pluronic-F127 was selected as modification surfactant, silica particles as template and thermosetting phenolic resin as carbon precursor to synthesize mesoporous carbons, the influence of Pluronic-F127 on the pore structure of as-prepared MCs was discussed.

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2. EXPERIMENTAL

2.1 Synthesis of mesoporous carbon

2.1.1 silica addition

Nanosized silica particles (particle size, ca. 10nm, surface area, 40m²/g, and skeletal density measured by Hg adsorption, 1.65g/cm³) were dispersed ultrasonically in the ethanol solution of TPR. After the solvent was evaporated, the mixture(SiO₂/TPR) was stabilized in air at 120 °C, heat-treated in N₂ at 700 °C for 1 hour to obtain the SiO₂/C composite. The composite was washed by excessive NaOH solution to remove the silica particles, followed by washing with distilled water to neutral and drying at 110 °C for 48hrs to obtain MC. The as-prepared MCs before and after washing with NaOH solution were labeled as SW-n and S-n, respectively, in which n represented the mass ratio of silica to TPR.

2.1.2 Pluronic-F127/silica addition

Pluronic-F127 and silica particles were added into ethanol solution of TPR orderly. The mixture was treated following the above processes to obtain the final MC. The kind of MC obtained by the modification of Pluronic-F127 with the concentration of 10g/L before and after washing was labeled as SFWm-n and SFm-n, respectively, in which m and n represent the mass ratio of silica to Pluronic-F127 and silica to TPR, respectively.

2.2 Characterization

Nitrogen adsorption-desorption isotherms were performed at 77K on a Micromeritics ASAP-2010 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 obtained from the 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 change of the surfactant was determined by thermogravimetric analysis (TGA, STA 409 PC). The sample was heated up to 900 °C at the rate of 5 °C/min in nitrogen.

The size of silica particle was observed by means of transmission electron microscopy (TEM). TEM measurement was conducted by using JEM-2010. The samples were prepared by dispersing the products in ethanol with an ultrasonic bath for 15mins and then a few drops of the resulting suspension were placed on a copper grid.

3. RESULTS AND DISCUSSION

As is well known, the surfactant could effectively promote the dispersion ability of nanosized particles, and accordingly the pore structure of the resultant MCs would change after the addition of surfactant. In this section the effect of the amount of the surfactant on the pore structure of as-prepared MCs was investigated. Table 1 listed the properties of MCs prepared by the modification of the surfactant of different content with the mass ratio of silica particles to TPR was 3. BET surface area and

total pore volume reached 1214m²/g and 5.60cm³/g, respectively for SF1-3. However, the micro-surface area of the sample was the minimum among these samples.

Table 1. Properties of MCs obtained by the modification of Pluronic F-127 with different content

Sample name	SiO ₂ /F-127 (g/g)	S _{BET} (m ² /g)	S _{micro} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	Ratio _{meso} (%)
SF1-3	1	1214	136	5.60	0.05	5.55	99
SF3-3	3	1171	182	3.70	0.07	3.63	98
SF5-3	5	1007	177	3.39	0.07	3.32	98
SF8-3	8	1115	285	3.47	0.12	3.35	97

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

Fig. 1 showed adsorption-desorption isotherms and BJH pore size distributions of MCs prepared by the modification of the surfactant with different content. The nitrogen adsorption amount of SF1-3 was the largest among the five samples(Fig. 1(a)), which was in accordance with the maximal values of BET surface area and total pore volume of the sample. BJH pore size distributions of S-3 and SF1-3 were centered at about 10nm, while that of the other samples centered at about 4nm and 10nm. Moreover, the peak of about 10nm of SF1-3 was more intense than that of the other samples(fig. 1(b)).

For SF1-3, the amount of surfactant used was the largest among the samples, the silica particles were dispersed fairly well according to the intense peak at about 10nm,

and the minimum value of micro-surface area might be ascribed to the deposition of the pyrolysate of the surfactant in the micropores. The surfactant can not be pyrolyzed completely till 900 °C, and there was about 10% pyrolysate remained when it was

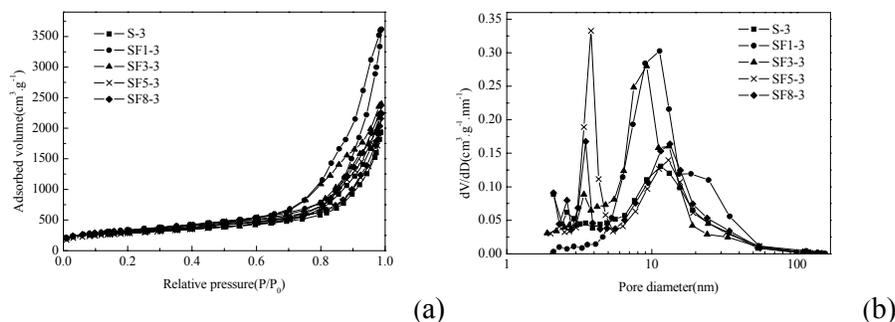


Fig. 1 Adsorption-desorption isotherms(a) and BJH pore size distributions(b) of MCs

obtained by the modification of the surfactant with different content

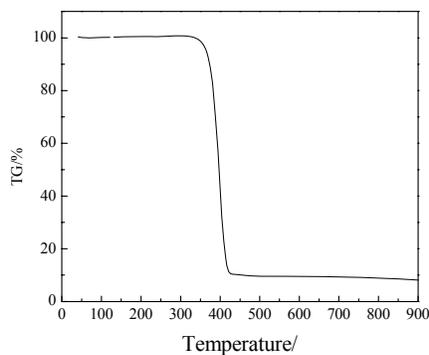


Fig.2 TG curve of Pluronic-P127

heated at 700 °C (Fig. 2). Since the mass ratio of silica to Pluronic F-127 was 1, and mass ratio of the surfactant to TPR was 3, the pyrolysate was fairly large compared to that of the carbon precursor, and therefore, a majority of micropores was blocked by the pyrolysate of the surfactant. For the sample of SF8-3, less surfactant was used, and the pyrolysate also participated in the blocking of micropores of the carbon, but

the quantity of the pyrolysate was too little to block more micropores, which led to the increase of micro-surface area. It was also found that the pores of about 4nm developed abundantly for the sample SF5-3, which meant that as the amount of the surfactant increased or decreased, the pores of about 4nm could not develop abundantly. It is supposed that the amount of the surfactant introduced in the modification of nanosized particles had a critical value, when it exceeded this value, the majority of the surfactant was used to modify the particles, and if it was less than the value, the majority would analyze to form pores about 4nm in the carbon. In the present study, mass ratio of silica particles to the surfactant of 5 was considered as the critical value. And the assumption was confirmed by the intenser peak of ca. 10nm of SF3-3 and the relatively same quantity of pores of about 10nm of SF5-3, SF8-3 and S-3. In order to further prove the conclusion, BJH pore size distributions of SW-3, SFW1-3 and SFW5-3 were proposed(Fig. 3). The quantity of pores larger than 10nm was almost the same for SW-3, SFW1-3 and SFW5-3, and there was a relative intense peak at ca. 4nm for SFW5-3, which indicated that the pyrolysis of the surfactant did not form larger mesopores, the majority of pores of about 10nm were formed through the removal of the template. The appearance of pores of about 4nm for SFW5-3 was in consistent with the assumption mentioned above. It was noticeable that pores of about 4nm of SF5-3 were more than those of SFW5-3, which might originate from the opened pores of the matrix after the template removal.

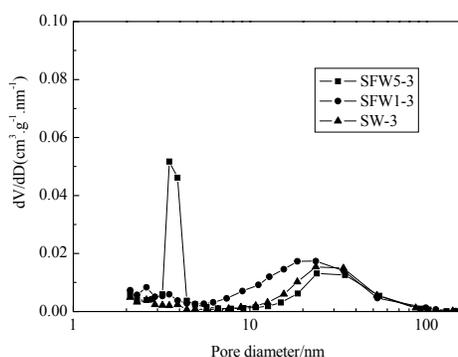


Fig. 3 BJH pore size distributions of MCs prepared with and without the addition of surfactant before washing

4. CONCLUSIONS

In order to improve the dispersion ability of nanosized particles, Pluronic-F127 was used to modify the surface of the silica particles. Results showed that Pluronic-F127 was effective to improve the dispersion capacity of nanosized silica particles when the proper amount added. Pore volume and BET surface area of MC increased up to $1214\text{m}^2/\text{g}$ and $5.60\text{cm}^3/\text{g}$, respectively after the addition of Pluronic-F127. The surfactant used in the present study not only participated in the dispersion of silica particles, but also took part in the formation of small mesopores as well as blocking the micropores.

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