Carbon – Science and Technology

ISSN 0974 – 0546

http://www.applied-science-innovations.com

ARTICLE Received : 10/03/2009, Accepted : 13/05/2009

The effect of PTSA on preparation of mesophase carbon spheres

Youliang Cheng, Tiehu Li, Deqi Jing, Fengjuan Li, Qiang Zhuang

Department of Material Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, P. R. China.

Mesophase spheres have been synthesized by heat-treating a medium coal tar pitch at 420 ºC for 2 hours in the presence of P-toluene sulphonic acid (PTSA). The effect of PTSA on synthesis of mesophase spheres had been studied. It was found that PTSA promotes the formation of mesophase spheres in coal tar pitch through accelerating polymerization of aromatic hydrocarbons. PTSA content between 3 and 5 wt % gave similar size spheres, beyond which as the PTSA content increases, the size of spheres increases. 5 wt % PTSA gives uniform spheres with small size, good spherical shape and smooth surface.

1. Introduction :

Mesocarbon microbeads (MCMB) are nematic liquid crystal materials formed by laminating polycyclic aromatic hydrocarbon with moderate molecular weight. MCMB with high electrical, magnetic and chemical activities, have great potent application in water and air purification as an excellent precursor for high surface active carbon [1 - 2] and ion exchanger [3 - 4]. Practical application aspects of MCMB are dependent on the size and shape of the particles, which have been believed to base on feedstocks, heat-treatment conditions, additives and so on [5].

Mesophase spheres are observed at the early stage of mesophase pitch formation [6]. Many authors found that some super strong acids, such as HF/BF_3 and $AlCl_3$, can enhance the formation of mesophase pitch [7 - 9]. P-toluene sulphonic acid (PTSA) is a super strong solid acid and widely used as catalyst in organic reactions. In the present study, the effect of PTSA on preparation of mesophase spheres had been studied.

2. Experiment :

2.1 Raw material :

In this work, a medium coal tar pitch, PTSA and pyridine were used. The coal tar pitch was supplied by WUHAN IRON AND STEEL COMPANY LIMITED. Some properties of the pitch are summarized in Table (1). PTSA with purity better than 99.5 % was used without further purification. Pyridine used for preparative extractions had a purity of 99.0 %.

2.2 Preparation of mesophase spheres :

The coal tar pitch was blended with PTSA of 3, 5 and 10 wt %, and then added into phenyl silicone oil. The mixture was agitated vigorously for 10 min. and dispersed in an ultrasonic bath for 5 min. to give further dispersion of PTSA. The pitch was heated to 420 °C with a heating rate of 2 °C/min under nitrogen gas flow in a tube and soaked for 2 hours at this temperature, and then free cooled to room temperature, black massive solid was obtained. Mesophase spheres were isolated from the massive solid by soxhlet extraction with pyridine after being washed, dried and ground. As a compared experiment, the coal tar pitch without PTSA was also heat-treated under the same conditions.

Table (1) : Properties of raw coal tar pitch.

C/H	SP (℃)	QI (wt%)	BI (wt%)	CY (wt%)
1.56	82.0	6.82	20	52.6

C/H :Atomic ratio, SP: Softening point,
QI : Quinoline insoluble, BI: Benzene insoluble,
CY : Carbon yield.

2.3 Characterization of mesophase spheres :

The isolated spheres and residue extracted from heat-treated coal tar pitch with or without PTSA were observed by a scanning electron microscope (JEOL, JSM 5800). The average diameters of the spheres were measured by a laser particle size analyzer (LS POP).

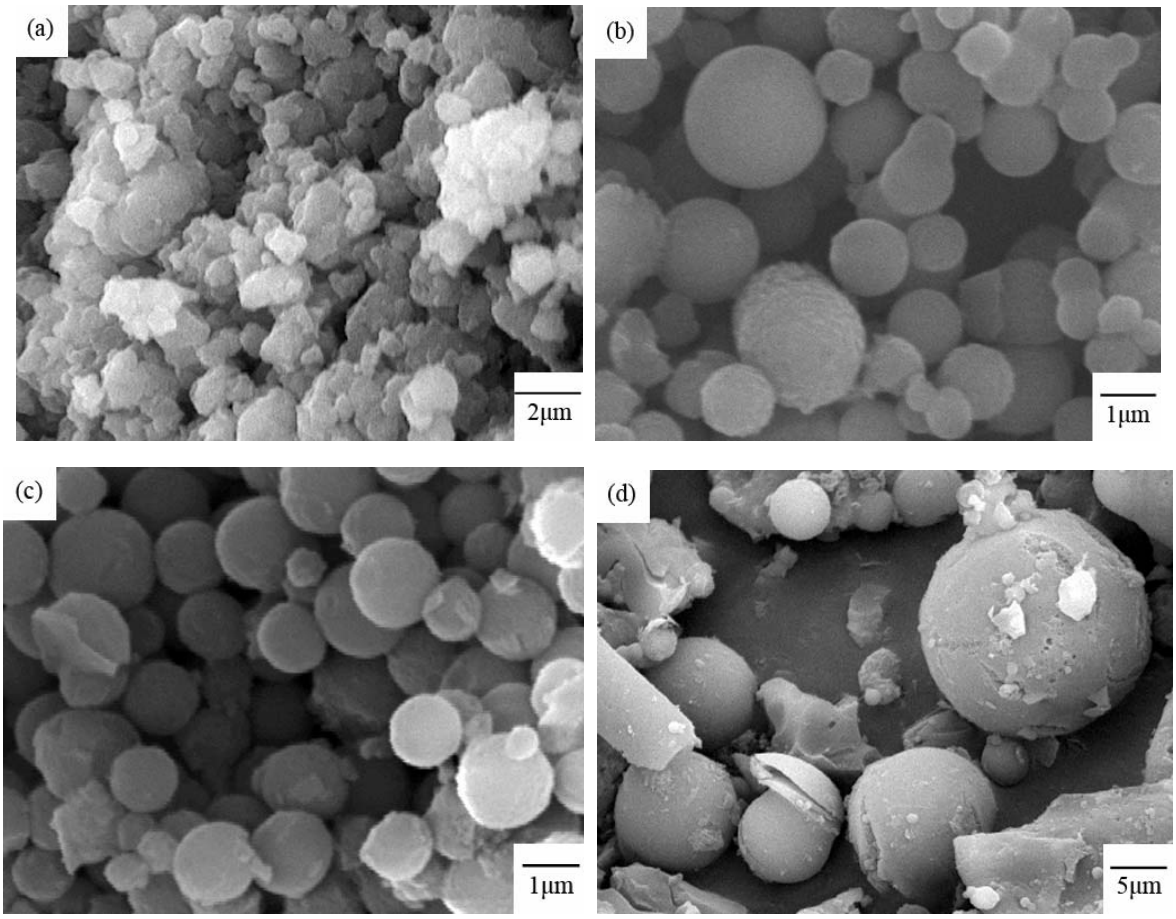

Figure (1) : SEM photographs of residue prepared from heat-treated coal tar pitch at 420 ºC for 2 h with or without PTSA. (a) without PTSA, (b) 3 wt % PTSA, (c) 5 wt % PTSA, (d) 10 wt % PTSA..

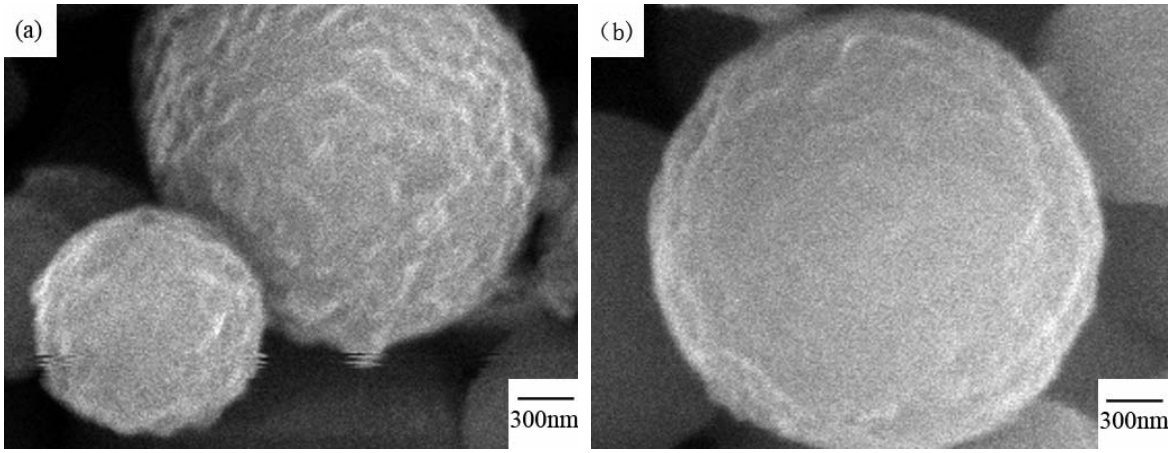

Figure (2) : Higher magnification photographs of spheres prepared from heat treated coal tar pitch at 420 ºC for 2 h in the presence of PTSA. The amount of PTSA : (a) 3 wt %, (b) 5 wt %.

3. Result and Discussion :

3.1 Shape and grain size of mesophase spheres :

The microphotographs of extracted spheres or residue are shown in Figure (1). The average diameters of the spheres are summarized in Table (2). Figure (1a) shows the scanning electron micrograph (SEM) of residue extracted from heat treated coal tar pitch at 420 ºC for 2 h without PTSA. Bulk mass were found in the residue, no sphere was observable. Figure (1b) shows the SEM photograph of mesophase spheres prepared with 3 wt % PTSA. 3 wt % PTSA produced a number of spheres. The diameter of the spheres ranged from 1 to 5 µm, their average diameter was 1.89 µm. Some coalesced spheres were also found. Higher magnification revealed the spheres had crinkled surface [Figure (2a)]. Figure (1c) shows the SEM photograph of mesophase spheres prepared with 5 wt % PTSA. The spheres had good sphere and uniform size. The average diameter of spheres was 1.83 µm. No coalesced spheres were observed. Higher magnification showed the surface of spheres was more smooth than that of 3 wt % PTSA, although ridged surface was still maintained [Figure (2b)].

Figure (1d) shows the SEM photograph of product prepared with 7 wt % PTSA. Sphere, broken-sphere and irregular bulk solid were produced, and some small pores were observed on the surface. The diameter of spheres in the product was over 10 µm, and the measured average diameter reached 26.8 µm.

Table (2) : Average diameters of extracted spheres.

Heat-treatment conditions *Temp.* (ºC)	*Time* (h)	**PTSA (wt %)**	**Average diameter (µm)**
420	2	-	-
420	2	3	1.89
420	2	5	1.83
420	2	10	26.8

4. Discussion :

The present study clarified the influence of PTSA on the preparation of mesophase spheres. It was found that a large number of mesophase spheres with small size were obtained through heat-treated medium coal tar pitch at 420 ºC for 2 hours in the presence of PTSA. The diameter of spheres depended on the amount of PTSA under this experimental condition. The size of spheres was similar when PTSA content was between 3 and 5 wt %, and then increasing with increasing of PTSA content.

At the beginning of the study, the formation processes of mesophase spheres have been reported extensively **[6, 10]**, it is recognized that the formation of mesophase spheres generally involves three elemental processes : nucleation, growth and coalescence of spheres. Furthermore, strong lewis acids have been proved to promote the formation of mesophase pitch by accelerating polymerization and condensation of aromatic hydrocarbons **[8 - 9]**. When coal tar pitch was heated in the presence of PTSA, aromatic hydrocarbons reacted at some temperature and leaded to the formation of high molecular weight nearly planar mesogen molecules. Some of the mesogen molecules formed the nucleation of spheres and tended to produce a large number of smaller size spheres, the other contributed to the growth of spheres. It is well known that the generation rate of these mesogen molecules is associated with the catalyst concentration in the pitch matrix. Lower PTSA concentration gave a small quantity of mesogen molecules, which formed smaller spheres with higher surface energy. The higher surface energy of spheres resulted in the spheres coalescence and more parent pitch adsorbed on the surface of spheres, the parent pitch was extracted by pyridine, causing crinkled surface of these spheres [Figure (1b)]. Whereas excess PTSA content may allow rapid nucleation and growth of spheres, carrying some lighter component of the parent pitch into spheres. Such lighter components could be removed by extraction with solvent, which is reason for the small pores on the surface of the spheres and broken-spheres [Figure (1d)]. Therefore, to get perfect mesophase spheres, the critical content of PTSA should be controlled. In this study, 5 wt % PTSA produced uniform mesophase spheres with good spherical shape and smooth surface.

5. Conclusions :

This study confirms that addition of PTSA in coal tar pitch promotes the formation of mesophase spheres through accelerating polymerization of aromatic hydrocarbons. PTSA content between 3 and 5 wt % gave similar size spheres through heat-treating pitch matrix at 420 ºC for 2 h, and then as the PTSA content increases, the size of spheres increases. 5 wt % PTSA is optimum to give uniform spheres with small size, good spherical shape and smooth surface.

Acknowledgements :

The work is supported by National Natural Science Foundation of China (No.50472801) and Graduates Innovative Foundation of Northwestern Polytechnical University (No.W016130).

References :

[1] Y. Ji, T. Li, L. Zhu, X. Wang and Q. Lin, Applied Surface Science 254 (2007) 506.
[2] K. Kaneko, C. Ishii, Colloids and Surfaces 67 (1992) 203.
[3] M. Haratake, S. Hidaka, M. Ono, M. Nakayama, Analytica Chimica Acta 589 (2007) 76.
[4] M. Kodama, N. Shimizu, T. Fujiura, K. Esumi, K. Meguro, H. Honda, Carbon 28 (1990) 199.
[5] R. A. Greinke, Newyork : Marcel Dekker 24 (1994).

[6] Y. Sanada, T. Furuta, H. Kimura, H. Honda, Fuel 52 (1973) 143.
[7] J. F. Rey Boero and J. A. Wargon, Carbon 19 (1981) 341.
[8] J. P. Boudou, D. Bégin, E. Alain, G. Furdin, J. F. Marêché, A. Albiniak, Fuel 77 (1998) 601.
[9] Y. Korai, M. Nakamura, I. Mochida, Y. Sakai, S. Fujiyama, Carbon 29 (1991) 561.
[10] R. Moriyama, H. Kumagai, J. -I. Hayashi, C. Yamaguchi, J. Mondori, H. Matsui, T. Chiba, Carbon 38 (2000) 749.