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Synthesis and characterization of carbon molecular sieve CMK-3

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Abstract. A nanoporous carbon material was prepared using silica SBA-15 as a template and characterized by several techniques: XRD, N_2-adsorption/desorption, SEM, and TEM. Carbonaceous material exhibits typical characteristics of nanostructed carbon family. The specific surface area and the mean pore size are about 1400 m^2/g and 4 -12 nm, respectively.

Keywords: CMK-3, mesopores, carbon molecular sieve.

1. Introduction

Ordered mesoporous materials have many advantages such as large surface area, uniform pore sizes and in some case high thermal stability [1,2]. These materials have shown many potential applications in heterogeneous catalysis, host-guest chemistry, adsorption, environmental technology and other fields [3-6]. Up to now, various types of well known mesoporous materials are mesoporous silica M41S, SBA-15 [7], but recent attention has been focused on the synthesis of ordered mesoporous carbons, such as CMK-n (n =1 - 9), carbon nanotubes, nanosheets, nanofibers… [2]. Compared to the silica families, porous carbons are chemically inert under various harsh reaction conditions, i.e. they are stable in strongly acidic or basic environments, and withstand high temperature treatment in the absence of oxidants. Moreover, these solids have a high carbon content and the large surface reactivity, due to the existence of remarkable amounts of surface oxygen and hydrogen on channel walls. Carbon materials normally have high surface area and porosity, tunable pore sizes, and large pore volume. Therefore, these materials can be used as efficient adsorbents, catalyst supports [3-6].

The present work deals with the way to prepare a porous carbon, named as CMK-3, using silica sieve SBA-15 as a template. The synthesized material is expected to manipulate the catalytic properties of the carbon-supported catalysts

2. Experimental

2.1. Synthesis of silica template and mesoporous carbon

Silica template SBA-15 was prepared accordingly as reported in Ref. [7]. For example, a quantity of 8.5 g copolymer P123 was dissolved in 300 ml of deionized water and 48.5 grams of 10 M HCl solution. The mixture was stirred for at least 2 hours at 35 ^oC before

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adding 17.2 grams of TEOS. This resultant was further stirred 24 h, and then aged at 75 °C for 48 h. The resulting solid was filtered, washed, dried overnight at room temperature, and then calcined at 550 °C in air for 6 h in order to obtain SBA-15 silica.

Mesoporous CMK-3 carbon was prepared using the SBA-15 silica template [1,5,8]. Typically, a mass of 5 g of SBA-15 was impregnated with a 10 ml aqueous solution containing 6.25 g sucrose and 0.72 g H_2SO_4. The resultant was heated in an oven at 100 °C for 6h and then 160 °C for another 6 h. Then, the composite was carbonized by pyrolysis in an argon flow at 900 °C for 2 h with a heating rate of 2 °C/min. Finally, the resulting solid was washed with 5 wt% HF twice to remove the silica template and dried at 378 K for 4 h. Thus, mesoporous carbon CMK-3 was obtained.

2.2. Material characterization

XRD patterns were collected in a range of 0.5-5° from a Philips X'pert diffractometer equipped using Cu Kα radiation. Scanning electron microscope (SEM) images of the catalysts are acquired on a Hitachi S-800 operating at 10 kV. TEM observation was conducted with a JEM-200CX electron microscope. The BET surface areas and pore size distributions of the CMK-3 sample were determined by N_2 adsorption on a Micrometrics ASAP 2020 apparatus at -196 °C.

3. Results and discussion

Figure 1 illustrates the power X-ray diffraction pattern of SBA-15 silica and corresponding CMK-3 carbon replica. For the parent SBA-15, XRD pattern clearly shows the three well-resolved reflections of the h k l = 1 0 0 ($2\theta = 0.91°$), 1 1 0 ($2\theta = 1.52°$), 2 0 0 ($2\theta = 1.76°$) planes, charactering the long-range ordering of the hexagonal structure [1,8]. Meantime, the small-angle X-ray diffraction pattern of carbon CMK-3 presents a strong reflection peak for the (1 0 0) plane and two very weak peaks of the (1 1 0) and (2 0 0) planes. The lower diffraction intensity signals are interpreted by an incomplete cross linking of carbon framework [2,9]

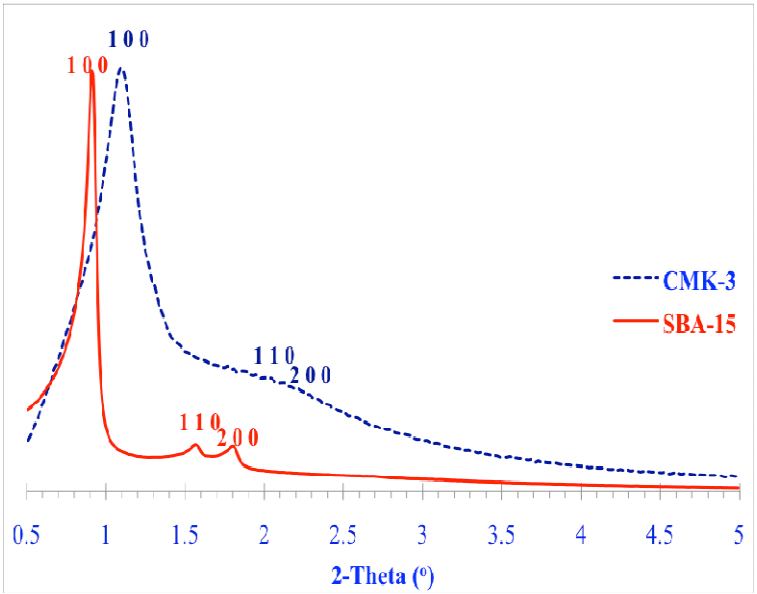

Fig. 1. XRD patterns of SBA-15 and CMK-3.

These characteristics demonstrate that the porous texture of the CMK-3 is exactly an inverse replica of the SBA-15 silica [10]. Therefore, CMK-3 has a well-ordered hexagonal structure analogous to the parent silica [11]. This is substantiated by the nitrogen adsorption/desorption data.

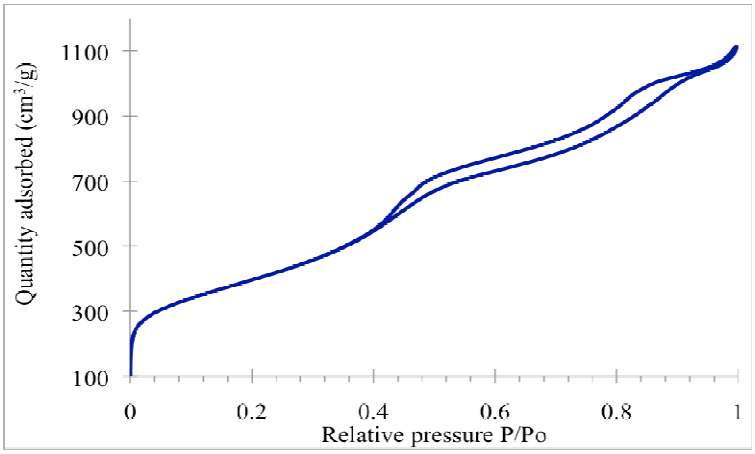

Fig. 2. Nitrogen adsorption/desorption isotherm of the prepared carbon material.

This isotherm of the prepared porous carbon, according to the IUPAC classification, is clearly of type IV and H1 hysteresis loop with capillary condensation at relative pressure P/Po of 0.4-0.5 as displayed in Figure 2. More interestingly, hysteresis loop of the isotherm shows a narrow at medium relative pressure and a slightly broader at a higher P/Po, being interpreted the existence of two pore systems with different pore sizes [8]. Indeed, the pore distribution estimated using the Barrett – Joyner – Halenda (BJH) method shows that the synthesized CMK-3 is typically mesoporous with a quite narrow pore size distribution centered mostly at 3.9 nm (Fig. 3) [9].

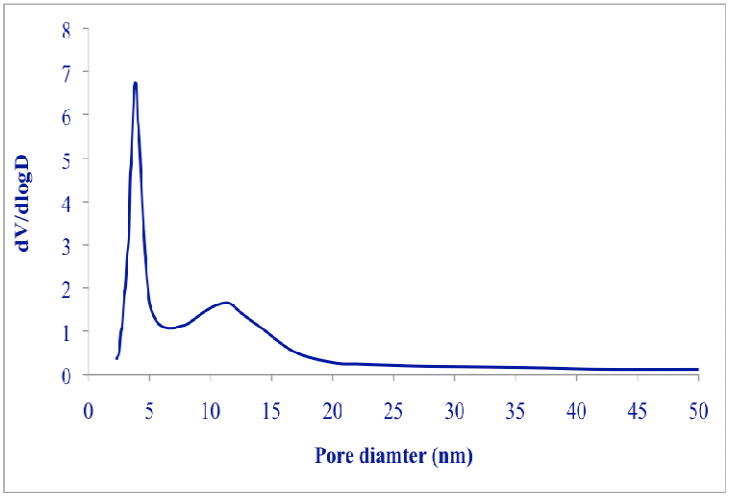

Fig. 3. BJH pore size distribution of CMK-3.

A second peak around at 11.5 nm is explained by the presence of the slit-shaped spaces between amorphous carbon rods [12]. The total pore volume reaches about 1.76 cm^3/g and the BET area of CMK-3 is about 1390.6 m^2/g. A high pore volume is probably associated with the void spaces between the carbon rods. This is strongly substantiated by SEM and TEM images.

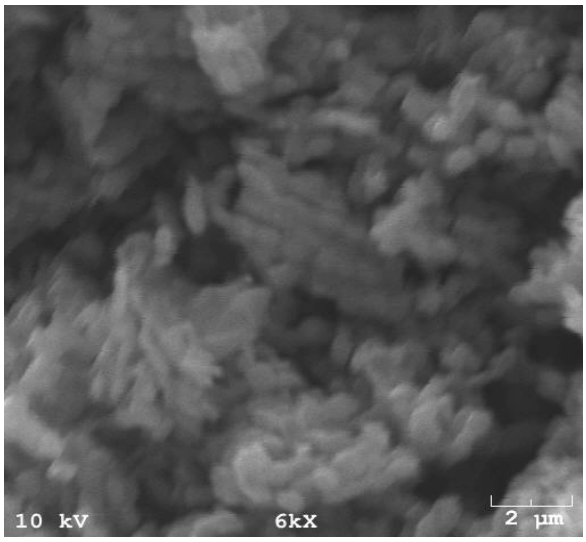

Fig. 4. SEM photograph of CMK-3.

Figure 4 presents a scanning electron micrograph of CMK-3. The porous carbon material is composed of several carbon rodlikes of 0.5-1 µ m in length. There are many void spaces formed between these rods, forming a high external surface area [1].

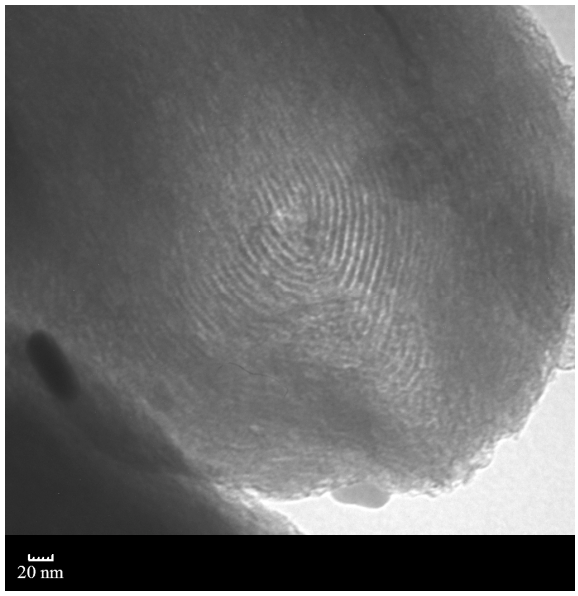

Fig. 5. TEM image of mesoporous carbon material.

The transmission electron image reveals the order of the CMK-3 porous texture. It is clear to see that CMK-3 possesses the uniformity of the mesopores from original inorganic wall structure of the SBA-15 precursor. The parallel lines are characteristic for the ordered nanotubes, with the average pore diameter of 4 nm [2,12]. This is consistent with the nitrogen adsorption/desorption calculation (Fig. 3). Therefore, it can be concluded that the structure of carbon molecular sieve CMK-3 consists of the hexagonal arrangement of cylinder nanoporous tubes.

4. Conclusions

An ordered, nanoporous carbon material is synthesized using SBA-15 silica as the template, sucrose as the carbon source, and sulfuric acid as the carbonizing agent. The synthesized carbon material has mesoporous structure and very high surface area. The pore diameter is about 4 nm while BET surface area

can reach about 1400 m^2/g. This carbon molecular sieve may open many new opportunities for applications as advanced materials.

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References

[1] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, and O. Terasaki, Synthesis of new, nanoporous carbon with hexagonally ordered mesostructure, *J. Am. Chem. Soc.* 122*,* (2000)10712.

[2] R. Ryoo, S.H. Joo, and S. Jun, Synthesis of highly ordered carbon molecular sieves via template-mediated structural transformation, *J. Phys. Chem.* B 103, (1999) 7743.

[3] T. Onfroy, F. Guenneau, M.-A. Springuel-Huet, A. Gedeon, First evidence of interconnected micro and mesopores in CMK-3 materials, *Carbon* 47 (2009) 2352.

[4] H. Huwe, M. Froba, Synthesis and characterization of transition metal and metal oxide nanoparticles inside mesoporous carbon CMK-3, *Carbon* 45 (2007) 304.

[5] Tamas I. Koranyi, Zdenk Vit, Janos B. Nagy, Support and pretreatment effects on the hydrotreating activity of SBA-15 and CMK-5 supported nickel phosphide catalysts, *Catal.Today* 130 (2008) 80.

[6] S. M. Holmes, P. Foran, E. P. L. Robertsa and J. M. Newton, Encapsulation of metal particles within the wall structure of mesoporous carbons, *Chem. Commun*. (2005) 1912.

[7] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores, *Science* 279 (1998) 548.

[8] S.H. Joo, S. Jun, R. Ryoo, Synthesis of ordered mesoporous carbon molecular sieves CMK-1, *Micro. and Meso. Mater*. 44-45 (2001) 153.

[9] W. Schmidt, Calculation of XRD patterns of simulated FDU-15, CMK-5, and CMK-3 carbon structures, *Micro. and Meso. Mater*. 117 (2009) 372.

[10] J. He, K. Ma, J. Jin, Z. Dong, J. Wang, R. Li, Preparation and characterization of octyl-modified ordered mesoporous carbon CMK-3 for phenol adsorption, *Micro. and Meso. Mater.* 121 (2009) 173.

[11] W.C. Choi, S.I. Woo, M.K Jeon, J.M. Sohn, M.R. Kim, and H.J. Jeon, Platinum nanoclusters studded in the microporous nanowalls of ordered mesoporous carbon, *Adv. Mater*. 17 (2005) 446.

[12] A. Lu, A. Kiefer, W. Schmidt, and F. Schuth, Synthesis of polyacrylonitrile-based ordered mesoporous carbon with tunable pore structures, *Chem. Mater*. 16 (2004) 100.

Tổng hợp và đặc trưng vật liệu cacbon rây phân tử CMK-3

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Cacbon rây phân tử được tổng hợp bằng các sử dụng chất định cấu trúc là SBA-15 silica và được đặc trưng bằng các phương pháp vật lý như XRD, hấp phụ/giải hấp nitơ, SEM, TEM. Vật liệu cacbon thu được thể hiện các đặc trưng của họ vật liệu cacbon mao quản trung bình. Diện tích bề mặt riêng đạt được 1400 m^2/g và kích thước mao quản trong khoảng 4-12 nm.