

Synthesis and Characterization of Microporous Carbon Material with High Surface Area

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Novel microporous carbon with very high surface area has been synthesized for the first time using MCM-22 zeolite as a template. The specific surface area of the microporous carbon materials is much higher than that of its parent zeolite template. As the textural characteristics of the microporous carbon are excellent, we believe that the material will definitely find many applications in the field of adsorption and separation of small organic molecules such as amino acids, dyes and vitamins.

Key words: MCM-22, microporous, carbon, nanocasting.

INTRODUCTION

Porous carbons have been attracted much attention due to their potential applications in catalysis, adsorption and separation process, storage of natural gas, electric double layer capacitors and fuel cells.¹⁻³ These applications require carbon materials with porous structure and controllable textural parameters such as specific surface area and specific pore volume which control the performance of the materials. Porosity in the carbon materials can be generated by various processes including activation of organic precursors, carbonization of polymers at high temperature and carbonization of organic molecules inside the porous matrix of inorganic templates. Among them, templating process is very attractive and highly successful for making well ordered porous carbon materials with very high surface area and pore volume.

Templated synthesis of new materials is focused in the literature because they possess interesting physical, magnetic and electronic properties. During the templated synthesis methods, substrate materials are included into the template porous matrix in such a way that their final structure reflects the shape of the template. Organic templates are commonly used to synthesize inorganic materials. For instance, well ordered mesoporous materials such as porous silicates, oxides, and sulfides can be easily synthesized using organic surfactant molecules as the template or structure directing agent. Furthermore, simpler templating materials, more exotic organic amines, self-assembled block copolymer films and colloids have also been utilized recently for the development of novel micro and mesoporous materials. In the same way, inorganic templates have also been used to synthesize a wide variety materials such as alumina, aluminum oxide, silica gel, silica sols, silica opal crystals,

sintered sodium chloride, layered double hydroxides, sepiolite, bentonite L and other clays.

Recently, Ryoo et al. obtained ordered mesoporous carbon materials from various mesoporous silica templates such as MCM-48, SBA-1, and SBA-15 using sucrose as a carbon source.^{4,5} Since then, the research on the development and applications of ordered mesoporous carbon materials is steadily grown.⁶⁻⁹ Very recently Vinu et al. successfully synthesized various mesoporous carbon materials with different pore diameters and structure type by simply varying the pore diameter of the silica template and choosing the template with different structure, respectively and studied their applications mainly in the adsorption of large biomolecules such as proteins, vitamins and aminoacids.⁶⁻¹⁶

Microporous carbon materials are very attractive and have been receiving much attention because these materials possess very high surface area and small pore diameter which are critical for the size selective adsorption of small organic and biomolecules. Recently, many novel microporous carbon materials have been prepared via template carbonization technique using zeolite Y, zeolite beta, zeolite L, mordenite and ZSM-5 as templates.¹⁷⁻¹⁹ Unfortunately, no report on the synthesis of microporous carbon using MCM-22 zeolite is available in the literature. Among the zeolites, MCM-22 is very particular zeolite. It possesses a unique pore structure of 12-membered ring side cups on the crystallites exterior as well as two independent 10-membered ring channel systems; one contains 12-membered ring supercages and other is of sinusoidal tortuosity. In addition, its thin platelet morphology results in high external surface area. The high surface area and the attractive pore structure and active sites in the porous matrix of MCM-22 makes it available for a variety of reactions such as isomerization and alkylation etc. Here

we tried for the first time to use the material as a template for the preparation of microporous carbon material. Microporous carbon material with very high surface area has been prepared using MCM-22 as the template and sucrose as the carbon source. The microporous carbon material has been unambiguously characterized by various sophisticated techniques like XRD, N₂ adsorption and HRSEM. It has been found that the specific surface area of the material is much higher than that of its parent zeolite template, which could offer great potential in many applications including the selective adsorption of small organic molecules and dyes and fuel cells.

EXPERIMENTAL

Zeolite MCM-22 was synthesized using hexamethyleneimine (HMI) as a structure-directing agent. The synthesis procedure was adopted from Marques et al.²⁰ Hydrothermal treatments were carried out in a stainless steel autoclave under rotating conditions at 150 °C for the crystallization period of 96 h. After quenching the autoclave to room temperature, the solid sample was washed with deionized water and then dried at 100 °C overnight. HMI was removed by heating at 540 °C for 24 h under oxygen flow.

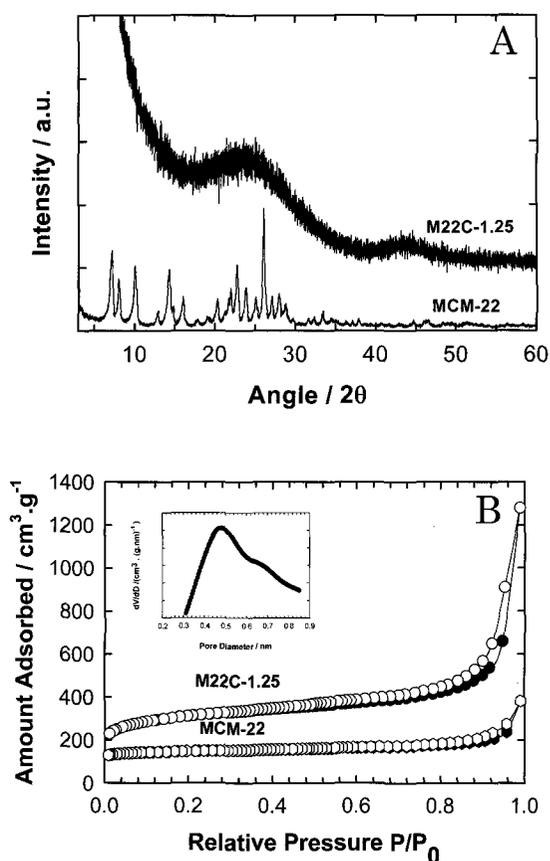
Microporous carbon material was prepared through template carbonization technique. In a typical synthesis of microporous carbon, 1 g of MCM-22 was added to a solution obtained by dissolving 0.75 g of sucrose, 0.08 g of H₂SO₄ and 5 g of water, and keeping the mixture in an oven for 6 h at 100 °C. Subsequently, the oven temperature was raised to 160 °C for another 6h. In order to obtain fully polymerized and carbonized sucrose inside the pores of silica template, 0.5 g of sucrose, 0.06 g of H₂SO₄ and 5 g of water were again added to the pretreated sample and the mixture was again subjected to thermal treatment described above. The total weight ratio of sucrose to MCM-22 was varied from 1.25 to 2 for the preparation of microporous carbons and the sample was labeled as M22C-x where x denoted as the sucrose to template weight ratio. The sucrose to sulfuric acid weight ratio of 9.4 and 8.3 was used in the first and second sucrose polymerization process, respectively. The template-polymer composite was then pyrolyzed in a nitrogen flow at 900 °C and kept under these conditions for 6 h to carbonize the polymer. The microporous carbon was recovered after dissolution of the silica framework in 5 wt % hydrofluoric acid, by filtration, washed several times with ethanol and dried at 100 °C.

The powder X-ray diffraction (XRD) patterns of microporous carbon material and MCM-22 were collected on a Rigaku diffractometer using CuK α ($\lambda = 0.154$ nm) radiation. The diffractograms were recorded in the 2θ range of 3 to 60° with a 2θ step size of 0.01 and a step time of 1 second. Nitrogen adsorption and desorption isotherms were measured at -196 °C on a Quantachrome Autosorb 1 sorption

analyzer. Samples were outgassed at 250 °C for 3 h prior to the nitrogen adsorption measurements. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore size was obtained from the adsorption branch of the nitrogen isotherms by HK method. The morphology of the materials was observed on a Hitachi S-4800 field emission scanning electron microscope (HR-FESEM) using an accelerating voltage of 5.0 kV.

RESULTS AND DISCUSSION

The structural order of microporous carbon material was investigated by XRD. The powder XRD patterns of MCM-22 and microporous carbon sample synthesized at sucrose to MCM-22 weight ratio 1.25 (M22C-1.25) are shown in Fig 1A. The XRD pattern of MCM-22 exhibits many sharp peaks which can be mainly attributed the framework topology of aluminosilicate network in MCM-22. The carbon material exhibits a broad peak in the range $2\theta = 23-27^\circ$, which is attributed to 002 diffraction of graphite-like carbon. However, the absence of a sharp diffraction pattern indicates that the resulting microporous carbon material possesses a low crystallinity and do not have any stacking structure of graphene layers. Nitrogen adsorption isotherms of the carbon sample



(M22C-1.25) along with the parent MCM-22 zeolite are shown in Fig. 1B.

Fig 1. (A) XRD patterns of MCM-22 and microporous carbon materials. (B) Nitrogen adsorption-desorption isotherms of MCM-22 and microporous carbon (close symbol adsorption, open symbols desorption). Inset: Pore

size distribution of M22C-1.25 calculated from HK method on basis of N₂ adsorption data.

Sample	A _{BET} /m ² /g	dp, /nm	V _p / cm ³ /g
MCM-22	526	1.04	0.24
M22C-1.25	1145	1.02	0.53

Table I. The textural parameters of the microporous carbon and the template

The isotherm of the carbon material prepared at sucrose to template weight ratio 1.25 is almost similar that of their parent zeolite template and is of type I which is typically observed for microporous solids. The absence of hysteresis loop and capillary condensation step in the isotherm confirms that the mesoporosity does not exist in the carbon sample. The linear branch at high relative pressures of the isotherm is almost horizontal for the template while the same is no longer horizontal for the M22C, suggesting a wider and heterogeneous microporosity in the carbon. The textural pore size of M22C-1.25 was calculated from the adsorption branch of the isotherm to be 0.53 nm.

Specific surface area, pore volume and pore diameter of the carbon and template are summarized in Table I. The specific surface area and the specific pore volume of M22C are higher than those of the zeolites template. The specific surface area and the specific pore volume are 526 m²/g and 0.24 cm³.g⁻¹ for MCM-22 and 1145 m²/g and 0.53 for M22C-1.25, respectively. The higher surface area and pore volume in the microporous carbon material reveals that the sucrose molecules are completely filled inside the micropore channels of the template. It should be also mentioned that the sucrose to template ratio has been varied from 1.25 to 2 to control the textural parameter of the materials. The specific surface area amounts to 860 m²/g for M22C-2.0 and increases to 1145 m²/g for M22C-1.25, while the specific pore volume increases from 0.41 cm³/g to 0.53 cm³/g for the same samples. The low specific surface area and pore volume of M22C-2.0 could be attributed to the fact that the excess of sucrose molecules in the synthesis mixture block the micropore channels and deposit on the external surface of the template. Among the carbons prepared, M22C-1.25 was the best sample, showing very high surface area and pore volume.

The microscopic features of the MCM-22 and M22C-1.25 displays a similar morphology with a thin plate aggregates (not shown). Moreover, the interconnected petals like structure and highly interconnected small and macro textural pores can be clearly observed for both the carbon and the template. The similarity of surface morphology in both the template and the carbon structure indicates that the sucrose molecules are completely filled in the zeolite macro channels without serious carbon deposition on the zeolite external surface.

In conclusion, novel microporous carbons with high surface area have been synthesized for the first time using MCM-22 as the template. The specific surface area and specific pore volume of the carbons are much higher as

compared with those of their zeolite template. Moreover, the textural parameters such as the specific surface area, pore volume and the surface morphology of the materials can be easily controlled by the simple adjustment of the weight ratio of the sucrose to template in the synthesis mixture. Thus, we believe that the above materials with tunable textural parameters will definitely find many applications in the field of adsorption and separation of small organic molecules such as amino acids, dyes and vitamins.

REFERENCES

- [1] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, *Nature* **386**, 377 (1997).
- [2] J. -S. Yu, S. Kang, S. B. Yoon, and G. Chai, *J. Am. Chem. Soc.* **124**, 9382 (2002).
- [3] G. Che, B. B. Lakshmi, E. R. Fisher, and C. R. Martin, *Nature* **393**, 346 (1998).
- [4] R. Ryoo, S.H. Joo, and S. Jun, *J. Phys. Chem. B* **103**, 7743 (1999).
- [5] S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, and O. Terasaki, *J. Am. Chem. Soc.* **122**, 10712 (2000).
- [6] A. Vinu, C. Streb, V. Murugesan, and M. Hartmann, *J. Phys. Chem. B* **107**, 8297 (2003).
- [7] A. Vinu, M. Miyahara, V. Sivamurugan, T. Mori, and K. Ariga, *J. Mater. Chem.* **15**, 5122 (2005).
- [8] A. Vinu, M. Miyahara and K. Ariga, *J. Phys. Chem. B* **109**, 6436 (2005).
- [9] A. Vinu, P. Srinivasu, M. Takahashi, T. Mori, V.V. Balasubramanian, and K. Ariga, *Micropor. Mesopor. Mater.* (2007, in press).
- [10] A. Hartmann, A. Vinu, and G. Chandrasekar, *Chem. Mater.* **17**, 829 (2005).
- [11] A. Vinu, K.Z. Hossain, G. Satishkumar, and K. Ariga, *Carbon* **44**, 530 (2006).
- [12] A. Vinu and M. Hartmann, *Catalysis Today* **102**, 189 (2005).
- [13] A. Vinu and K. Ariga, *Chem. Lett.* **34**, 674 (2005).
- [14] A. Vinu, M. Miyahara, and K. Ariga, *J. Nanosci. Nanotech.* **6**, 1510 (2006).
- [15] A. Vinu, M. Miyahara, T. Mori, and K. Ariga, *J. Porous. Mater.* **13**, 379 (2006).
- [16] A. Vinu, T. Mori, and K. Ariga, *Sci. Tech. Adv. Mater.* (2006, in press).
- [17] T. Kyotani, N. Sonobe, and A. Tomita, *Nature* **331**, 331 (1988).
- [18] T. Kyotani, T. Nagai, S. Inouce, and A. Tomita, *Chem. Mater.* **9**, 609 (1997).
- [19] J. R. Mirasol, T. Cordero, L. R. Radovic, and J. Rodriguez, *Chem. Mater.* **10**, 550 (1998).
- [20] A. L. S. Marques, J. L. F. Monteiro, H. O. Pastore, *Micropor. Mesopor. Mater.* **32**, 131 (1999)

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