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Synthesis of ordered mesoporous carbon molecular sieve and its adsorption capacity for H₂, N₂, O₂, CH₄ and CO₂

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Abstract

Ordered mesoporous carbon is a recently developed material. To test its potential application for adsorption, such a material was synthesized using silica SBA-15 as the template and sucrose as the carbon source. The ordered structure and the mesopore dimension of the material were proven with XRD, SEM and TEM examinations. Adsorption data of H₂, N₂, O₂, CH₄ and CO₂ on the ordered mesoporous carbon were collected with a typical volumetric method for a pressure range up to 11 MPa. Potential application for the separation of CO₂–CH₄–air mixture was indicated. © 2005 Elsevier B.V. All rights reserved.

1. Introduction

Ordered mesoporous material has been recently developed [1–3]. This kind of material attracted much research interest on its potential application due to the favorable property: the large pore volume, high specific surface area, high thermal stability, high stability in strong acids and bases, high mechanical stability, chemical inertness, solidity, and the ordered mesopore structure [4–10]. To further test the potential usage of the material for adsorptive storage of hydrogen and methane, and for the separation of gas mixtures, especially those of air with carbon dioxide and methane, based on adsorption, such a material was synthesized, and adsorption isotherms of hydrogen, nitrogen, oxygen, methane and carbon dioxide on the material were collected.

2. Experiment

SBA-15 silica with 2-dimensional ordered channels was synthesized in acidic condition. A non-ionic oligo-

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meric alky-ethylene oxide surfactant (Pluronic P123) was used as the structure-directing agent and tetraethyl orthosilicate (TEOS) of analysis grade was used as the silica source. After filtration and drying, the as-synthesized product was calcinated at 823 K to obtain the SBA-15 structure. Using SBA-15 as the template and sucrose as the carbon source, the carbon replica was produced. The quantity ratio of sucrose to the silica SBA-15 (C/Si) was kept at 1.25. The as-synthesized product was heated in vacuum to 1173 K with a heating rate of 5 K/min to complete the carbonization of sucrose. The silica template was washed out with 1 M NaOH (in solution of 50% ethanol in water) at temperature 373 K. The template-free carbon product thus obtained was filtered, washed with ethanol, and dried at 393 K. The carbon material obtained was indeed CMK-3-1.25 according to the conventional nomination rule and the initial C/Si ratio.

The synthesized carbon material was examined by small angle X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and the adsorption of nitrogen at 77 K, from which the specific surface area, pore volume and pore size distribution was determined based on the BET [11] and BJH [12] theory.

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The adsorption isotherms of the testing gases on the synthesized material were collected on a typical volumetric apparatus adapted for high-pressure adsorption studies. Working principle and details of the apparatus were previously presented [13]. Sample was first dried at 300 °C for 12 h in a vacuum oven. All gases used are of purity above 99.99%. Pressure was measured with sensitivity of 0.05% up to 11 MPa. Temperature was kept constant within ± 0.1 °C.

3. Results and analyses

The ordered structure of the synthesized carbon material is clearly shown in the SEM and TEM photos of Figs. 1 and 2. Since the template, SBA-15, consists of channels in hexagonal arrangement, its inverse replica, carbon CMK-3-1.25, consists of hexagonally arranged nanorods. The TEM analysis reports that the nanorods are 9.6-nm apart. Because there are some micropores connecting the cylindrical channels in the SBA-15 templates, the carbon nanorods are interconnected due to the micropore filling of the silica template with carbon source. The peak indicating the existence of the reflection $(1\ 0\ 0)$ is clearly identified in the XRD spectrum, which is in agreement with the hexagonal ordered structure. The BET surface area is 1098 m²/g and the total pore volume is $1.30\ \text{cm}^3$ /g based on nitrogen adsorption data. Pore size distribution of CMK-3-1.25, determined on treating the nitrogen data at 77 K with the BJH theory, is shown in Fig. 3. It is shown that the synthesized carbon material is mesoporous with quite narrow pore-size distribution centered at 3.8 nm, which is consistent with the results of TEM and XRD analysis.

To test the storage capacity of the material for hydrogen, an adsorption isotherm was collected at 273 K. As shown in Fig. 4, the isotherm shows the type-I feature and the highest capacity is less than 0.5% at 10 MPa and 273 K. This is reasonable because the adsorption



Fig. 1. SEM photo of the synthesized carbon material in two scales.



Fig. 2. TEM photos of the synthesized carbon material taken along the nanorod direction and the direction perpendicular to it (the circular black dots are nanorods).



Fig. 3. Pore size distribution of the synthesized carbon material.



Fig. 4. Adsorption isotherm of H₂ at 273 K.

amount of hydrogen is proportional to the specific surface area of the adsorbent [14] according to the monomolecular coverage mechanism [15]. Adsorption isotherms of N₂, O₂, CH₄ and CO₂ on the carbon material were collected at 298 K and shown in Fig. 5. The isotherms of N₂ and O₂ are almost coincided, but that for the other gases are quite much separated. The material seems prefer to adsorb CO₂; therefore, is potentially applicable for the separation of CO₂/N₂ or CO₂/O₂, and may also be applicable for the separation of CO₂/CH₄. The large pore size and large pore volume leave a large room for surface modification to improve the selectivity.



Fig. 5. Adsorption isotherms of N_2 , O_2 , CH_4 and CO_2 at 298 K.

4. Conclusion

An ordered mesoporous molecular sieve consists of hexagonally arranged carbon nanorods was synthesized with a template technique. It has a specific surface area of about 1100 m²/g and pore volume of $1.30 \text{ cm}^3/\text{g}$ centered at 3.8 nm. Although it is not suitable for hydrogen storage, it shows preferable adsorption affinity for CO₂ than for methane, oxygen and nitrogen; therefore, it might have potential application for the important separation task of CO₂-containing gas mixtures.

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