

SYNTHESIS OF ORDERED MESOPOROUS CARBON MATERIALS USING NEW MESOPOROUS SILICA AS TEMPLATES

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Abstract

MCM-48, SBA-1/15/16, as well as other mesocellular foam are all used as the templates frequently for the replication of ordered mesoporous carbons (OMC). However, the preparation of OMC using ordered mesoporous silica (OMS) synthesized from non-aqueous solvent evaporation method has not been reported. In this work, OMC materials were synthesized by OMS template using sucrose as the carbon source, and the samples were characterized by transmission electron microscope (TEM) and nitrogen adsorption. The results of observation shown that the OMS used in the experiment is an excellent hard template.

Keywords: Porous carbon; Impregnation; Carbonization

1. Introduction

Ordered mesoporous carbon (OMC) materials with high surface area and large pore volume have been attracted more attentions in the last decade because of their uses in catalysis, energy storage, and double-layer capacitors. The templating approach, based on the existing materials, is one of the most suitable preparation routes to synthesize OMC. So far, many kinds of inorganic silica templates such as MCM-48, SBA-1/15/16 [1-6] have been selected as fugitive phase to duplicate different structure carbon materials. Those silica templates are always prepared by hydrothermal synthesis method, and this long and complicated synthesis procedure is extravagant and will limit the utility of OMC. Moreover, the reported ordered mesoporous carbon materials are in the form of powders or particles, formation of these materials in a thin-film or membrane geometry [7] is therefore an active area of research.

In this paper, silica template with a hexagonally arranged mesoporous structure was synthesized by the combination of sol-gel and evaporation-induced self-assembly (EISA) process. Ordered mesoporous carbon materials were synthesized by means of the liquid impregnation using sucrose solution followed by carbonization and the subsequent silica removal. It is shown that the as-synthesized silica is an excellent template to fabricate OMC. Thus this work is time-saving and energy-saving.

2. Experiment

2.1 Synthesis of the template

The general procedure to prepare silica template is described as follows, using modification of the technique established by Zhao et al. [8] and Alberius et al. [9] TEOS was added to the mixture of water,

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HCl and CH₃OH. After being hydrolyzed for 2h at room temperature, the ethanol solution of P123 was added to the sols. The typical weights in grams of each component are tetraethyl orthosilicate/EtOH/HCl/P123=2.0 g/15 g/0.1 g/1 g. The obtained solution was stirring for 2h at the same temperature. The resulting sol was then aged in 20-40% humidity environment at room temperature until a translucent substance obtained. The surfactant/silica nanocomposites were subsequently maintained at 333 K in aqueous vapour to increase the extent of silica cross-linking. The silica template designated as OMS was obtained by the removal of P123 template using calcination.

2.2 Fabrication of OMC

OMC based sucrose was synthesized by the procedure as indicated by Ryoo et al. [4] except for the amount of sucrose introduced into silica pores. Briefly, the silica template was added to a liquid solution of sucrose, water, and H₂SO₄, and the weights in grams of each component are 1: 1: 5: 0.1. The mixture was placed in drying oven for 6 h at 373 K, and subsequently the oven temperature was increased to 433 K for 6 h. the another impregnation with 0.8 g of sucrose and 0.1 g of H₂SO₄ in 5 g of H₂O, the mixture was then treatment at the same process. The carbonization was completed by heating at typical 1173k in a nitrogen atmosphere for 3 h. the carbon-silica composites were then dissolved by stirring in a 10 wt% HF at room temperature to remove the silica template. The resulting dark materials were denoted as CS.

2.3 Characterization of materials

The sample morphology was observed by a JEOL (JEM 3010) transmission electron microscope (TEM) operation at 160 V. N₂ adsorption/desorption isotherms at 77 K were obtained using a Micromeritics ASAP2010 sorptometer. The surface area was deduced from the BET method, and pore size distributions were calculated using the BJH (Barett- Joyner-Harenda) method.

3. Result and Discuss

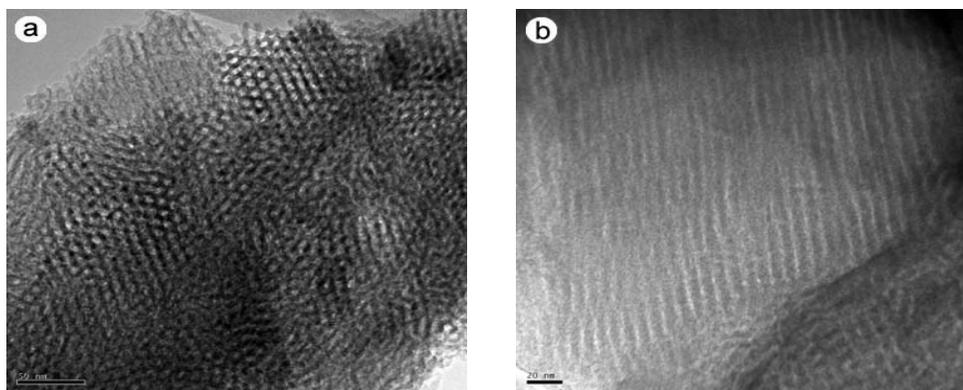


Figure 1. TEM image silica template and OMC

The TEM images of OMS and OMC were shown in Figure 1 to illustrate the mesopore structure. The mesopore of OMS with a hexagonal structure was uniform and distributed on the surface, its pore size distribution centered at 6.5 nm, which was consistent with the result derived from the BJH equation. However, unlike the SBA-15, the OMS synthesized from EISA process has an ordered asymmetric structure, and not all the hexagonal arrangement of cylindrical mesoporous tubes is

perforative. The TEM images of OMC clearly show a regular organized porous structure, which is exactly an inverse replica of OMS materials, and is similar to CMK-3 [4].

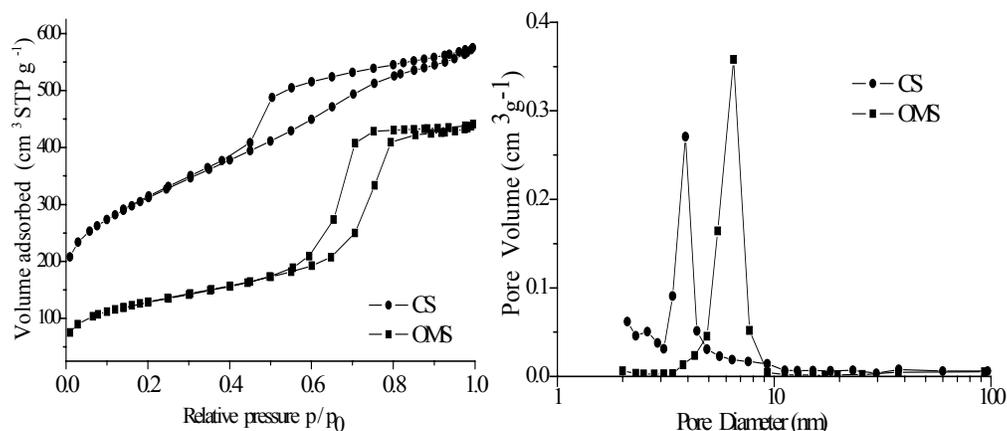


Figure 2. Nitrogen adsorption/desorption isotherms and their corresponding pore size distributions of silica template and OMC.

Nitrogen adsorption/desorption isotherms of OMS and OMC and the corresponding pore size distribution are shown in figure 2. Both of the samples show hysteresis loops at relatively high pressure P/P_0 because of capillary condensation, which is typical characteristic of mesostructure. For the carbon materials, both the adsorption and desorption isotherms have higher uptake at lower or greater relative pressure than that of silica template, and this indicates the OMS possesses an additional microporous structure and a macroporous structure. In this case, OMC materials have the BET area of $1086 \text{ m}^2/\text{g}$, which is two times than that of OMS. The pore-size distribution obtained for OMC is centered at 3.9 nm, while the distribution for OMS is centered at 6.5 nm. Both of them have a unimodal distribution, which suggests that the mesoporous networks of OMC are mainly contributed by the walls of the silica template.

4. Conclusions

In summary, ordered silica materials synthesized from EISA were selected as a hard template for the first time. The advantage of this hard template is that the process is simple and low cost. Especially, mesoporous material with thin film shape can also be fabricated by EISA process.

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