

ADSORPTION PROPERTIES OF ORDERED MESOPOROUS CARBONS

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Introduction

Ordered mesoporous carbons constitute a new group of carbonaceous adsorbents reported for the first time by Ryoo et al. in 1999 [1]. The synthesis of these carbons involves the infiltration of the porous structure of an ordered mesoporous material with three-dimensional porous structure with an appropriate carbon precursor; carbonization; and dissolution of the silica template. Ordered mesoporous carbons have periodic carbon frameworks with unit-cell sizes of about 10 nm, but the frameworks themselves are disordered on the atomic scale. These carbons exhibit uniform mesopores several nanometers in width, which are accompanied by micropores in the carbon framework. First ordered mesoporous carbon was synthesized using MCM-48 silica as a template, but was not a faithful replica of the template because of a structural transformation that accompanied the template dissolution [1]. Subsequently, a disordered mesoporous carbon that retained the structure of the HMS silica template was also reported [2]. Later, the first ordered mesoporous carbon that was a faithful replica of the template was synthesized using SBA-15 silica template [3]. There is currently an appreciable interest in the synthesis, and characterization of ordered mesoporous carbons, as well as in their assessment for applications ranging from electronic devices to adsorbents and catalyst supports [4-7].

Experimental

Ordered mesoporous carbons were synthesized via repeated infiltration of ordered mesoporous host (MCM-48 or SBA-15) with sucrose in the presence of sulfuric acid. The resultant samples were carbonized at 1173 K under vacuum or inert atmosphere. The silica template was dissolved using either NaOH solution in water/ethanol, or aqueous solution of HF to obtain the ordered mesoporous carbon. The details can be found elsewhere [1,3]. Nitrogen and argon adsorption isotherms were measured at 77 K using an ASAP 2010 volumetric adsorption analyzer. Weight change curves were recorded under air atmosphere using a TA Instruments TGA 2950 thermogravimetric analyzer in a high-resolution mode with maximum heating rate of 20 K min⁻¹.

Results and Discussion

After carbon precursor infiltration and carbonization, the carbon/silica composites contain about 35% of carbon and about 60% of silica, as can be inferred from the weight change curves (Figure 1). The subsequent dissolution of silica results in carbons that typically contain less than 3% of ash. Under air atmosphere, carbons burn in a narrow temperature range (for instance at ca. 713 K, see Figure 1), which indicates their high degree of homogeneity [5]. The carbons exhibit high degree of structural ordering as seen from the appearance of several distinct peaks on X-ray diffraction patterns at low angles (2θ below $\sim 4^\circ$) [1,3,7]. Highly ordered periodic structure is also evident on transmission electron microscopy (TEM) images [1,3,7]. As seen from nitrogen and argon isotherms, ordered mesoporous carbons exhibit uniform mesopores and high adsorption capacities. Shown in Figure 2 is argon adsorption isotherm at 77 K for CMK-3 carbon synthesized using SBA-15 as a template. This carbon consists of 2-dimensionally hexagonally ordered array of connected uniform rods of diameter about 7 nm [3]. The isotherm exhibits a distinct step on the adsorption branch at relative pressures of about 0.5, which can be related to adsorption in ordered mesopores of size about 4.5 nm, as determined using nitrogen adsorption and TEM [3]. The adsorption in ordered mesopores is accompanied with hysteresis, and the fact that the hysteresis loop is relatively narrow indicates facile pore connectivity. Low-pressure part of argon adsorption isotherm at 77 K is shown in Figure 3. The carbon adsorbs a significant amount of argon at low pressures, which is indicative of some degree of microporosity. The microporosity is also observed for the carbon/SBA-15 composite and therefore can be regarded as an inherent feature of framework of carbons prepared using sucrose as carbon precursor.

Acknowledgments

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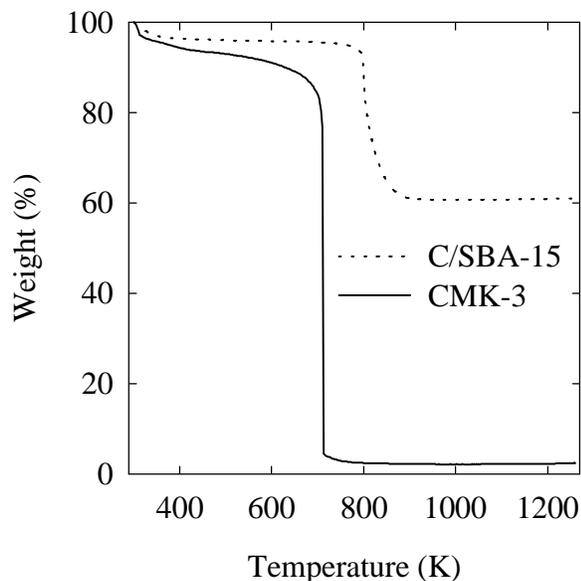


Figure 1. Weight change curves under air atmosphere for the carbon/SBA-15 composite and CMK-3 carbon obtained after SBA-15 silica dissolution.

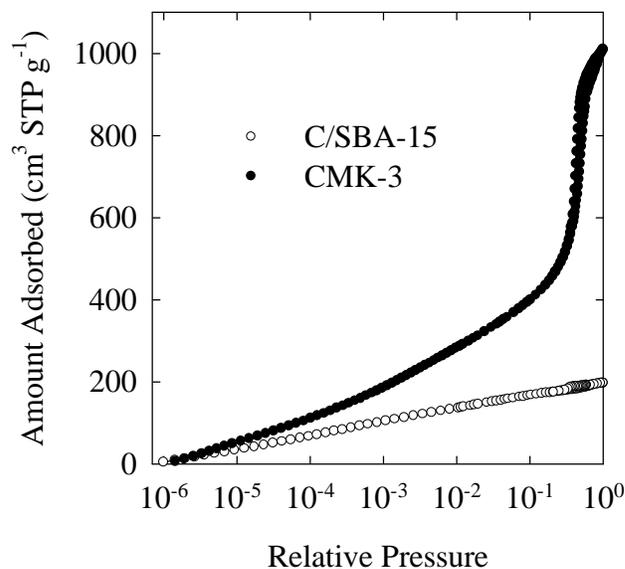


Figure 3. Argon adsorption isotherms at 77 K shown in a logarithmic scale for the carbon/SBA-15 composite and CMK-3 carbon obtained after SBA-15 silica dissolution.

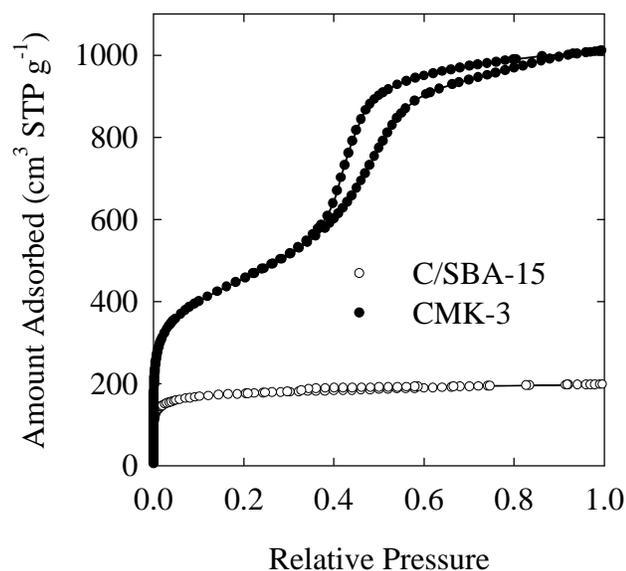


Figure 2. Argon adsorption isotherms at 77 K for the carbon/SBA-15 composite and CMK-3 carbon obtained after SBA-15 silica dissolution.

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