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SHORT COMMUNICATION

Sucrose-derived graphitic porous carbon replicated by mesoporous silica

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Abstract−A method for preparing porous graphitic carbon in the presence of an Fe salt using sucrose and mesoporous silica (SBA-15) as a carbon precursor and a removable template, respectively, is described. Hydrothermal treatment was essential for the development of a graphitic structure in the final carbon. Characterization of the porous graphitic carbon indicated a high surface area (490 m^2/g) and large pore volume (0.5 cm^3/g).

Key words: Carbon Precursor, Graphitic Carbon, Carbonization, Catalyst Support

INTRODUCTION

Preparation of porous carbon materials using inorganic oxides as a removable template has attracted considerable attention because of their unique structural properties, which includes high surface area and large pore volume [Hou et al., 2005]. Porous carbon materials are extensively used in many fields of science and engineering, including adsorption [Li et al., 2005], catalysis, and electrochemistry [Su et al., 2005; Kim et al., 2005, 2006]. In particular, their excellent physical properties make them well suited for use as catalyst supports for fine dispersions of metal particles with high loading [Hyeon et al., 2003]. It has been reported that a carbon material with a graphic structure has a positive effect on the performance of carbon-supported metal catalysts [Hyeon et al., 2003]. However, it is difficult to prepare a carbon material with both a high surface area and a crystalline phase. One of the promising methods for preparing such a carbon material is a templating method, in which a carbon precursor is deposited on a removable template via a gas-phase reaction [Xia and Mokaya, 2004].

Many types of carbon precursors have been used for the preparation of porous carbons [Su et al., 2005; Hyeon et al., 2003; Xia and Mokaya, 2004; Kim et al., 2003; Yang et al., 1999]. Among the various candidates, sucrose has many advantages in terms of non-toxicity and availability. However, a carbon material prepared using sucrose usually has an amorphous structure, unless harsh pyrolysis conditions or additional graphitization processes are employed [Kim et al., 2003].

In this work, we propose a method for preparing a porous graphitic carbon that involves a hydrothermal method and a mild pyrolysis temperature, using sucrose and mesoporous silica as a carbon precursor and a removable template, respectively. To the best of our knowledge, this is the first example of the preparation of porous graphitic carbon using sucrose as a carbon source at a moderate pyrolysis temperature.

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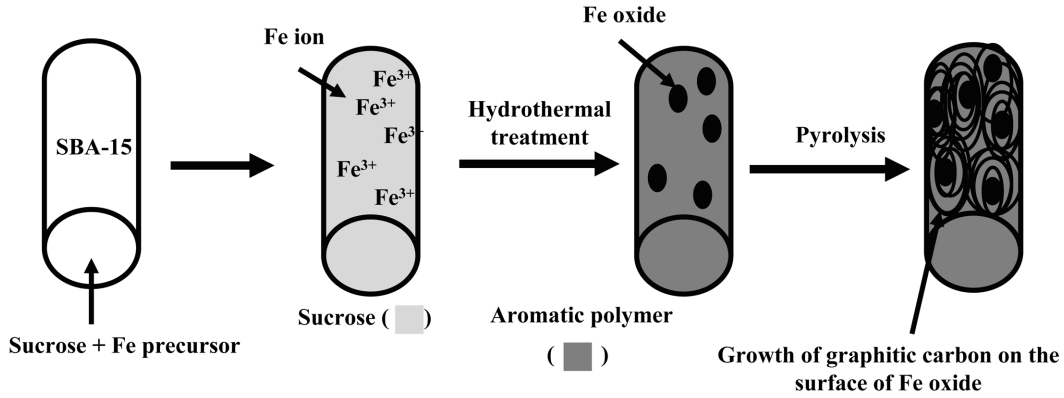
EXPERIMENTAL

Porous carbon with graphitic characteristics was prepared by a hydrothermal method, as shown in Scheme 1. Fe salt ($FeNO_3 \cdot 9H_2O$, Aldrich) was impregnated on the mesoporous silica (SBA-15), followed by drying for 3 h at 80 °C. The pores of the Fe-loaded SBA-15 were then filled with sucrose (Aldrich) dissolved in de-ionized water. After drying, this composite was charged into a Teflon-coated stainless steel autoclave filled with an aqueous solution of sucrose (molar ratio of Fe : sucrose : SiO_2=1 : 1.4 : 3.5). The autoclave was placed in a convection oven at 190 °C for 7 h. After the autoclave was cooled to room temperature, the black precipitate was isolated by filtration. The precipitate was dried and then pyrolyzed at 900 °C. The final porous carbon (hereafter referred to as G-carbon) was obtained by removing the mesoporous silica template and Fe species by treatment with concentrated solutions of NaOH and HNO_3, respectively. FE-SEM-EDX analyses revealed that Fe and Si species were not present at detectable levels in the G-carbon, indicating the complete removal of these species. For comparison purposes, a carbon material (CMK-3) was prepared by using the same template (SBA-15) and carbon precursor (sucrose), while the samples were prepared without hydrothermal treatment or Fe precursor [Kim et al., 2003].

RESULTS AND DISCUSSION

FE-SEM analyses (not shown here) showed that the replicated carbon materials exhibited rod-like morphologies with an average diameter of 1-2 μm, similar to the morphology of the mesoporous silica template. The pore structures of the carbon materials were examined in detail by TEM analyses. As shown in Fig. 1, both replicated carbons showed one-dimensional channel-like pores within the rods, although a few small pores were observed in the G-carbon. In particular, (002) lattice fringes representing a graphitic structure, which were not found in the CMK-3, were clearly observed in the G-carbon, as shown in Fig. 1(c) and (d). It should be noted from the above results that the morphology of G-carbon completely mim-



Scheme 1. Schematic representation for the preparation of G-carbon.

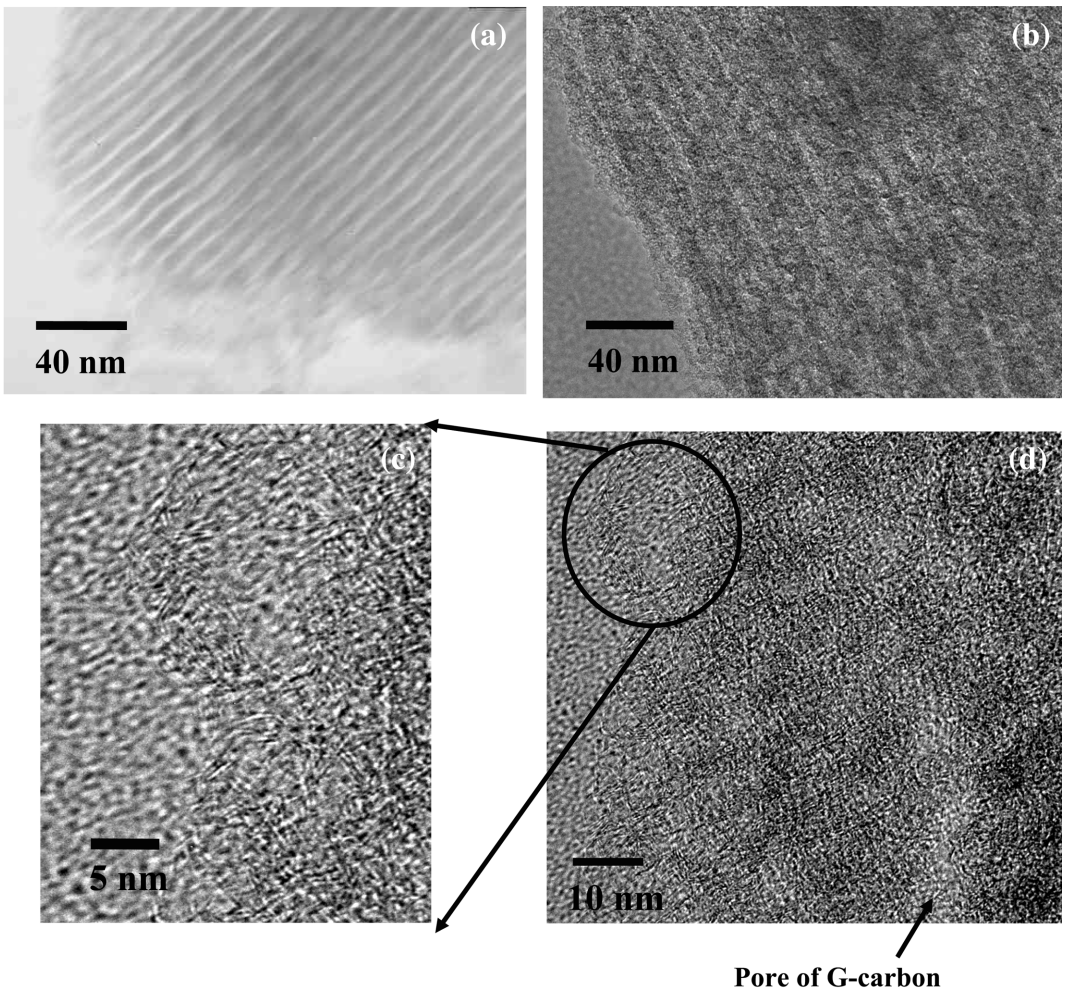


Fig. 1. TEM images of (a) CMK-3 and (b) G-carbon: (c) and (d) are high magnification images of G-carbon.

icked the mesoporous silica template. The G-carbon exhibited a relatively high surface area (490 m^2/g) and a large pore volume (0.5 cm^3/g).

Fig. 2 shows the XRD patterns of CMK-3 and G-carbon. The amorphous feature that is typical for the carbon material prepared using sucrose was observed in the CMK-3, while the characteristic peaks for graphite showing (002) and (100) diffractions were observed in the G-carbon. The crystalline sizes measured perpendicular to the basal plane and the d_{002}-spacings in the G-carbon were determined to be 4.8 nm and 3.41 Å, respectively. The degree of graphitization estimated by applying the equation $0.344\text{-}d_{002}/0.0086$ [Maldonado et al., 2000], was calculated to be 0.359, indicating the highly graphitized structure of G-carbon.

The graphitic characteristics of G-carbon were further confirmed by Raman spectroscopy measurements, as shown in Fig. 3. For comparison purposes, the Raman spectrum of multi-wall carbon nano-

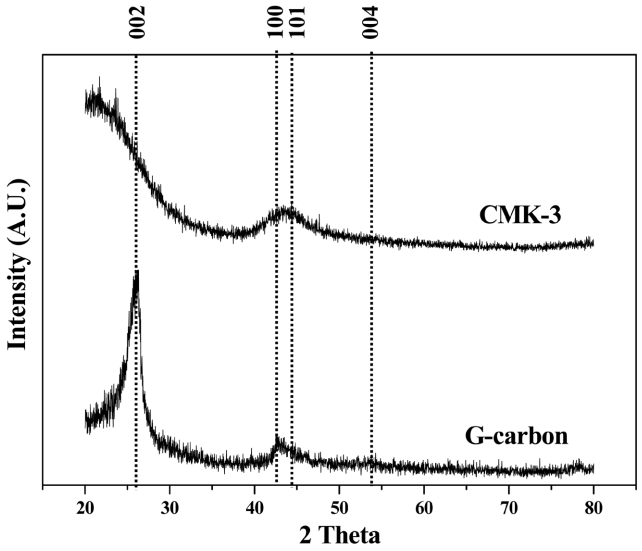


Fig. 2. XRD patterns of CMK-3 and G-carbon.

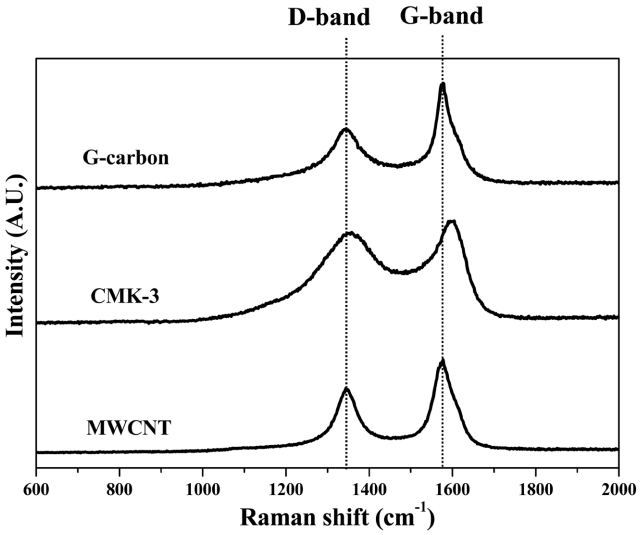


Fig. 3. Raman spectra of CMK-3, G-carbon, and MWCNT.

tube (MWCNT) was also measured under the same conditions. All the carbon materials exhibited two distinct bands at around 1,350 cm^{-1} (D-band) and 1,580 cm^{-1} (G-band). However, the ratio of the intensity of two bands (I_D/I_G), another index of the degree of graphitization [Maldonado et al., 2000], was smaller in the G-carbon than in the CMK-3, demonstrating a higher graphitic structure of G-carbon. In addition, the similar values for I_D/I_G between G-carbon and MWCNT indicate that the G-carbon retained graphitic characteristics comparable to MWCNT.

It is noteworthy that the graphitic carbon material was produced at a mild carbonization temperature (900 °C) in this work. To investigate the effect of synthesis parameters on the development of the graphitic structure, we attempted to prepare a carbon material using the same preparation method as was used for CMK-3 using Fe salt without hydrothermal treatment. The XRD pattern of the prepared carbon material was similar to that of amorphous CMK-3, implying that the hydrothermal treatment was essential for the formation of a graphitic structure in the final carbon material. As illustrated in Scheme 1, the aromatization of polymer derived from sucrose occurs during the hydrothermal treatment [Sun and Li, 2004; Wang et al., 2001]. In the case of G-carbon, it appears that both the polymerization of sucrose and the subsequent aromatization were aided by the catalytic action of Fe species, resulting in the development of an aromatic polymer on the surface of the Fe oxide. It has also been reported that the graphitization of carbon was accelerated in the presence of a catalyst such as a metal or a metal oxide [Inagaki et al., 1998]. Therefore, it can be concluded that a graphitized structure cannot be developed without hydrothermal treatment even when the carbon material is prepared in the presence of Fe salt.

CONCLUSIONS

A porous graphitic carbon was successfully prepared in the presence of Fe salt using sucrose and mesoporous silica (SBA-15) as a carbon precursor and a removable template, respectively. Both the hydrothermal treatment and the catalytic action of Fe species were essential for the formation of graphitic structure in the G-carbon. Because a non-toxic carbon precursor and mild carbonization temperature were employed in the preparation of G-carbon, the method described herein would be an easy and environmentally benign process for producing porous carbon with graphitic characteristics.

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