Catalytic Excavation and Graphitization of Activated Carbon by Cobalt Nanoparticles

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Cobalt nanoparticles loaded on an activated carbon catalytically excavated the activated carbon when it was heat-treated in a 1 atm stream of a mixture of hydrogen and argon gases at high temperature. The BET surface area of the activated carbon decreased from 2210 to 1750 $m^2\,g^{-1}$, and the mesopore volume increased from 0.14 to 0.25 $cm^3\,g^{-1}$ by heat-treatment at 900 °C for 8 h. As for the XRD pattern of the heat-treated specimen, diffraction peaks from the turbostratic carbon phase were observed. This phase was confirmed by TEM both around the cobalt particles and the walls of the pores formed by the excavation.

Activated carbons have widely been used for the electrodes of electrochemical capacitors owing to their high specific surface area. For the capacitors, mesopores are more convenient for the transportation of the solvated ions than micropores.[1] Although the use of metal salts and complexes for the preparation of activated carbons with mesopores has widely been reported,[2,3] the method using metal nanoparticles to create mesopores has scarcely been reported before.[3] We have previously demonstrated that nonochannels and holes can be catalytically created by the heat treatment of both highly oriented pyrolytic graphite (HOPG) and diamond crystallites loading metal particles in a hydrogen atmosphere.[4] This report presents the finding that mesopores can be created in an activated carbon loading cobalt nanoparticles by a gasification when it is heated in a hydrogen atmosphere.

An amorphous activated carbon (Kansai Coke and Chemicals; MSP-20) was suspended in an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (Wako Chemicals), and dried at 80 °C. The loading amount of cobalt as metal on the carbon was 5 mass %. After drying of the suspension, the specimen was heat-treated in 1 atm stream of the mixed gas of H_2 (10%) and Ar (90%) at 800 and 900 °C for 8 h. These specimens are denoted as Co/MSP-800 and Co/MSP-900, respectively. During this heat-treatment process, cobalt nitrate decomposed into cobalt nanoparticles at around 300 °C, and the cobalt nanoparticles began to excavate the carbon above around 500 °C. Gas chromatography detected methane as the gaseous product of the excavation of the carbon by cobalt nanoparticles in the hydrogen atmosphere. The evaluation of the specific surface area by Brunauer–Emmett–Teller (BET) method and the X-ray diffraction (XRD) for the specimens was conducted after the complete elution of the cobalt with 1 M HCl at 40 °C. These specimens are denoted as Co_{elu}/MSP-800 and Co_{elu}/MSP-900, respectively. For the characterization of the specimens, scanning electron microscopy (SEM) with a Hitachi S-5000 transmission electron microscope (TEM) with a JEOL JEM-2010, BET method with a BEL Japan

Table 1. Specific surface area, micro and mesopore volumes of the activated carbons

Sample	Specific surface area /$m^2\,g^{-1}$	Micropore volume /$cm^3\,g^{-1}$	Mesopore volume /$cm^3\,g^{-1}$
MSP-20	2210	0.96	0.14
MSP-20-900	2015	0.87	0.13
Co_{elu}/MSP-20-800	2410	1.05	0.19
Co_{elu}/MSP-20-900	1750	0.71	0.25

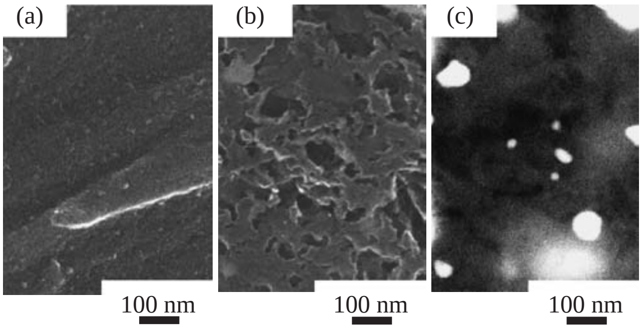

Figure 1. SEM images of (a) MSP-20, (b) Co/MSP-20-900 (secondary electron image), and (c) Co/MSP-20-900 (reflection electron image of the same part of (b)).

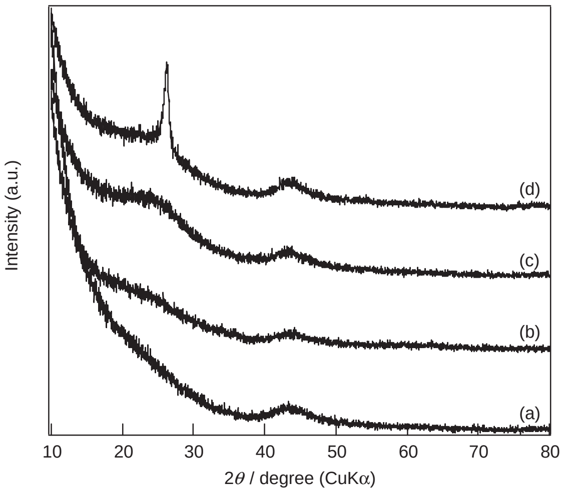

Figure 2. The XRD patterns of (a) MSP-20, (b) MSP-20-900, (c) Co_{elu}/MSP-20-800, and (d) Co_{elu}/MSP-20-900.

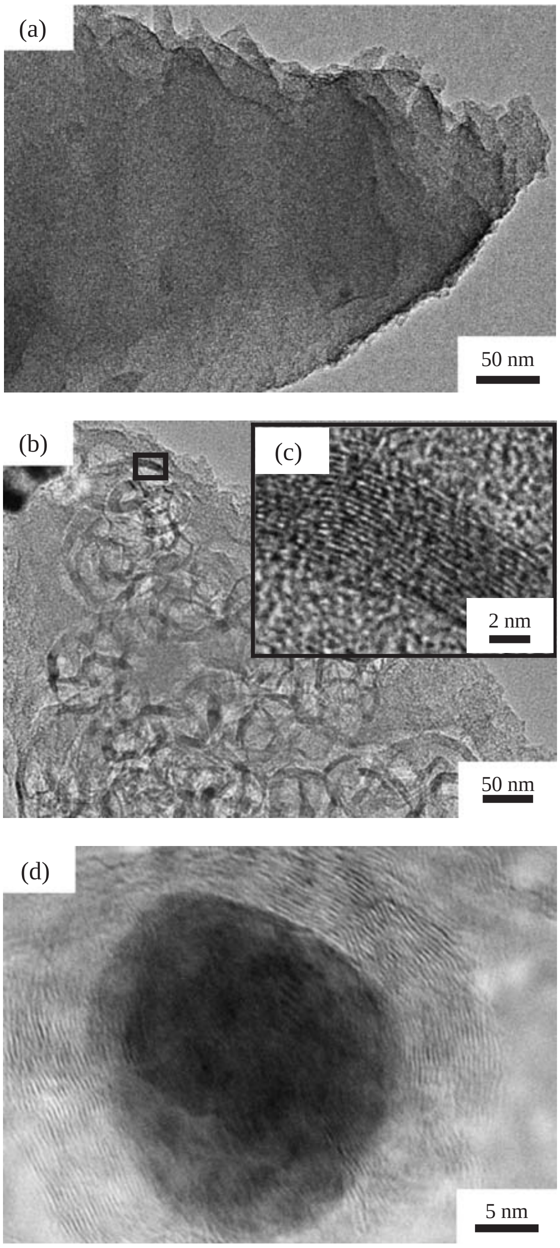

Figure 3. TEM images of (a) MSP-20, (b) Co/MSP-20-900, (c) a high-magnification image of the part surrounded with black square in (b), and (d) a cobalt particle surrounded with turbostratic carbon layers in Co/MSP-20-900.

BELSORP28, and XRD with a Rigaku RINT-2550 (with monochromated Cu Kα radiation at 40 kV and 80 mA) were adopted.

The adsorption isotherms of nitrogen gas for MSP-20, MSP-20-900, and $\mathrm{Co_{elu}}$/MSP-20-800 produced the I-type, while $\mathrm{Co_{elu}}$/MSP-20-900 produced the IV-type suggesting the existence of mesopores. Table 1 lists the BET specific surface area, micropore volume evaluated by the MP method and the mesopore volume of the BJH-method for each specimen. In the case of the $\mathrm{Co_{elu}}$/MSP-20-800, the specific surface area, micro- and mesopores are all greater than the pristine carbon; however, a considerable decrease in the specific surface area and micropores are observed in the case of $\mathrm{Co_{elu}}$/MSP-20-900, in spite of the fact that there was a substantial increase in the mesopores. Figure 1 shows the SEM images of MSP-20 and Co/MSP-20-900. Many holes are observed in Figure 1b, and the cobalt particles that made their way into the activated carbon are observed by the comparison of the secondary electron image (Figure 1b) and the reflection image (Figure 1c). As shown in Figure 2, the evident diffraction peak due to the turbostratic carbon phase, 26°, is observed only on the XRD pattern of the $\mathrm{Co_{elu}}$/MSP-20-900. Since the heat treatment of the activated carbon without cobalt particles (MSP-20-900) rendered no such peak, the partial graphitization must be caused by the existence of the cobalt nanoparticles at 900 °C. The TEM images of the pristine carbon and the Co/MSP-20-900 are shown in Figure 3. The band-shaped layered structure seen in Figure 3b is a turbostratic carbon phase,[5] because the higher-magnification image presented in Figure 3c shows the distance of the interlayer to be about 0.35 nm. As shown in Figure 3d, the cobalt particle is surrounded by the turbostratic carbon layers.

In conclusion, the mesopore volume of an activated carbon was increased through the excavation by cobalt nanoparticles in a hydrogen atmosphere of 900 °C. Through excavation, the turbostratic carbon layer was created surrounding cobalt particles. The movement of the cobalt particles contributing to excavating the activated carbon walls composed of a band-shaped turbostratic carbon layer.

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