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CHARACTERIZATION OF SURFACE STRUCTURES ON THERMAL TREATED CARBON BLACK

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Introduction

Carbon black (CB) has been widely applied as an anchor material, a conductive additive and a colorant. They are usually provided through a stage of high temperature treatment for adding functionality. Since the surface structures such as functional groups and size of basal plane critically affect interaction between CBs and guest molecules or ions, they are key factor determining the physical properties of the CBs. It is quite important to clarify the surface structure including functional groups and bonding states (sp^2 and sp^3) for the fabrication of the desired CB. Heat of adsorption determined from gas adsorption isotherms becomes one of the effective indicators for understanding the carbon surface.[1-5] In this study, we characterized micro-structures of thermal-treated CBs by linking the structural factor with the heat of adsorption.

Materials and Methods

We used two types of commercial CB as a model carbon material. One is provided by Asahi Carbon Co., Ltd. (CB: ASAHI #51), and the other is a graphitized carbon black (GCB: TOKA BLACK #3845) provided by Tokai Carbon Co., Ltd. The thermal treated samples were prepared under H_2 or He gas flow up to 800 or 1000 ˚C. The CB samples treated under H_2 and He gases are named as CB-H*t* and CB-*t* (*t* = 800 or 1000 ˚C), respectively. The GCB are also named as GCB-H*t* and GCB-*t*. The initial surface structures of CB and GCB were determined from X-ray photoelectron spectroscopy (XPS), thermal gravimetry (TG), Temperature-programmed desorption (TPD) and N_2 adsorption isotherm at 77 K. The ratio of hydrogen and oxygen containing functional groups terminating on carbon edges were determined from TPD method. The porosity changes by thermal treatment were examined by N_2 adsorption isotherm at 77 K and water adsorption isotherm at 298 K. The heat of adsorptions were calculated from Clausius-Clapeyron equation applying to N_2 adsorption isotherm at 77 and 87 K.

Results and Discussion

Figure 1 shows TEM images of CB and GCB. The CB is a nonporous particle constructed mainly from micrographites with curvature (Fig. 1(a)), and the GCB is a hollow sphere with graphitic layers (Fig. 1(b)). After thermal treatment, clear edge parts of micrographites are disappeared on the surface of CB (Fig. 1(c)). On the GCB, structural relaxation is not occurred on graphite layers but on carbon fragments (Fig. 1(d)). The calculated amount from TPD measurement represented that CB has a larger amount of functional group compared with GCB; the surface roughness obviously reflect the amount of oxygen-containing functional groups. Both of the BET specific

surface area of CB and GCB were slightly increased by the thermal treatment. Especially, the increase in the surface area of CB possibly stem from formation of new micropores. The porosity change was obviously indicated from vapor adsorption isotherms. The dramatical increase in vapor adsorption on thermal treated CB started from the lower relative pressure compared with the original CB. The change of vapor adsorption isotherms implies that ultramicropores are formed in the CB by thermal treatment. The heats of adsorption of CB and GCB were determined from N_2 adsorption isotherm at 77 K and 87 K. The heat of adsorption curves in GCB show an initial increase in heat of adsorption derived from fluid-fluid interaction, and heat spike by rearrangement of N_2 adsorbates. The previous reports suggested that such heat of adsorption behavior is appeared on flat carbon surface.[1,3] On the other hand, the heat of adsorption curves of CB samples except for CB-H*800* sample showed that the fluid-fluid interaction and rearrangement of N_2 adsorbate hardly occurred due to the wavy surface. Our theoretical calculation revealed that 28% more N_2 were localized around hydroxyl group than hydrogen on nanowindows in a graphene. The slight hold of N_2 molecules by oxygen-containing functional groups should restrict the rearrangement of N_2 adsorbate with exothermic reaction. Therefore, in CB-H*800* sample with less oxygen-containing functional groups, heat spike was appeared in the heat of adsorption curves.

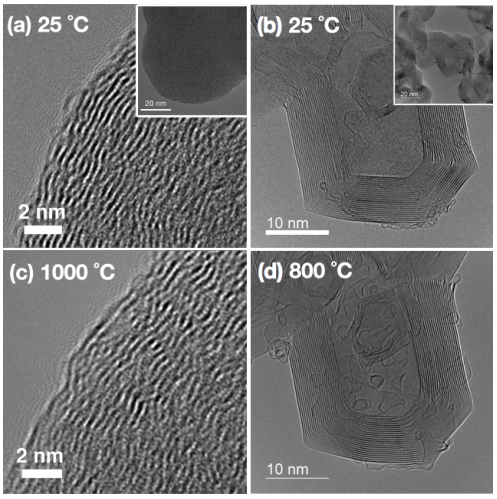

Figure 1. TEM images of (a) CB, (b) GCB and (c) thermal treated CB at 1000 ˚C and (d) thermal treated GCB at 800 ˚C.

Conclusions

Carbon surfaces constructed by micrographites are effectively terminated by H_2 around 800 ˚C. However, the terminated hydrogens are also removed from carbon edges, and the bonding between micrographites are formed above the temperature. These surface structures including functional groups were clarified by using gas adsorption technique, TEM observation and TPD methods, and the heat of adsorption provides a useful index of surface structural change in carbon materials.

Acknowledgment

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