MAGNETIC PROPERTIES AND POROSITY OF NOVEL POROUS CARBONS

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Introduction

Activated carbon is less-crystalline, but the fundamental structures are composed of the sp^2 carbon atoms, that is, high surface area carbons are composed of nanographite units. The basal plane of the nanographite has the sp^2 carbon atoms, while the edge carbon atoms have both of sp^2 and sp^3 bonding natures. Thus, the mixed valence state of carbon atoms should be important in the high surface area carbon.

Activated carbon fibers (ACFs) having uniform micropores show an excellent adsorption characteristics and unusual physical properties due to the high surface area.[1] Activated mesocarbon microbeads (a-MCMB) prepared from mesocarbon microbeads (MCMB) with oriented polycyclic aromatic layer have large surface area, which should be regarded as a representative high surface area carbon. According to our preceding studies[2], a-MCMB shows behavior of spin glass or mictomagnetism. The preparation of a more pure a-MCMB is requested. Activated carbon aerogels (a-AC) have both of micropores and mesopores, which are expected unusual physical properties. This article describes the relationship between the pore structures and magnetic properties of these nobel porous carbons.

Experimental

The a-MCMB was produced with KOH activation using the platinum crucible. The a-MCMBs were prepared under the different KOH ratios (in weight). The obtained samples is denoted Mx; The x of Mx is KOH ratio. The products were washed with distilled water and 0.1 N HCl to remove the residual potassium hydroxide and metal potassium[3]. a-AC was prepared in the same way as published.[4] Cellulose-based ACFs were supplied by Toyobo Co. The N_2 adsorption isotherm was measured at 77 K by a gravimetric method with a high-resolution adsorption apparatus. The magnetic susceptibility χ was measured by a SQUID magnetometer (Quantum Design, MPMSR2) at the magnetic field of 1 T over the temperature range 1.9 – 300 K. The a-MCMB samples were sealed in an ESR tube after evacuation at 423 K and 10^{-4} Torr for 2 h before the magnetic measurement.

Results and Discussion

Figure 1 shows adsorption isotherms of N_2 on a-MCMB samples obtained by activation at 1173 K for 1 h with the different KOH ratios of 1 to 5. The N_2 adsorption isotherms are basically of type I, indicating that predominant pores are micropores. There is a linear increase in adsorption until P/P_0= 0.6 after the low pressure uptake in M3 and M5, suggesting the presence of larger micropores of more than 1 nm in width. The N_2 adsorption isotherms were analyzed by the high resolution α_s- plots.[5] The high resolution α_s-plots were constructed using the standard data on nonporous carbon black. The high resolution α_s- plot of M3 has a filling swing below α_s = 0.5 due to an enhanced micropore field and a cooperative swing between α_s = 0.5 and 1.0 due to filling in the residual pore-space. M1 has only the filling swing and M5 has the slight cooperative swing. The α_s analysis indicated that the KOH activation develops micropores in the MCMB and the pore structure depends on the KOH ratio. The detailed pore analysis for a-AC and ACFs were carried out by use of the high resolution α_s-plot, which gave the reliable data on the pore structures.

The Curie plots (χ^{-1}- T plots) of M0 and M3 were constructed. The χ -T relation of M0 (nonavtivaed MCMB) showed the representative paramagnetism, in particular, at the low temperature region, because the χ^{-1}-T linear plot passed through the origin. This result suggests the

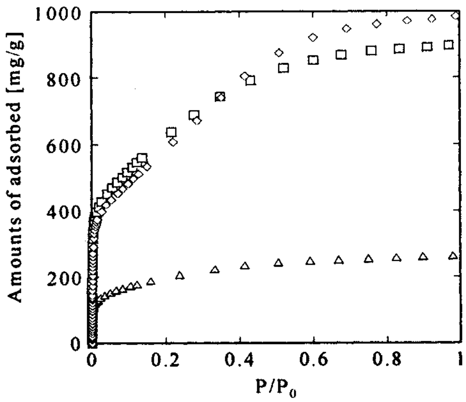

Fig.1 Adsorption isotherms of nitrogen on a-MCMB activated by KOH
△: M1, □: M3, ◇: M5

presence of free spins in MCMB at low temperature. On the other hand, the magnetic susceptibility of MCMB has negative values in the high temperature region, indicating the diamagnetism. It is well known that the remarkable diamagnetism of graphite comes from the highly conjugated π-electron structure. The diamagnetism of MCMB can be attributed to the nanographite structure. However the linear Curie-plot was limited to the low temperature range of 1.9 to 20 K and the observed χ^{-1}-T relation showed an upward deviation above 20 K. Accordingly the effective spin concentration showed the decrease as increasing temperature, suggesting the weak spin-spin interaction above 20 K. The χ-T relation of a-MCMB depended on the KOH ratio; the χ-T curve was different from each other. The χ of M1 was positive only at the low temperature and became negative above 30 K. On the other hand M3 and M5 of high surface area had positive χ-values over the whole temperature range. Also the M5 having the greatest surface area showed an irreversible χ-T behavior. M5 suggest a strong spin-spin interaction, because the χ-T curve of M5 had a maximum at 3 K in the heating course.

Figure 2 shows the χ-T relations for ACF, AC, and a-AC. The χ decreases with the increase of temperature and becomes negative above about 30 K. These carbons have more marked diamagnetism than a-MCMB. Therefore the spin concentration of AC and ACF are smaller that of a-MCMB. The analysis of the Curie-Weiss plot supported this. AC showed a remarkable change of χ with time at 2 K and 1 T, indicating the presence of a weak interaction between spins. The decrease of the χ value was 40 % and it became smaller (10 %) at 5 K. At 300 K no time dependence was observed. This time dependence of χ suggested the presence of the spin glass behavior even in carbon aerogel samples.

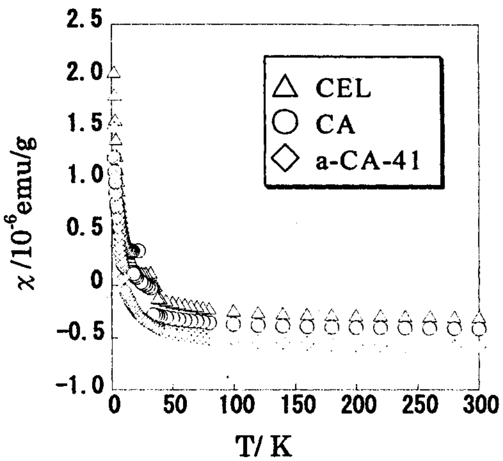

Fig.2 χ-T plots of Cellulose-based ACF (CEL), CA, and a-CA.
△: CEL, ○: CA, ◇: a-CA

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