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Interaction between Copper(I) Chloride and Active Carbon in Active Carbon-Supported Copper(I) Chloride as Solid Carbon Monoxide Adsorbent

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Synopsis. Magnetic susceptibility (-4.7×10^{-9} m^3 kg^{-1}) of the carbon monoxide adsorbent prepared from 10.0 g of active carbon and 1.4 g of copper(I) chloride is in paramagnetic side with respect to the value (-10.1×10^{-9} m^3 kg^{-1}) estimated from the susceptibilities of the components. Almost all the copper atoms are in their monovalent states, as shown by X-ray photoelectron spectroscopy. These results have indicated specific interaction between active carbon and copper(I) chloride in the adsorbent.

Separation of carbon monoxide from gas mixtures is an important process in industry, since carbon monoxide is usually obtained as mixtures with nitrogen, hydrogen, methane, and carbon dioxide.[1]

In previous papers,[2,3] the authors showed that the active carbon-supported copper(I) chloride rapidly and reversibly adsorbed carbon monoxide under mild conditions. The adsorbing capacities of the adsorbents were much larger than the sum of the capacities of the active carbon and copper(I) chloride, indicating some interaction between them in the adsorbents.

This paper reports the results of magnetic susceptibility measurements and X-ray photoelectron spectroscopy on the active carbon-supported copper(I) chloride, which shed light on the interaction between active carbon and copper(I) chloride in the adsorbents.

Experimental

Active carbon was purchased from Kureha Chemical Industries Co. (BAC G-70R, Lot No. 810117; beads of average diameter ca 0.7 mm) and was subjected to a reduced pressure (6 mmHg) at 200 °C for 5 h immediately before use. The active carbon-supported copper(I) chloride was prepared by stirring 10.0 g of the active carbon in 15 cm^3 of aqueous hydrochloric acid solution (3 mol dm^{-3}) containing various amounts of copper(I) chloride at room temperature for 1 h, followed by the removal of the liquid phase at 6 mmHg, 100 °C.[2,3] The amount of copper(I) chloride supported onto the active carbon was determined by atomic absorption spectroscopy.

Magnetic susceptibilities were measured at room temperature by use of a CAHN Instrument Co. Model RG Automatic Electrobalance, which took advantage of the Gouy's method.[4] The permanent magnetic field, the magnetic field gradient, and the balance sensitivity were 5 kG (1 G$=10^{-4}$ T), 4.841×10^6 G^2 cm^{-1}, and 0.1 µg, respectively. Specimens (100—500 mg) were charged into Pyrex glass vessels of diameter 8 mm and depth 10 mm under nitrogen. The susceptibilities of the specimens were determined by subtraction of the susceptibilities for the vessels without the specimens from the values for the vessels with them.

X-Ray photoelectron spectra were measured on a Shimadzu Electron Spectrometer ESCA 750 with Mg X-ray anode. Chemical shifts were determined by use of the $4f_{7/2}$ band of metallic gold at 84.0 eV as reference.

Results and Discussion

Figure 1 depicts the X-ray photoelectron spectra for the Cu_{2p} region of the active carbon-supported copper(I) chloride as carbon monoxide adsorbents, copper(I) chloride, and copper(II) chloride. The adsorbents exhibit spectra (a and b) having two bands at 933 and 953 eV, which are virtually identical with that (c) of copper(I) chloride. The spectra of the adsorbents, however, are significantly different from that (d) of copper(II) chloride, which shows four bands at 937, 944, 957, and 964 eV. Thus, almost all the copper atoms in the adsorbents are present in the monovalent states.

Table 1 lists the mass magnetic susceptibility of the adsorbent (Active Carbon/CuCl) composed of 10.0 g of the active carbon (Active Carbon) and 1.4 g of copper(I) chloride (CuCl) together with the values of the components. All of the adsorbent, the active carbon, and copper(I) chloride are diamagnetic, as shown by the negative values of the susceptibilities. The absolute value (4.7×10^{-9} m^3 kg^{-1}) of the susceptibility of the adsorbent is considerably smaller than that (10.1×10^{-9} m^3 kg^{-1}) estimated from the susceptibilities (-11.0×10^{-9} and -3.9×10^{-9} m^3 kg^{-1}, respec-

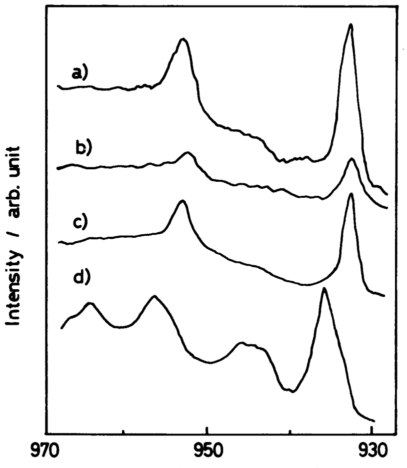

Fig. 1. X-Ray photoelectron spectra in the Cu_{2p} region for (a) the adsorbent prepared from 2.5 g of copper(I) chloride and 10.0 g of the active carbon, (b) the adsorbent prepared from 1.5 g of copper(I) chloride and 10.0 g of the active carbon, (c) solid of copper(I) chloride, and (d) solid of copper(II) chloride.

Table 1. Mass Magnetic Susceptibility of the Carbon Monoxide Adsorbent Prepared from 10.0 g of the Active Carbon and 1.4 g of Copper(I) Chloride as well as the Values for the Components

Specimen	Magnetic susceptibility[a)] 10^{-9} m^3 kg^{-1}
Active carbon/CuCl	−4.7
Active carbon	−11.0
CuCl	−3.9

a) Negative signs refer to diamagnetic properties.

tively) of the active carbon and copper(I) chloride under the assumption that the additivity rule is applicable here. In the rule proposed by Wiedemann,[5)] the susceptibility is expressed by linear combination of the values of the components with the use of weight fractions as coefficients. This indicates that some paramagnetic species are formed by the interaction between the active carbon and copper(I) chloride.

The open circles in Fig. 2 depict the plot of the mass magnetic susceptibility for the adsorbent composed of the active carbon and copper(I) chloride as a function of the weight ratio of copper(I) chloride to the active carbon. The broken line refers to theoretical values evaluated by use of the additivity rule. All the experimental points are located in considerably paramagnetic sides with respect to the theoretical line. The magnitude of the deviation of the experimental point from the theoretical line significantly increases with increase in the weight ratio of copper(I) chloride to the active carbon.

These results show that some electronic interaction is operative between the active carbon and copper(I) chloride in the adsorbent. The interaction is probably associated with formation of pi-type complex between them. Electron donation from the active carbon to the copper(I) chloride as well as back donation from the copper atoms to the active carbon results in unpaired electrons both on the copper atoms and in the condensed aromatic rings of the active carbon, giving rise to the increase in the paramagnetic characters of the adsorbents.

These arguments are supported by the formation of pi-complexes between copper(I) ion and various olefins.[6)] In the present adsorbents almost all the copper(I) chloride are present in their monomeric or dimeric forms.[3)]

Virtually the same X-ray photoelectron spectra (a and b in Fig. 1) of the adsorbents with that (c) of copper(I) chloride is ascribed to rather small dependence of the chemical shifts of copper(I) ions on their chemical circumstances. The chemical shifts of Cu_{2p} bands for the complexes between copper(I) chloride and various ligands are identical with each other within 1.6 eV.[7)]

The interaction between copper(I) chloride and active carbon in the adsorbents has been also examined by electron spin resonance spectroscopy. Detection of signals from the paramagnetic species in the adsorbents, however, has not been successful yet, probably due to both effective shielding of them from magnetic field by the active carbon and background signals from the active carbon.

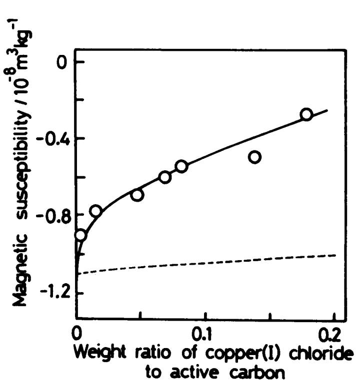

Fig. 2. Plot of mass magnetic susceptibility of the carbon monoxide adsorbent prepared from the active carbon and copper(I) chloride against the weight ratio of copper(I) chloride to the active carbon: the negative signs in the susceptibilities refer to diamagnetic properties; the broken line is a theoretical line evaluated from the susceptibilities of the components under the assumption that the additivity rule is valid.

High dispersion of copper(I) chloride on the surface of the active carbon in the active carbon-supported copper(I) chloride, which is essential for the large adsorbing ability of the adsorbents,[3)] is attributable to the specific interaction between the active carbon and the copper(I) chloride. Without the interaction, copper(I) chloride is promptly bound each other through chlorine bridges, forming aggregates with minimal adsorbing capacities. In addition, decreases of the electron densities in the d-orbitals of the copper(I) ions, due to back donation from them to the active carbon, suppress back donation from the copper atoms to carbon monoxide. This weakens coordination bonds between the carbon monoxide and the copper(I) ions in the adsorbents, resulting in the effective desorption of the adsorbed carbon monoxide under mild conditions.

In conclusion, the magnetic susceptibility measurements as well as X-ray photoelectron spectroscopy have showed specific interaction between active carbon and copper(I) chloride in the active carbon-supported copper(I) chloride as solid carbon monoxide adsorbents. Effective and reversible adsorptions of carbon monoxide by the adsorbents are ascribed to the interaction.

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