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PREPARATION OF CARBON MONOXIDE ADSORBENT FROM COPPER(II) CHLORIDE AND ACTIVE CARBON

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A novel adsorbent of carbon monoxide is prepared by stirring 15.0 mmol of copper(II) chloride and 10.0 g of active carbon in water, followed by removal of the liquid phase at 0.06 mmHg, 180 °C. The adsorbent rapidly adsorbs carbon monoxide from 9:1 carbon monoxide-helium mixture under 1 atm at 20 °C, and the equilibrium amount of adsorbed carbon monoxide is 10.0 mmol.

In industry, carbon monoxide is obtained as gas mixtures with nitrogen, hydrogen, methane, and carbon dioxide. Thus, separation of carbon monoxide from gas mixtures is necessary for effective use of carbon monoxide.[1)] Considerable number of liquid absorbents of carbon monoxide were proposed.[2)] However, solid adsorbents for carbon monoxide have been rather scanty.

Zeolite-supported copper(I) ions exhibited carbon monoxide adsorbing abilities.[3,4)] However, the adsorption was so strong that desorption of the adsorbed carbon monoxide required rather severe conditions such as 10^{-4} mmHg at room temperature.

Previously, the authors reported that active carbon-supported copper(I) chloride,[5,6)] active carbon-supported aluminium copper(I) chloride,[7)] and polystyrene resin-supported aluminium copper(I) chloride [8,9)] reversibly adsorbed carbon monoxide under mild conditions.

This paper describes preparation of a novel solid carbon monoxide adsorbent from copper(II) chloride and active carbon. The adsorbent, prepared without the use of any additional reducing agent, exhibits much larger adsorbing ability than that of active carbon, although copper(II) chloride without active carbon has no adsorbing ability.

The adsorbent was prepared either under nitrogen or under air by the addition of 10.0 g of active carbon (Kureha Chemical Industry Co., BAC G-70R, Lot. No. 810117) to 15 cm^3 of water containing 15.0 mmol of copper(II) chloride. The mixture was stirred for 1 h, and then the liquid phase was removed at 0.06 mmHg, 180 °C. The adsorbent was obtained as black beads of average diameter 0.7 mm.

Adsorption of carbon monoxide by the adsorbent was carried out at 20 °C under 1 atm. Carbon monoxide gas was connected with a flask which contained the adsorbent under helium. The adsorption was initiated by circulating the carbon monoxide-helium mixture with a gas circulating pump, and was followed by measuring the uptake of carbon monoxide with the use of a gas burette.

The open circles in Fig. 1 show the adsorption of carbon monoxide from 9:1 carbon monoxide-helium mixture by the adsorbent prepared under nitrogen from 15.0 mmol of copper(II) chloride and 10.0 g of the active carbon. The adsorption is rapid, and the equilibrium amount of the adsorbed carbon monoxide is 10.0 mmol.

On heating the adsorbent to 120 °C, all of the adsorbed carbon monoxide is promptly desorbed to the gas phase. In the second adsorption, shown by the closed circles in Fig. 1, both the rate of adsorption and the equilibrium amount of adsorbed carbon monoxide are virtually identical with the values in the first adsorption. Adsorption-desorption cycles were repeated five (the maximum number examined) times without measurable deterioration.

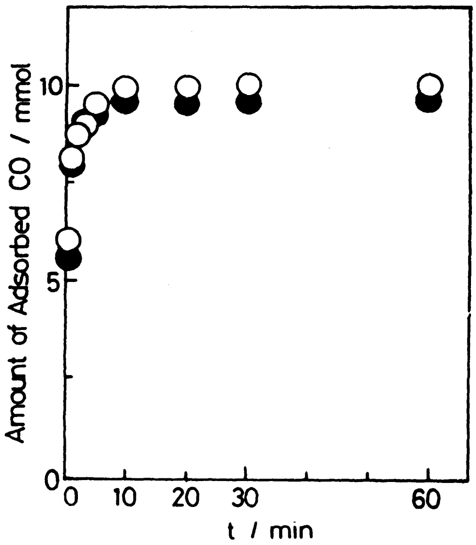

Fig. 1. Adsorption of carbon monoxide from 9:1 carbon monoxide-helium mixture at 20 °C under 1 atm by the adsorbent prepared from 15.0 mmol of copper(II) chloride and 10.0 g of the active carbon: the first (○) and the second (●) adsorptions; the desorption of the adsorbed carbon monoxide was carried out by heating the adsorbent to 120 °C under 1 atm.

Table 1 shows the carbon monoxide adsorbing capacity of the present adsorbent as well as those for the components. The adsorbing capacity (10.0 mmol) of the present adsorbent

($CuCl_2$/Active Carbon) is three times as large as that (3.3 mmol) of the active carbon (Active Carbon) without copper(II) chloride. Both the solid of copper(II) chloride ($CuCl_2$ (solid)) and 1.0 mol dm^{-3} of aqueous solution of copper(II) chloride ($CuCl_2$ (aq. soln.)) exhibit no measurable adsorbing abilities. Thus, the large adsorbing ability of the present adsorbent is definitely attributable to cooperation of the active carbon and copper(II) chloride.

Table 1. Adsorbing capacities of the carbon monoxide adsorbents and absorbent [a,b)]

Adsorbent or absorbent	Adsorbing Capacity mmol
$CuCl_2$/Active Carbon	10.0
$CuCl_2$ (solid)	0.0
$CuCl_2$ (aq. soln.)	0.0
Active Carbon	3.3

a) The charged amounts of copper(II) chloride and the active carbon are 15.0 mmol and 10.0 g, respectively.
b) Under 1 atm at 20 °C; the initial partial pressure of carbon monoxide was 0.9 atm.

The adsorbent prepared from the active carbon and copper(II) chloride under air showed exactly identical adsorbing ability with that of the adsorbent prepared under nitrogen. This is ascribed to stabilities of both of copper(II) chloride and the active carbon against oxygen.

Figure 2 (a) depicts an X-ray photoelectron spectrum in the Cu_{2p} region for the present adsorbent. The spectrum, which exhibits two bands at 953 and 933 eV, is almost identical with that (b) of the solid of copper(I) chloride. In the spectrum (c) of the solid of copper(II) chloride, however, four bands are observed at 964, 957, 944, and 937 eV. This result shows that virtually all the copper atoms in the present adsorbent are in the univalent states. Thus, the copper(II) ions are

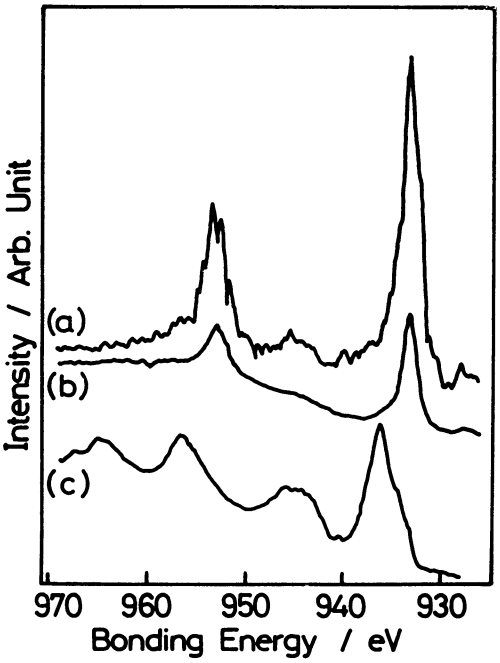

Fig. 2. X-Ray photoelectron spectra of (a) the adsorbent prepared from 15.0 mmol of copper(II) chloride and 10.0 g of the active carbon, (b) solid of copper(I) chloride, and (c) solid of copper(II) chloride.

reduced to copper(I) ions by the active carbon during the preparation of the present adsorbent, giving rise to the large carbon monoxide adsorbing ability.

The reduction of copper(II) ions to copper(I) ions in the present adsorbent is probably associated with electrophilic chlorination of the active carbon by copper(II) chloride, in which copper(II) chloride is converted to copper(I) chloride. The active carbon, composed of accumulation of conjugated aromatic rings, should have many reactive sites for the above reaction. The interpretation is consistent with the formation of copper(I) chloride together with 9,10-dichloroanthracene by the reaction between copper(II) chloride and anthracene.10)

The preparation of the present adsorbent is achieved at 180 °C in the absence of any additional reducing agent. These conditions are much milder than those employed for the preparation of zeolite-supported copper(I) ion.3) There, the reduction of the copper(II) ions, supported onto the zeolite, required both higher temperature (400 °C) and use of carbon monoxide as reducing agent.

In conclusion, solid adsorbent of carbon monoxide, which reversibly adsorbs carbon monoxide under mild conditions, is prepared from copper(II) chloride and active carbon. Stability of the starting materials against oxygen is an important advantage of the present adsorbent from the viewpoint of practical application.

References

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