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ACTIVE CARBON-SUPPORTED COPPER(I) CHLORIDE AS CARBON MONOXIDE SOLID ADSORBENT

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An active carbon-supported copper(I) chloride is prepared as a solid adsorbent for carbon monoxide. It adsorbs carbon monoxide at 20°C under 1 atm and releases almost all of the adsorbed carbon monoxide by elevating the temperature to 120°C under 1 atm, or by reducing the pressure to 0.4 mmHg at 20°C.

Importance of separation of carbon monoxide from gas mixtures is rapidly increasing, since almost all of the sources of carbon monoxide are mixtures with hydrogen, nitrogen, methane, carbon dioxide, and others.[1,2]

Although many liquid absorbents for carbon monoxide were reported,[2,3] solid adsorbents have been scant. In a patent,[4] copper(I) ion supported by zeolite was claimed as a solid adsorbent for carbon monoxide. Recently, the present authors reported polystyrene-supported aluminium copper(I) chloride [5] and active carbon-supported aluminium copper(I) chloride [6] as water-resistant solid adsorbents for carbon monoxide.

In this paper, preparation of a simple but novel solid adsorbent for carbon monoxide, active carbon-supported copper(I) chloride, and its character will be described.

Active carbon (Kureha Chemical Industry Co., BAC, G-70R, Lot No. 810117, beads of ca. 0.7 mm diameter) was kept under reduced pressure (6 mmHg) at 200°C for 5 h in order to remove adsorbed materials, and was directly subjected to the preparation of adsorbent. Copper(I) chloride (Koso Chemical Co., guaranteed grade) was reprecipitated from concentrated hydrochloric acid solution by the addition of water, followed by washing successively with ethanol and ethyl ether, and then dried in vacuo. Carbon monoxide gas and nitrogen gas, which had the purities of 99.95% and 99.999%, respectively, were passed through the columns of molecular sieve 3A immediately before use.

The preparation of the active carbon-supported copper(I) chloride adsorbent was as follows. First, hydrochloric acid solution of copper(I) chloride was prepared from 15 mmol of copper(I) chloride and 15 ml of 3 N hydrochloric acid by incubating these components at room temperature under an atmosphere of dry nitrogen for 1 h. Then, 10 g of active carbon was added to the solution. After the mixture was stirred for 1 h, hydrochloric acid and water were thoroughly removed in vacuo at 100°C for 1 h, resulting the active carbon-supported adsorbent as black to grey beads.

For comparison, the following solid adsorbents and liquid absorbent were obtained. A hydrochloric acid solution of copper(I) chloride (CuCl(HCl soln.)) was prepared by keeping 15 mmol of copper(I) chloride in 15 ml of 3 N hydrochloric acid at room temperature under nitrogen for 1 h. Copper(I) chloride solid without active carbon (CuCl(solid)) was prepared as a white and rather sticky powder spreading over the inner surface of a flask, by removing hydrochloric acid and water from the above hydrochloric acid solution of copper(I) chloride in vacuo at 100°C for 1 h. An active carbon without copper(I) chloride (Active Carbon) was obtained by the same procedure as described for the preparation of the present adsorbent except for the absence of copper(I) chloride.

The adsorption of carbon monoxide by the adsorbent, continuously stirred by use of a magnetic stirrer, from 1500 ml of carbon monoxide-nitrogen mixture (the total pressure, 1 atm; the initial partial pressures of carbon monoxide and nitrogen, 0.9 and 0.1 atm, respectively) was followed by use of a gas burette at 20°C under the atmospheric pressure. During the first 10 min, the carbon monoxide-nitrogen mixture was made to flow on the adsorbent at a rate of 30 ml per second by use of a gas pump.

The release of the adsorbed carbon monoxide was made at 20°C by reducing the total pressure in the flask to 0.4 mmHg for 10 min. Alternatively, the release of the adsorbed carbon monoxide was effected by elevating temperature from 20°C to 120°C under 1 atm.

As depicted in Fig. 1, the active carbon-supported copper(I) chloride rapidly adsorbs carbon monoxide at 20°C. After 10 min, the amount of the adsorbed carbon monoxide is 11.6 mmol, which is 94% of the equilibrium value (12.4 mmol) determined after 60 min. After being subjected to a reduced pressure (0.4 mmHg) at 20°C for 10 min or elevating temperature from 20°C to 120°C under 1 atm, the adsorbent was again brought into contact with the 9 : 1 carbon monoxide-nitrogen mixture. The adsorbent adsorbed carbon monoxide rapidly and the equilibrium value was 12.4 mmol. The carbon monoxide adsorption-release cycle composed of the adsorption of 12.4 mmol of carbon monoxide at 20°C under 1 atm and the release of carbon monoxide at 20°C under a reduced pressure (0.4 mmHg) or at 120°C under 1 atm was repeated more than five times without apparent deterioration.

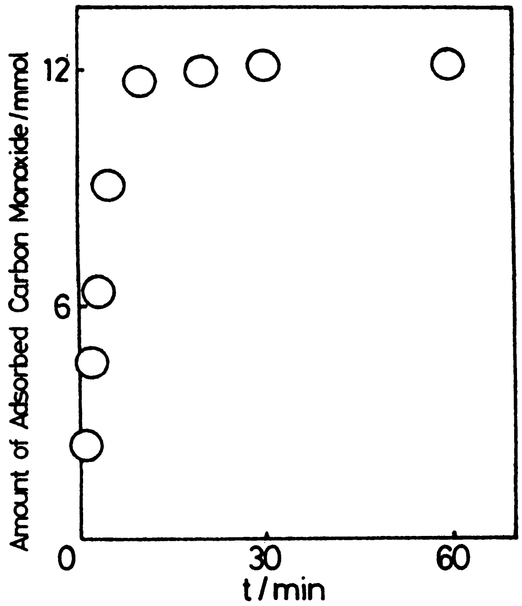

Fig. 1 Carbon monoxide adsorption by the solid adsorbent composed of 15 mmol of copper(I) chloride and 10 g of active carbon at 20°C under 1 atm: The initial volume of the gas mixture, 1500 ml; the initial partial pressures of carbon monoxide and nitrogen, 0.9 and 0.1 atm, respectively.

Table 1 shows the carbon monoxide adsorbing activity, determined immediately after the preparation, of the present active carbon-supported copper(I) chloride adsorbent (CuCl/Active Carbon) together with the values for the active carbon without copper(I) chloride (Active Carbon), copper(I) chloride solid (CuCl(solid)), and the hydrochloric acid solution of copper(I) chloride (CuCl (HCl soln.)). The amount of adsorbed carbon monoxide (12.4 mmol), determined after 60 min, for the present adsorbent is much larger than either the value (0.7 mmol) for the active carbon alone or that (0.0 mmol) for the solid copper(I) chloride alone. Thus, high adsorbing activity of the present adsorbent is definitely attributable to cooperation of copper(I) chloride and active carbon. The

Table 1 Amounts of carbon monoxide adsorbed by adsorbents for 60 min [a)]

Adsorbent	Adsorbed carbon monoxide (mmol)
CuCl/Active Carbon [b,c)]	12.4
Active Carbon [c)]	0.7
CuCl(solid) [b)]	0.0
CuCl(HCl soln.) [b)]	6.5

a) feed gas: p_{CO}=0.9 atm, p_{N_2}=0.1 atm, volume=1500 ml, 20°C.
b) CuCl:15 mmol. c) active carbon:10g.

activity of the present solid adsorbent is about two times as large as that of hydrochloric acid solution of copper(I) chloride.

Disproportionation of copper(I) chloride is largely suppressed in the present adsorbent. After being stored under nitrogen at room temperature for 60 days, the carbon monoxide adsorbing activity of the present adsorbent was 80% in comparison with the value exhibited immediately after the preparation. Moreover, the loss of about 20% in the activity occurred only during the first 7 days, and later the activity remained constant at 80% of the initial value. Probably, most of the charged copper(I) chloride are highly dispersed on the large surface of active carbon, resulting in the inhibition of collision of two copper(I) ions. The minor deactivation only in the early stage is associated with the disproportionation of a small portion of copper(I) chloride in insufficient dispersion.

After the incubation under air at room temperature for 1 h, the present adsorbent adsorbed in equilibrium 8.9 mmol of carbon monoxide on the first contact with the 9 : 1 carbon monoxide-nitrogen mixture at 20°C. Almost all of the adsorbed carbon monoxide was released by elevating temperature from 20°C to 120°C. In the following second adsorption, the equilibrium amount of the adsorbed carbon monoxide was 12.3 mmol, which was virtually identical with the value (12.4 mmol) exhibited immediately after the preparation of the adsorbent. After this, the equilibrium amounts remained constant at 12.3 mmol for five carbon monoxide adsorption-release cycles. This result shows that the present adsorbent successfully exhibits a high ability of carbon monoxide adsorption even after the incubation under air.

Detailed study on the roles of active carbon in the present adsorbent is currently under way.

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