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Preparation of Efficient Carbon Monoxide Adsorbent from Iron(II) Chloride, Copper(II) Chloride, and Active Carbon

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An adsorbent for carbon monoxide is prepared from 30.0 mmol of copper(II) chloride, 30.0 mmol of iron(II) chloride, and 20.0 g of active carbon. The adsorbing capacity (28.4 mmol) of the adsorbent is 2.1 times as large as the sum (13.7 mmol) of the capacity (11.8 mmol) of the active carbon-supported copper(II) chloride and that (1.9 mmol) of the active carbon-supported iron(II) chloride.

Carbon monoxide, an important starting material in industry, is usually obtained as gas mixtures with nitrogen, hydrogen, methane, carbon dioxide, and so on. Thus, carbon monoxide must be separated from gas mixtures prior to effective use.1) Considerable number of proposals on liquid absorbents of carbon monoxide were made.2) However, information on solid adsorbents for carbon monoxide has been rather scanty.

Previously, the present authors reported that active carbon-supported copper(I) chloride,3) active carbon-supported aluminium copper(I) chloride,4) and polystyrene resin-supported aluminium copper(I) chloride 5) reversibly adsorbed carbon monoxide under mild conditions. Furthermore, an adsorbent for carbon monoxide (active carbon-supported copper(II) chloride) was successfully prepared from active carbon and copper(II) chloride.6)

This paper describes preparation of carbon monoxide adsorbent from iron(II) chloride, copper(II) chloride, and active carbon. The adsorbent exhibits much larger adsorbing capacity than the active carbon-supported copper(II) chloride and the active carbon-supported iron(II) chloride.

The adsorbents were prepared by the addition of 20.0 g of active carbon (Kureha Chemical Industry Co., BAC G-70R, Lot. No. 810117) to 30 cm^3 of water containing 30.0 mmol of copper(II) chloride and various amounts of iron(II) chloride. The mixture was stirred for 1 h, and then the liquid was removed at 100 °C under 2.5 mmHg. The adsorbents were obtained as black beads of average diameter 0.7 mm. The active carbon-supported copper(II) chloride and the active carbon-supported iron(II) chloride were prepared in similar ways except for the absence of iron(II) chloride and copper(II) chloride, respectively.

Adsorptions of carbon monoxide by the adsorbents were carried out at 20 °C under 1 atm, and were followed by measuring the uptake of carbon monoxide by a gas burette. The adsorption was initiated by circulating carbon monoxide-nitrogen mixture with a gas circulating pump.

On the contact with 9:1 carbon monoxide-nitrogen mixture at 20 °C under 1 atm, the adsorbent prepared from 30.0 mmol of iron(II) chloride, 30.0 mmol of copper(II) chloride, and 20.0 g of the active carbon rapidly adsorbed carbon monoxide. The equilibrium amount of the adsorbed carbon monoxide was 28.4 mmol.

The adsorbed carbon monoxide was desorbed by subjecting the adsorbent to a reduced pressure (2.5 mmHg) at 20 °C for 30 min. In the second adsorption, the adsorption was rapid and the equilibrium amount of adsorbed carbon monoxide was 25.5 mmol. In the third and the later adsorptions, both the rate of adsorption and the equilibrium amount of adsorbed carbon monoxide were identical with the values in the second adsorption.

The difference between the equilibrium amount in the first adsorption and that in the second or the successive adsorption corresponds to the amount of carbon monoxide which has not been desorbed under the desorption conditions employed (2.5 mmHg, 20 °C for 30 min).

Table 1 shows the carbon monoxide adsorbing capacity (the amount of carbon monoxide adsorbed in equilibrium in the first adsorption) of the present adsorbent ($FeCl_2/CuCl_2/AC$) as well as those for the active carbon-supported copper(II) chloride ($CuCl_2/AC$) and the active carbon-supported iron(II) chloride ($FeCl_2/AC$). The adsorbing capacity (28.4 mmol) of the present adsorbent is 2.4 times as large as that (11.8 mmol) of the active carbon-supported copper(II) chloride. The adsorbing capacity (1.9 mmol) of the active carbon-supported iron(II) chloride is minimal. Thus, the adsorbing capacity of the present adsorbent is much larger

Table 1. Adsorbing capacities of the carbon monoxide adsorbents at 20 °C under 1 atm[a)]

Adsorbent	Adsorbing capacity/mmol [b)]
$FeCl_2/CuCl_2/AC$	28.4
$CuCl_2/AC$	11.8
$FeCl_2/AC$	1.9

a) The charged amounts of iron(II) chloride ($FeCl_2$), copper(II) chloride ($CuCl_2$), and the active carbon (AC) are 30.0 mmol, 30.0 mmol, and 20.0 g, respectively.

b) The initial partial pressure of carbon monoxide is 0.9 atm.

than the sum (13.7 mmol) of the capacity of the active carbon-supported copper(II) chloride and that of the active carbon-supported iron(II) chloride.

Figure 1 depicts a plot of the adsorbing capacity vs. the charged amount of iron(II) chloride for the adsorbent prepared from iron(II) chloride, copper(II) chloride, and the active carbon. The capacity monotonously increases with increase in the charged amount of iron(II) chloride, showing saturation at the amount of iron(II) chloride around 30 mmol. Here, the charged molar ratio of iron(II) chloride to copper(II) chloride is unity.

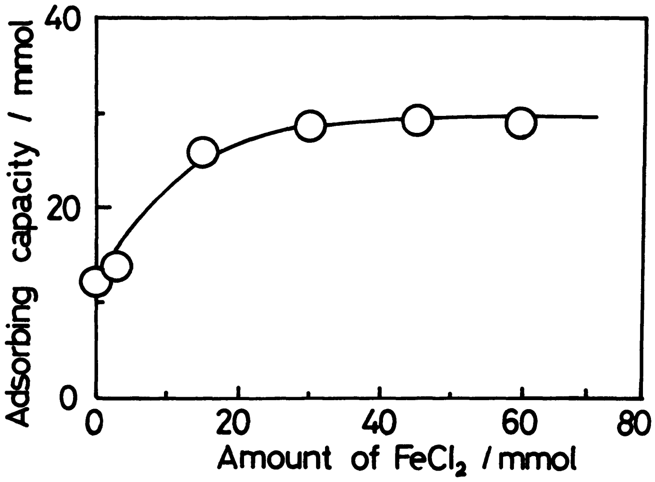

Fig. 1. Plot of the adsorbing capacity vs. the charged amount of iron(II) chloride for the adsorbent prepared from iron(II) chloride, copper(II) chloride, and the active carbon: The charged amounts of copper(II) chloride and the active carbon were kept constant at 30.0 mmol and 20.0 g, respectively.

The enhancement of iron(II) chloride on the adsorbing capacity is probably associated with weak interaction between iron(II) chloride and the active species of the adsorbent, copper(I) chloride, on the surface of the active carbon, although detailed mechanism has not been clear yet. The copper(I) chloride is produced during the preparation of the adsorbents by the electrophilic chlorination of the active carbon by copper(II) chloride, in which copper(II) chloride is converted to copper(I) chloride.6) Because of the interaction with iron(II) chloride, the copper(I) chloride is effectively dispersed in the adsorbent, resulting in larger adsorbing capacity. Possibility that the enhancement by iron(II) chloride is simply due to stoichiometric reduction of copper(II) ions by iron(II) ions is unlikely, since the standard electrode potential (-0.62 V)7) for this reaction is largely negative.

The present adsorbents have an advantage over the active carbon-supported copper(I) chloride that the preparation is successfully achieved by use of water as solvent. For the preparation of the active carbon-supported copper(I) chloride, however, use of aqueous hydrochloric acid solution is required.3) Furthermore, the present adsorbents contain no aluminium chloride as component, which is in contrast with the adsorbents such as the active carbon- and the polystyrene resin-supported aluminium copper(I) chloride.4,5)

In conclusion, solid adsorbents of carbon monoxide are prepared from iron(II) chloride, copper(II) chloride, and active carbon. The adsorbents exhibit larger adsorbing capacities than the active carbon-supported copper(II) chloride, and thus can have still larger potentialities of practical applications.

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