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Reaction between Copper(II) Chloride and Active Carbon for the Formation of Solid Carbon Monoxide Adsorbent

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Synopsis Evolution of hydrochloric acid on the preparation of carbon monoxide adsorbents from copper(II) chloride and active carbon has been experimentally confirmed. Relationship between the amount of hydrochloric acid evolved and the adsorbing capacity shows that the efficient adsorption by the adsorbents is attributable to the function of the copper(I) chloride, which is formed during the preparation by the reaction between copper(II) chloride and active carbon.

In industry, carbon monoxide is usually obtained as gas mixtures with nitrogen, hydrogen, methane, and carbon dioxide. Thus carbon monoxide must be separated from gas mixtures for the effective utilization.[1)]

Previously,[2)] the present authors have reported that solid adsorbents, prepared from copper(II) chloride and active carbon, adsorb carbon monoxide efficiently and reversibly under mild conditions. These adsorbents have an advantage from the viewpoint of practical application that both of the starting materials are stable against oxygen and thus the preparations are successfully achieved even under air. The adsorbing capacities of the adsorbents are much larger than the sum of the values for copper(II) chloride and active carbon. Thus it has been proposed that copper(II) chloride ($CuCl_2$) and active carbon (AC-H) react during the preparation as shown by Eq. 1, resulting in the formation of copper(I) chloride (CuCl).[2)] The resultant copper(I) chloride supported on the active carbon effectively adsorbs carbon monoxide.[3)]

$$\text{AC-H} + 2\,CuCl_2 \rightarrow \text{AC-Cl} + 2\,CuCl + HCl \qquad (1)$$

In this article, evolution of hydrogen chloride during the preparation of the adsorbents from copper(II) chloride and active carbon are quantitatively analyzed. The relationship between the amounts of hydrogen chloride evolved and the adsorbing capacities of the adsorbents is described.

Experimental

Active carbon (Kureha Chemical Industry Co., BAC G-70R, Lot. No. 810117) was subjected to a reduced pressure (5 mmHg (1 mmHg=133.322 Pa)) at 200 °C for 5 h prior to use.

The adsorbents were prepared by refluxing 20 g of the active carbon and 30 mmol of copper(II) chloride in 30 cm^3 of water, followed by removal of the liquid phase under 5 mmHg. Here, hydrogen chloride evolved was trapped with the use of liquid nitrogen traps, and was titrated with 1.0 mol dm^{-3} aqueous solution of sodium hydroxide. The amount of copper atoms, which were supported onto the active carbon, was 28.2 g-atoms as determined by atomic absorption spectroscopy.

Results and Discussion

When aqueous solution of silver nitrate was added to the contents obtained in the liquid nitrogen traps on the preparation of the adsorbents from copper(II) chloride and the active carbon, white precipitates (AgCl) were immediately formed. This result definitely shows that the reaction of Eq. 1 in fact takes place, yielding hydrogen chloride.

No hydrogen chloride was trapped, when only water-active carbon mixtures were evaporated at 180 °C under 2.5 mmHg. On evaporation of 30 cm^3 of aqueous solution of copper(II) chloride (1.0 mol dm^{-3}), the amount of hydrogen chloride was only 0.2 mmol.

Table 1 shows the amounts of hydrogen chloride trapped in the liquid nitrogen traps under various preparation conditions, together with the carbon monoxide adsorbing capacities of the resultant adsorbents. When the adsorbent is prepared by refluxing copper(II) chloride and the active carbon in water for 6 h, followed by the evaporation of the liquid phase at 180 °C, the amount of hydrogen chloride trapped is 13.5 mmol. The adsorbing capacity of the adsorbent is 19.3 mmol. On increase of the evaporation temperature from 180 to 200 °C, the amount of hydrogen chloride trapped is slightly increased to 14.1 mmol.

According to Eq. 1, 28.2 mmol of copper(I) chloride should be formed during the preparation of the adsorbent, when 14.1 mmol of hydrogen chloride is evolved. The molar ratio (0.68) of the adsorbing capacity (19.3

Table 1. Carbon Monoxide Adsorbing Capacities of the Adsorbents Prepared from the Active Carbon and Copper(II) Chloride as well as the Amounts of Hydrogen Chloride Trapped on Their Preparation

Preparation condition		Adsorbing capacity/ mmol	Amount of HCl/ mmol[c)]
Refluxing[a)] period/h	Evaporation[b)] temp/°C		
6	180	19.3	13.5
6	200	19.3	14.1
0	180	16.5	9.5

a) The period in which the active carbon and copper(II) chloride are refluxed in water. b) The temperature of the removal of the liquid phase under 2.5 mmHg. c) The amount of hydrogen chloride trapped in the liquid nitrogen traps on the preparation of the adsorbents.

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mmol) of the adsorbent to the estimated amount (28.2 mmol) of copper(I) chloride formed is almost identical with the corresponding value (0.64)[3] for the adsorbent, which is prepared directly from copper(I) chloride and active carbon in water. Thus the carbon monoxide adsorbing activity of the present adsorbent is ascribed to the function of the copper(I) chloride, which is formed during the preparation and is supported on the active carbon.

The adsorbent, prepared by the removal of the liquid phase at 180 °C without refluxing the mixture in water, shows a smaller adsorbing capacity (16.5 mmol). The amount (9.5 mmol) of hydrogen chloride trapped during the preparation is about 2/3 of the value (13.5 mmol) for the adsorbent obtained by the evaporation at 180 °C after refluxing.

These results indicate that the reaction of Eq. 1 occurs both during the refluxing and during the evaporation of the liquid phase. Refluxing of the reaction mixture in water probably facilitates the dissolution of hydrogen chloride, which is formed in the micropores of the active carbon and is adsorbed there, into aqueous phase.

The reaction of Eq. 1 proceeds in a similar way as electrophilic chlorination of anthracene by copper(II) chloride,[4] in which 9,10-dichloroanthracene and copper(I) chloride are formed. Active carbons have many reaction sites for this reaction, since they are composed of conjugated aromatic rings.

In conclusion, it has been experimentally established that the reaction of Eq. 1 occurs during the preparation of carbon monoxide adsorbents from copper(II) chloride and active carbon. The resultant copper(I) chloride supported on the active carbon is responsible for the efficient adsorption of carbon monoxide by the adsorbents.

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