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ACTIVE CARBON-SUPPORTED ALUMINIUM COPPER CHLORIDE AS WATER-RESISTANT CARBON MONOXIDE ADSORBENT

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A solid adsorbent of carbon monoxide, aluminium copper(I) chloride supported on active carbon, is prepared from copper(I) chloride, aluminium chloride, and active carbon. The adsorbent is stable against water and is applicable to separation of carbon monoxide from gas mixture containing water.

Carbon monoxide is a valuable raw material for the syntheses of variety of chemicals in industry.[1)] Since most of main sources of carbon monoxide are gas mixtures of carbon monoxide, nitrogen, hydrogen, carbon dioxide, methane, and others, and additionally they are usually saturated with water, devices for the separation of carbon monoxide from gas mixtures containing water are quite important.[2)]

In previous papers,[3,4)] it was shown that the solution composed of copper(I) chloride, aluminium chloride, polystyrene, and toluene was highly water-resistant and was applicable to direct separation of carbon monoxide from gas mixtures containing considerable amount of water. The water-resistivity of the absorbents was attributed to specific interactions between aluminium copper(I) chloride ($AlCuCl_4$) and adjacent aromatic rings of polystyrene.

In this paper, the preparation of water-resistant solid carbon monoxide adsorbent from copper(I) chloride, aluminium chloride, and active carbon, which is an assembly of microcrystals of accumulated layers of condensed aromatic rings, will be described.

Active carbon (Kureha Chemical 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. Aluminium chloride (Kishida Chemical Co., guaranteed grade) was purified by sublimation. 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 aluminium copper(I) chloride adsorbent was as follows. First, toluene solution of aluminium copper(I) chloride was prepared from 20 mmol of aluminium chloride, 20 mmol of copper(I) chloride, and 20 ml of toluene by incubating these components at 40°C under atmosphere of dry nitrogen for 4 h. Then, the dark-colored solution was added to 10g of active carbon, kept in an evacuated 100 ml flask, avoiding contamination of nitrogen and air by using a dropping funnel. The liquid phase was soon decolorized, which was attributable to specific interaction of aluminium copper(I) chloride with active carbon. After the mixture was stirred for 1 h, toluene was thoroughly removed in vacuo at 80°C for 1 h, which resulted in the formation of active carbon-supported adsorbent as black to grey beads.

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.

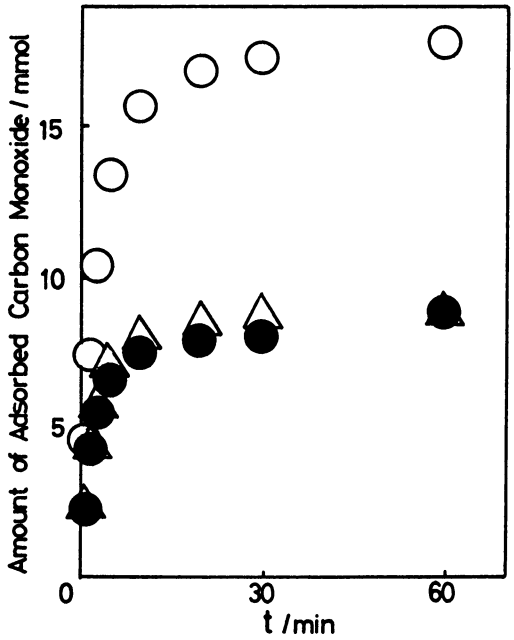

Fig. 1 Time dependence of the amount of carbon monoxide adsorbed at 20°C under 1 atm by a solid adsorbent composed of 20 mmol of aluminium copper(I) chloride and 10g of active carbon: The release of the adsorbed carbon monoxide was carried out by reducing the total pressure to 6 mmHg for 10 min; the first adsorption(○), the second one(●), and the one measured after the contact of the adsorbent with 5000 ml of nitrogen containing 2 mmol of water(△); initial volume of the gas mixture 1500 ml; initial pressures of carbon monoxide and nitrogen, 0.9 and 0.1 atm, respectively.

The release of the adsorbed carbon monoxide was made at 20°C by reducing the total pressure in the flask to 6 mmHg for 10 min. Alternatively, the release of the adsorbed carbon monoxide was effected by elevating temperature from 20°C to 100°C.

The contact of the adsorbent with water was effected by circulating 5000 ml of nitrogen gas, which had the total pressure of 1 atm and contained 2 mmol of water, on the magnetically stirred adsorbent for 10 min. The nitrogen-water mixture was prepared by the introduction of water into an evacuated 5000 ml vessel using a microsyringe, followed by the addition of nitrogen gas in an amount required to make the total pressure atmospheric.

As shown in Fig. 1, the adsorbent rapidly adsorbs carbon monoxide at 20°C. After 10 min, the amount of the adsorbed carbon monoxide is 15.6 mmol, which is 88% of the equilibrium value (17.7 mmol) determined after 60 min. After being subjected to a reduced pressure (6 mmHg) at 20°C for 10 min, the adsorbent is again brought into contact with 9 : 1 carbon monoxide-nitrogen mixture. The adsorbent shows rapid adsorption and the equilibrium value of the adsorbed carbon monoxide is 8.8 mmol, as shown in Fig. 1. The equilibrium value for the third adsorption by the adsorbent, which has been subjected to 6 mmHg at 20°C for 10 min after the second adsorption, is also 8.8 mmol. Thus, the difference (8.9 mmol) between the equilibrium adsorbed value (17.7 mmol) in the first adsorption and that (8.8 mmol) in the second or third adsorption corresponds to the carbon monoxide adsorbed in equilibrium at 6 mmHg, 20°C. The carbon monoxide adsorption-release cycle composed of the adsorption of 8.8 mmol of carbon monoxide at 760 mmHg and the release of almost identical amount of carbon monoxide at 6 mmHg is repeated more than five times without apparent deterioration.

The triangles in Fig. 1 depict the time course of carbon monoxide adsorption by the adsorbent, which has contacted with 5000 ml of nitrogen containing 2 mmol of water for 10 min at 20°C and then is subjected to 6 mmHg for 10 min at 20°C. The rate of adsorption and the equilibrium value of the adsorbed carbon monoxide after the contact of the adsorbent with water are virtually identical with the values prior to the contact. The contacts of the adsorbent with nitrogen gas containing 2 mmol of water, prepared separately for each contact, were repeated more than five times. The rate of adsorption and the equilibrium adsorbed value, measured after each of the contacts, were also identical with those for the adsorbent prior to the contacts with water within experimental error. Thus, water shows no measurable deactivation effect on the present solid adsorbent.

This result is markedly in contrast with rapid deactivation of the solid adsorbent without active carbon on the contact with water. The solid adsorbent without active carbon was prepared by evaporation of the solvent from the solution composed of 20 mmol of aluminium chloride, 20 mmol of copper(I) chloride, and 20 ml of toluene. Prior to the contact with 5000 ml of nitrogen containing 2 mmol of water for 10 min, the adsorbent without active carbon repeatedly adsorbed 6.3 mmol of carbon monoxide during 10 min from 9 : 1 carbon monoxide-nitrogen mixture at 20°C under 1 atm. The release of the adsorbed carbon monoxide was effected by keeping the adsorbent at 6 mmHg for 10 min. Thus, the adsorbent without active carbon showed reversible adsorption of carbon monoxide in the absence of water, although the rate of adsorption was smaller than that by the adsorbent with active carbon. The smaller rate of adsorption by the adsorbent without active carbon is probably ascribed to the smaller surface area of the solid of aluminium copper(I) chloride. After the contact of the adsorbent with water, however, the amount of carbon monoxide adsorbed for 10 min was decreased to 3.5 mmol.

In addition to the pressure swing method described above, separation of carbon monoxide using the adsorbent is successfully achieved by changing temperature, as shown in Fig. 2. The adsorbent, which has adsorbed 17.7 mmol of carbon monoxide at 20°C exactly in the same way as the first adsorption depicted in Fig. 1, rapidly releases 11.0 mmol of carbon monoxide on the elevation of temperature from 20°C to 100°C. In the following adsorption, the equilibrium value of the adsorbed carbon monoxide is 11.0 mmol. The cycle involving the adsorption of 11.0 mmol of carbon monoxide at 20°C, followed by the release of 11.0 mmol of carbon monoxide at 100°C, is repeated more than five times.

The adsorption of carbon monoxide by the adsorbent is due to molecular complex formation between aluminium copper(I) chloride, probably showing specific interactions with aromatic rings of active carbon, and carbon monoxide. On elevating temperature or reducing the partial pressure of carbon monoxide, the molecular complex is decomposed and carbon monoxide is released. Strong water-resistivity of the present solid adsorbent is associated with the protection of aluminium copper(I) chloride by active carbon, since in the absence of active carbon the complex is rapidly deactivated by the irreversible reaction with water. Aluminium copper(I) chloride is probably located in apolar micropores of active carbon, composed of walls of condensed aromatic rings, and is shielded from water in gas mixtures.

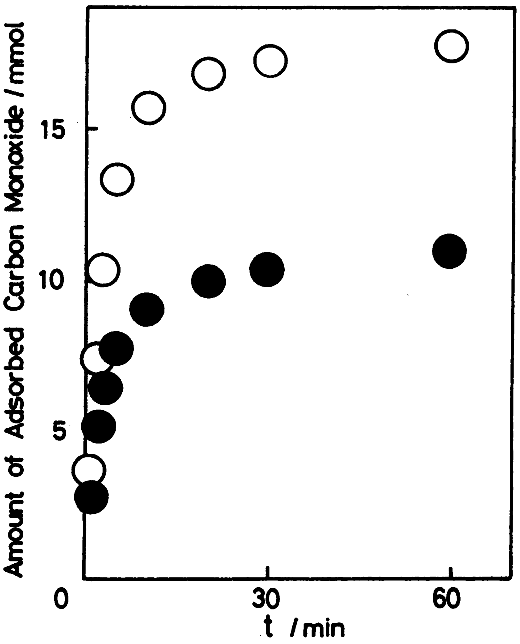

Fig. 2 Time dependence of the amount of carbon monoxide adsorbed at 20°C under 1 atm by a solid adsorbent composed of 20 mmol of aluminium copper(I) chloride and 10g of active carbon: The release of the adsorbed carbon monoxide was carried out by elevating temperature from 20°C to 100°C; the first adsorption(○) and the second one(●); initial volume of the gas mixture 1500 ml; initial pressures of carbon monoxide and nitrogen, 0.9 and 0.1 atm, respectively.

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