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POLYSTYRENE-SUPPORTED ALUMINIUM COPPER CHLORIDE AS WATER-RESISTANT SOLID CARBON MONOXIDE ADSORBENT

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A solid adsorbent of carbon monoxide, polystyrene-supported aluminium copper(I) chloride, is prepared by use of carbon disulfide as solvent. The adsorbing activity of the resulting adsorbent shows no measurable decrease after the repeated contact with nitrogen gas containing a considerable amount of water.

Recently the importance of carbon monoxide as a starting material in industry is rapidly increasing.[1)] Usually carbon monoxide is obtained as gas mixtures with hydrogen, carbon dioxide, nitrogen, methane, and others. In addition, the gas mixtures are mostly saturated with water.[2)] Thus, effective and low-cost separation process of carbon monoxide from gas mixtures containing water is highly required.[3,4)]

In the present study, a polystyrene-supported aluminium copper(I) chloride ($AlCuCl_4$) is prepared by use of carbon disulfide as solvent and the resulting solid carbon monoxide adsorbent is found to be highly stable against water in gas mixtures.

The polystyrene resin "Bio-Beads SM-2" of Bio-Rad Laboratories, a 20 % cross-linked macroreticular polystyrene-divinylbenzene copolymer, was purified by stirring successively in the following solvents under the specified conditions: aqueous hydrochloric acid solution, 7 M, 55 °C, 1 h; aqueous sodium hydroxide solution, 4 M, 55 °C, 1 h; distilled water, 55 °C, 1 h; methanol, 20 °C, 1 h; dichloromethane, 20 °C, 1 h. The resin was then dried overnight in vacuo at 80 °C. Copper(I) chloride (Koso Chemical Co., guaranteed grade) was reprecipitated from concentrated hydrochloric acid with water, followed by washing successively with ethanol and ethyl ether, then dried overnight in vacuo at 95 °C. Aluminium chloride (Kishida Chemical Co., guaranteed grade) was sublimed. Carbon disulfide was distilled after being dried by phosphorus pentoxide. 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 solid carbon monoxide adsorbent was as follows. 2.6 grams (25 milli equivalents) of the polystyrene resin, 2.1 g (21 mmole) of copper(I) chloride, 2.8 g (21 mmole) of aluminium chloride, and 10 ml of carbon disulfide were stirred and refluxed in a 100 ml flask under dry nitrogen. After 6 h, carbon disulfide was thoroughly removed from the mixture by evaporation at 4 mmHg, 40 °C, for 4 h. The resulting dark orange colored beads were used as the solid carbon monoxide adsorbent.

The adsorption of carbon monoxide by the solid adsorbent, continuously stirred, was observed at 20 °C by following the carbon monoxide uptake at the carbon monoxide pressure of 760 mmHg using a gas burette.

The release of the adsorbed carbon monoxide was achived at 20 °C by reducing the pressure in the flask to 7 mmHg for 10 min.

The contact of the adsorbent with water was effected by circulating 10 liters of nitrogen gas, which had the total pressure of 760 mmHg and contained 10 mole% water (water content: 5000 ppm) to charged copper(I) chloride, on the magnetically stirred adsorbent for 10 min. The nitrogen / water mixture (water content: 5000 ppm) was prepared by introduction of water into an evacuated vessel (10 liters) using a microsyringe, followed by the addition of nitrogen gas in an amount required to

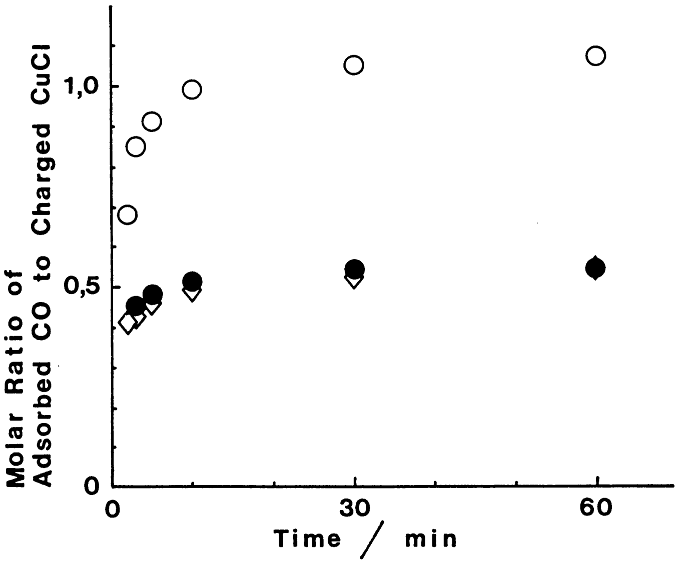

Fig. 1. Adsorption of carbon monoxide at 20 °C, 760 mmHg by the polystyrene-supported aluminium copper(I) chloride prepared by use of carbon disulfide as solvent:
(○) the first adsorption; (●) the second adsorption by the adsorbent which was subjected to 7 mmHg at 20 °C for 10 min after the first adsorption; (◇) the third adsorption by the adsorbent which contacted with 10 mole% water and was subjected to 7 mmHg at 20 °C for 10 min after the second adsorption.

make total pressure 760 mmHg.

Fig. 1 depicts the adsorption of carbon monoxide at 20 °C, 760 mmHg by the solid adsorbent of polystyrene-supported aluminium copper(I) chloride. The adsorption was rapid, and the molar ratio of the adsorbed carbon monoxide to the charged copper(I) chloride at 3 min was 0.85. The equilibrium molar ratio, determined at 60 min, was 1.07.

Then, the adsorbed carbon monoxide was released by contacting with 10 liters of dry nitrogen gas for 10 min, followed by subjecting the adsorbent to a reduced pressure 7 mmHg at 20 °C for 10 min. On the second contact with carbon monoxide at 760 mmHg, the adsorbent rapidly adsorbed carbon monoxide, and the equilibrium value of the adsorbed carbon monoxide was 54 mole% to the charged copper(I) chloride.

The contact of the adsorbent with dry nitrogen gas prior to the treatment at 7 mmHg was made simply for the purpose of comparison with the following results involving the contacts of the adsorbent with nitrogen gas containing water. The adsorbent, which was directly subjected to 7 mmHg at 20 °C for 10 min without the contact with nitrogen gas, also adsorbed about 54 mole% of carbon monoxide in the second adsorption.

Later, the adsorbent, which was contacted with dry nitrogen for 10 min after the foregoing adsorption, followed by the standing at 7 mmHg, 20 °C for 10 min, adsorbed about 54 mole% of carbon monoxide at 760 mmHg, more than three times without apparent deterioration.

As shown in Fig. 1, the rate of adsorption and the equilibrium molar ratio of the adsorbed carbon monoxide after the contact of the adsorbent with 10 mole% water to the charged copper(I) chloride were identical with the values prior to the contact within experimental errors. Furthermore, repeated five contacts of the adsorbent with water, for each of which nitrogen gas containing 10 mole% water was prepared separately, did not show appreciable changes in the rate and the equilibrium molar ratio.

Thus, water showed no measurable deactivation effect on the adsorbent prepared from copper(I) chloride, aluminium chloride, and polystyrene resin by use of carbon disulfide as solvent.

In contrast, the aluminium copper(I) chloride salt, prepared in solid without polystyrene beads, was rapidly deactivated by water in gas. The molar ratio of the adsorbed carbon monoxide to the charged copper(I) chloride at 60 min decreased from 0.23 to 0.15 after the contact with 10 mole% water to the charged copper(I) chloride.

The polystyrene-supported aluminium copper(I) chloride prepared by use of toluene as solvent,5) in place of carbon disulfide in the present study, was also deactivated by water in gas. The molar ratio of the adsorbed carbon monoxide to the charged copper(I) chloride at 60 min decreased from 0.55 to 0.45 after the contact with 10 mole% water to the charged copper(I) chloride.

The adsorption of carbon monoxide by the present adsorbent is associated with molecular complex formation of carbon monoxide with the $AlCuCl_4$ salt, showing specific interactions with aromatic rings of polystyrene resin. On the reduction of the partial pressure of carbon monoxide, the molecular complex is decomposed and carbon monoxide is released.

In the present adsorbent prepared by use of carbon disulfide as solvent, the $AlCuCl_4$ salt is mostly located in the interior of the resin, since rather poor solubility of the salt in carbon disulfide should induce deep penetration of the salt into the resin. Thus, the salt may be firmly shielded from water by the aromatic rings of polystyrene resin. In the adsorbent prepared by use of toluene as solvent, however, the salt is largely located on the surface of the resin, since toluene favorably dissolves the salt.

A detailed study on the water resistivity of the polystyrene-supported aluminium copper(I) chloride prepared by use of carbon disulfide is currently under way.

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