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Polystyrene Resin-Supported Aluminium Copper(I) Chloride as Selective Ethylene Adsorbent

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Synopsis. Solid adsorbents for ethylene are prepared by stirring copper(I) chloride, aluminium chloride, and a macroreticular type polystyrene resin in carbon disulfide, followed by removal of the liquid phase. The adsorbents effectively adsorb ethylene at 20 °C under 1 atm, and exhibit no measurable adsorptions of nitrogen, hydrogen, and methane.

Ethylene, one of the most important raw materials in chemical industry, is usually obtained as gas mixtures with nitrogen, hydrogen, methane, carbon monoxide, and others. Thus, ethylene must be separated from the gas mixtures prior to utilization.1)

Previously, the authors have reported that toluene solutions of aluminium silver chloride2) and the macroreticular type polystyrene resin-supported aluminium silver chloride3) reversibly and selectively absorb ethylene under mild conditions.

This paper reports preparation of solid adsorbents for ethylene from copper(I) chloride, aluminium chloride, and a macroreticular type polystyrene resin. The ethylene adsorbing and desorbing abilities as well as selectivities of the ethylene adsorptions with respect to the adsorptions of other gases are described.

Experimental

A macroreticular type polystyrene resin, purchased from Bio-Rad Laboratories (Bio-Beads SM-2; divinylbenzene content, 20 mol%; diameter, 296—740 µm; average pore diameter, 9 nm; surface area, 300 m^2/g),4) was successively washed with aqueous hydrochloric acid solution (6 mol dm^{-3}), with aqueous sodium hydroxide solution (4 mol dm^{-3}), with water, with methanol, and with dichloromethane, and then was dried in vacuo at 80 °C for 12 h. Aluminium chloride was purified by sublimation. Copper(I) chloride was reprecipitated using concentrated aqueous hydrochloric acid solution-water system, was washed with ethanol and diethyl ether, and was dried in vacuo at 80 °C for 12 h. Ethylene, nitrogen, hydrogen, methane, and carbon monoxide were passed through columns of molecular sieve 3A immediately before use.

The adsorbents were prepared by refluxing copper(I) chloride, aluminium chloride, and the polystyrene resin in carbon disulfide under dry nitrogen for 6 h. The charged molar ratios of copper(I) chloride and the aromatic residue of the polystyrene resin, respectively, to aluminium chloride were 1.0 and 1.2. Then the liquid phase was removed at 4 mmHg, where the temperature was gradually elevated from 20 to 60 °C. The adsorbents were obtained as orange colored beads.

Adsorptions of gases by the adsorbents were carried out at 20 °C under 1 atm, and were followed by the gas uptake using a gas burette. Gas compositions were determined by gas chromatography (Ohkura Model 701; column, Porapak Q; column temperature, 80 °C; carrier gas, helium).

Results and Discussion

The open circles in Fig. 1 depict the adsorption of ethylene at 20 °C under 1 atm by the adsorbent prepared from copper(I) chloride, aluminium chloride, and the macroreticular type polystyrene resin. The adsorption is rapid, and the equilibrium molar ratio of adsorbed ethylene to the charged copper(I) chloride is 1.40. The amount of ethylene adsorbed by 1 g of the adsorbent is 89 cm^3 (standard temperature and pressure).

Then, desorption of the adsorbed ethylene has been carried out by subjecting the adsorbent to a reduced pressure (8 mmHg) at 20 °C for 10 min. In the second adsorption, shown by the closed circles in Fig. 1, the equilibrium molar ratio of the adsorbed ethylene to the charged copper(I) chloride is 0.29. Both the time courses of the adsorptions and the equilibrium molar ratios in the third, the fourth, and the fifth adsorptions are identical with those in the second adsorption within experimental error. Reversible adsorption of ethylene is successfully achieved by use of the present adsorbent.

The difference between the molar ratio (1.40) of the adsorbed ethylene to the charged copper(I) chloride in the first adsorption and that (0.29) in the second and the later adsorptions corresponds to the amount of ethylene, which is not desorbed under the desorption conditions employed (8 mmHg, 20 °C for 10 min).

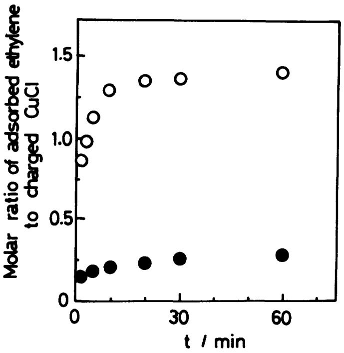

Fig. 1. Adsorption of ethylene under 1 atm at 20 °C by the polystyrene resin-supported aluminium copper (I) chloride: The first adsorption (○); the second adsorption (●) by the adsorbent which was subjected to a reduced pressure (8 mmHg) at 20 °C for 10 min after the first adsorption; the adsorbent was prepared from 2.57 g (26.0 mmol) of copper(I) chloride, 3.47 g (26.0 mmol) of aluminium chloride, and 3.24 g (31.1 milliequivalents in phenyl residue) of the macroreticular type polystyrene resin by use of 30 cm^3 of carbon disulfide.

The desorption of the ethylene adsorbed by the present adsorbent was also effectively carried out by heating the adsorbent to 90 °C under 1 atm for 10 min. The molar ratio of the desorbed ethylene to the charged copper(I) chloride was 0.47, as followed by the gas burette. In the following adsorption, the molar ratio of adsorbed ethylene to the charged copper(I) chloride was 0.47, which was exactly identical with the value for the ethylene desorbed in the foregoing desorption.

When the desorption of adsorbed ethylene was carried out under 8 mmHg at 142 °C for 10 min, the molar ratio of the desorbed ethylene to the charged copper(I) chloride was 0.87.

The present adsorbents exhibited no measurable adsorptions of nitrogen, hydrogen, and methane under 1 atm at 20 °C.

Separation of ethylene from ethylene–carbon monoxide mixture was examined by use of the adsorbent prepared from 12.0 mmol of copper(I) chloride, 12.0 mmol of aluminium chloride, and 1.50 g of the resin. Here, 1050 cm^3 of ethylene–carbon monoxide mixture having initial molar fraction 0.47 of ethylene was contacted with the adsorbent at 20 °C under 1 atm. The adsorbent rapidly adsorbed both ethylene and carbon monoxide[5] from the gas mixture, and the equilibrium amounts of adsorbed ethylene and adsorbed carbon monoxide were 9.0 mmol and 1.8 mmol, respectively. These values were evaluated by use of both the molar fraction (0.35) of ethylene in the gas phase after the contact with the adsorbent, measured by gas chromatography, and the total amount (264 cm^3) of the adsorbed gas, determined by a gas burette. Thus the amount of adsorbed ethylene was 5 times as large as that for carbon monoxide.

The efficient adsorptions of ethylene by the present adsorbents are ascribed to coordination of ethylene to the aluminium copper(I) chloride, which is formed from copper(I) chloride and aluminium chloride and is highly dispersed in the polystyrene resin.[5] The aluminium copper(I) chloride forms molecular complexes with carbon monoxide[5] and with various aromatic compounds.[6,7] The adsorbing capacity of the adsorbent, prepared from copper(I) chloride and the polystyrene resin in the absence of aluminium chloride, is minimal: the molar ratio of adsorbed ethylene to the charged copper(I) chloride is only 0.03.

Rather low price of copper(I) chloride, in comparison with the price of silver chloride used for the preparation of the polystyrene resin-supported aluminium silver chloride as selective ethylene adsorbent,[3] is an advantage of the present adsorbents from the viewpoints of practical applications.

In conclusion, solid adsorbents for ethylene are prepared from copper(I) chloride, aluminium chloride, and a macroreticular type polystyrene resin. The adsorbents are applicable to selective separation of ethylene from gas mixtures containing ethylene together with nitrogen, hydrogen, methane, and carbon monoxide.

References

1) "Encyclopedia of Chemical Technology," 1st ed, ed by R. E. Kirk and D. F. Othmer. The Interscience Encyclopedia Inc., New York (1950), Vol. 5, p. 894.

2) H. Hirai, S. Hara, and M. Komiyama, *Chem. Lett.*, **1986**, 257.

3) H. Hirai, S. Hara, and M. Komiyama, *Angew. Makromol. Chem.*, **130**, 207 (1985).

4) "Materials, Equipment, and Systems for Chromatography, Electrophoresis, Immunochemistry, and HPLC," Catalog G, Bio-Rad Laboratories Ltd., (1981), p. 28.

5) H. Hirai, S. Hara, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **59**, 1051 (1986).

6) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).

7) H. Hirai, M. Nakamura, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **56**, 2519 (1983).