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SELECTIVE ETHYLENE ADSORBENTS COMPOSED OF COPPER(I) CHLORIDE AND POLYSTYRENE RESINS HAVING AMINO GROUPS

Hidefumi HIRAI,* Kazunori KURIMA, Keiichiro WADA, and Makoto KOMIYAMA
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

A selective adsorbent for ethylene is prepared by stirring 15 g of copper(I) chloride and 10 g of polystyrene resin having primary and secondary amino groups in 1:1 (v/v) acetonitrile-water mixture, followed by removal of the liquid phase. The adsorbent adsorbs 15.0 mmol of ethylene at 20 °C, 1 atm, which is 7.9 fold larger than the value (1.9 mmol) for ethane.

In industry, ethylene is usually obtained as gas mixtures with methane, ethane, propane, hydrogen, and nitrogen. Thus, separation of ethylene from gas mixtures is quite important.[1] However, there have been few reports on solid adsorbents for ethylene.

A process of ethylene separation using activated carbon as adsorbent was proposed.[2] However, selective separation of ethylene from gas mixtures, especially from the ones containing methane, ethane, and propane, is difficult for the process using activated carbon, since activated carbon also adsorbs these saturated hydrocarbons.[3]

Although zeolite-supported copper(I) or silver(I) ion adsorbs ethylene,[4] the adsorption is so strong that severe conditions are required for the release of the adsorbed ethylene from the adsorbents.

Previously, the authors reported ethylene adsorbents composed of cross-linked polystyrene resins and aluminium copper(I) chloride [5] or aluminium silver chloride.[6]

In this paper, preparation of ethylene adsorbents composed of copper(I) chloride and polystyrene resins having amino groups is reported. These ethylene adsorbents are significantly different from the previous ones [5,6] in that aluminium chloride is not employed as a component here, and that polystyrene resins with amino groups are used in place of polystyrene resins without functional groups. The present adsorbents show effective adsorption of ethylene, whereas the adsorption of ethane is minimal. Highly selective adsorption of ethylene can be achieved by using these adsorbents.

Macroreticular type of polystyrene resin having primary and secondary amino groups (Mitsubishi Chemical Industries, Ltd., DIAION WA20; pale yellow beads with diameter 0.35 - 0.55 mm, amino residue 2.5 equiv./dm^3, apparent density 650 g/dm^3) and macroreticular type of polystyrene resin having tertiary amino groups (Rohm and

Haas Co., Ltd., Amberlite IRA-93; pale yellow beads with diameter 0.37 - 0.47 mm, amino residue 4.6 equiv./dm^3, apparent density 640 g/dm^3) were washed with ethyl alcohol, and were dried in vacuo at 80 °C for 12 h. Copper(I) chloride was reprecipitated from concentrated aqueous hydrochloric acid solution with water, washed successively with ethyl alcohol and ethyl ether, and was dried in vacuo at 100 °C for 12 h.

Ethylene adsorbents were prepared as follows. 10 g of the polystyrene resin having amino groups and various amounts of copper(I) chloride were stirred in 80 cm^3 of acetonitrile-water mixture (volume ratio 1:1) at 20 °C for 4 h, and then the liquid phase was thoroughly removed at 80 °C, 7 mmHg for 4 h. The adsorbents were obtained as green beads.

Adsorption of ethylene or ethane by the adsorbents was carried out at 20 °C, 1 atm, and was followed by use of a gas burette. The release of adsorbed gas was effected either by heating the adsorbents or by subjecting them to a reduced pressure.

Figure 1 shows time courses for the adsorption of ethylene by the adsorbent prepared from 10 g of the polystyrene resin having primary and secondary amino groups and 10 g of copper(I) chloride. On the contact with ethylene at 20 °C, 1 atm, the adsorbent rapidly adsorbs ethylene (○). The adsorption virtually attains an equilibrium in 1.5 h, where 13.5 mmol of ethylene is adsorbed. This value corresponds to the adsorption of 0.68 mmol ethylene per 1 g of the adsorbent. Then, the adsorbent was subjected to a reduced pressure (5 mmHg) at 20 °C for 1 h. In the following adsorption (◑), the adsorption is also rapid, and the equilibrium amount of ethylene adsorbed is 10.7 mmol. In the third and the fourth adsorptions, both the rate of adsorption and the equilibrium amount of ethylene adsorbed were almost identical with the values for the second

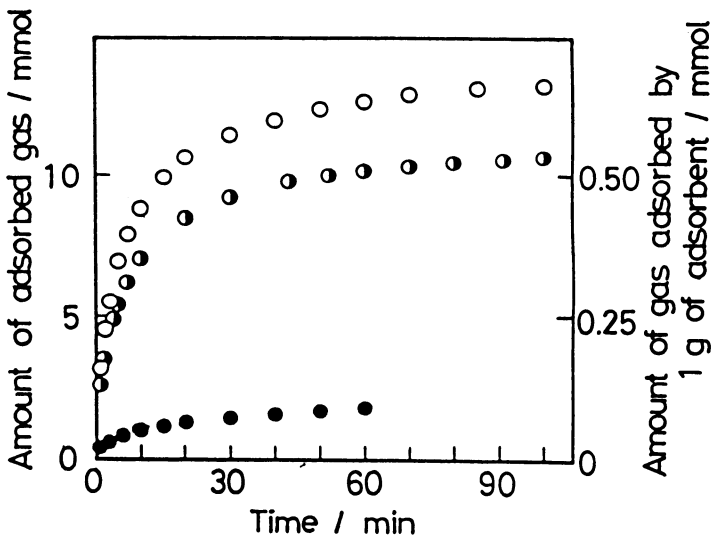

Fig. 1. Adsorption of ethylene and ethane at 20 °C, 760 mmHg by the solid adsorbent prepared from 10 g (101 mmol) of copper(I) chloride and 10 g of the polystyrene resin having primary and secondary amino groups by using acetonitrile-water mixture (volume ratio 1:1) as solvent: the first adsorption of ethylene (○); the second adsorption of ethylene (◑) by the adsorbent which was subjected to 5 mmHg at 20 °C for 1 h after the first adsorption; the adsorption of ethane (●) by the adsorbent which was subjected to 5 mmHg at 20 °C for 1 h after an adsorption of ethylene.

adsorption.

The closed circles in Fig. 1 depict the adsorption of ethane by the same adsorbent, which is carried out after the adsorbed ethylene is released at 5 mmHg, 20 °C for 1 h. The adsorption is rapid, but the equilibrium amount of ethane adsorbed is only 1.9 mmol. This value is 7.1 fold smaller than the value for ethylene. Thus, this adsorbent exhibits selective adsorption of ethylene. A possibility that the ethane adsorption is suppressed by ethylene preadsorbed is definitely ruled out by the following result. Time course for ethane adsorption by a virgin adsorbent, prepared exactly in the same way but separately, superimposed that shown by the closed circles in Fig. 1.

The adsorbent exhibited no measurable adsorption of methane at 20 °C, 1 atm. Adsorptions of hydrogen and nitrogen were not detected at all either.

Figure 2 depicts the plots of the amounts of adsorbed ethylene and ethane as a function of the charged amount of copper(I) chloride. Here, the amount of the polystyrene resin having primary and secondary amino groups is kept constant at 10 g. The amount of the adsorbed ethylene increases with increasing amount of the charged copper(I) chloride. In contrast, the amount of ethane adsorbed decreases with increasing amount of copper(I) chloride. As a result, the selectivity for the ethylene adsorption, defined as the ratio of the amount of adsorbed ethylene to the value for ethane, significantly increases as the charged amount of copper(I) chloride increases. The selectivity is 7.9, when the charged amount of copper(I) chloride is larger than 15 g (152 mmol). The amount of adsorbed ethylene at the charged amount of copper(I) chloride 152 mmol is 15.0 mmol, that is, 0.60 mmol per 1 g of the adsorbent.

An adsorbent prepared from 10 g of the polystyrene resin and 10 g (101 mmol) of copper(I) chloride using water as solvent, in place of 1:1 acetonitrile-water mixture, also showed high selectivity (6.4). The rate of ethylene adsorption, however, was considerably smaller than that by the adsorbent obtained using the acetonitrile-water mixture. On the other hand, usage of acetonitrile, in place of the mixture, provided

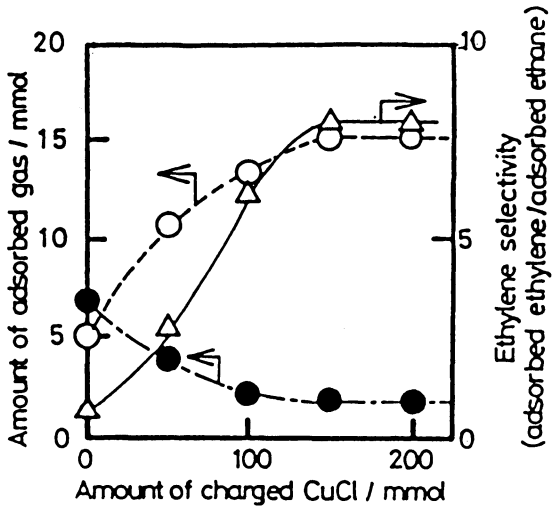

Fig. 2. Dependence of adsorbing capacity and ethylene selectivity on the charged amount of copper(I) chloride for the solid adsorbent composed of copper(I) chloride and the polystyrene resin having primary and secondary amino groups: ethylene adsorption (○), ethane adsorption (●), and the ethylene selectivity (△); polystyrene resin, 10 g.

an ethylene adsorbent with larger rate of adsorption. However, the ethylene selectivity (3.4) was smaller.

Adsorbents prepared from a polystyrene resin having tertiary amino groups and copper(I) chloride also selectively adsorbed ethylene. However, the adsorbents obtained with the use of polystyrene resins having either quaternary ammonium residues, carboxyl acid groups, iminodiacetic acid groups, or sulfonic acid groups, in place of the resins having amino groups, showed only poor activities as ethylene adsorbents with respect to both the amount of adsorbed ethylene and the selectivity. These results definitely show that complex formation of copper(I) chloride with amino residues is essential for the adsorption of ethylene by the present adsorbents. Ethylene is adsorbed by coordination to the copper(I) ion in the copper-amino complex.

In the adsorbents composed of the resins having amino groups and copper(I) chloride, some portion of the charged copper(I) chloride can form layers on the surface of the micropores of the resins. Thus, physical adsorption of saturated hydrocarbons on the surface of the resins is suppressed, especially in the presence of sufficient amount of copper(I) chloride (see Fig. 2). In the absence of copper(I) chloride, however, physical adsorption of ethane takes place more effectively than that of ethylene and the selectivity of ethylene adsorption is only 0.79.

In conclusion, selective adsorbents for ethylene were prepared from coppper(I) chloride and polystyrene resins having amino groups. These adsorbents are applicable to separation of ethylene from gas mixtures containing saturated hydrocarbons.

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