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SELECTIVE ABSORPTION OF ETHYLENE BY TOLUENE SOLUTION OF ALUMINIUM SILVER CHLORIDE

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Toluene solutions of aluminium silver chloride rapidly absorb ethylene from ethylene-nitrogen (0.94:0.06) mixture at 20 °C under 1 atm. The equilibrium molar ratio of absorbed ethylene to the charged silver chloride is 0.65. In contrast, the solutions show no measurable absorption of carbon monoxide under comparable conditions.

Ethylene, the most important and fundamental material in petrochemical industry, is usually obtained as gas mixtures with carbon monoxide, hydrogen, nitrogen, oxygen, methane, ethane, and carbon dioxide.[1] Thus, separation of ethylene from gas mixtures is necessary. A patent [2] claimed a method which took advantage of complex formations of ethylene with metal complexes. With the use of metal complexes, however, selective separation of ethylene from gas mixtures containing both ethylene and carbon monoxide is generally impossible, since the modes of coordination of these two kinds of gaseous molecules to metal ions are similar.[3] Zeolite-supported silver(I) or copper(I) ion adsorbed both ethylene and carbon monoxide.[4]

This paper reports that toluene solutions of aluminium silver chloride ($AgAlCl_4$) can be selective absorbents of ethylene. The solutions effectively absorb ethylene under mild conditions and in contrast show no absorption of carbon monoxide.

Aluminium chloride (kishida Chemical Co., guaranteed grade) was purified by sublimation. Silver chloride (Kojima Chemical Co., guaranteed grade) was used without further purification. Copper(I) chloride (Koso Chemical Co., guaranteed

grade) was reprecipitated from concentrated hydrochloric acid solution with water, followed by washing successively with ethanol and diethyl ether, and then was dried overnight in vacuo at 100 °C. Toluene was distilled after being dried over metallic sodium. Ethylene gas, nitrogen gas, and carbon monoxide gas, which had purities of 99.9, 99.999, and 99.95%, respectively, were passed through columns of molecular sieve 3A immediately before use.

Toluene solutions of aluminium silver chloride were prepared by incubating silver chloride and aluminium chloride in toluene under nitrogen at 50 °C for 4 h. The charged molar ratio of silver chloride to aluminium chloride was 1.0 unless otherwise noted.

Absorption of ethylene by the liquid absorbent, continuously stirred with a magnetic stirrer, from 2980 cm^3 of ethylene-nitrogen mixture (total pressure: 1 atm; the partial pressures of ethylene and nitrogen: 0.94 and 0.06 atm, respectively) was followed by reading the uptake of ethylene with a gas burette. During the first 3 min, the ethylene-nitrogen mixture was made to flow over the absorbent by use of a gas pump. Absorption of carbon monoxide was investigated in the same way as above.

Both in the preparation of the toluene solutions of aluminium silver chloride and in the measurements of their gas absorbing

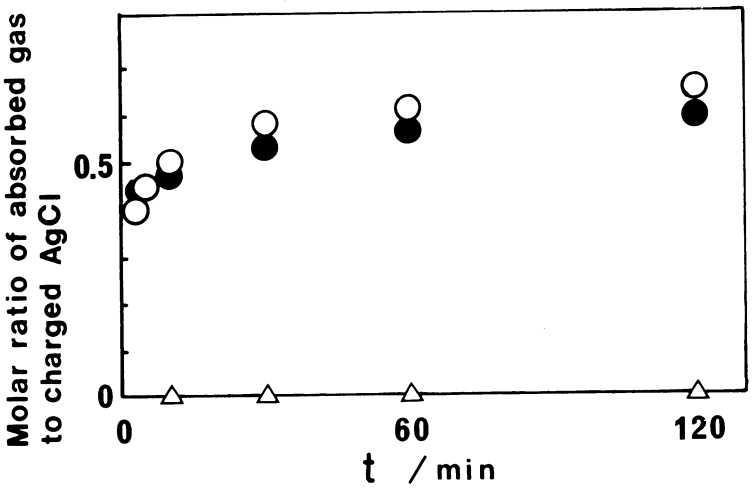

Fig. 1. Absorption of ethylene at 20 °C under 1 atm by the toluene solution of aluminium silver chloride: the first absorption (○) from ethylene-nitrogen (0.94 : 0.06) mixture; the second absorption (●) by the absorbent which was subjected to 111 °C under 1 atm to release the absorbed ethylene; the absorption of carbon monoxide (△) from carbon monoxide-nitrogen (0.94 : 0.06) mixture; the absorbent was prepared from 7.93 g (55.3 mmol) of silver chloride, 7.38 g (55.3 mmol) of aluminium chloride, and 55 cm^3 of toluene.

activities, the apparatuses containing the solutions were wrapped with aluminium foil to shield from ambient light.

Open circles in Fig. 1 show the absorption of ethylene from 0.94:0.06 ethylene-nitrogen mixture at 20 °C under 1 atm by the toluene solution of aluminium silver chloride. The absorption is rapid and the amount of absorbed ethylene at 3 min is 40 mol% with respect to the charged silver chloride. The value at 120 min is 65 mol%, where an equilibrium is virtually attained.

The toluene solution of aluminium silver chloride, however, does not absorb carbon monoxide in a measurable amount from 0.94:0.06 carbon monoxide-nitrogen mixture, as shown by the triangles. Thus, the solution of aluminium silver chloride absorbs ethylene selectively.

This is markedly in contrast with the result that toluene solutions of aluminium copper(I) chloride ($AlCuCl_4$), prepared from copper(I) chloride, aluminium chloride, and toluene, absorbed both ethylene and carbon monoxide. The toluene solution of aluminium copper(I) chloride absorbed 178 mol% of ethylene with respect to the charged copper(I) chloride from 0.94:0.06 ethylene-nitrogen mixture at 23 °C under 1 atm for 120 min. The solution also absorbed 85 mol% of carbon monoxide to the charged copper(I) chloride on the contact with carbon monoxide at 20 °C under 1 atm for 60 min.

Release of absorbed ethylene from the toluene solution of aluminium silver chloride to the vapor phase was carried out by the elevation of temperature from 20 °C to 111 °C. In the following contact with 0.94:0.06 ethylene-nitrogen mixture, the solution rapidly absorbed ethylene. The time course of this absorption, shown by the closed circles in Fig. 1, almost perfectly superimposed the open circles for the first absorption.

A gas chromatography (Silicone OV-1 column, 1 m, 160 °C) on the toluene solution of aluminium silver chloride indicated that Friedel-Crafts reaction between the absorbed ethylene and toluene concurrently took place to some extent during the ethylene absorption-release cycles. The Friedel-Crafts reaction proceeded mostly on the release of the absorbed ethylene, which was effected at 111 °C. The rate of the reaction was highly dependent on the charged molar ratio of silver chloride to aluminium chloride. At the charged molar ratio 1.0, 17% of the absorbed ethylene reacted with toluene in each of the cycles, yielding ethyltoluene. At the charged molar ratio 1.1, however, the reaction was largely

suppressed and only 6% of the absorbed ethylene reacted with toluene. Thus, the Friedel-Crafts reaction is attributable to the catalysis by free aluminium chloride existing in the solution in an equilibrium. A possibility that aluminium silver chloride itself exhibits catalytic activity is ruled out.

Absorption of ethylene by the toluene solution of aluminium silver chloride involves replacement of toluene, originally coordinating to the silver(I) ion,[5] with ethylene. Carbon monoxide is not absorbed by the solution, since it can not effectively repel the toluene from the silver(I) ion due to weaker coordinating ability than ethylene.

In conclusion, toluene solutions of aluminium silver chloride show prompt absorptions of ethylene and no measurable absorptions of carbon monoxide. Selective separation of ethylene from gas mixtures containing both ethylene and carbon monoxide is possible with the use of these solutions.

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