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WATER-RESISTANT CARBON MONOXIDE ABSORBENTS COMPOSED OF ALUMINIUM COPPER(I) CHLORIDE AND TWO-AROMATIC RING-COMPOUNDS

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Solutions composed of aluminium copper(I) chloride and 1,3-diphenylpropane, 1,2-diphenylethane, diphenyl ether or styrene oligomer rapidly absorbed carbon monoxide at 60-70 °C under 1 atm ($CO:N_2$=0.94:0.06). The absorbing power of the solutions remained unchanged even after the contacts with a nitrogen gas containing 10 mol% water to the charged copper(I) chloride.

It is important to separate carbon monoxide, a chief material for one carbon chemistry, from a gas mixture with hydrogen, nitrogen, oxygen, methane, carbon dioxide, and water. One of the proposed separating processes for carbon monoxide takes advantage of complex formation of aluminium copper(I) chloride ($AlCuCl_4$) with carbon monoxide in toluene.[1] However, the aluminium copper(I) chloride reacts with water in a gas mixture, resulting in irreversible decrease of the carbon monoxide absorbing power of the toluene solution.

In previous papers,[2,3] water-resistant absorbents for carbon monoxide in liquid and solid forms were prepared by protection of aluminium copper(I) chloride with linear polystyrene and cross-linked polystyrene resin, respectively.

In this paper, it will be shown that the carbon monoxide absorbents composed of aluminium copper(I) chloride and some two-aromatic ring-compounds as solvents are stable against gaseous water.

Aluminium chloride (Kishida Chemical Co., guaranteed grade) was purified by sublimation. Copper(I) chloride (Koso Chemical Co., guaranteed grade) was reprecipitated from a concentrated hydrochloric acid solution with distilled water, followed by washing successively with ethanol and ethyl ether, and then dried overnight in vacuo at 100 °C.

1,3-Diphenylpropane was prepared from 1,3-diphenylpropanone according to the literatures.[4,5] Biphenyl, diphenylmethane, 1,2-diphenylethane, diphenyl ether, and diphenylmethanol were obtained from Tokyo Kasei Kogyo Co., Ltd., and were used without further purification. Styrene oligomer (number-averaged degree of polymerization 4) was purchased from Toyo Soda Manufacturing Co., Ltd. Toluene was distilled after being dried over metallic sodium. Carbon monoxide gas and nitrogen gas, which had the purities of 99.95 and 99.999%, respectively, were passed through columns of molecular sieve 3A immediately before use.

The carbon monoxide absorbents were prepared by incubating copper(I) chloride, aluminium chloride, and aromatic solvent (molar ratio; 1:1:1) in a 100 ml flask under nitrogen at 50-80 °C for 4 h.

The absorption of carbon monoxide by the absorbent at 60 or 70 °C, continuously stirred with a magnetic stirrer, from 2980 ml of carbon monoxide / nitrogen mixture (total pressure: 1 atm; the initial partial pressures of carbon monoxide and nitrogen: 0.94 and 0.06 atm, respectively) was followed by measuring the uptake of carbon monoxide with a gas burette. The release of carbon monoxide from the absorbent was effected by heating the absorbent under atmospheric pressure.

The contacts of the absorbents with water were effected by circulating 10 liters of nitrogen gas, which had the total pressure of 1 atm and contained 10 mol% water to the charged copper(I) chloride, on the magnetically stirred absorbents for 10 min at 60 or 70 °C (the same temperature as that used for the absorption of carbon monoxide). The nitrogen / water mixture was prepared by introduction of water into an evacuated vessel of 10 liters using a microsyringe, followed by the addition of dry nitrogen gas in an amount required to make total pressure 1 atm.

Figure 1 depicts the absorption of carbon monoxide by the 1,3-diphenylpropane solution of aluminium copper(I) chloride. As shown by the open circles, the liquid absorbent rapidly absorbs

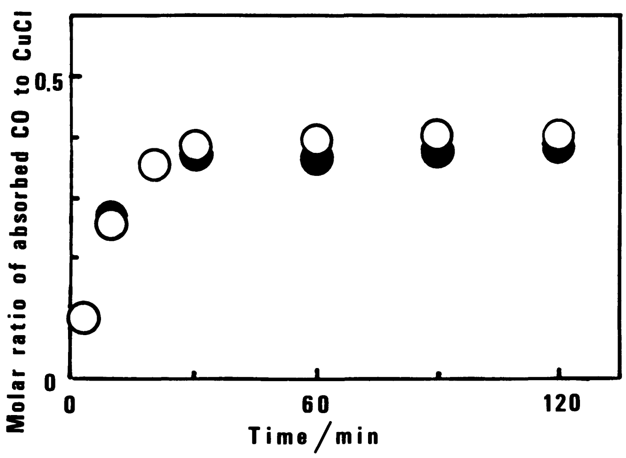

Fig. 1. Absorption of carbon monoxide by the solution composed of 5.0 g (51 mmol) of copper(I) chloride, 6.7 g (50 mmol) of aluminium chloride, and 11 ml (51 mmol) of 1,3-diphenylpropane at 60 °C: before contact of the absorbent with 10 mol% water to the charged copper(I) chloride (○); after the contact (●). Initial volume of the gas mixture: 2980 ml. Initial partial pressures of carbon monoxide and nitrogen: 0.94 and 0.06 atm, respectively.

carbon monoxide at 60 °C and the equilibrium amount of absorbed carbon monoxide is 40 mol% with respect to the charged copper(I) chloride.

On the elevation of the temperature from 60 °C to 121 °C, the absorbed carbon monoxide was released to the vapor phase.

Closed circles in Fig. 1 show the absorption of carbon monoxide after the contact of the absorbent at 60 °C with a nitrogen gas containing 10 mol% water to the charged copper(I) chloride (water content: 13800 ppm). The absorbing power is virtually identical with the value prior to the contact with gaseous water.

Table 1 shows the equilibrium amount of carbon monoxide absorbed by the absorbent composed of aluminium copper(I) chloride and various aromatic solvents, before and after the contact with a nitrogen gas containing 10 mol% water with respect to the charged copper(I) chloride. All the absorbents are homogeneous throughout the absorption and desorption. The amount of the desorbed carbon monoxide was identical with that of absorbed carbon monoxide within experimental error for all the absorbents. In the case using 1,2-diphenylethane, diphenyl ether, or styrene oligomer as solvent, the absorbing power is not decreased by the contact with gaseous water, similarly as described above for the 1,3-diphenylpropane solution. These results are markedly in contrast with the fact that a toluene solution of aluminium copper(I) chloride

Table 1. Effect of water on the activity of the carbon monoxide absorbent composed of aluminium copper(I) chloride and aromatic solvent

Solvent	Absorption conditions		Equilibrium molar ratio of absorbed CO to CuCl	
	Temp/ °C	P_{CO}/atm	before[a)]	after[b)]
1,3-Diphenylpropane	60	0.94	0.40	0.38
1,2-Diphenylethane	70	0.94	0.27	0.28
Diphenylmethane	70	0.94	0.29	0.24
Biphenyl	70	0.94	0.40	0.33
Diphenyl ether	60	0.94	0.33	0.33
Styrene oligomer	70	1	0.30	0.32
Toluene	70	0.94	0.41	0.32
Toluene	20	0.8	0.68	0.51

a) Before contact with 10 mol% water to the charged copper(I) chloride; contact with gaseous water was made at the same temperature as that of carbon monoxide absorption.

b) After the contact with water.

rapidly loses its absorbing power on the contact with gaseous water. Thus, the use of aromatic solvents possessing two aromatic rings or more is definitely essential for the absorbents to exhibit water resistance. This is consistent with the previous results showing the protection of aluminium copper(I) chloride with polystyrene in toluene against water.[2)]

In spite of virtually no effect of water on the activity of the absorbents with 1,2-diphenylethane and 1,3-diphenylpropane, the activity of the absorbent with diphenylmethane as solvent slightly decreased on the contact with water. The decrease of the activity for the absorbent with biphenyl was still larger. These results indicate importance of the carbon chains between the two aromatic rings in the two-aromatic ring-compounds for the water resistance of the absorbents.

A homogeneous absorbent was not prepared by using diphenylmethanol as solvent, probably due to the reaction of the hydroxyl group of diphenylmethanol with aluminium copper(I) chloride.

All the two-aromatic ring-compounds used here possess higher boiling points than that of toluene. Thus, the present absorbents are available for separation of carbon monoxide at high temperatures where a toluene solution of aluminium copper(I) chloride is hard to be used.

In the absorbents, the two-aromatic ring-compounds probably take a conformation in which one of the two aromatic rings interacts with the copper(I) ion in an aluminium copper(I) chloride and the other one interacts with the aluminium chloride moiety in the same complex salt. The aluminium copper(I) chloride is protected against water by the two aromatic rings. This argument is supported by the fact the carbon chains between the two aromatic rings are necessary for the sufficient water resistance, since they are required for the two-aromatic ring-compounds to take the conformation. The water resistance of the absorbent with diphenyl ether is associated with some interaction between the ether oxygen atom and aluminium copper(I) chloride.

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