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MACROMOLECULE-METAL COMPLEXES FOR GAS SEPARATION

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ABSTRACT

Macromolecule-copper(I) chloride complexes have been prepared for the separation of carbon monoxide and ethylene from gas mixtures with hydrogen, nitrogen, carbon dioxide, methane, and water. A toluene solution of a polystyrene-aluminum copper(I) chloride complex can separate carbon monoxide selectively and retains this function even on contact with gas containing water. Strong charge-transfer absorption bands have been found in the 380-500 nm region for the toluene solution of polystyrene-aluminum copper(I) chloride complex. A solution of 1,3-diphenylpropane-aluminum copper(I) chloride complex also exhibits similar absorption bands. A continuous variation plot using the chemical shift change in ^{13}C -NMR shows a 1 : 1 interaction between 1,3-diphenylpropane and aluminum copper(I) chloride. These results suggest a two-way interaction between the adjacent phenyl groups of polystyrene and aluminum copper(I) chloride. A resin bead of crosslinked polystyrene-aluminum copper(I) chloride complex has been prepared as a solid adsorbent. The water resistance of the solid macromolecular complex depends on the nature of the solvent used in the preparation of the solid adsorbent. Carbon disulfide is a suitable solvent. A selective adsorbent of ethylene has been prepared from a macroreticular polystyrene resin with primary and secondary amino groups and

copper(I) chloride. The selectivity of ethylene against ethane and that of carbon monoxide against carbon dioxide increase with an increasing amount of supported copper(I) chloride.

INTRODUCTION

In industry, carbon monoxide (CO) is usually produced as a gas mixture with hydrogen, nitrogen, methane, carbon dioxide, and other gaseous compounds. Ethylene is also obtained, in most cases, as a gas mixture with carbon monoxide, hydrogen, nitrogen, oxygen, methane, ethane, carbon dioxide, etc. The gas mixtures are usually saturated with water. A toluene solution of aluminum copper(I) chloride (AlCuCl_4) was used for the separation of carbon monoxide from such gas mixtures [1]. However, the water content in the feed gas for this process must be reduced below 1 ppm by pretreatment [2].

In the present paper, the protecting effect of polystyrene for aluminum copper(I) chloride against water is investigated with respect to the interaction of metal complexes with macromolecules. A complex of copper(I) chloride with crosslinked polystyrene containing amino groups for the selective separation of ethylene is also described.

EXPERIMENTAL

Preparation of Complex Solutions

The complex solution of aluminum copper(I) chloride was prepared by incubating copper(I) chloride, aluminum chloride, and polystyrene or related aromatic compounds in the corresponding solvents between room temperature and 50°C for 4 h under nitrogen [3]. The molar ratio of copper(I) chloride to aluminum chloride was kept at 1.0.

Preparation of Complex Solids

The complex of aluminum copper(I) chloride with crosslinked polystyrene as a solid CO-adsorbent was prepared by refluxing aluminum chloride, copper(I) chloride, and the macroreticular-type polystyrene resin in carbon disulfide, dichloromethane, toluene, or benzene under dry nitrogen. After 6 h the solvents were removed from the mixtures by evaporation at 4 mmHg for 4–6 h [4, 5].

The complex of copper(I) chloride with crosslinked polystyrene having amino groups as a solid ethylene adsorbent was prepared by stirring copper(I) chloride and a macroreticular-type polystyrene resin containing

primary and secondary amino groups in a 1 : 1 acetonitrile-water mixture at 20°C for 4 h, and then the liquid phase was removed at 5 mmHg, 80°C [6].

RESULTS AND DISCUSSION

Carbon Monoxide Absorbing and Releasing Capacities of Complex Solutions

The AlCuCl_4 complex solution composed of copper(I) chloride (20 mmol), aluminium chloride (20 mmol), and toluene (20 mL) absorbed carbon monoxide rapidly from 8 : 2 carbon monoxide/nitrogen mixture at 20°C and 1 atm. In 30 min the molar ratio of absorbed carbon monoxide to the admitted CuCl reached 0.70. The absorbed carbon monoxide was released in 5 min at 90°C. After contact with 5 L nitrogen containing 2 mmol water [corresponding to 10 mol% of the admitted copper(I) chloride], the carbon monoxide absorbing capacity decreased by 20%.

A polystyrene- AlCuCl_4 complex solution composed of copper(I) chloride (20 mmol), aluminum chloride (20 mmol), polystyrene (number-average degree of polymerization 420; 20 meq), and toluene (20 mL) exhibited almost the same carbon monoxide absorbing and releasing capacities [7]. Both the rate of absorption and the equilibrium value of the absorbed carbon monoxide after contact with the nitrogen gas containing water (10 mol% to admitted CuCl) were identical with those prior to the contact. Thus, the water showed no measurable deactivation effect on the polystyrene- AlCuCl_4 complex solution.

Interaction of Polystyrene with Metal Complex

The equimolar mixture of copper(I) chloride and aluminum chloride became homogeneous on being stirred in toluene at 50°C for 10–30 min, indicating formation of aluminum copper(I) chloride. The aluminum copper(I) chloride molecule in toluene has been proposed to have a structure with two chlorine bridges between one aluminum atom and one copper atom based on the result of ^{27}Al -NMR spectroscopy [8].

The toluene solution of aluminum copper(I) chloride and polystyrene exhibits a strong charge-transfer band in the 380–500 nm region, as shown by the solid line in Fig. 1. The charge-transfer band has two peaks at 370–380 and 460 nm. In contrast, benzene [9] and toluene solutions of aluminum copper(I) chloride without polystyrene shows a very weak charge-transfer band around 370–380 nm, and no band is observed at a wavelength longer than 400 nm.

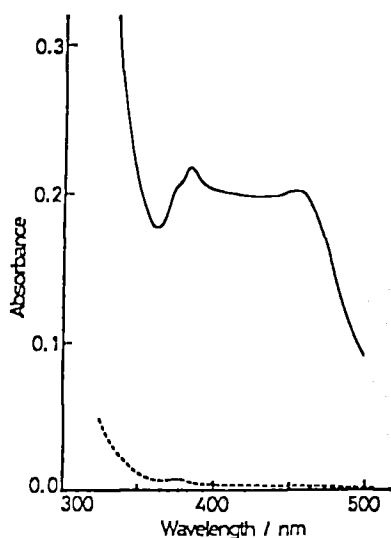


FIG. 1. Electronic absorption spectra of toluene solutions of AlCuCl_4 (dashed line) and of polystyrene- AlCuCl_4 (solid line); $[\text{AlCuCl}_4] = 0.63 \text{ mol/L}$, $[\text{polystyrene}] = 0.63 \text{ phenyl residue mol/L}$; cell length, 1 mm.

A 1,3-diphenylpropane solution of the aluminum copper(I) chloride complex exhibits a strong absorption band similar to that of the polystyrene- AlCuCl_4 solution [10]. On the other hand, both 1,2-diphenylethane and 1,4-diphenylbutane solutions of aluminum copper(I) chloride do not have such strong charge-transfer bands. Consequently, the strong charge-transfer interaction with aluminum copper(I) chloride requires two phenyl groups connected to each other by the linkage of three methylenes. Thus, 1,3-diphenylpropane is found to be a suitable monomer-model for the styrene in the macromolecule-metal complex.

Interaction of Diphenylpropane with Metal Complex

The chemical shift of carbon atoms of 1,3-diphenylpropane in 1,2-dichloroethane changed on the addition of aluminum copper(I) chloride [8]. The chemical shifts of phenyl carbons at the meta and para positions shifted to higher magnetic fields, while those of other carbons of phenyl group and methylene groups shifted toward lower magnetic fields.

A continuous variation plot using the chemical shift changes of the

meta and para carbons clearly indicates a 1 : 1 interaction between 1,3-diphenylpropane and aluminum copper(I) chloride in 1,2-dichloroethane, as shown in Fig. 2.

The equilibrium constant (K) for complex formation was determined by a curve-fitting method [11] by using the relations between the chemical shift and the concentration of aluminum copper(I) chloride. The changes in enthalpy ($-\Delta H$) and entropy ($-\Delta S$) for the complex formation of aluminum copper(I) chloride were also obtained by an Arrhenius plot of the equilibrium constants. As shown in Table 1, the equilibrium constant and the binding energy for AlCuCl_4 complex formation in 1,3-diphenyl-

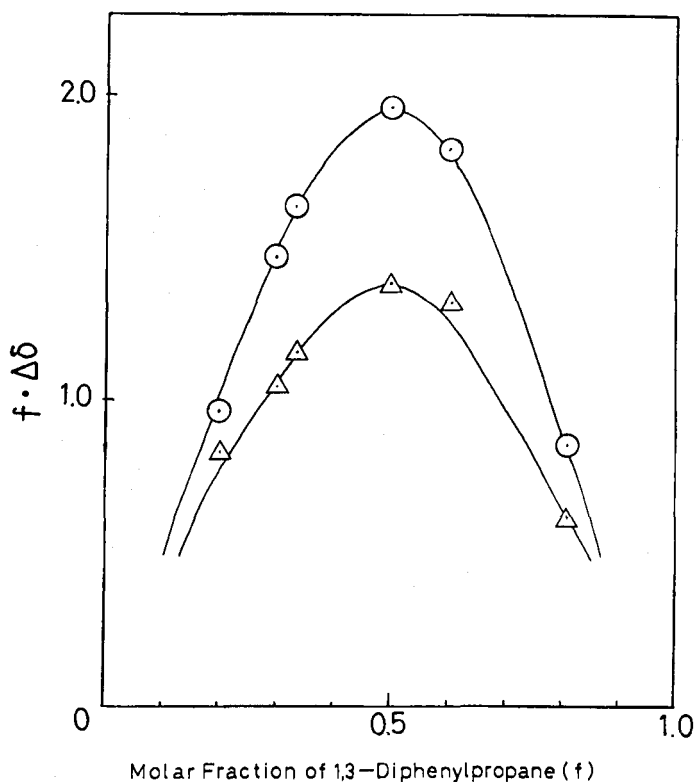


FIG. 2. Continuous variation plot for 1,3-diphenylpropane- AlCuCl_4 in 1,2-dichloroethane using chemical shift changes ($\Delta\delta$, ppm) of meta (Δ) and para (\circ) carbons of diphenylpropane; $[1,3\text{-diphenylpropane}] + [\text{AlCuCl}_4] = 0.2 \text{ mol/L}$.

TABLE 1. Equilibrium Constant at 273 K and Thermodynamic Parameters for Complex Formation between AlCuCl_4 and Aromatic Compound in 1,2-Dichloroethane

Aromatic compound	K , mol/L	$-\Delta H$, kJ/mol	$-\Delta S$, $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1,3-Diphenylpropane	167	16.3	16.5
Toluene	3.8	5.5	9.1

propane are much larger than those for AlCuCl_4 complex formation in toluene.

In consideration of all the results, the proposed structure of 1,3-diphenylpropane- AlCuCl_4 complex is shown in Fig. 3. A two-way interaction of 1,3-diphenylpropane with aluminum copper(I) chloride through π -coordination of two phenyl groups should be much stronger than a one-way interaction through one phenyl group.

The solution of the 1,3-diphenylpropane- AlCuCl_4 complex absorbed carbon monoxide selectively and was not deactivated by the water contained in the gas [12].

In conclusion, the proposed structure of the polystyrene- AlCuCl_4 complex is shown in Fig. 4. The two-way interaction between the adjacent phenyl groups of polystyrene and aluminum copper(I) chloride makes the complex formation effective, and the hydrophobic polystyrene chain may inhibit the approach of water to the metal complex.

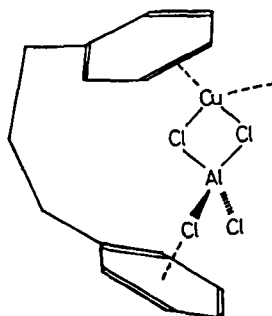


FIG. 3. Proposed structure of 1,3-diphenylpropane- AlCuCl_4 complex.

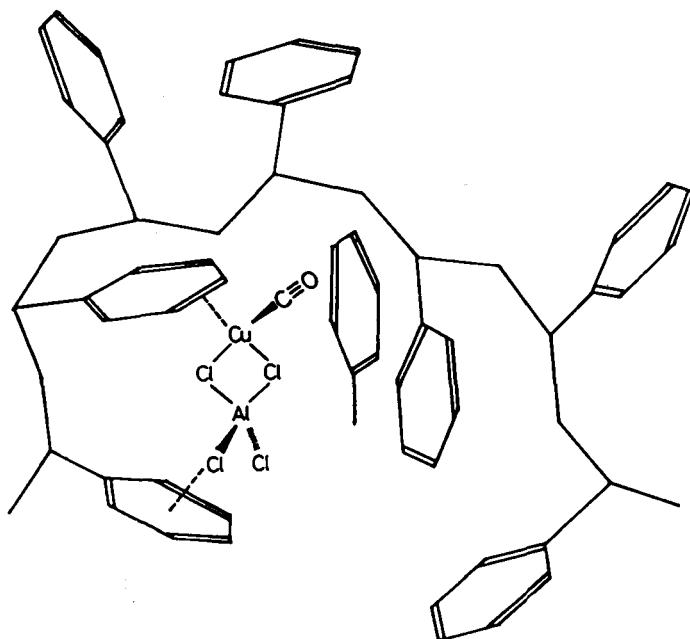


FIG. 4. Proposed structure of polystyrene-AlCuCl₄ complex.

Crosslinked Polystyrene-Metal Complex

The crosslinked polystyrene-AlCuCl₄ complex solid exhibited rapid and reversible adsorption of carbon monoxide [13]. For the complex solid prepared by using carbon disulfide as solvent, the equilibrium molar ratio of adsorbed CO to admitted CuCl was 1.07 at 25°C and 1 atm [14]. Desorption of carbon monoxide was carried out at 7 mmHg, 20°C for 10 min. The equilibrium molar ratio of adsorbed CO to the admitted CuCl in the second adsorption was 0.54. In subsequent adsorptions, the equilibrium molar ratios were constant at 0.54.

The absorbing capacities of the complex solids prepared by the use of carbon disulfide and dichloromethane remained virtually unchanged after repeated contacts of the adsorbents with nitrogen gas containing 10 mol% water with respect to the admitted CuCl. The complex solids obtained with the use of benzene and toluene as preparation solvents, however, exhibited small but gradual decreases in the adsorbing capacities on repeated contact with nitrogen gas containing water [14].

Scanning electron microscopy (SEM) and energy dispersive x-ray microanalysis on the cross-section of the beads of the complex solids were carried out. In beads of the complex solid prepared by the use of toluene, Al atoms exist largely on or near the surface of the bead, and a number of crystalline deposits are observed in the inner portion of the bead, as shown in Fig. 5(a). In the beads of the complex solid obtained with the use of carbon disulfide, Al atoms distributed uniformly in the cross-section of the bead, and no crystalline deposits are seen in the whole cross-section, as shown in Fig. 5(b). Obviously, benzene and toluene compete with the phenyl groups of the polystyrene and prevent effective bonding of aluminum copper chloride.

Crosslinked Polystyrene with Amino Group–Metal Complex

The complex of a macroreticular-type polystyrene resin (Fig. 6) containing primary and secondary amino groups and copper(I) chloride exhibits rapid and reversible adsorptions of ethylene [6] and carbon monoxide [15].

Figure 7 shows plots of the amounts of adsorbed ethylene and ethane as a function of the supported amount of copper(I) chloride. In these

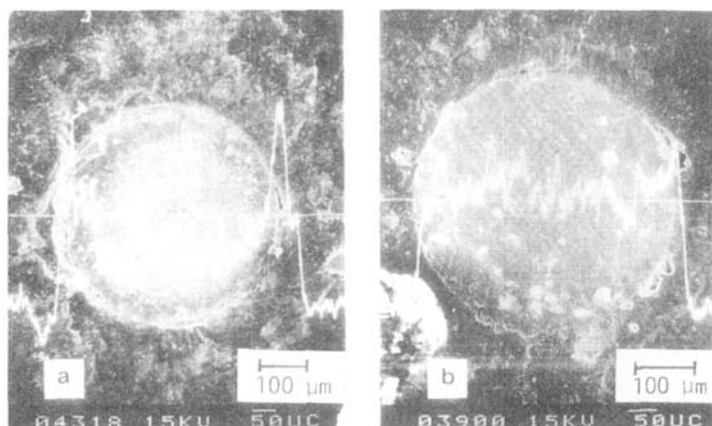


FIG. 5. SEM photographs and Al atom distribution for the cross section of the CO-adsorbent beads prepared from the macroreticular-type polystyrene resin, AlCl_3 , and CuCl by use of toluene (a) and carbon disulfide (b) as solvent.

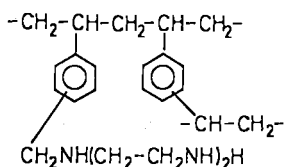


FIG. 6. Polystyrene with primary and secondary amino groups in macroreticular-type resin.

examples the amount of the polystyrene resin containing primary and secondary amino groups was kept constant at 10 g. The amount of adsorbed ethylene increases with an increasing amount of the supported CuCl. In contrast, the amount of ethane adsorbed decreases with an increasing amount of copper(I) chloride. As a result, the selectivity for ethylene adsorption, defined as the ratio of the amount of adsorbed ethylene to adsorbed ethane, significantly increases as the supported amount of copper(I) chloride increases.

The adsorbent efficiently adsorbs ethylene by coordination of ethylene to the copper(I) ions in the complexes between copper(I) chloride and the amino residues of the polystyrene resin. The amounts of copper(I) chlo-

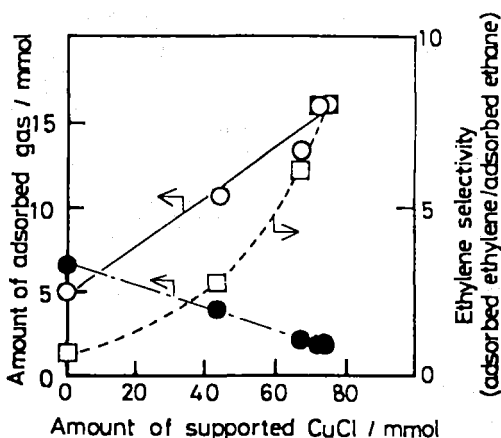


FIG. 7. Dependence of adsorbing capacity on the supported amount of CuCl for the adsorbent composed of CuCl and polystyrene resin with primary and secondary amino groups: ethylene adsorption (○), ethane adsorption (●), and ethylene selectivity (□); resin, 10 g, with adsorption at 20°C, 1 atm.

ride supported on the polystyrene resin containing amino groups in the present adsorbents were larger than the ion-exchange capacity (38 mmol) of 10.0 g of the resin. Considerable amounts of copper(I) chloride were supported on the resin without the formation of complexes with amino residues of the resin. These CuCl molecules were connected by chloride bridges to each other and with the CuCl molecules, which were complexed to the amino residues of the resin, resulting in the formation of layers of copper(I) chloride on the surface of the micropores of the resin [15]. Thus, the physical adsorption of ethane on the surface of the resin is suppressed by the layers of copper(I) chloride formed on the surface of the micropores.

As shown in Table 2, this present adsorbent also adsorbs carbon monoxide selectively in mixtures containing carbon dioxide, whereas the resin itself without copper(I) chloride adsorbs exceedingly larger amounts of carbon dioxide through both chemical and physical adsorption. The chemical adsorption of carbon dioxide due to interaction with the amino groups of the resin is inhibited by the formation of a complex between the amino groups and copper(I) chloride. The physical adsorption of carbon dioxide on the surface of the resin is also suppressed by the layers of copper(I) chloride formed on the surface of the micropores.

TABLE 2. Adsorbing Capacity of the Adsorbent Composed of CuCl (70 mmol) and Polystyrene Resin with Amino Group (10 g)

Gas	Adsorbing capacity, mmol	
	Adsorbent	Resin without CuCl
Methane	0.1	0.1
Ethylene	15.1	4.9
Ethane	1.9	6.7
Propylene	9.9	8.1
Propane	2.8	7.6
Carbon monoxide	15.8	0.1
Carbon dioxide	2.3	13.5
Hydrogen	0.1	—
Nitrogen	0.1	—
Argon	0.1	—

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