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Polymer-Protected Metal Complex for Gas Separation. I. A Solution of Polystyrene-Protected Aluminium Copper(I) Halide as Water-Resistant Carbon Monoxide Absorbent

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Carbon monoxide absorbents composed of linear polystyrene (PSt), aluminium halide, copper(I) halide, and toluene are prepared. The toluene solutions of polystyrene-protected aluminium copper(I) chloride (PSt-$AlCuCl_4$) rapidly absorb CO at 20 °C under 1 atm (initial partial pressure of CO: 0.90 atm) and the equilibrium molar ratio of absorbed CO to the charged CuCl is 0.78. On the elevation of the temperature from 20 °C to 82 °C under 1 atm, the absorbed CO is released completely. The absorption-release cycles are repeated many times without measurable decrease in the absorbing capacity. The CO absorbing capacities of toluene solutions composed of aluminium halides, copper(I) halides, and polystyrene decrease as follows: $AlCl_3$–CuCl system> $AlBr_3$–CuBr system≫AlI_3–CuI system=0. The CO absorbing activity of the toluene solution of PSt-$AlCuCl_4$ remains virtually unchanged on the contact of the solution with nitrogen gas containing 10 mol% water to the charged CuCl (water content: 9000 ppm), when the molar ratio of phenyl residue of polystyrene (number-averaged degree of polymerization: 420, 50, or 4.0) to $AlCuCl_4$ is unity or larger. This result is markedly in contrast with the fact that the activity of the toluene solution of $AlCuCl_4$ without polystyrene significantly (25%) decreases on the contact.

The importance of carbon monoxide (CO) as one of chief raw materials in chemical industry is increasing.[1,2] Carbon monoxide is usually produced as gas mixtures with nitrogen, hydrogen, oxygen, methane, carbon dioxide, and water[3] by steam reforming of hydrocarbons, partial oxidation processes, and coal gasification. Thus, separation of CO from gas mixtures is significant.

Copper liquor and cryogenic separation processes are known as CO separation methods.[3] Recently, a separating process using an absorbent, which takes advantage of selective complex formation of a double salt, aluminium copper(I) chloride ($AlCuCl_4$), with CO in toluene, has been proposed.[4] With this absorbent, CO is separated under mild conditions and the absorbent is stable against oxygen and carbon dioxide.[4,5] However, the CO absorbing activity of the absorbent rapidly and irreversibly decreases on the contact with gas mixture containing water, since $AlCuCl_4$ vigorously reacts with water as follows.[6,7]

$$H_2O + 2AlCuCl_4 \longrightarrow HCl + AlCuCl_4Al(OH)Cl_2 + CuCl \qquad (1)$$

$$AlCuCl_4Al(OH)Cl_2 \xrightarrow{\Delta} HCl + AlCuCl_4AlOCl \qquad (2)$$

Thus, the water content in feed gas mixtures must be reduced to 1 ppm or less by pretreatment for CO separation in industry.[4]

In a preliminary communication,[8] the authors showed that a solution composed of linear polystyrene (PSt), copper(I) chloride (CuCl), aluminium chloride ($AlCl_3$), and toluene reversibly absorbed CO under mild conditions and in addition was stable against water vapor.

This paper reports the results of detailed study on the toluene solutions of polystyrene-protected $AlCuCl_4$ (PSt-$AlCuCl_4$). The effects of the degree of polymerization and the amount of polystyrene on the water resistivity are revealed. The CO absorbing activities of the absorbents composed of $AlCuCl_4$ and other polymers are also shown. Furthermore, the infrared spectra of the PSt-$AlCuCl_4$ complex in the presence and the absence of CO are presented. The mechanism of protection of $AlCuCl_4$ by polystyrene in the CO absorbents is discussed.

Experimental

Materials. Linear polystyrene, purchased from Wako Pure Chemical Co. or prepared in toluene by use of benzoyl peroxide as initiator, was reprecipitated using the chloroform–methanol system and was dried in vacuo for 12 h at 60 °C. The number-averaged degrees of polymerization (DP_n) of these polystyrenes were 420 and 50, respectively, as estimated from the number-averaged molecular weight (M_n) and weight-averaged molecular weight (M_w): M_n=4.4×10^4 and M_w=1.5×10^5 for the first polystyrene, and M_n=5.2×10^3 and M_w=1.2×10^4 for the second one. The molecular weights were determined by gel permeation chromatography using columns of TSK-GEL, G5000H+G3000H, Toyo Soda Manufacturing Co. Styrene oligomer of DP_n 4.0, which contained oligomers of degrees of polymerization 2, 3, 4, 5, 6, 7, and 8 in 16, 27, 23, 16, 10, 5, and 3 mol%, respectively, was obtained from Toyo Soda Manufacturing Co.

Poly[oxy(2,6-dimethyl-1,4-phenylene)], M_n=3.2×10^4 and M_w=2.4×10^5, and polybutadiene (45% vinyl and 55% *cis* and *trans*-1,4), M_n=4.5×10^3, respectively, were purchased from Scientific Polymer Products and Aldrich Chemical Co. Styrene-butadiene block copolymer composed of 41.6 wt% styrene part and 58.4 wt% butadiene part and hydrogenation product (Kraton-G 1650) of styrene-butadiene block copolymer composed of 30 wt% of styrene part and 70 wt%

of butadiene part were obtained from Asahi Chemical Industry Co. and Shell Co., respectively. Alternating copolymer of styrene and methyl methacrylate was prepared by photopolymerization in the presence of boron chloride.[9]

Aluminium chloride (Kishida Chemical Co.) was purified by sublimation. Copper(I) chloride (Koso Chemical Co.) was reprecipitated from an aqueous concentrated hydrochloric acid solution by the addition of distilled water, followed by washing successively with ethanol and diethyl ether, and then dried overnight in vacuo at 100 °C. Aluminium bromide, copper(I) bromide, aluminium iodide, and copper(I) iodide were commercially (guaranteed grades) obtained and were used without further purification. Titanium(IV) chloride and tin(IV) chloride were purified by distillation.

Toluene and benzene were distilled after being dried over metallic sodium. Chlorobenzene was dried over diphosphorus pentaoxide and was distilled.

Carbon monoxide and nitrogen gas, which had the purities of 99.95 and 99.999%, respectively, were passed through columns of molecular sieves 3A immediately before use.

Preparation of CO Absorbents. Carbon monoxide absorbents were prepared by heating polymer, aluminium halide, copper(I) halide, and aromatic solvent at 50 °C for 4 h. The charged molar ratio of CuCl to $AlCl_3$ was kept constant at unity unless otherwise noted.

For example, the preparation procedure for toluene solution of PSt–$AlCuCl_4$ was as follows. 2.08 g (20 mequiv in phenyl residue) of linear polystyrene, 2.67 g (20 mmol) of $AlCl_3$, 1.98 g (20 mmol) of CuCl, and 20 cm^3 (192 mmol) of toluene were placed in a 100 cm^3 flask and were heated at 50 °C for 4 h under dry nitrogen with stirring by use of a magnetic stirrer. The nitrogen in the flask was several times replaced with fresh dry nitrogen during the preparation.

Toluene solution of $AlCuCl_4$ without polystyrene was prepared in a similar manner as above, except for the absence of polystyrene.

Absorption and Release of CO. The absorption of CO by the absorbent, continuously stirred by use of a magnetic stirrer, from CO–N_2 mixture (the total pressure: 1 atm) was carried out at room temperature under 1 atm using the apparatus depicted in Fig. 1. The amount of absorbed CO was determined at room temperature under 1 atm by a gas burette (6) using toluene as leveling liquid (7). During the first 10 min, the CO–N_2 mixture was made to flow over the absorbent (1), stirred magnetically in the flask, by a gas-circulating pump (5) (Iwaki Co., BA-106TN). The initial partial pressure of CO was in the range of 0.8 to 1.0 atm and the decrease of the partial pressure of CO during CO absorption was at most 0.07 atm.

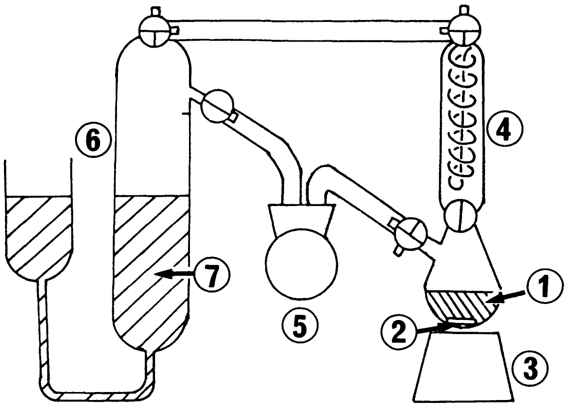

Fig. 1. Apparatus for measuring the amount of carbon monoxide absorbed by the absorbents or released from them; 1: CO absorbent, 2: rotor, 3: magnetic stirrer, 4: Dimroth condenser, 5: gas-circulating pump, 6: gas burette, 7: leveling liquid (toluene).

The release of CO from the absorbent was accomplished by heating the absorbent and the amount of released CO was determined by the gas burette ((6) in Fig. 1). Toluene vapor, produced from the absorbent on heating, was refluxed by a Dimroth condenser (4). After CO was released, the absorbent was cooled to room temperature under dry nitrogen, and then the second absorption by the absorbent was carried out by the same method as described above.

Contact of the Absorbent with Water Vapor. The contact of the absorbent with water vapor was effected by circulating 5000 or 10000 cm^3 of N_2 gas, containing 10 mol% water to the charged CuCl, over the absorbent for 10 min by use of a gas-circulating pump. During the contact, the absorbent was continuously stirred using a magnetic stirrer (Fig. 1, (3)). The N_2 gas containing water vapor was prepared by the introduction of distilled water into 5000 or 10000 cm^3 of evacuated vessel using a microsyringe, followed by the addition of dry nitrogen in an amount required to make the total pressure atmospheric.

After the contact with water, the gas phase in the flask was replaced by dry nitrogen, and then the following CO absorption was carried out.

Infrared Spectroscopy. Infrared spectra were taken with a Japan Spectroscopic Co. Model A-3 recording spectrophotometer by use of a KBr cell. Specimens were toluene solutions of PSt–$AlCuCl_4$ before and after the contact with CO under atmospheric pressure for 1 h.

Results

Preparation of CO Absorbent. The color of polystyrene (PSt) immediately changed from white to orange when aluminium chloride, copper(I) chloride, linear polystyrene, and toluene were mixed in a flask. The toluene solutions were reddish brown in the early stage of the preparation, and gradually became dark brown.

The CO absorbents were thoroughly homogeneous at the charged molar ratio unity of CuCl to $AlCl_3$. When the charged molar ratio of CuCl was larger than unity, however, CuCl in excess precipitated as white to gray powder in the mixture. In all the CO absorbents described hereinafter, the charged molar ratios of copper(I) halides to aluminium halides were maintained at 1.0.

Toluene and benzene solutions of $AlCuCl_4$ without polystyrene were black and brown homogeneous solutions, respectively.

Chlorobenzene solutions of PSt-$AlCuCl_4$ were prepared from $AlCl_3$, CuCl, polystyrene, and chlorobenzene as homogeneous dark brown solutions. The charged molar ratio of phenyl residue in polystyrene to CuCl was 1.0. In the absence of polystyrene, however, considerable amounts of gray precipitates were formed under reddish brown solutions and homogeneous absorbents were not obtained.

Toluene solution of polystyrene-protected aluminium copper(I) bromide complex was prepared as homogeneous solution from aluminium bromide, copper(I) bromide, polystyrene, and toluene. In the case of polystyrene-protected aluminium copper(I) iodide complex in toluene, however, the resulting mixture was composed of precipitates and a reddish brown solution.

CO Absorbing and Releasing Activities of PSt-$AlCuCl_4$ Complex in Aromatic Solvents. Figure 2 shows the absorption of CO at 20 °C under 1 atm by the absorbent composed of 0.96 g (7.2 mmol) of $AlCl_3$, 0.72 g (7.3 mmol) of CuCl, 0.67 g, (6.4 mequiv in phenyl residue) of linear polystyrene (DP_n: 420), and 10 cm^3 (96 mmol) of toluene. As depicted by the open circles, the absorbent rapidly absorbs CO and the equilibrium molar ratio of the absorbed CO to the charged CuCl is 0.85. On the elevation of the temperature of the absorbent from 20 °C to 82 °C, almost all the absorbed CO is released in 5 min from the absorbent to the vapor phase.

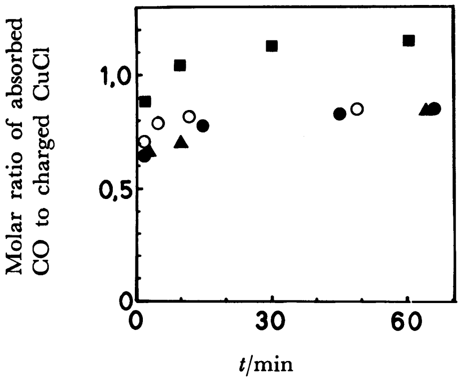

Fig. 2. Absorption of carbon monoxide at 20 °C under 1 atm by toluene or chlorobenzene solutions of polystyrene-$AlCuCl_4$: The first absorption by the toluene solution (○), the second absorption by the toluene solution which was heated to 82 °C to release CO after the first absorption (●), the third absorption by the toluene solution (▲); the first absorption by the chlorobenzene solution (■); For the toluene solution, $[AlCl_3]_0=[CuCl]_0=0.73$ and [phenyl residue of polystyrene (DP_n: 420)$]_0=0.64$ mol dm^{-3} in 10 cm^3 of toluene, and the initial $P_{CO}=1.0$ atm. For the chlorobenzene solution, $[AlCl_3]_0=[CuCl]_0=$ [phenyl residue of polystyrene (DP_n: 420)$]_0=1.0$ mol dm^{-3} in 22 cm^3 of chlorobenzene, and the initial volume of the gas mixture is 3000 cm^3 with initial pressures of CO and N_2, 0.9 and 0.1 atm, respectively.

In the second absorption, which is carried out after the cooling of the absorbent to 20 °C under dry nitrogen, the absorbent rapidly absorbs CO again as shown by the solid circles in Fig. 2. The equilibrium molar ratio of the absorbed CO to the charged CuCl is 0.85, which is exactly identical with the value (0.85) of the first absorption. The equilibrium molar ratio of the absorbed CO to the charged CuCl in the third absorption (the solid triangles) is also 0.85.

Table 1 shows the equilibrium molar ratios of the absorbed CO to the charged copper(I) halide for the various absorbents prepared from aluminium halides, copper(I) halides, polystyrene (DP_n: 420), and toluene. The absorbing capacities of the absorbents are as follows:

$AlCl_3$–CuCl system>$AlBr_3$–CuBr system ≫ AlI_3–CuI system=0.

Solid squares in Fig. 2 depict the absorption of CO by the chlorobenzene solution of PSt-$AlCuCl_4$ complex. The equilibrium molar ratio (1.15) of the absorbed CO to the charged CuCl is larger than the value (0.85) of the toluene solution even though the initial partial pressure of CO (0.9 atm) is smaller than the value (1.0 atm) for the toluene solution.

Effect of Water Vapor on CO Absorbing Activity of Toluene Solutions of PSt-$AlCuCl_4$ Complex. Open circles in Fig. 3 depict the absorption of CO from 1500 cm^3 of CO–N_2 mixture (initial partial pressure of CO: 0.80 atm) under 1 atm at 20 °C by the absorbent composed of 2.98 g (22.3 mmol) of $AlCl_3$, 2.22 g (22.4 mmol) of CuCl, 2.33 g (22.4 mequiv in phenyl residue) of polystyrene (DP_n: 420), and 15 cm^3 (144 mmol) of toluene. The absorption of CO is rapid and the equilibrium molar ratio of the absorbed CO to the charged CuCl is 0.71. On the elevation of the temperature from 20 °C to 95 °C,

Table 1. Molar Ratios of Equilibrium Amounts of the Absorbed CO to the Charged Copper(I) Halide for Toluene Solutions of Aluminium Halide (AlX_3) and Copper(I) Halides (CuX) with of without Polystyrene (PSt)[a]

Absorbent	Halogen (X)		
	Cl	Br	I
PSt-AlX_3–CuX	0.78	0.45	0.00
AlX_3–CuX	0.83	0.45	—

a) CO absorbing conditions; at room temperature under 1 atm; the initial volume of the gas mixture is 3000 cm^3 and the initial pressures of CO and N_2 are 0.9 and 0.1 atm, respectively; $[AlX_3]_0=[CuX]_0=$ [phenyl residue of polystyrene$]_0=1.0$ mol dm^{-3}; the subscript 0 is used to designate the charged concentration; number-averaged degree of polymerization of polystyrene: 420.

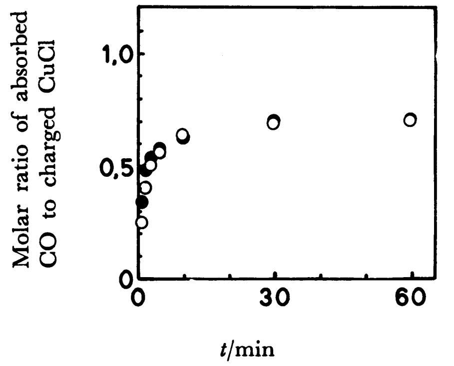

Fig. 3. Effect of water vapor on the CO absorbing activity of toluene solution of polystyrene–$AlCuCl_4$; the first absorption (○); the second absorption after the contact of the solution with 10 mol% water to the charged CuCl (●); CO absorbing conditions, 20 °C under 1 atm; the initial volume of the gas mixture is 1500 cm^3 and the initial pressures of CO and N_2 are 0.8 and 0.2 atm, respectively; $[AlCl_3]_0$= $[CuCl]_0$= [phenyl residue of polystyrene (DP_n: 420)]$_0$ = 1.5 mol dm^{-3} in 15 cm^3 of toluene.

Table 2. Effects of the Degree of Polymerization and the Amount of Polystyrene (PSt) on the Water Resistivity of Toluene Solution of PSt-$AlCuCl_4$[a)]

PSt		Water resistivity of the CO absorbent[d)]
DP_n[b)]	Charged amount[c)]	
420	3.0	1.01
420	1.0	1.01
420	0.5	0.94
420	0.1	0.92
50	1.0	1.01
4	1.0	0.99
—	0	0.75

a) $[AlCl_3]_0$ = $[CuCl]_0$ = 1.0 mol dm^{-3}. CO absorbing conditions: at room temperature under 1 atm; the initial volume of the gas mixture is 1500 cm^3 and the initial pressures of CO and N_2 are 0.8 and 0.2 atm, respectively. b) Number-averaged degree of polymerization. c) The charged molar ratio of phenyl residue in polystyrene to CuCl. d) The ratio of the equilibrium amount of the absorbed CO after the contact of the absorbent with water vapor to the value before the contact. The charged molar ratio of water to CuCl is 0.10.

almost all the absorbed CO is released.

After being cooled to 20 °C under dry nitrogen, the absorbent is contacted with 5000 cm^3 of nitrogen containing 10 mol% water to the charged CuCl (water content: 9000 ppm) for 10 min. In the following CO absorption, the absorbent quickly absorbs CO from 1500 cm^3 of CO–N_2 mixture (initial pressure of CO: 0.80 atm), as shown by the solid circles in Fig. 3. The equilibrium molar ratio of the absorbed CO to the charged CuCl is 0.71, which is identical with the value (0.71) for the absorbent prior to the contact with water vapor. No decrease in the CO absorbing activity was detected at all even after the repeated (five times) contacts of the absorbent with water vapor. Thus, the water vapor exhibits no measurable deactivation effect on the absorbent containing polystyrene (DP_n: 420) equimolar in phenyl residue to the charged CuCl.

Table 2 shows the effects of the degree of polymerization and the amount of polystyrene used on the water resistivity of the toluene solution of PSt-$AlCuCl_4$ complex. Here, the ratio of the amount of CO absorbed by the absorbent after the contact with water vapor (10 mol% to the charged CuCl) to the value before the contact is used as an index of the water resistivity of the absorbents.

When the charged molar ratio of the phenyl residue of polystyrene (DP_n: 420) to CuCl is larger than unity, no decrease in the activity is observed after the contact with 10 mol% water to the charged CuCl. At the molar ratios 0.5 and 0.1, however, the CO absorbing activity decreases by 6 and 8%, respectively, after the contact. The decrease of the CO absorbing activity of the absorbents, even at the molar ratio 0.5 or 0.1, is much smaller than that (25%) of the toluene solutions of $AlCuCl_4$ without polystyrene.

At the charged molar ratio 1.0 of the phenyl residue of polystyrene to CuCl, no measurable decrease of the CO absorbing activity of the absorbents by the contact with water vapor is observed irrespective of the degree of polymerization (420, 50, and 4.0) of polystyrene.

CO Absorbing Activity and Water Resistivity of Toluene Solution of $AlCuCl_4$ without PSt. As shown by the open circles in Fig. 4, the toluene solution of $AlCuCl_4$ without polystyrene rapidly absorbs CO from 1500 cm^3 of CO–N_2 mixture (initial partial pressure of CO: 0.80 atm) at 20 °C under 1 atm and the equilibrium molar ratio of the absorbed CO to the charged CuCl is 0.68. Almost all the absorbed CO is released when the absorbent is heated to 80 °C. The CO absorbing activity remains constant on repeated absorption-release cycles, as long as sufficiently dried CO is used.

However, the activity of the absorbent without polystyrene rapidly decreases on the contact with water vapor. The equilibrium molar ratio (0.51) of the absorbed CO to the charged CuCl after the contact of the absorbent with N_2 gas containing 10 mol% water to the charged CuCl (the solid circles in Fig. 4) is much smaller than that (0.68) before the contact.

After the second contact with 10 mol% water to the charged CuCl, the equilibrium molar ratio of the absorbed CO to the charged CuCl is further decreased to 0.30.

The activity of the absorbent without polystyrene did not change on the contact with oxygen. The contact was carried out under 1 atm of oxygen for 1 h at room temperature, while the absorbent was magnetically stirred.

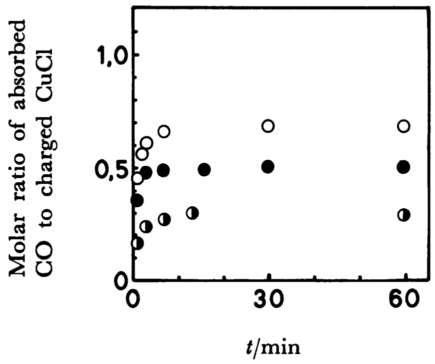

Fig. 4. Effect of water vapor on the CO absorbing activity of toluene solution of $AlCuCl_4$ without polystyrene; the first absorption (○); the second absorption after the contact of the solution with 10 mol% water to the charged CuCl (●); the third absorption after the second contact with 10 mol% water (◑); CO absorbing conditions, 20 °C under 1 atm; the initial volume of the gas mixture is 1500 cm^3 and the initial pressures of CO and N_2 are 0.8 and 0.2 atm, respectively; $[AlCl_3]_0=[CuCl]_0=1.5$ mol dm^{-3} in 19 cm^3 of toluene.

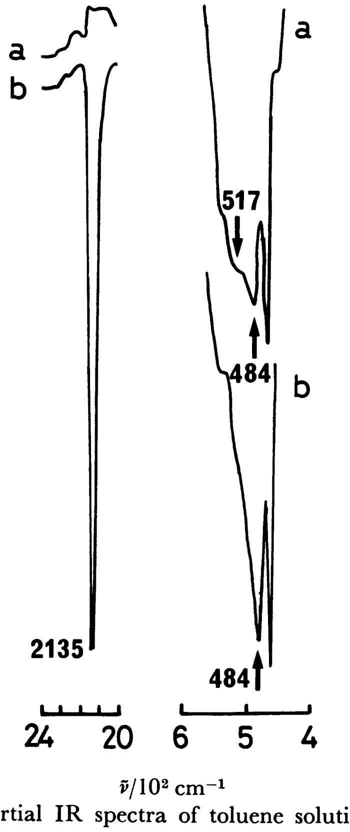

Fig. 5. Partial IR spectra of toluene solution of polystyrene-$AlCuCl_4$ before the contact with CO (a) and after the contact (b); $[AlCl_3]_0=[CuCl]_0=$[phenyl residue of polystyrene (DP_n: 420)]$_0=1.0$ mol dm^{-3}.

Infrared Spectra of the Solution of PSt-$AlCuCl_4$ with or without Absorbed CO. In the absence of CO, the solution of PSt-$AlCuCl_4$ exhibits a strong absorption at 484 cm^{-1} and a shoulder peak at 517 cm^{-1} as shown in Fig. 5, (a). All other signals are assignable to polystyrene and toluene.

When the absorbent absorbs CO, a strong and sharp absorption band appears at 2135 cm^{-1} and the band at 517 cm^{-1} weakens, as shown in Fig. 5, (b). The band at 2135 cm^{-1} is due to stretching vibration (ν_{CO}) of the absorbed CO. Otherwise, no change in the spectrum is observed on the CO absorption.

In benzene and chlorobenzene solutions of $AlCuCl_4$, ν_{CO} bands were observed at 2132 and 2135 cm^{-1}, respectively. No band assignable to the absorbed CO was observed for toluene itself without $AlCuCl_4$, which was stored under CO for 1 d.

CO Absorbents Composed of Various Polymers and $AlCuCl_4$. Homogeneous toluene solution of polymer-$AlCuCl_4$ complex was prepared using poly[oxy(2,6-dimethyl-1,4-phenylene)] or hydrogenated styrene-butadiene block copolymer (Kraton G) instead of polystyrene. These absorbents slowly absorbed CO as depicted by the open circles and solid circles in Fig. 6.

When polybutadiene, styrene-butadiene block copolymer, or alternating copolymer of styrene and methyl methacrylate were used, however, aggregates were formed and homogeneous solutions were not obtained. These aggregates showed no absorption of CO under 1 atm at 20 °C.

CO Absorbing Activities of the Absorbents with-

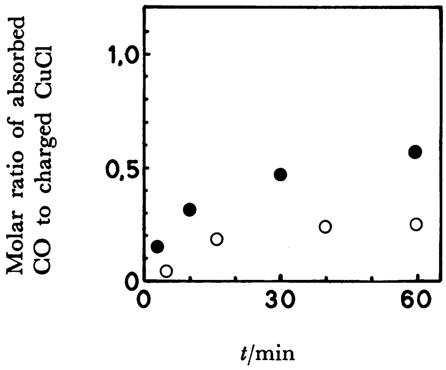

Fig. 6. Absorption of carbon monoxide at 20 °C under 1 atm CO by toluene solutions of $AlCuCl_4$ with poly[oxy(2,6-dimethyl-1,4-phenylene)] (○) or hydrogenated styrene-butadiene block copolymer (●): for the absorbent with poly[oxy(2,6-dimethyl-1,4-phenylene)], $[AlCl_3]_0=[CuCl]_0=1.3$ and [phenyl residue of the polymer]$_0=1.6$ mol dm^{-3} in 20 cm^3 of toluene; for the absorbent with hydrogenated styrene–butadiene block copolymer, $[AlCl_3]_0=[CuCl]_0=0.7$ and [phenyl residue of the polymer]$_0=0.25$ mol dm^{-3} in 40 cm^3 of toluene.

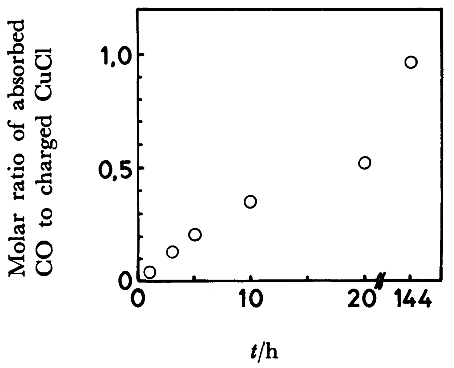

Fig. 7. Absorption of carbon monoxide at 20 °C under 1 atm CO by toluene suspension of CuCl composed of 25.0 mmol of CuCl and 20 cm^3 of toluene.

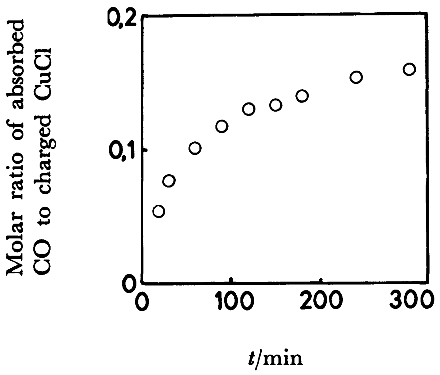

Fig. 8. Absorption of carbon monoxide at 30 °C under 1 atm by concentrated hydrochloric acid solution of CuCl composed of 3.0 mmol of CuCl and 20 cm^3 of aqueous HCl solution (12 mol dm^{-3}); the initial volume of the gas mixtures is 3000 cm^3 and the initial pressures of CO and N_2 are 0.9 and 0.1 atm, respectively.

out $AlCl_3$. In the absence of $AlCl_3$, CuCl does not dissolve in toluene either in the presence or the absence of polystyrene, and only toluene suspension of CuCl is obtained. The suspension without polystyrene slowly absorbs CO and the molar ratio of the absorbed CO to the charged CuCl is 0.04 at 60 min and 0.97 at 144 h under 1 atm at 20 °C, as shown in Fig. 7.

Concentrated hydrochloric acid solution of CuCl also slowly absorbs CO and the molar ratio of the absorbed CO to the charged CuCl is 0.10 at 60 min and 0.16 at 300 min, as shown in Fig. 8.

Dark reddish brown solution prepared from 0.85 g (8.2 mequiv in phenyl residue) of linear polystyrene (DP_n: 420), 1.55 g (8.2 mmol) of titanium(IV) chloride, 0.81 g (8.2 mmol) of CuCl, and 20 cm^3 of toluene did not absorb CO. Yellow solution from 0.95 g (9.1 mequiv in phenyl residue) of linear polystyrene (DP_n: 420), 2.39 g (9.2 mmol) of tin(IV) chloride, 0.91 g (9.2 mmol) of CuCl, and 20 cm^3 of toluene did not absorb CO either. In both cases, considerable amounts of precipitates were formed under homogeneous solutions.

Discussion

Formation of PSt-$AlCuCl_4$ Complex. Copper(I) chloride, which hardly dissolves in toluene alone, satisfactorily dissolves in toluene in the presence of $AlCl_3$ equimolar to CuCl. When the molar ratio of CuCl to $AlCl_3$ is larger than unity, CuCl present in excess forms precipitates. These results definitely show that CuCl and $AlCl_3$ form a double salt $AlCuCl_4$ in a molar ratio 1 : 1. Formation of $AlCuCl_4$ in toluene either in the presence or the absence of polystyrene was further confirmed by the infrared absorption band at 484 cm^{-1} (Fig. 5 (a)), which was assigned to antisymmetric stretching mode ν_a of $AlCl_4^-$ residue in $AlCuCl_4$.[10]

In the CO absorbents composed of polystyrene, $AlCl_3$, CuCl, and aromatic solvents, polystyrene and $AlCuCl_4$ form a polymer complex PSt-$AlCuCl_4$. This is shown by the fact that chlorobenzene solution of $AlCuCl_4$ was homogeneous only in the presence of polystyrene. Here, aromatic rings of polystyrene formed charge-transfer complexes with $AlCuCl_4$, which satisfactorily dissolved in chlorobenzene. In the absence of polystyrene, however, considerable portion of $AlCuCl_4$ precipitated, since the equilibrium constant for the charge-transfer complex formation between $AlCuCl_4$ and chlorobenzene was small due to small electron donating ability of chlorobenzene (ionization potential (I_p): 9.60 eV).[11] Toluene, which had a larger electron donating ability (I_p: 9.18 eV)[11] than chlorobenzene, efficiently formed charge-transfer complex with $AlCuCl_4$, resulting in a homogeneous toluene solution of $AlCuCl_4$ even in the absence of polystyrene.

The formation of the PSt-$AlCuCl_4$ complex has been further confirmed by a very strong charge-transfer band in the 380—500 nm region.[12] Such a charge-transfer band has not been found in a toluene solution of $AlCuCl_4$ without polystyrene.

Marked difference in absorption spectra between the $AlCuCl_4$-PSt system and the $AlCuCl_4$-toluene system indicates that the PSt-$AlCuCl_4$ complex involves interactions of two aromatic rings of polystyrene with $AlCuCl_4$. Probably an aromatic ring in polystyrene interacts with the Cu(I) ion in $AlCuCl_4$ and another aromatic ring interacts with the $AlCl_3$ part in the same $AlCuCl_4$ molecule.[11] The interaction between polystyrene and $AlCuCl_4$ is promoted by the chelate effect of these two types of interactions. The proposed conformation of the PSt-$AlCuCl_4$ complex is consistent with the result of crystallography on the $AlCuCl_4$-benzene complex,[13] where a benzene molecule interacts with the Cu(I) ion in $AlCuCl_4$. Alternatively, two aromatic rings of polystyrene can interact with the two Cl atoms of the $AlCl_3$ part of $AlCuCl_4$ in the PSt–$AlCuCl_4$ complex.

When poly[oxy(2,6-dimethyl-1,4-phenylene)] and hydrogenated styrene–butadiene block copolymer were used in place of polystyrene, homogeneous solutions were obtained also by the interactions between the aromatic rings of the polymers and $AlCuCl_4$. Formation of the aggregates on the usage of polybutadiene and the alternating copolymer of styrene and methyl methacrylate, respectively, were associated with cross-linking of polybutadiene by cationic polymerization with $AlCl_3$ catalyst and the coordination of the ester groups in the alternating copolymer to $AlCl_3$.

CO Absorption by Solutions of PSt-$AlCuCl_4$ Complex. The frequency (2135 cm^{-1}) of the stretching vibration for the CO absorbed by the toluene solution of PSt–$AlCuCl_4$ (Fig. 5) is smaller than the value (2143 cm^{-1})[14] for free CO by about 10 cm^{-1}. This fact shows that CO absorption by the PSt–$AlCuCl_4$ absorbent is attributable to the coordination of CO to Cu(I) ion in $AlCuCl_4$. The coordination results in π-back donation from the Cu(I) ion to CO, reducing the bond order of C–O bond in CO.[14]

On the coordination of CO to the Cu(I) ion in $AlCuCl_4$, the aromatic ring of polystyrene or the toluene molecule, which is originally interacting with Cu(I) ion, is liberated from the Cu(I) ion and instead CO coordinates to the resultant unoccupied coordination site.[15] The larger equilibrium amount of the absorbed CO for the chlorobenzene solution of PSt–$AlCuCl_4$ than that for the toluene solution (Fig. 2) is consistent with this argument, since the ligand exchange from chlorobenzene to CO is easier than that from toluene to CO. The coordination of chlorobenzene to the Cu(I) ion in $AlCuCl_4$ is weaker than that of toluene, because of smaller electron donating ability (I_P=9.60 and 9.18 eV, respectively, for chlorobenzene and toluene).

Both the CO absorption rate and the amount of absorbed CO for the toluene solution of PSt–$AlCuCl_4$ complex (Fig. 2) are much larger than those of the concentrated hydrochloric acid solution of CuCl (Fig. 8). Formation of the double salt between $AlCl_3$ and CuCl decreases the electron density on the Cu(I) ion, which enhances the electron donation from CO to the Cu(I) ion, and promotes the coordination of CO to the Cu(I) ion.

The halogen dependence for the amount of CO absorbed by the toluene solutions of PSt–$AlCuX_4$ ($Cl>Br \gg I=0$) (Table 1) is identical with that for the coordination of CO to copper(I) halides.[16] As the electronegativity of halogen decreases, the electron density on the Cu(I) ion in $AlCuCl_4$ increases and thus the capacity of CO absorption decreases.

In the coordination of CO to Cu(I) ion in $AlCuCl_4$, electron donation from CO to the Cu(I) ion makes predominant contribution, and the contribution of back donation from the Cu(I) ion to CO is less important. The ν_{CO} (2135 cm^{-1}) of the CO coordinating to the Cu(I) in $AlCuCl_4$ is larger than the ν_{CO} (2063 cm^{-1} in water,[17] and 2080 cm^{-1} in methanol)[18] of CO coordinating to CuCl. The back donation is suppressed by the decrease of electron density on the Cu(I) ion due to the formation of double salt $AlCuCl_4$.

In addition to the promotion of CO coordination to the Cu(I) ion by decreasing electron density on the ion, $AlCl_3$ in the solutions of PSt–$AlCuCl_4$ accelerates the CO absorption by dissolving CuCl, which is not soluble in toluene alone, with the formation of the double complex. CO absorption of homogeneous toluene solution of PSt–$AlCuCl_4$ complex (Fig. 2) is much faster than that by the toluene suspension of CuCl (Fig. 7).

Protection of $AlCuCl_4$ by PSt. The toluene solution of PSt–$AlCuCl_4$ shows no measurable deactivation on the repeated contacts with 10 mol% water to the charged CuCl (Fig. 3). This is markedly in contrast with significant decrease of the absorbing capacity of the toluene solutions of $AlCuCl_4$ without polystyrene. The amount of the $AlCuCl_4$ deactivated by water in the absence of polystyrene, estimated from the decrease in the CO absorbing capacity, is about twice in mole as large as that of the water (Fig. 4). This result is consistent with the irreversible reaction between $AlCuCl_4$ and water expressed by Eqs. 1 and 2.

No deterioration of the toluene solution of PSt–$AlCuCl_4$ on the contact with water vapor is probably due to the protection of $AlCuCl_4$ against water by the hydrophobic field of polystyrene. As described above, polystyrene and $AlCuCl_4$ form a polymer complex, in which two aromatic rings of polystyrene interact with one $AlCuCl_4$ molecule. The interactions of the two aromatic rings function cooperatively, and thus the interaction between aromatic ring and the $AlCl_3$ moiety is largely enhanced due to chelate effect. As the result, the $AlCl_3$ moieties, which otherwise rapidly react with water, are sufficiently protected by the aromatic rings of polystyrene. The water vapor remains in the gas phase here.[19]

In case of the toluene solution of $AlCuCl_4$ without polystyrene, however, protective effects of toluene on $AlCuCl_4$ are not so large, since the chelate effect does not take place. Water vapor promptly penetrates into the absorbent and hydrolyzes the $AlCuCl_4$.[19]

No dependence of the water-resistivity of CO absorbent on the degree of polymerization of polystyrene used (Table 2) indicates that the water resistivity of the absorbent is not attributable to the increase of the viscosity of the absorbent resulting from the addition of polystyrene.

The proposed mechanism of water resistivity of the absorbent is also supported by the fact that water-resistive CO absorbent can be prepared by use of 1,3-diphenylpropane, a low molecular weight model of polystyrene, as solvent.[20)]

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