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Polymer-Protected Metal Complex for Gas Separation. II. Cross-Linked Polystyrene-Supported Aluminium Copper(I) Halide as Solid Carbon Monoxide Adsorbent

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Macroreticular (MR) type cross-linked polystyrene-supported aluminium copper(I) chloride is prepared by refluxing MR type polystyrene (divinylbenzene content 20%), aluminium chloride, and copper(I) chloride in benzene, toluene, carbon disulfide, or dichloromethane, followed by evaporation of the liquid phase. All the polystyrene-supported aluminium copper(I) chloride exhibit rapid and reversible adsorptions of carbon monoxide (CO). For the adsorbent prepared by using toluene as solvent, the equilibrium molar ratio of adsorbed CO to the charged copper(I) chloride is 0.83 at 20 °C under 1 atm (initial partial pressure of CO: 0.90 atm). Desorption of CO is carried out at 7 mmHg, 20 °C for 10 min. The equilibrium molar ratio of adsorbed CO to the charged copper(I) chloride in the second adsorption is 0.56. In the following adsorptions, the equilibrium molar ratios are virtually constant at 0.56. Usage of either gel type cross-linked polystyrenes or a linear polystyrene in place of the MR type cross-linked polystyrene results in CO adsorbents having poor abilities with respect to both adsorption rates and capacities. The adsorbing capacities of the CO adsorbents prepared from aluminium halide, copper(I) halide, and the MR type cross-linked polystyrene decrease as follows: $AlCl_3$-CuCl system > $AlBr_3$-CuBr system ≫ AlI_3-CuI system ≈ $AlCl_3$-CuI system ≈ AlI_3-CuCl system ≈ 0.

Carbon monoxide (CO), which is one of the important raw materials in chemical industry,[1] is usually obtained as gas mixtures.[2] Thus, separation of CO from gas mixtures is required for effective utilization of CO.

Previously,[3,4] the authors reported on CO absorbents composed of linear polystyrene, aluminium chloride ($AlCl_3$), copper(I) chloride (CuCl), and toluene. The absorbents reversibly absorbed CO under mild conditions, and were stable against water vapor due to protection of water-sensitive aluminium copper(I) chloride ($AlCuCl_4$), a double salt formed from $AlCl_3$ and CuCl, by the polystyrene. Separation of CO from gas mixtures containing water vapor was successfully achieved with the use of the absorbents.

In spite of many proposals on liquid CO absorbents,[2–5] informations on solid adsorbents of CO are rather scanty. Although Y zeolite-supported copper(I) ions adsorbed CO, the adsorption was so strong that the adsorbed CO was not sufficiently released even at 10^{-4} mmHg (1 mmHg=133.3 Pa).[6] A patent[7] claimed that copper(I) ions supported on zeolites having high SiO_2/Al_2O_3 molar ratios adsorbed CO. The equilibrium amount of CO adsorbed by 1 g of the adsorbent at 50 °C was 16 cm^3 (standard temperature and pressure), which was almost independent of partial pressure of CO at the partial pressure 100 mmHg or larger.

In preliminary communications,[8,9] the authors showed that the macroreticular (MR) type cross-linked polystyrene-supported $AlCuCl_4$ adsorbed and desorbed CO under mild conditions.

This paper describes the results of detailed studies on the MR type cross-linked polystyrene-supported $AlCuCl_4$. Dependences of CO adsorbing capacities of the adsorbents either on adsorbing temperature, on partial pressure of CO, or on the preparation solvent are described. The adsorbing and desorbing abilities of the adsorbents are compared with those for the adsorbents prepared by use of gel type cross-linked polystyrene or linear polystyrene in place of MR type cross-linked polystyrene. Furthermore, the adsorbing capacities of the adsorbents prepared from various aluminium halides, copper(I) halides, and MR type cross-linked polystyrene are shown.

Experimental

Materials. A macroreticular (MR) type cross-linked polystyrene (styrene-divinylbenzene (DVB) copolymer, divinylbenzene content 20%; 20—50 mesh; diameter, 296—740 μm; average pore diameter, 9 nm; surface area, 300 m^2/g)[10] was obtained from Bio-Rad Laboratories (Bio-Beads SM-2). A cross-linked (DVB 12%) gel type polystyrene (200—400 mesh; diameter, 37—74 μm) and a cross-linked (DVB 1%) gel type polystyrene (200—400 mesh; diameter, 37—74 μm) were purchased also from Bio-Rad Laboratories (Bio-Beads S-X12 and Bio-Beads S-X1, respectively). They were purified by stirring successively in the following solvents under the specified conditions: aqueous hydrochloric acid solution, 4 mol dm^{-3}, 55 °C, 2 h; aqueous sodium hydroxide solution, 2 mol dm^{-3}, 55 °C, 2 h; distilled water, 55 °C, 2 h; methanol, room temperature, 1 h; dichloromethane, room temperature, 1 h. The resins were dried in vacuo at 80 °C for 12 h.

Linear polystyrene, purchased from Wako Pure Chemical Co., was reprecipitated using the chloroform–methanol system and was dried in vacuo at 60 °C for 12 h. The number-averaged molecular weight and the weight-averaged molecular weight were 4.4×10^4 and 1.5×10^5, respectively, as determined by the gel permeation chromatography using columns of TSK-GEL, G5000H+G3000H, Toyo Soda Manufacturing Co.

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 was dried overnight in vacuo at 100 °C. Aluminium bromide, copper(I) bromide, aluminium iodide, and copper(I) iodide were commercially obtained (guaranteed grades) and were used without further purification.

Carbon disulfide and dichloromethane were dried over diphosphorus pentaoxide and were distilled. Toluene and benzene were distilled after being dried over metallic sodium.

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

Preparation of CO Adsorbents. Preparation of the solid CO adsorbent was carried out as follows. Aluminium halide, copper(I) halide, and the macroreticular type polystyrene resin were refluxed in various solvents under dry nitrogen for 4—6 h, during which the mixture was magnetically stirred. Then, the solvent was thoroughly removed from the mixture by evaporation at 4 mmHg for several hours. Evaporation temperature was gradually elevated from room temperature to 60 °C, as the evaporation proceeded.

Charged molar ratio of aluminium halide to copper(I) halide was 1.0 unless otherwise noted and the ratio of phenyl residue in the polystyrene resin to copper(I) halide was 1.2—2.0.

Adsorption and Desorption of CO. Adsorption of CO by the adsorbent (1), continuously stirred by use of a magnetic stirrer (3), from atmospheric CO or CO–N_2 mixtures (total pressure: 1 atm) was carried out under 1 atm, using the apparatus depicted in Fig. 1. The amount of adsorbed CO was determined by a gas burette (4) using liquid paraffin as leveling liquid (5). Adsorption from atmospheric CO was initiated by introduction of CO to a flask containing the adsorbent. The flask was evacuated to 7 mmHg prior to the introduction. In case of adsorption from CO–N_2 mixtures, the gas mixtures were made to flow over the adsorbent by use of a gas-circulating pump (6) for the first 10 min in the adsorption.

Desorption of CO from the adsorbent was carried out at 7 mmHg for 10 min at room temperature or prescribed temperatures.

Fourier Transfer Infrared (FT-IR) Spectroscopy. FT-IR spectra were taken at room temperature with a JEOL FT-IR model 10 spectrometer at various CO pressures. Specimen was prepared from 2.05 g (15.4 mmol) of $AlCl_3$, 1.52 g (15.4 mmol) of CuCl, and 3.35 g (30.7 mequiv in phenyl residue) of the macroreticular type cross-linked polystyrene by use of 10 cm^3 of carbon disulfide as solvent. The adsorbent was mixed with silica gel (Cab-O-Sil, Wako Pure Chemical Co.) after being thoroughly ground. The content of copper atom in disk was 2.5 wt%.

Results

Preparation of Macroreticular Type Polystyrene-Supported $AlCuCl_4$. When $AlCl_3$, CuCl, and the macroreticular type polystyrene resin (DVB 20%) were refluxed in toluene or benzene for 6 h, both the polystyrene beads and the liquid phase turned dark brown. Solid adsorbents were obtained as yellowish green beads by evaporating the solvents thoroughly at 4 mmHg from the mixtures.

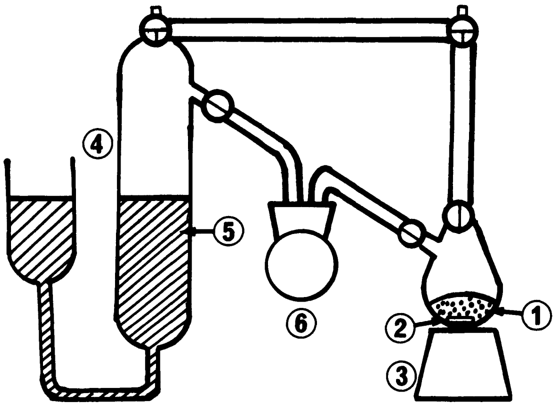

Fig. 1. Apparatus for measuring the amounts of carbon monoxide adsorbed by the adsorbents; 1: CO adsorbent, 2: rotor, 3: magnetic stirrer, 4: gas burette, 5: leveling liquid (liquid paraffin), 6: gas-circulating pump.

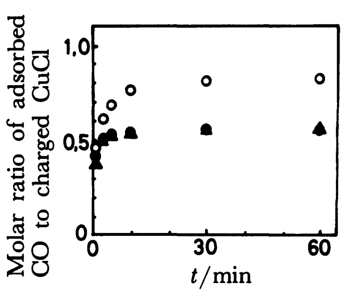

Fig. 2. Adsorption of carbon monoxide from 9:1 CO–N_2 mixture at 20 °C under 1 atm by the macroreticular (MR) type polystyrene-supported aluminium copper(I) chloride prepared by use of toluene as solvent: The first adsorption (○), the second adsorption (●), and the third adsorption (▲); the desorption of CO was carried out at 7 mmHg for 10 min; the adsorbent was prepared from 5.21 g (39.1 mmol) of $AlCl_3$, 3.87 g (39.1 mmol) of CuCl, and 7.04 g (64.6 mequiv in phenyl residue) of the MR type polystyrene with the use of 20 cm^3 of toluene; the initial volume of the gas mixture was 2000 cm^3 with initial pressures of CO and N_2, 0.9 and 0.1 atm, respectively.

On the refluxing of $AlCl_3$, CuCl, and the polystyrene resin in carbon disulfide or dichloromethane, however, only the polystyrene beads turned dark brown after refluxing. The liquid phase was almost transparent with quite a faint dark orange color. The adsorbents obtained after evaporation of the solvent were reddish brown beads.

Depositions of metal salts on the inside walls of the flasks, used for the preparation of the adsorbents, were hardly observed in any of these cases. These results show that almost all of the charged metal salts are incorporated to the adsorbents.

CO Adsorbing and Desorbing Abilities of Macroreticular Type Polystyrene-Supported $AlCuCl_4$. Figure 2 depicts the adsorption of CO at 20 °C from 9:1 CO–N_2 mixture (initial partial pressure of CO: 0.9 atm) under 1 atm by the adsorbent prepared from 5.21

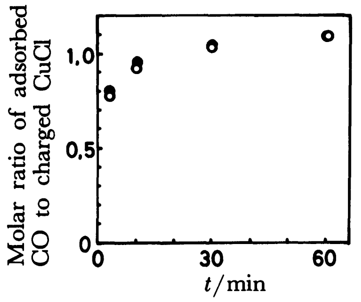

Fig. 3. Adsorption of carbon monoxide from atmospheric CO at 20 °C under 1 atm by the macroreticular (MR) type polystyrene-supported aluminium copper(I) chloride prepared by use of toluene as solvent: The first adsorption (○), and the second adsorption (●); the desorption of CO was carried out at 7 mmHg, 90 °C for 30 min after the first adsorption; the adsorbent was prepared from 2.75 g (20.6 mmol) of $AlCl_3$, 2.04 g (20.6 mmol) of CuCl, and 2.58 g (23.7 mequiv in phenyl residue) of the MR type polystyrene using 10 cm^3 of toluene.

g (39.1 mmol) of $AlCl_3$, 3.87 g (39.1 mmol) of CuCl, and 7.04 g (64.6 mequiv in phenyl residue) of the macroreticular type polystyrene resin with the use of 20 cm^3 of toluene. As shown by the open circles, the adsorbent rapidly adsorbs CO and the equilibrium molar ratio of the adsorbed CO to the charged CuCl is 0.83 (45 cm^3 (standard temperature and pressure) of CO per 1 g of the adsorbent).

Desorption of adsorbed CO is carried out at 7 mmHg, 20 °C for 10 min. On the second contact with 9:1 CO–N_2 mixture, the adsorbent rapidly adsorbs CO and the equilibrium molar ratio of adsorbed CO to the charged CuCl is 0.56 (31 cm^3 (standard temperature and pressure) of CO per 1 g of the adsorbent; solid circles in Fig. 2).

The third adsorption of CO by the adsorbent, which is subjected to a reduced pressure (7 mmHg) at 20 °C for 10 min after the second adsorption, from 9:1 CO–N_2 mixture is also rapid and the equilibrium molar ratio of adsorbed CO to the charged CuCl is 0.57 (solid triangles in Fig. 2). This molar ratio is identical with the value (0.56) in the second adsorption within experimental error.

The open circles in Fig. 3 depict CO adsorption by the adsorbent, prepared separately using toluene as solvent, from atmospheric CO at 20 °C. The adsorption is rapid and the equilibrium molar ratio of adsorbed CO to the charged CuCl is 1.10 (69 cm^3 (standard temperature and pressure) of CO per 1 g of the adsorbent). The adsorbed CO is desorbed by heating the adsorbent at 90 °C under 7 mmHg for 30 min. In the second adsorption, shown by the closed circles, the equilibrium molar ratio of adsorbed CO to the charged CuCl is 1.10, which is identical with the value for the first adsorption.

Table 1. CO Adsorbing Capacities of the Macroreticular Type Polystyrene-Supported Aluminium Copper(I) Chloride Prepared by Use of Various Solvents[a]

Preparation solvent	Molar ratio[b]	
	1st[c]	2nd[d]
Toluene	1.05	0.55
Benzene	1.03	0.43
Carbon disulfide	1.07	0.54
Dichloromethane	1.11	0.35
Tetrachloromethane	0.55	0.23

a) Charged molar ratios of $AlCl_3$ and phenyl residue in the cross-linked polystyrene to CuCl are 1.0 and 1.2, respectively. b) Equilibrium molar ratios of adsorbed CO to the charged CuCl at room temperature under 1 atm of CO. c) The value in the first adsorption by a virgin adsorbent. d) The value in the second adsorption by the adsorbent which has been subjected to a reduced pressure (7 mmHg) for 10 min at room temperature after the first adsorption.

Effect of Preparation Solvent on CO Adsorbing Capacity of Macroreticular Type Polystyrene-Supported $AlCuCl_4$. Table 1 shows the equilibrium molar ratios of adsorbed CO to the charged CuCl for the polystyrene-supported $AlCuCl_4$ prepared by using various solvents. All the adsorbents, except for the one prepared by use of tetrachloromethane as solvent, adsorb CO around equimolar to the charged CuCl in the first adsorptions. The equilibrium amounts of the adsorbed CO in the second adsorptions are about one half to one third of the values in the first adsorptions. The desorptions are carried out at 7 mmHg, room temperature for 10 min.

When the desorptions were achieved at 7 mmHg, 90 °C for 30 min, the amount of adsorbed CO in the second adsorption for the adsorbent prepared by use of carbon disulfide as solvent was 67% of the value in the first adsorption.

On the usage of tetrachloromethane as solvent, liquid phase gradually turned black on refluxing and gray precipitates were formed. The adsorbent, obtained as black beads after evaporation, showed considerably smaller CO adsorbing capacity than the adsorbents prepared by use of toluene, benzene, carbon disulfide, and dichloromethane (Table 1).

Effects of Adsorbing Temperature and CO Partial Pressure on Adsorbing Capacity of Macroreticular Type Polystyrene-Supported $AlCuCl_4$. Open circles in Fig. 4 show the plot of the equilibrium molar ratio of adsorbed CO to the charged CuCl vs. adsorption temperature for the adsorbent prepared by using dichloromethane. Below 50 °C, the molar ratio is larger than unity. The adsorbing capacity markedly decreases with increasing temperature above 70 °C and the amount of adsorbed CO at 145 °C is nearly zero.

Solid circles in Fig. 4 are for the second adsorptions by the adsorbent which desorbs CO at 7 mmHg for 10 min after the first adsorptions. The desorptions are carried out at the same temperatures as the first adsorptions are achieved. The amounts of CO adsorbed in the second adsorptions are almost identical with

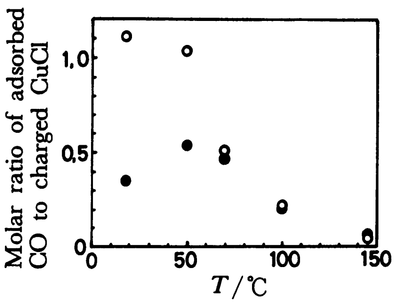

Fig. 4. Temperature dependence of the adsorbing capacity for the macroreticular (MR) type polystyrene-supported aluminium copper(I) chloride prepared by use of dichloromethane as solvent: The first adsorption at a prescribed temperature under 1 atm (○) and the second adsorption at the same temperature (●); prior to the second adsorption, the adsorbed CO was desorbed at 7 mmHg for 10 min at the temperature that was employed for the first and the second adsorptions; the charged molar ratios of $AlCl_3$ and phenyl residues in the polystyrene to CuCl were 1.0 and 1.2, respectively.

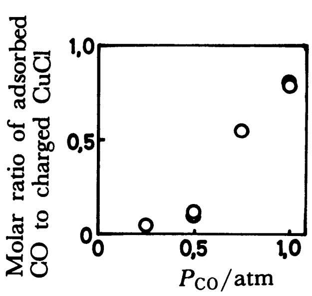

Fig. 5. Effect of partial pressure (P_{CO}) of carbon monoxide on the carbon monoxide adsorption at room temperature by the MR type polystyrene-supported aluminium copper(I) chloride prepared using dichloromethane as solvent: The adsorbent was subjected to a reduced pressure (7 mmHg) at 90 °C for 60 min after a CO adsorption in order to desorb virtually all of the adsorbed CO, and was then used for the following adsorption at a different partial pressure of carbon monoxide; the adsorbent was prepared from 1.35 g (10.1 mmol) of $AlCl_3$, 1.00 g (10.1 mmol) of CuCl, and 1.05 g (9.6 mequiv in phenyl residue) of the MR type polystyrene with the use of 10 cm^3 of dichloromethane.

those in the first adsorptions, when the desorption temperatures are 70 °C or higher. This result shows that almost all of the adsorbed CO is desorbed at 7 mmHg at a temperature higher than 70 °C.

Figure 5 depicts dependence of the equilibrium molar ratio of adsorbed CO to the charged CuCl on CO partial pressure. The amount of adsorbed CO gradually decreases with decreasing CO partial pressure. Decrease in CO partial pressure during CO adsorption was at most 0.02 atm.

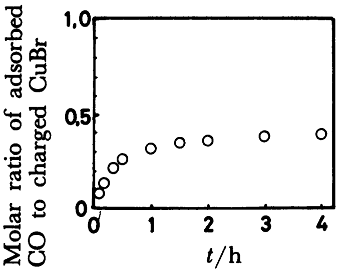

Fig. 6. Adsorption of carbon monoxide from 9:1 CO–N_2 mixture at 30 °C under 1 atm by the macroreticular (MR) type polystyrene-supported aluminium copper(I) bromide prepared by use of toluene as solvent: The adsorbent was prepared from 11.80 g (44.2 mmol) of $AlBr_3$, 6.35 g (44.3 mmol) of CuBr, and 4.60 g (42.2 mequiv in phenyl residue) of the MR type polystyrene using 20 cm^3 of toluene.

CO Adsorbing Abilities of Adsorbents Prepared from Macroreticular Type Polystyrene, Various Aluminium Halides, and Various Copper(I) Halides. The adsorbent, prepared from 11.8 g (44.2 mmol) of aluminium bromide, 6.35 g (44.3 mmol) of copper(I) bromide, and 4.60 g (42.2 mequiv in phenyl residue) of the macroreticular (MR) type polystyrene resin using 20 cm^3 of toluene as solvent, adsorbs CO from 9:1 CO–N_2 mixture (partial pressure of CO: 0.9 atm) at 30 °C, as shown in Fig. 6. The equilibrium molar ratio of the adsorbed CO to the charged copper(I) ion is 0.38, which is smaller than that (0.83) of the MR type polystyrene-supported $AlCuCl_4$. The adsorption of CO by the MR type polystyrene-supported $AlCuBr_4$ is considerably slower than that by the MR type polystyrene-supported $AlCuCl_4$.

The adsorbent, prepared from aluminium iodide, copper(I) iodide, and the MR type polystyrene resin using carbon disulfide as solvent, showed quite a small capacity of CO adsorption : The molar ratio of the CO adsorbed in 3 h to the charged copper(I) iodide was 0.01. Either the adsorbent prepared from aluminium iodide, copper(I) chloride, and the resin or the one from aluminium chloride, copper(I) iodide, and the resin exhibited no measurable CO adsorption.

FT-IR Spectra of CO Adsorbed by Macroreticular Type Cross-Linked Polystyrene-Supported $AlCuCl_4$. A peak appeared at 2121 cm^{-1} on the contact of the adsorbent with 20 mmHg of CO (Fig. 7 (a)). The peak completely disappeared when CO was pumped off from the adsorbent at 10^{-4} mmHg, as shown in Fig. 7 (b). The height of the peak increased with increasing pressure of CO: (d, 760 mmHg)>(c, 300 mmHg) >(a, 20mmHg)>(b, 10^{-4} mmHg) = 0. This signal is definitely attributable to stretching vibration of CO, which is adsorbed by the adsorbent.

The bands in the 1600—2050 cm^{-1} region are assignable to the vibrations for the MR type polystyrene backbone.

Effect of Molar Ratio of $AlCl_3$ to CuCl on CO Adsorbing Ability. The CO adsorbent, prepared as white beads from CuCl and the macroreticular type polystyrene resin in the absence of $AlCl_3$ using carbon

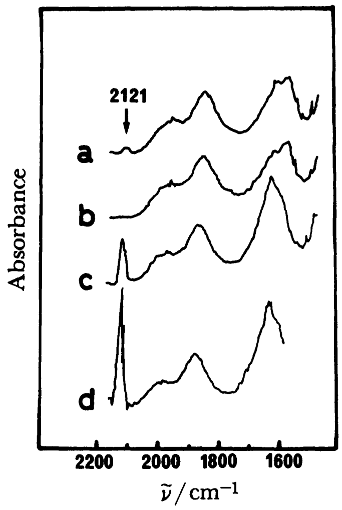

Fig. 7. Partial FT-IR spectra of the macroreticular type polystyrene-supported aluminium copper(I) chloride at various partial pressures of CO: Partial pressures of CO were 20 mmHg (a), 10^{-4} mmHg (b), 300 mmHg (c), and 760 mmHg (d); the spectra were measured in the order of a, b, c, and d.

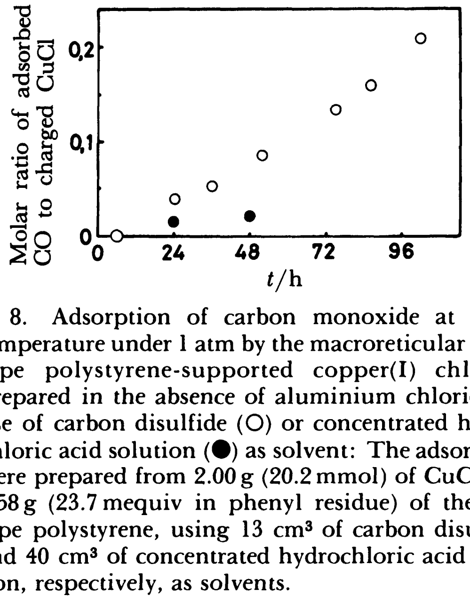

Fig. 8. Adsorption of carbon monoxide at room temperature under 1 atm by the macroreticular (MR) type polystyrene-supported copper(I) chloride prepared in the absence of aluminium chloride by use of carbon disulfide (○) or concentrated hydrochloric acid solution (●) as solvent: The adsorbents were prepared from 2.00 g (20.2 mmol) of CuCl and 2.58 g (23.7 mequiv in phenyl residue) of the MR type polystyrene, using 13 cm^3 of carbon disulfide and 40 cm^3 of concentrated hydrochloric acid solution, respectively, as solvents.

disulfide (open circles) or concentrated hydrochloric acid (solid circles) as solvent, exhibited very small adsorbing ability (Fig. 8). The molar ratios of the CO adsorbed in 24 h to the charged CuCl were 0.04 and 0.02, respectively.

Figure 9 shows the plot of the molar ratio of the adsorbed CO to the charged CuCl as a function of the charged molar ratio (r) of $AlCl_3$ to CuCl for the adsorbents composed of $AlCl_3$, CuCl, and the macroreticular type polystyrene resin. Here, the charged amount of $AlCl_3$ is changed, keeping the amounts of CuCl and the polystyrene resin constant. The amount of adsorbed CO proportionally increases with increasing ratio r in the range of r value from 0.0 to 1.0. At the r value larger than 1.0, however, the amount is almost independent of r.

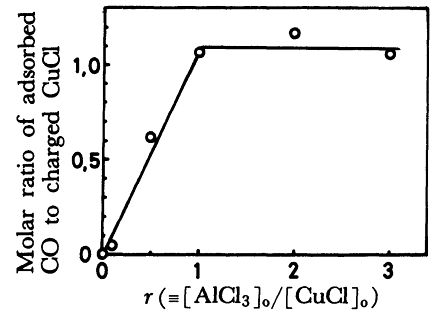

Fig. 9. Plot of the molar ratio of adsorbed carbon monoxide to the charged copper(I) chloride vs. the charged molar ratio (r) of $AlCl_3$ to CuCl for the macroreticular (MR) type polystyrene-supported $AlCuCl_4$: The adsorption at 25 °C under 1 atm for 60 min by the adsorbent prepared from the MR type polystyrene, $AlCl_3$, and CuCl using carbon disulfide; the charged molar ratio of phenyl residue in the polystyrene to CuCl was 1.2.

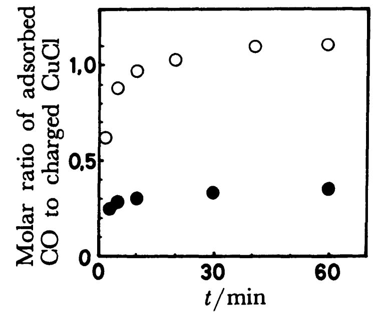

Fig. 10. Adsorption of carbon monoxide at 18 °C under 1 atm by the adsorbent prepared from the macroreticular (MR) type (DVB 20%) polystyrene, $AlCl_3$, and CuCl by use of dichloromethane as solvent: The first adsorption (○) and the second adsorption (●); the desorption of CO was carried out at 18 °C for 10 min under 7 mmHg after the first adsorption; the adsorbent was prepared from 2.47 g (18.5 mmol) of $AlCl_3$, 1.83 g (18.5 mmol) of CuCl, and 2.31 g (21.2 mequiv in phenyl residue) of the MR type polystyrene with the use of 10 cm^3 of dichloromethane.

Adsorbing Abilities of CO Adsorbents Prepared from $AlCl_3$, CuCl, and Various Polystyrenes. Figure 10 depicts the adsorption of CO by the reddish brown adsorbent prepared from $AlCl_3$, CuCl, and the macroreticular (MR) type polystyrene by use of dichloromethane as solvent.

Yellowish brown beads were obtained as CO adsorbents, when $AlCl_3$, CuCl, and gel type polystyrene resins (divinylbenzene (DVB) contents; 1 and 12%) were refluxed in dichloromethane for 6 h and then the liquid phase was removed by evaporation. Figures 11 and 12 show the adsorptions of CO by these adsorbents. The adsorptions are much slower than that (Fig. 10) for the adsorbent prepared from the macroreticular (MR) type polystyrene resin as support.

Table 2. CO Adsorbing Capacities of Adsorbents Prepared from Various Types of Polystyrenes, $AlCl_3$, and CuCl[a]

Polystyrene		Preparation solvent	Molar ratio of adsorbed CO to charged CuCl[b]	
Type	DVB content %		at 10 min	at 60 min
MR	20	Carbon disulfide	0.99	1.07
Gel	1		0.60	0.77
Gel	12		0.55	0.64
None	—		0.63	0.79
MR	20	Toluene	0.92	1.05
Gel	1		0.30	0.71
Gel	12		0.58	0.76
None	—		0.44	0.76
MR	20	Dichloromethane	0.97	1.11
Gel	1		0.52	0.64
Gel	12		0.51	0.63
Linear	0		0.02	0.02
None	—		0.66	0.78

a) Charged molar ratios of $AlCl_3$ and phenyl residue in polystyrene to CuCl are 1.0 and 1.2, respectively. b) The first adsorption of CO by a virgin adsorbent at room temperature under 1 atm.

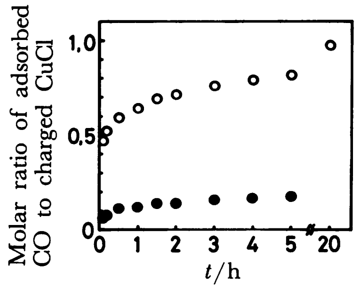

Fig. 11. Adsorption of carbon monoxide at 25 °C under 1 atm by the adsorbent prepared from the gel type (DVB 1%) polystyrene, $AlCl_3$, and CuCl by use of dichloromethane as solvent: The first adsorption (○) and the second adsorption (●); the desorption of CO was carried out at 25 °C for 10 min under 7 mmHg after the first adsorption; the adsorbent was prepared from 3.96 g (29.7 mmol) of $AlCl_3$, 2.94 g (29.7 mmol) of CuCl, and 3.71 g (35.5 mequiv in phenyl residue) of the gel type (DVB 1%) polystyrene with the use of 40 cm³ of dichloromethane.

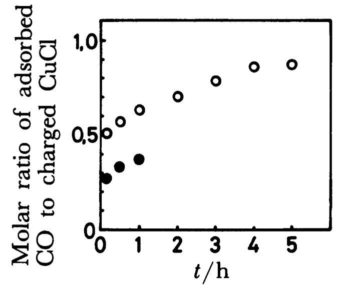

Fig. 12. Adsorption of carbon monoxide at 25 °C under 1 atm by the adsorbent prepared from the gel type (DVB 12%) polystyrene, $AlCl_3$, and CuCl by use of dichloromethane as solvent: The first adsorption (○) and the second adsorption (●); the desorption of CO was carried out at 25 °C for 10 min under 7 mmHg after the first adsorption; the adsorbent was prepared from 3.50 g (26.3 mmol) of $AlCl_3$, 2.60 g (26.3 mmol) of CuCl, and 3.28 g (30.9 mequiv in phenyl residue) of the gel type (DVB 12%) polystyrene with the use of 20 cm³ of dichloromethane.

On the refluxing of linear polystyrene, $AlCl_3$, and CuCl in dichloromethane, dark orange precipitates were formed under a yellow solution after refluxing. On the evaporation of dichloromethane, dark yellow aggregates were produced. The aggregates, however, did not show measurable adsorption of CO.

When $AlCl_3$ and CuCl were refluxed in dichloromethane in the absence of polystyrene and the liquid phase was evaporated, solid of $AlCuCl_4$ was obtained as a dark yellowish green powder. The solid without polystyrene support showed only a slow adsorption of CO (Fig. 13).

Table 2 lists the molar ratios of the CO adsorbed in 10 and 60 min to the charged CuCl for the adsorbents prepared from various types of polystyrenes. All the molar ratios for the MR type polystyrene-supported $AlCuCl_4$, prepared by use of either carbon disulfide, toluene, or dichloromethane, are significantly larger than the corresponding values both for the adsorbents prepared from gel type polystyrenes or linear polystyrene and for the adsorbents prepared in the absence of polystyrene. The adsorptions by the MR type polystyrene-supported $AlCuCl_4$ are much faster than those by the other adsorbents. Here, the rates of adsorption are evaluated from the ratio of the value at 10 min to that at 60 min.

A film, prepared by evaporation of the solvent from a toluene solution of linear polystyrene-protected

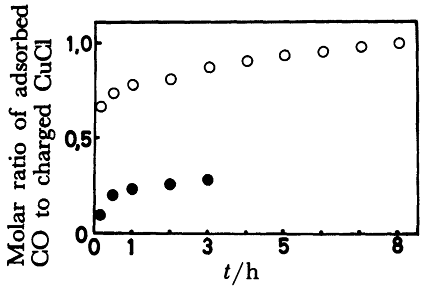

Fig. 13. Adsorption of carbon monoxide at 25 °C under 1 atm by the adsorbent prepared from $AlCl_3$ and CuCl in the absence of polystyrene by use of dichloromethane as solvent: The first adsorption (○) and the second adsorption (●); the desorption of CO was carried out at 25 °C for 10 min under 7 mmHg after the first adsorption; the adsorbent was prepared from 3.32 g (24.9 mmol) of $AlCl_3$ and 2.46 g (24.9 mmol) of CuCl with the use of 15 cm^3 of dichloromethane.

$AlCuCl_4$, did not adsorb CO.

Discussion

Preparation of CO Adsorbents. Carbon disulfide and dichloromethane are good solvents for macroreticular (MR) type polystyrene resin, whereas they are poor solvents for $AlCuCl_4$. When $AlCl_3$, CuCl, and the MR type polystyrene resin are refluxed in these solvents, the metal salts are effectively incorporated into the resin during refluxing. Thus, almost transparent liquid phase, which does not contain the metal salts any more, is obtained after refluxing, prior to evaporation of the liquid phase. $AlCuCl_4$ promptly penetrates into the polystyrene beads, since it favorably interacts with aromatic rings of the polystyrene due to formation of molecular complexes. $AlCuCl_4$ forms molecular complexes with various aromatic compounds such as benzene,[11,12] toluene,[12] and mesitylene.[12] The color of the adsorbents, reddish brown, is in accord with the position of the charge transfer absorption band (λ_{max}: 460 nm)[13] for the molecular complex between $AlCuCl_4$ and linear polystyrene in toluene solutions.

On the usage of toluene or benzene as preparation solvent, however, both the polystyrene beads and the solution part were colored after refluxing. Here, a considerable portion of the $AlCuCl_4$ remains in the liquid phase and only the rest penetrates into the polystyrene resin, since both toluene and benzene are quite good solvents for $AlCuCl_4$. On evaporation of the solvents, the $AlCuCl_4$ in the liquid phase deposits at the surface of the beads.

These arguments are confirmed by the results of a scanning electron microscopy and an energy dispersive X-ray microanalysis.[14,15] For the polystyrene-supported $AlCuCl_4$, prepared by use of carbon disulfide as solvent, $AlCuCl_4$ uniformly distributes in the beads of the adsorbent. For the polystyrene-supported $AlCuCl_4$ prepared with toluene, however, distribution of the double salt in the beads is not uniform and considerable amounts of $AlCuCl_4$ are located on the surface of the beads.

In the present adsorbents with the charged molar ratio unity of $AlCl_3$ to CuCl, most of the charged CuCl and $AlCl_3$ form a double salt $AlCuCl_4$. If only small part of the charged metal salts were forming $AlCuCl_4$ and large part were present as the single salts, the adsorbing capacity at the charged molar ratio 1.0 should be significantly smaller than the values at the charged molar ratios larger than 1.0, due to smaller amount of $AlCuCl_4$, the active species for adsorption (vide infra). Obviously, it is not the case (see Fig. 9).

Adsorption of CO. The plot of the adsorbing capacity vs. the charged molar ratio (r) of $AlCl_3$ to CuCl (Fig. 9), which involves linear increase of the capacity with increasing r below $r=1$ and virtually constant capacity irrespective of r above $r=1$, shows that the active component in the polystyrene-supported $AlCuCl_4$ is the double salt $AlCuCl_4$, composed of CuCl and $AlCl_3$ in a molar ratio 1:1. On the CO adsorption by the adsorbent, CO forms a complex with $AlCuCl_4$, where CO coordinates to the copper(I) ion.

Terminal coordination of CO to $AlCuCl_4$ in the polystyrene-supported $AlCuCl_4$ is supported by the fact that the frequency (2121 cm^{-1}) of the stretching vibration of the adsorbed CO (Fig. 7) is smaller than the value (2143 cm^{-1}) for free CO.[16] This decrease in frequency is mainly attributable to back donation from the copper(I) ion in $AlCuCl_4$ to the CO, which decreases bond order of the C–O bond. The frequency for the CO adsorbed by the present adsorbent is slightly smaller than the value (2135 cm^{-1}) for the CO absorbed by toluene solution of linear polystyrene-protected $AlCuCl_4$.[4]

Formation of a bridging CO from CO and two $AlCuCl_4$ molecules in the adsorbents is ruled out by the stretching frequency (2121 cm^{-1}) of the adsorbed CO. Bridging CO should exhibit stretching vibration mode around 1800 cm^{-1}.[16]

In the macroreticular (MR) type polystyrene-supported $AlCuCl_4$, high dispersion of $AlCuCl_4$ in the beads of the polystyrene, due to formation of molecular complexes of the double salt with the aromatic rings, promotes adsorption of CO. In the absence of $AlCl_3$, however, dispersion of CuCl in the polystyrene beads is not sufficient, resulting in an adsorbent with poor ability (Fig. 8). Furthermore, effective adsorption of CO by the MR type polystyrene-supported $AlCuCl_4$ is associated with decrease of electron density on the copper(I) ion by the formation of the double salt. The decrease of electron density enhances electron donation from CO to the copper(I) ion. On the complex formation of CO with $AlCuCl_4$, contribution of donation from CO to the copper(I) ion is larger than that of back donation from the ion to CO.[4]

The amounts (103—111 mol% with respect to the charged CuCl: Table 1) of CO adsorbed by the macroreticular type polystyrene-supported $AlCuCl_4$, prepared using benzene, toluene, carbon disulfide, or dichloromethane, are larger than the amount (85 mol%) of CO absorbed by toluene solution of linear polystyrene-protected $AlCuCl_4$.4) This is ascribed to absence of competition between CO and toluene in the coordination to $AlCuCl_4$ for the solid adsorbents. In the CO absorption by the toluene solutions, CO coordinates to $AlCuCl_4$ by replacing a toluene molecule which originally coordinates to the $AlCuCl_4$.12)

The macroreticular type polystyrene-supported $AlCuCl_4$ prepared using carbon disulfide adsorbs 67 cm^3 (standard temperature and pressure) of CO per 1 g of the adsorbent under 1 atm of CO at 25 °C. When the cycles involving adsorption of CO at 760 mmHg, 25 °C and desorption at 7 mmHg, 25 °C are repeated using the adsorbent, 34 cm^3 (standard temperature and pressure) of CO is separated for each of the cycles per 1 g of the adsorbent.

The order in the adsorbing capacities of various adsorbents, prepared from the macroreticular type cross-linked polystyrene, aluminium halides, and copper(I) halides, is as follows: $AlCl_3$–CuCl system>$AlBr_3$–CuBr system $\gg AlI_3$–CuI system≈ 0. This order is identical with that in the absorbing capacities for toluene solutions of linear polystyrene-protected aluminium copper(I) halide.4)

Effect of Polystyrene Support on CO Adsorbing and Desorbing Abilities. Efficient adsorption and desorption of CO for the macroreticular (MR) type polystyrene-supported $AlCuCl_4$ (Figs. 2, 3, and 10 and Table 2) are attributable to the presence of macroporosity and microporosity in the MR type resin.17) Through the porosities, $AlCuCl_4$ is effectively introduced into the polystyrene beads in preparation of the adsorbent. The porosities are also important for prompt diffusion of CO either to the metal salt on CO adsorption or from the metal salt on CO desorption. Furthermore, $AlCuCl_4$ is highly dispersed in the adsorbent due to large surface area (300 m^2/g) of the MR type polystyrene, providing sufficient contact of the double salt with CO.

These arguments are confirmed by quite slow adsorptions of the gel type polystyrene-supported $AlCuCl_4$ (Figs. 11 and 12). Here, $AlCuCl_4$ is poorly dispersed in the gel type polystyrene beads having so small surface area. CO can not promptly diffuse to the $AlCuCl_4$ in the adsorbent due to absence of porosity, since porosity of the gel type resin exists only in swollen states in good solvents.17,18) Absence of porosity is also responsible for inefficient desorption of adsorbed CO.

Either the adsorbent, prepared from the linear polystyrene, $AlCl_3$, and CuCl or the film of linear polystyrene-$AlCuCl_4$ complex, prepared by evaporating toluene solution of linear polystyrene-protected $AlCuCl_4$,3,4) which has no porosity, exhibits no measurable adsorbing capacity. The CO adsorption by $AlCuCl_4$ solid without polystyrene (Fig. 13) is much slower than that by the MR type polystyrene-supported $AlCuCl_4$ (Fig. 10).

In conclusion, usage of macroreticular type cross-linked polystyrene as support is essential for the preparation of CO adsorbents having large abilities both in adsorption and desorption.

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