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Active Carbon-Supported Copper(I) Chloride as Solid Adsorbent for Carbon Monoxide[1)]

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An active carbon-supported copper(I) chloride (CuCl) is prepared by stirring active carbon in aqueous hydrochloric acid solution of CuCl, followed by removal of the liquid phase under 6 mmHg at 100 °C. The resulting solid rapidly adsorbs carbon monoxide (CO) at 20 °C from 9:1 CO–N_2 mixture under 1 atm (the CO partial pressure 0.9 atm) and the equilibrium molar ratio of adsorbed CO to CuCl is 0.88. All of adsorbed CO is promptly desorbed either by reducing CO partial pressure to 0.4 mmHg at 20 °C or by elevating temperature from 20 °C to 120 °C under 1 atm (the CO partial pressure 0.9 atm). Reversible adsorption-desorption cycles are repeated four times without measurable decrease in the adsorbing capacity. The adsorbing capacity of the active carbon-supported CuCl is much larger than either that of CuCl solid or that of active carbon. Effective CO adsorption by the present adsorbent is attributed to formation of complex between CO and CuCl, which is highly dispersed on the surface of active carbon.

Efficient methods for separation of carbon monoxide (CO) from gas mixtures are important in industry, since almost all CO sources are gas mixtures with nitrogen, hydrogen, methane, and carbon dioxide.[2)] Many liquid absorbents for CO were proposed.[3–5)] However, reports on solid adsorbents for CO have been scanty. Solid adsorbents have an advantage over liquid absorbents that pressure-swing methods are available for separation of CO. In addition, CO separated from gas mixtures by use of solid adsorbents is free from contamination with solvent vapor.

Although a Y-type zeolite-supported copper(I) ion adsorbed CO,[6)] the interaction between CO and the copper(I) ion was so strong that adsorbed CO could not be sufficiently desorbed even at the CO partial pressure 10^{-4} mmHg (1.0 mmHg=1.33×10^2 Pa). A patent[7)] claimed that copper(I) ion supported on zeolites, which had high ratios of silica to alumina, had CO adsorbing abilities. The amount of adsorbed CO was rather independent of CO partial pressure at the partial pressure larger than 10 mmHg.

Previously, the authors reported that aluminium copper(I) chlorides supported both on polystyrene resin[8)] and on active carbon[9,10)] reversibly adsorbed CO under mild conditions.

In this paper, preparation of active carbon-supported copper(I) chloride (CuCl) as solid CO adsorbents is reported. Their CO adsorbing and desorbing abilities as well as effects of preparation solvent on the ability are shown. Pore size distribution, BET surface area, and distribution of CuCl of the adsorbents are also described. Mechanism of effective and reversible adsorption of CO is discussed on the basis of these results.

Experimental

Materials. Active carbon was obtained from Kureha Chemical Industry Co. (Petroleum pitch, BAC G-70R, Lot No. 810117, average diameter ca. 0.7 mm) and was subjected to a reduced pressure (6 mmHg) at 200 °C for 5 h. Copper(I) chloride (guaranteed grade) was purchased from Koso Chemical Co. All other metal salts and solvents were commercially obtained.

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

Preparation of CO Adsorbents. A predetermined amount of CuCl was magnetically stirred in 15 cm^3 of various solvents under dry nitrogen at room temperature for 1 h, and then 10 g of the active carbon was added to the mixture. After stirring the mixture for 1 h, the liquid phase was removed at 6 mmHg, 100 °C for 1 h.

Solid of CuCl without active carbon was prepared as white powder in the same way as described above except for the absence of the active carbon.

Determination of the Amount of CuCl in the Adsorbent. The adsorbent was thoroughly washed by stirring for 24 h at room temperature in four portions of aqueous hydrochloric acid solution (3 mol dm^{-3}, total volume 2000 cm^3). Total amount of copper atoms in the solution was determined by atomic absorption spectroscopy (Shimadzu Co., model AA-646).

Measurements of Pore Size Distribution and BET Surface Area. Pore size distribution in the adsorbent was determined from desorption isotherm of nitrogen at 77 K by the method of Dollimore.[11)] The method takes advantage of capillary condensation theory and is based on the assumption of cylindrical pores with radii r. The value $\Delta v/\Delta r$ is obtained as a function of r, where Δv is sum of volume for the pores having radii between r and $r+\Delta r$. Desorption isotherm of nitrogen at 77 K was measured on a Calroerba Co. Sorptomatic Series 1800.

The BET surface area was measured by nitrogen adsorption at 77 K with a Micromeritics Instrument Model 2200A Rapid Surface Area Analyzer.

Electron Microscopy and X-Ray Microanalysis. Scanning electron microscopy and X-ray microanalysis on the beads of the adsorbents were carried out by use of a Hitachi Micro Scanning X-ray Analyzer Model X-650, which had resolution ability of X-ray image around 100 Å. The beads were embedded in epoxy resin, and the composites were cut with a stainless steel cutter and then were coated with gold so that cross-sections of the beads were irradiated by electron beam. The distributions of copper and chlorine atoms were evaluated from intensity of characteristic X-ray.

Measurement of CO Adsorption and Desorption. Adsorption of CO from CO–N_2 mixtures by the adsorbents was achieved at 20 °C under the atmospheric pressure using the apparatus depicted in Fig. 1. Uptake of CO was followed by a gas burette (3) using water as leveling liquid (5). The flask (2) containing the adsorbent (1) under nitrogen was connected with CO in the gas burette, and the adsorption was initiated by circulating the gases with the use of a gas pump (4). The circulation was effected for the first 10 min at a rate of 30 $cm^3 s^{-1}$ in order to mix the gas phase sufficiently.

Desorption of the adsorbed CO was carried out either by reducing the total pressure in the flask to 0.4 mmHg at 20 °C for 10 min or by heating the adsorbent to 120 °C under 1 atm for 10 min.

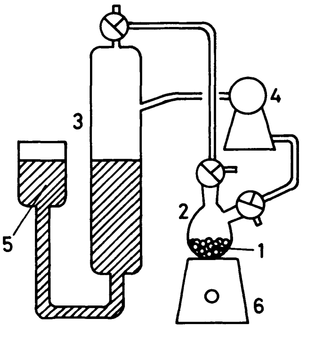

Fig. 1. Apparatus for measuring the amount of CO adsorbed by the adsorbents or desorbed from them. 1: adsorbent; 2: flask; 3: gas burette; 4: gas pump; 5: leveling liquid (water); 6: magnetic stirrer.

Results

Preparation of Active Carbon-Supported CuCl. Active carbon-supported CuCl adsorbents were obtained as black beads. The amount of CuCl supported on 10 g of the active carbon was 14.1 mmol, as determined by atomic absorption spectroscopy, when the charged amount of CuCl was 15.0 mmol and 15 cm^3 of aqueous hydrochloric acid solution (3 mol dm^{-3}) was used as preparation solvent. Thus, 94% of the charged CuCl was supported on the active carbon under these conditions.

BET surface area of the active carbon-supported CuCl composed of 14.1 mmol of CuCl and 10 g of the active carbon is 744 $m^2 g^{-1}$. This value is about 70% of the value (1044 $m^2 g^{-1}$) for the original active carbon.

Figure 2 depicts pore size distribution either in the present adsorbent (the solid line) or in the original active carbon (the broken line). The ordinate ($\Delta v/\Delta r$) approximately corresponds to number of pores. The number of pores with radii smaller than 10 Å for the present adsorbent is significantly smaller than the value for the original active carbon. In contrast, the number of pores with radii larger than 10 Å is almost identical with the value for the original active carbon.

Figure 3 shows scanning electron micrographs of a cross-section of a bead of the active carbon-supported CuCl. Waved white lines depict the distributions of copper atoms (a) and chlorine atoms (b) along the white straight lines on the cross-section. Both copper atoms and chlorine atoms are uniformly distributed in the bead. No deposition of CuCl is observed either on the surface of the bead or inside the bead.

Adsorption and Desorption of CO by the Active Carbon-Supported CuCl. Figure 4 shows repeated adsorption-desorption cycles using the active carbon-supported CuCl by temperature change. The adsorbent rapidly adsorbs CO on the contact with 9:1 CO–N_2 mixture at 20 °C under 1 atm (the region I-a), and the amount of CO adsorbed in 10 min is 11.8 mmol. An equilibrium is attained in 30 min, where the amount of adsorbed CO is 12.4 mmol. This value corresponds to molar ratio 0.88 of adsorbed CO to supported CuCl: 24 cm^3 (standard temperature and pressure) per 1 g of the adsorbent.

All of the adsorbed CO is desorbed in 10 min to the gas phase, as followed with the use of the gas burette, by heating the adsorbent to 120 °C at 1 atm (the region I-d in Fig. 4).

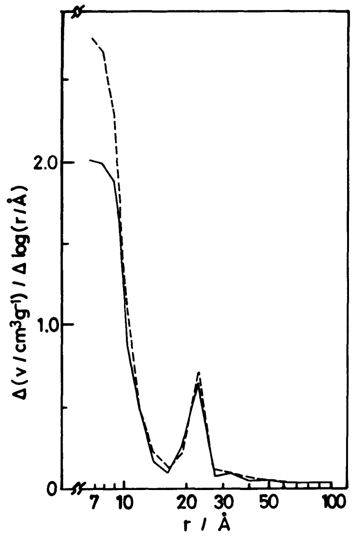

Fig. 2. Pore size distributions in the active carbon-supported CuCl (——) and the original active carbon (----): Δv is sum of volume for the pores having radii between r and $r+\Delta r$; the active carbon-supported CuCl was prepared from 15.0 mmol of CuCl and 10 g of the active carbon using 15 cm^3 of aqueous hydrochloric acid solution (3 mol dm^{-3}) as solvent, and contained 14.1 mmol of CuCl.

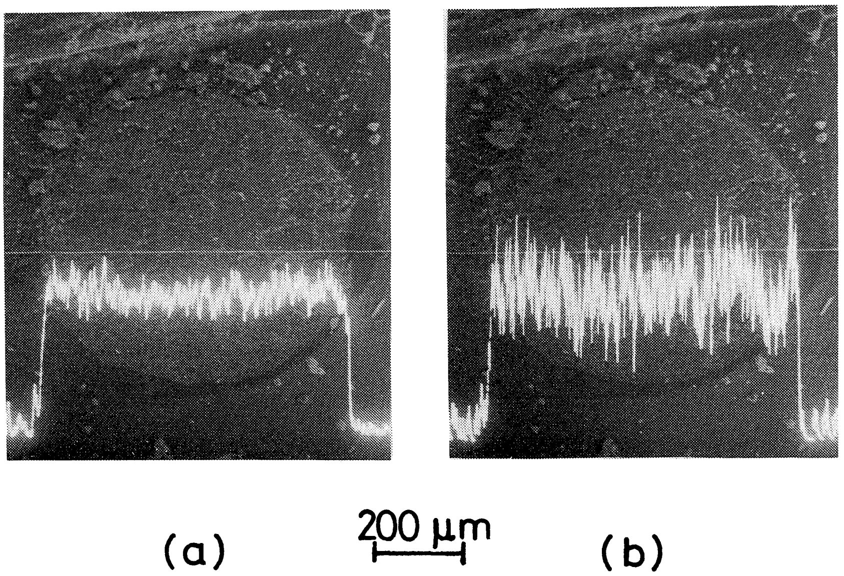

Fig. 3. Scanning electron micrographs for the cross-section of the active carbon-supported CuCl composed of 14.1 mmol of CuCl and 10 g of the active carbon: The waved white lines show distributions of copper atoms (a) and chlorine atoms (b) along the corresponding white straight lines.

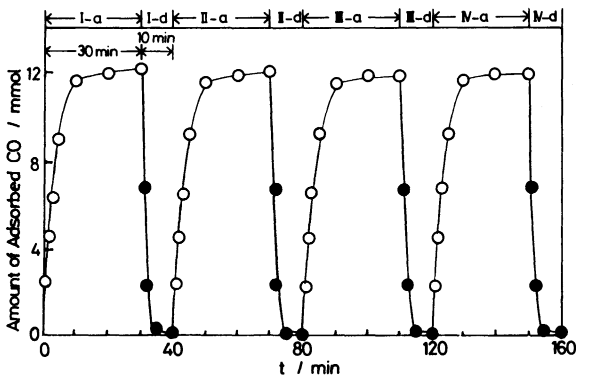

Fig. 4. Time courses of repeated CO adsorption-desorption cycles by the active carbon-supported CuCl using a change in temperature: CO adsorptions (○) from 9 : 1 CO-N_2 mixtures were carried out at 20 °C under 1 atm, and desorptions (●) of adsorbed CO were effected by heating the adsorbent to 120 °C under 1 atm for 10 min; the adsorbent was composed of 14.1 mmol of CuCl and 10 g of the active carbon.

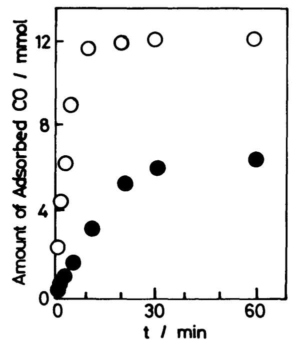

Fig. 5. CO adsorption and absorption from 9 : 1 CO-N_2 mixtures at 20 °C under 1 atm by the active carbon-supported CuCl (○) and by 2 mol dm^{-3} aqueous hydrochloric acid solution of CuCl (●): The charged amount of CuCl was 15.0 mmol.

On the next contact with 9:1 CO-N_2 mixture, the adsorbent rapidly adsorbs CO, as shown in the region II-a in Fig. 4, and the time course is almost identical with that in the first adsorption. The equilibrium amount of adsorbed CO is 12.4 mmol (24 cm^3 per 1 g of the adsorbent). The adsorption-desorption cycles are repeated four times without measurable deterioration.

Adsorption-desorption cycles for the present adsorbent were successfully carried out also by use of partial pressure change of CO in place of temperature change. Almost all of the adsorbed CO was rapidly desorbed by subjecting the adsorbent to a reduced pressure (0.4 mmHg) at 20 °C. In the following adsorptions, the time courses were virtually the same as the ones depicted by the open circles in Fig. 4. The cycles were repeated four times without measurable decrease in the adsorbing capacity.

As shown in Table 1, CO adsorbing capacity (12.4 mmol) of the active carbon-supported CuCl is much larger than either that (0.0 mmol) of the solid of CuCl or that (3.3 mmol) of the active carbon without CuCl. The capacity (6.5 mmol) of the aqueous hydrochloric acid solution of CuCl is about half of the value (12.4 mmol) of the active carbon-supported CuCl. The rate of adsorption for the active carbon-supported CuCl is much larger than that for the aqueous hydrochloric acid solution of CuCl, as depicted in Fig. 5.

Table 1. Adsorbing Capacities of the CO Adsorbents and Absorbent[a)]

Adsorbent or absorbent	Amount of CuCl / mmol	CO adsorbed in 60 min	
		Amount / mmol	Molar ratio to CuCl
Active carbon-supported CuCl[b)]	14.1	12.4	0.88
Solid of CuCl	15.0	0.0	0.00
Original active carbon[b)]	—	3.3[c)]	—
Hydrochloric acid solution of CuCl	15.0	6.5	0.43

a) At 20 °C; initial volume of gas mixture 1500 cm^3; initial partial pressures of CO and N_2, respectively, were 0.9 and 0.1 atm. b) Active carbon, 10 g. c) The value was measured using helium, in place of N_2, as balance, since the magnitudes of adsorptions of CO and N_2 to the active carbon were comparable with each other, and adsorption of helium was negligibly small.

Table 2. CO Adsorbing Capacities of Solid Adsorbents Composed of Various Copper(I) Halides and the Active Carbon[a)]

Copper(I) halide	Equilibrium amount of adsorbed CO / mmol
CuCl	12.4
CuBr	9.5
CuI	1.7

a) At 20 °C, under 1 atm; initial volume of gas mixture 1500 cm^3; initial partial pressures of CO and N_2, respectively, were 0.9 and 0.1 atm; the adsorbents were prepared from 15.0 mmol of copper(I) halide and 10 g of the active carbon using 15 cm^3 of 28% ammoniacal aqueous solution as solvent.

Table 2 lists CO adsorbing capacities of the adsorbents prepared from the active carbon and various copper(I) halides by use of 28% ammoniacal aqueous solution as solvent. The capacity decreases in the following order: CuCl>CuBr$\gg$CuI. The adsorbing capacities (0.8, 0.9, and 0.9 mmol, respectively) for the adsorbents prepared from 10.0 g of the active carbon and 15.0 mmol of either sodium chloride, zinc chloride, or magnesium chloride were small.

Effect of Preparation Solvent on CO Adsorbing Capacity. Figure 6 depicts the dependence of the CO adsorbing capacity of the active carbon-supported CuCl on the concentration of aqueous hydrochloric acid solution used as preparation solvent. The concentration of CuCl in the solution is kept constant at 1.0 mol dm^{-3}. The adsorbing capacity of the active carbon-supported CuCl increases with increasing concentration of aqueous hydrochloric acid solution up to the concentration 1.0 mol dm^{-3}. At the concentration larger than 1.0 mol dm^{-3}, however, the capacity is constant irrespective of the concentration.

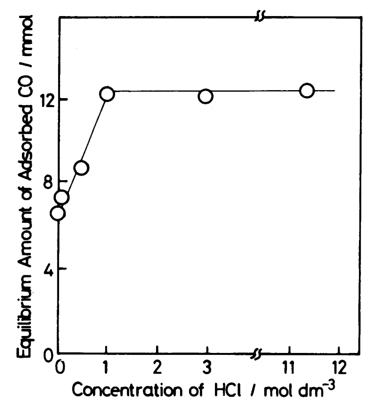

Fig. 6. Dependence of CO adsorbing capacity of the active carbon-supported CuCl on the concentration of aqueous hydrochloric acid solution used as preparation solvent; $[\mathrm{CuCl}]_0 = 1.0$ mol dm^{-3}.

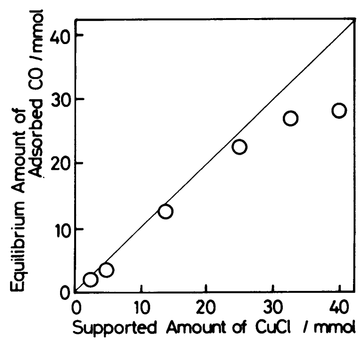

Fig. 7. Plot of CO adsorbing capacity of the active carbon-supported CuCl against the supported amount of CuCl.

Active carbon 10 g; the straight line is theoretical one calculated under the assumption that the supported CuCl forms 1 : 1 complex with CO.

Table 3 shows the CO adsorbing capacities of the active carbon-supported CuCl prepared by using various solvents. The adsorbent prepared using aqueous hydrochloric acid solution exhibits much larger adsorbing capacity and larger ratio of adsorbed CO to supported CuCl than those of the ones prepared using water, acetonitrile, and toluene.

Effect of Supported Amount of CuCl on CO Adsorbing Capacity. As shown in Table 4, both the ratio of the supported amount of CuCl to the charged amount and BET surface area of the active carbon-supported CuCl decrease with increasing charged amount of CuCl. Here, the amount of the active carbon is kept constant at 10 g.

Figure 7 depicts plot of CO adsorbing capacity of the active carbon-supported CuCl against the charged amount of CuCl. When the supported amount is smaller than 25 mmol, all the experimental points

Table 3. CO Adsorbing Capacities of the Active Carbon-Supported CuCl Prepared by Using Various Preparation Solvents[a)]

Solvent	Ratio of supported CuCl to charged CuCl	Amount of adsorbed CO / mmol	Molar ratio of adsorbed CO to supported CuCl
Aqueous hydrochloric acid solution (3 mol dm^{-3})	0.94	12.4	0.88
Water	0.70	5.6	0.64
Acetonitrile	0.87	6.1	0.47
Toluene	0.69	1.3	0.13

a) At 20 °C; initial volume of gas mixture 1500 cm^3; initial partial pressures of CO and N_2, respectively, were 0.9 and 0.1 atm; the adsorbents were prepared from 15.0 mmol of CuCl and 10 g of the active carbon using 15 cm^3 of one of the solvents.

Table 4. Supported Amounts of CuCl, Ratios of the Supported CuCl to the Charged CuCl, and BET Surface Areas for the Active Carbon-Supported CuCl Prepared from 10 g of the Active Carbon and Various Amounts of CuCl[a)]

Amount of CuCl / mmol		Ratio of supported CuCl to charged CuCl	BET surface area / m^2 g^{-1}
Charged	Supported		
0.0	0.0	—	1044
2.5	2.5	0.99	897
5.0	4.8	0.96	887
10.0	9.3	0.93	811
15.0	14.1	0.94	744
20.0	18.2	0.91	661
30.0	24.9	0.83	676
40.0	33.2	0.83	565
50.0	40.5	0.81	531

a) 15 cm^3 of 3 mol dm^{-3} aqueous hydrochloric acid solution was used as preparation solvent.

satisfactorily fit the theoretical line (the solid straight line) calculated under the assumption that the supported CuCl forms 1 : 1 complex with CO. At the supported amount larger than 25 mmol, however, CO adsorbing capacity is considerably smaller than the value estimated under the assumption.

Discussion

Preparation of the Active Carbon-Supported CuCl. Significant decrease of the BET surface area of the active carbon on the formation of the active carbon-supported CuCl adsorbents (Table 4) shows that CuCl is supported on the surface of the active carbon in the adsorbents. There, CuCl molecules probably exist in both monomeric and dimeric forms, resulting in effective adsorption of CO. Formation of large aggregates of CuCl is unlikely, since solid of CuCl shows no measurable adsorbing ability (Table 1) at 20 °C under the CO partial pressure 0.9 atm.

The proposed structure of the adsorbent involving CuCl in monomeric and dimeric forms is consistent with pore size distribution (Fig. 2) which indicates the presence of CuCl in the pores having radii smaller than 10 Å. The number of these micro-pores in the adsorbents is much smaller than that for the original active carbon, whereas the number of pores with radii larger than 10 Å is almost identical with each other. Molecular dimensions of monomeric form of CuCl and its dimeric form, respectively, are approximately 3.4 Å×3.4 Å×4.5 Å and 3.4 Å×3.9 Å× 6.7 Å. These dimensions are evaluated from the bond length (2.05 Å)[12)] of the Cu–Cl bond in solid of CuCl and the ionic radii (0.74 Å for copper(I) ion and 1.67 Å for chlorine anion).[12)]

These arguments are further supported by the result of X-ray microanalysis (Fig. 3) showing uniform distribution of CuCl in the beads of the adsorbents without formation of any deposits of metal salts. Gradual decrease of BET surface area of the active carbon with increasing amount of supported CuCl (Table 4) is also consistent with them.

Rough estimation using the decrease (300 m^2 g^{-1}) of the BET surface area for the adsorbent composed of 10 g of the active carbon and 14.1 mmol of CuCl indicates that one molecule of CuCl occupies around 35 Å^2 of the surface area of the active carbon.

CO Adsorbing and Desorbing Ability of the Active Carbon-Supported CuCl. By use of the active carbon-supported CuCl, CO separation is successfully achieved both by temperature-swing method (Fig. 4) and by pressure-swing method. All the CO adsorbed at 20 °C under 1 atm (the CO partial pressure 0.9 atm) is desorbed both by heating the adsorbent to 120 °C under 1 atm and by reducing CO partial pressure to 0.4 mmHg at 20 °C. The amount of CO separated with the use of the present adsorbent for each of the cycles involving CO adsorption at 20 °C under 1 atm and desorption at 120 °C or for each of the cycles involving adsorption at 20 °C under 1 atm and desorption at 0.4 mmHg, 20 °C is

24 cm^3 (standard temperature and pressure) per 1 g of the adsorbent.

Complete desorption of adsorbed CO for the present adsorbent is highly in contrast with the fact that CO adsorbed by Y-type zeolite-supported copper(I) ion is not effectively desorbed even at 10^{-4} mmHg.[6] Desorption of CO, which is adsorbed by the adsorbent composed of copper(I) ion and zeolites having high SiO_2/Al_2O_3 ratios, is also difficult, as indicated by rather small dependence of the amount of adsorbed CO on CO partial pressure.[7]

The amount of CO adsorbed by 1 g of the active carbon-supported CuCl composed of 24.9 mmol of CuCl and 10 g of the active carbon is 38 cm^3 (standard temperature and pressure). The value is 2.4 times as large as the value (16 cm^3) for the adsorbent composed of copper(I) ion and high SiO_2/Al_2O_3 ratio zeolite.[7]

Mechanism of CO Adsorption by the Active Carbon-Supported CuCl. Much larger adsorbing capacity (12.4 mmol) of the active carbon-supported CuCl than both the value (0.0 mmol) for CuCl solid and that (3.3 mmol) for the active carbon (Table 1) shows that the presence of both of CuCl and active carbon is essential for the effective adsorption of CO by the active carbon-supported CuCl.

In the present adsorbent, CO is adsorbed by formation of 1:1 complex with the CuCl supported on the active carbon. This is clearly seen by the satisfactorily straight line with a slope unity for the plot between the CO adsorbing capacity and the supported amount of CuCl (Fig. 7). Deviation of the plot from the straight line at the supported amount 25 mmol or larger is ascribed to formation of small aggregates of CuCl at such large supported amounts. Furthermore, quite small capacities of the active carbon-supported sodium chloride, zinc chloride, and magnesium chloride confirm that the copper(I) ions are active species of CO adsorption by the present adsorbent. A possibility that surface of the active carbon treated with CuCl in aqueous hydrochloric acid solution has a CO adsorbing ability is ruled out by the independence of the capacity from the concentration of aqueous hydrochloric acid solution in the concentration range from 1.0 to 11.2 mol dm^{-3} (Fig. 6).

The order ($CuCl > CuBr \gg CuI$) in the CO adsorbing capacities of the active carbon-supported copper(I) halides (Table 2) is identical with that for copper(I) halides in various solvents.[13]

Effective adsorbing ability of the active carbon-supported CuCl is attributed to sufficient dispersion of CuCl on the surface of the active carbon, which produces vacant coordination sites at the copper(I) ions. Both the adsorbing capacity and the ratio of adsorbed CO to supported CuCl for the active carbon-supported CuCl prepared by use of aqueous hydrochloric acid solution are larger than the corresponding values for the ones prepared by use of acetonitrile, water, and toluene (Table 3). Aqueous hydrochloric acid solutions effectively dissolve CuCl in the form of $CuCl_2^-$,[14] whereas CuCl exhibits small solubility in acetonitrile or water, and virtually no solubility in toluene. When active carbon is stirred in hydrochloric acid solution of CuCl, most of the $CuCl_2^-$ ions, which are solvated with water, are supported on the surface of the active carbon due to mutual interactions. In the active carbon-supported CuCl obtained after evaporation of the liquid phase, CuCl molecules are satisfactorily dispersed on the surface of the active carbon. With the use of acetonitrile and water, however, the amount of CuCl supported on the active carbon is smaller due to small solubility of CuCl in them, and dispersion of CuCl molecules in the resultant adsorbents is poorer. The adsorbent prepared by use of toluene exhibits the smallest ability.

These arguments are further confirmed by the fact that the adsorbing capacity increases with increasing concentration of hydrochloric acid up to 1.0 mol dm^{-3}, when the charged amount of CuCl is 1.0 mol dm^{-3} (Fig. 6). One molecule of CuCl requires one molecule of hydrogen chloride for the formation of $CuCl_2^-$.

Adsorption of CO by the active carbon-supported CuCl is faster than that by a hydrochloric acid solution of CuCl (Fig. 5). This is due to the fact that diffusion of CO in liquid phase, which is rate-determining in the absorption by the solution, is not required for the present solid adsorbent to adsorb CO from gas phase.

In conclusion, the active carbon-supported CuCl is a solid adsorbent of CO having high abilities with respect to both adsorption and desorption. CO is efficiently adsorbed by the formation of complex with the CuCl, which is highly dispersed on the surface of the active carbon.

References

1) A preliminary communication: H. Hirai, K. Wada, and M. Komiyama, *Chem. Lett.*, **1983**, 361.

2) A. L. Kohl and F. C. Riesenfeld, "Gas Purification," 3rd ed., Gulf Publishing Co., Houston (1979).

3) A. T. Larson and C. S. Teitsworth, *J. Am. Chem. Soc.*, **44**, 2878 (1922).

4) H. Deringer, *Chimia*, **1**, 125 (1947).

5) D. J. Haase, *Chem. Eng. News*, **1975**, August 4, 52.

6) Y.-Y. Huang, *J. Catal.*, **30**, 187 (1973).

7) J. A. Rabo, J. N. Francis, and C. L. Angell, U.S. Patent 4019879 (1977).

8) H. Hirai, M. Komiyama, and S. Hara, *Chem. Lett.*, **1982**, 1685.

9) H. Hirai, M. Komiyama, and K. Wada, *Chem. Lett.*, **1982**, 1025.

10) H. Hirai, K. Wada, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **59**, 1043 (1986).

11) D. Dollimore and G. R. Heal, *J. Appl. Chem.* (London), **14**, 109 (1964).

12) "Kagaku Binran, Kiso-hen," ed by the Chemical Society of Japan, Maruzen, Tokyo (1984), pp. II-715 and II-718.

13) M. I. Bruce, *J. Organomet. Chem.*, **44**, 209 (1972).

14) D. D. Davis, K. L. Stevenson, and C. R. Davis, *J. Am. Chem. Soc.*, **100**, 5344 (1978).