April, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 1043—1049 (1986)* 1043

Active Carbon-Supported Aluminium Copper(I) Chloride as Solid Carbon Monoxide Adsorbent

Hidefumi HIRAI,* Keiichiro WADA, and Makoto KOMIYAMA
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received October 21, 1985)

Active carbon-supported aluminium copper(I) chloride ($AlCuCl_4$) is prepared by mixing active carbon with toluene solution of $AlCuCl_4$, followed by the removal of the liquid phase at 6 mmHg, 100 °C. The active carbon-supported $AlCuCl_4$ rapidly adsorbs carbon monoxide (CO) at 20 °C under 1 atm from 9:1 $CO-N_2$ mixture and the equilibrium molar ratio of adsorbed CO to $AlCuCl_4$ is 1.03. Adsorbed CO is desorbed either by reducing pressure or by elevating temperature. In the second adsorption, which is carried out after the desorption at 6 mmHg, 20 °C for 10 min, the molar ratio of adsorbed CO to $AlCuCl_4$ is 0.51. The molar ratios are constant at 0.51 in the third and later adsorptions. The CO adsorbing ability of the active carbon-supported $AlCuCl_4$ remains virtually unchanged on repeated contacts with nitrogen gas containing 9000 ppm of water.

Carbon monoxide (CO), a valuable raw material in chemical industry,[1] is produced in large scale by partial oxidation and water gas reaction of petroleum or coal.[2] In addition, considerable amounts of CO are present in exhausted gases from various chemical plants. Since all of these sources of CO are gas mixtures with methane, hydrogen, nitrogen, carbon dioxide, and water, separation and purification of CO from gas mixtures are necessary.[2,3]

Many liquid absorbents for CO have been proposed.[2-8] The toluene solution of polystyrene-aluminium copper(I) chloride ($AlCuCl_4$) complex, devised by the present authors,[7,8] has reversibly absorbed CO under mild conditions. $AlCuCl_4$, which is highly reactive with water vapor, is protected from water vapor by the polystyrene in the polymer-metal complex, and thus separation of CO from gas mixtures containing water vapor is successfully achieved with the absorbent.

In contrast to a number of proposals on liquid CO absorbents, reports on solid adsorbents for CO are scanty. Although Y zeolite-supported Cu(I) ion adsorbed CO, the adsorption was so strong that adsorbed CO did not effectively desorb even at 10^{-4} mmHg (1.0 mmHg=1.33×10^2 Pa).[9] In the case of the adsorbents composed of Cu(I) ion and zeolites having high SiO_2/Al_2O_3 molar ratios,[10] the amounts of Cu(I) ion, and thus the amounts of adsorbed CO, per 1 g adsorbents were small due to small ion-exchange capacities of the zeolites.

In preliminary communications, the authors reported solid CO adsorbents composed of $AlCuCl_4$ and active carbon[11] or polystyrene resin.[12] These adsorbents exhibited reversible adsorptions of CO under mild conditions and were stable against water in gas mixtures.

In this paper, CO adsorbing and desorbing abilities of adsorbents composed of $AlCuCl_4$ and active carbon as well as their water-resistance are reported in detail. The selectivity of the adsorbents for the adsorption of CO with respect to the adsorptions of other gases is shown. Furthermore , results of measurements of pore size distributions both for the adsorbents and for the original active carbon are presented. The mechanism of the water-resistance of the present adsorbents is discussed in terms of these results.

Experimental

Materials. Active carbon, prepared from petroleum pitch, was obtained from Kureha Chemical Industry Co. (BAC G-70R, Lot No. 810117, average diameter ca. 0.7 mm), and was subjected to a reduced pressure (6 mmHg) at 200 °C immediately before use.

Aluminium chloride (Kishida Chemical Co., guaranteed grade) was purified by sublimation. Copper(I) chloride (Koso Chemical Co., guaranteed grade) was reprecipitated from concentrated hydrochloric acid solution by the addition of water, followed by washing successively with ethanol and diethyl ether, and then was dried in vacuo.[13] Toluene was dried over metallic sodium and was distilled.

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

Preparation of Adsorbent. 20.0 mmol of aluminium chloride and 20.0 mmol of copper(I) chloride were magnetically stirred in 20 cm^3 of toluene at 50 °C for 4 h under dry nitrogen. The resultant homogeneous dark-colored toluene solution of $AlCuCl_4$ was added to 10 g of active carbon, kept in an evacuated 100 cm^3 vessel, avoiding contamination of air with the use of a dropping funnel. The mixture was stirred with a magnetic stirrer for 1 h, and then the liquid phase was thoroughly removed at 6 mmHg, 100 °C for 1 h. The adsorbents were obtained as black to grey beads.

Solid of $AlCuCl_4$ without active carbon was prepared as described above except for the absence of active carbon. The solid was white to grey aggregates.

Determination of the Amount of Metal Salt in the Adsorbent. The adsorbent was thoroughly washed by stirring for 6 h in three portions of aqueous hydrochloric acid solution (3 mol dm^{-3}, total volume 1500 cm^3). The total amounts of copper atoms in the solution were evaluated by atomic absorption spectroscopy (Shimadzu Co., model AA-646).

Measurement of BET Surface Area and Pore Size Distribution. BET surface area was calculated from desorption isotherm of nitrogen at 77 K. Pore size distribution was determined also from the isotherm by the method of Dollimore.[14] The method takes advantage of capillary condensation theory and is based on the assumption of cylindrical pores with

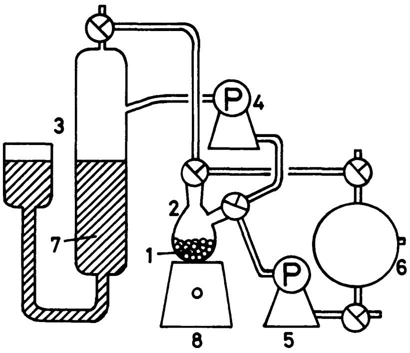

Fig. 1. Apparatus for measuring the amount of CO adsorbed by the adsorbents or desorbed from them; **1**: adsorbent; **2**: flask; **3**: gas burette; **4**: gas pump A; **5**: gas pump B; **6**: gas reservoir for nitrogen containing water; **7**: leveling liquid (toluene); **8**: magnetic stirrer.

radius 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.

Measurement of CO Adsorption and Desorption. The adsorptions of CO from CO–N_2 mixtures by the adsorbents were carried out 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 toluene as leveling liquid (7). The flask (2) containing the adsorbent (1) under nitrogen was connected with CO or CO–N_2 mixtures, and the adsorption was initiated by circulating the gas with the use of gas pump A (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.

The desorption of the adsorbed CO was carried out either by reducing the total pressure in the flask at 20 °C for 10 min or by elevating temperature from 20 °C to a predetermined temperature.

Contacts of the Adsorbent with Water Vapor. The contact of the adsorbent with water vapor was effected by circulating 5000 cm^3 of nitrogen gas, which had total pressure of 1 atm and contained 2.0 mmol of water (water content 9000 ppm), for 10 min on the magnetically stirred adsorbent with the use of a gas pump B (5). The nitrogen–water mixture was prepared by the introduction of water into an evacuated 5000 cm^3 vessel ((6) in Fig. 1) using a microsyringe, followed by the addition of dry nitrogen gas in an amount required to make the total pressure atmospheric.

Results

Preparation of Active Carbon-Supported $AlCuCl_4$. Toluene solutions of $AlCuCl_4$ were obtained as homogeneous dark-colored solutions by heating aluminium chloride and copper(I) chloride at charged molar ratio unity in toluene. On the addition of the toluene solution of $AlCuCl_4$ to active carbon, the color of the liquid phase rapidly decolorized. This result shows specific interactions between active carbon and $AlCuCl_4$. On removal of the liquid phase, active carbon-supported $AlCuCl_4$ was obtained as black to grey beads.

Table 1. BET Surface Areas of Adsorbents

Adsorbent	BET surface area $m^2 g^{-1}$
Active carbon-supported $AlCuCl_4$[a]	870
Original active carbon	1230

a) The adsorbent was prepared from 20.0 mmol of $AlCuCl_4$ and 10 g of active carbon, and contained 17.2 mmol of $AlCuCl_4$.

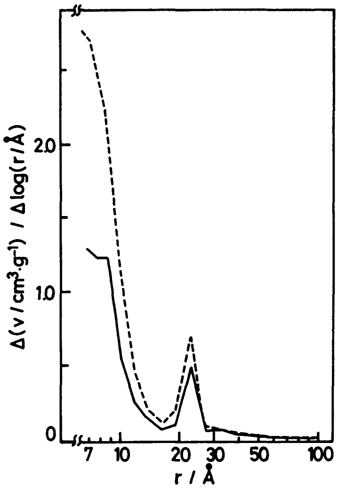

Fig. 2. Pore size distributions in the active carbon-supported $AlCuCl_4$ (——) and original active carbon (---): Δv is sum of volume for the pores having radii between r and $r+\Delta r$.

The atomic absorption spectroscopy showed that 17.2 mmol of $AlCuCl_4$ was supported to 10 g of active carbon, when 20.0 mmol of $AlCuCl_4$ in 20 cm^3 of toluene was treated with the active carbon. Thus, 86% of the charged $AlCuCl_4$ was supported to the active carbon under these conditions.

Table 1 shows the results on the measurement of BET surface area. The surface area (870 $m^2 g^{-1}$) for the adsorbent is about 70% of the value (1230 $m^2 g^{-1}$) 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 dotted line). The ordinate ($\Delta v/\Delta r$) approximately corresponds to number of pores. The number of pores with radii smaller than 15 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 15 Å is almost identical with the value for the original active carbon. This result shows that small BET surface area (870 $m^2 g^{-1}$) of the present adsorbent, compared with the value (1230 $m^2 g^{-1}$) of the original active carbon, is almost totally attributable to decrease in the number of pores with radii smaller than 15 Å.

Adsorption and Desorption of CO by the Active Carbon-Supported $AlCuCl_4$. As shown by the open

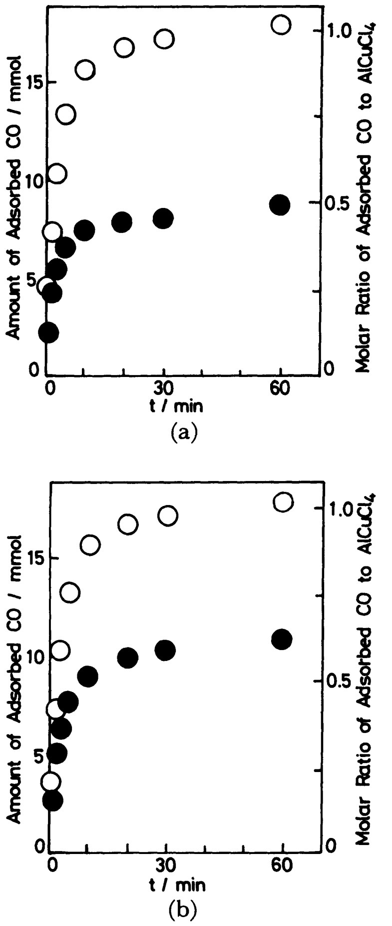

Fig. 3. Adsorption of CO by the active carbon-supported $AlCuCl_4$ at 20 °C under 1 atm: the desorption conditions were 6 mmHg at 20 °C for 10 min for (a), and 100 °C, 1 atm for (b); the first adsorption by a virgin adsorbent (○); the second adsorption by the adsorbent which was subjected to the desorption conditions after the first adsorption (●); the adsorbent was prepared from 20.0 mmol of $AlCuCl_4$ and 10 g of active carbon, and contained 17.2 mmol of $AlCuCl_4$; the initial volume of gas mixture was 1500 cm^3 and the initial partial pressures of CO and N_2 were 0.9 and 0.1 atm, respectively.

circles in Fig. 3(a), the adsorbent rapidly adsorbs CO on the contact with 9:1 CO–N_2 mixture at 20 °C under 1 atm. After 10 min, the amount of adsorbed CO is 15.6 mmol, which is 88% of the equilibrium value (17.7 mmol) determined after 60 min. The equilibrium molar ratio of adsorbed CO to the $AlCuCl_4$ supported to active carbon is 1.03; the amount of the supported $AlCuCl_4$ is 17.2 mmol.

After being subjected to a reduced pressure (6 mmHg) at 20 °C for 10 min, the adsorbent was again contacted with 9:1 CO–N_2 mixture. The adsorbent showed a rapid adsorption and the equilibrium value of adsorbed CO was 8.8 mmol (● in Fig. 3(a)). The equilibrium value for the third adsorption by the adsorbent, which was subjected to a reduced pressure (6 mmHg) at 20 °C for 10 min after the second adsorption, was also 8.8 mmol. The CO adsorption-desorption cycle, composed of the adsorption of 8.8 mmol of CO at 760 mmHg and the desorption of almost the identical amount of CO at 6 mmHg, was repeated five (the maximum number examined) times without measurable deterioration.

Table 2. Effect of CO Partial Pressure on the Amount of CO Adsorbed by the Active Carbon-Supported $AlCuCl_4$ at 20 °C[a)]

CO partial pressure / mmHg	Molar ratio of CO adsorbed in 60 min to $AlCuCl_4$
152	0.13
380	0.36
684	1.03
760	1.05

a) $AlCuCl_4$, 17.2 mmol; active carbon, 10 g.

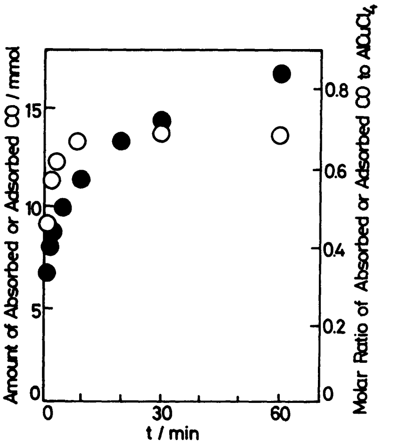

Fig. 4. Absorption or adsorption of CO by a toluene solution of $AlCuCl_4$ (○) or by a solid of $AlCuCl_4$ (●) at 20 °C under 1 atm: the initial partial pressure of CO for the absorption by the toluene solution was 0.8 atm, whereas that for the adsorption by the solid was 0.9 atm; the amount of $AlCuCl_4$, 20.0 mmol.

The adsorbed CO was also desorbed by elevating temperature (Fig. 3(b)). The active carbon-supported $AlCuCl_4$, which was prepared separately, adsorbed 17.7 mmol of CO on the first contact with 9:1 CO–N_2 mixture at 20 °C (the open circles). On the elevation of temperature from 20 to 100 °C under 1 atm, the adsorbent rapidly desorbed 11.0 mmol of CO. In the following adsorption, the equilibrium value of the adsorbed CO was 11.0 mmol (the closed circles in Fig. 3(b)). The cycle involving the adsorption of 11.0 mmol of CO at 20 °C, followed by the desorption of 11.0 mmol of CO at 100 °C, was repeated five times without deterioration.

Table 2 shows the dependence of the amount of CO adsorbed by the active carbon-supported $AlCuCl_4$ on the partial pressure of CO in CO–N_2 mixtures. The molar ratio of the adsorbed CO to $AlCuCl_4$, supported to active carbon, decreases with decreasing partial

Table 3. Adsorbing Capacities of the CO Adsorbents and Absorbent[a]

Adsorbent or absorbent	CO adsorbed in 60 min	
	Amount/mmol	Molar ratio to $AlCuCl_4$
Active carbon-supported $AlCuCl_4$[b,c]	17.7	1.03
Solid of $AlCuCl_4$[b]	14.6[d]	0.85
Toluene solution of $AlCuCl_4$[b]	14.4	0.84
Original active carbon [c]	3.3[e]	—

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) $AlCuCl_4$, 17.2 mmol. c) Active carbon, 10 g. d) This value was estimated from the result in Fig. 4, using the fact that the amount of adsorbed CO was proportional to the amount of $AlCuCl_4$. e) The measurement was carried out using helium, in place of nitrogen, as balance, since the magnitudes of adsorptions of CO and N_2 to active carbon were comparable with each other, and adsorption of helium was negligibly small (Table 5).

pressure from 1.05 at 760 mmHg to 0.13 at 152 mmHg.

For the purpose of comparison, the time course of the CO absorption by a toluene solution of $AlCuCl_4$ (○) and the time course of the adsorption by a solid of $AlCuCl_4$ (●) without active carbon are depicted in Fig. 4. The toluene solution of 20.0 mmol of $AlCuCl_4$ in 20 cm^3 of toluene rapidly absorbs CO from 8:2 CO–N_2 mixture. The equilibrium amount of absorbed CO, determined after 60 min, is 14.0 mmol ($CO/AlCuCl_4$= 0.70). The solid of 20.0 mmol of $AlCuCl_4$ also adsorbs CO on the contact with 9:1 CO–N_2 mixture. The rate of adsorption, however, is much smaller than the value for the active carbon-supported $AlCuCl_4$ adsorbent, and the adsorption does not attain an equilibrium even after 6 h.

Table 3 lists the amounts of CO adsorbed or absorbed for 60 min by the three types of the adsorbents and absorbent as well as the value for the original active carbon. The active carbon-supported $AlCuCl_4$ adsorbs CO about equimolar to $AlCuCl_4$, and shows larger adsorbing capacity either than the toluene solution of $AlCuCl_4$ or than the solid of $AlCuCl_4$. The CO adsorbing ability of the original active carbon itself is small under these conditions.

Desorption of Adsorbed CO under Various Desorption Conditions. The effect of desorption conditions on the degree of desorption of adsorbed CO from the adsorbent is shown in Table 4. Here, the degrees of desorption under the specified conditions are expressed in terms of the ratios of the amounts of desorbed CO to the capacities of the adsorbent (the amounts of CO adsorbed in the first adsorption by a virgin adsorbent). The first adsorption and the second one by the adsorbent, which was subjected to the specified desorption conditions after the first adsorption, were carried out, keeping the adsorption conditions constant: 20 °C and the initial CO pressure 0.9 atm. The amount of the CO desorbed under the desorption conditions was evaluated from the amount of CO adsorbed in the second adsorption.

When the desorption conditions are 20 °C, 6.0 mmHg, the amount of adsorbed CO in the second and later adsorptions is 8.8 mmol, as depicted in Fig. 3(a). Thus, 50% of CO with respect to the amount (17.7 mmol) adsorbed in the first adsorption is desorbed under the above conditions.

Table 4. Dependence of the Amount of Desorbed CO on the Desorption Conditions for the Active Carbon-Supported $AlCuCl_4$[a]

Desorption conditions		Ratio of amount of desorbed CO to adsorbing capacity[b]
T/°C	Pressure/mmHg	
20	6.0	0.50
20	0.4	0.61
100	0.4	0.91
180	0.4	0.99
180	760.0	0.72
100	760.0	0.62

a) $AlCuCl_4$, 17.2 mmol; active carbon, 10 g. b) The ratio of the amount of desorbed CO under specified conditions to the amount of CO adsorbed in the first adsorption by a virgin adsorbent.

Table 5. Adsorbing Capacities of the Active Carbon-Supported $AlCuCl_4$ and the Original Active Carbon for Various Kinds of Gases[a]

Gas	Amount of gas adsorbed by 1 g of Adsorbent/cm^3 g^{-1}	
	Active carbon-supported $AlCuCl_4$	Original active carbon
H_2	0.0	0.0
He	0.0	0.0
N_2	0.8	7.2
Ar	0.9	6.3
CH_4	4.2	21.5
CO	24.1	9.5

a) Gas pressure 1 atm, 20 °C.

Almost all of the adsorbed CO is desorbed at a reduced pressure and a high temperature: 0.4 mmHg and 180 °C. When these desorption conditions are used, 17.7 mmol of CO is separated by each of adsorption-desorption cycles.

Selectivity of CO Adsorption for the Active Carbon-Supported $AlCuCl_4$. Table 5 shows adsorbing capacities on various gases for the active carbon-supported $AlCuCl_4$. The adsorbent exhibits no measurable ad-

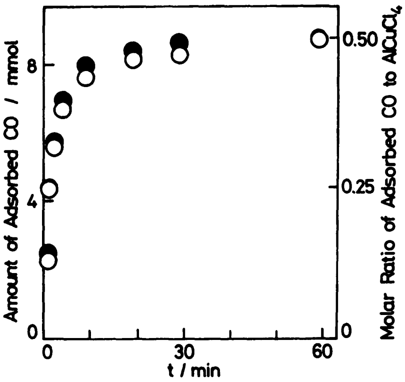

Fig. 5. CO adsorbing capacity of the active carbon-supported $AlCuCl_4$ before (○) and after (●) the contact of the adsorbent with 5000 cm^3 nitrogen gas containing 2.0 mmol of water (water content 9000 ppm) for 10 min: The adsorptions of CO were carried out by the contacts with 9:1 CO–N_2 gas mixtures at 20 °C, 1 atm; the desorptions of CO were achieved at 20 °C, 6 mmHg for 10 min.

sorption of hydrogen or helium at 1 atm, 20 °C. Adsorption of nitrogen or argon is not significant either. The amount of methane adsorbed is only 17% of the value of CO.

In contrast, the amount of methane adsorbed by the original active carbon is more than two times as large as the value of CO. The active carbon also shows considerable adsorptions on nitrogen and argon, although the adsorptions of hydrogen and helium are minimal.

Water-Resistivity of the Active Carbon-Supported $AlCuCl_4$. The open circles in Fig. 5 exhibit the adsorption of CO by the active carbon-supported $AlCuCl_4$, which has adsorbed 17.7 mmol of CO on the first contact with 9:1 CO–N_2 mixture (see Fig. 3), and then has been subjected to a reduced pressure (6 mmHg) at 20 °C for 10 min. Without contacts of the adsorbent with water vapor, almost identical time courses were obtained for repeated CO adsorptions (Fig. 3(a)).

The closed circles in Fig. 5, which are for the adsorption after the contact of the adsorbent with nitrogen containing 2.0 mmol of water (water content 9000 ppm) for 10 min, almost perfectly superimpose the open circles for the adsorption prior to the contact. Thus, water vapor has no measurable effects on the activity of the active carbon-supported $AlCuCl_4$ with respect to both the rate of CO adsorption and the adsorbed amount. Even after the contacts of the adsorbent with nitrogen gas containing 2.0 mmol of water, prepared separately for each contact, are repeated five times (total period of the contact is 50 min and total amount of water is 10 mmol), both the rate of adsorption and the equilibrium value of adsorbed CO are also identical with the values prior to the contacts (Table 6).

In contrast, the CO adsorbing activity of solid of $AlCuCl_4$ without active carbon largely decreases on the contacts with water vapor, as also shown in Table 6.

Table 6. Water Resistivities of the Adsorbents[a)]

Number of repeated contacts of the adsorbents with water vapor	Relative adsorbing capacity[b)]	
	Active carbon-supported $AlCuCl_4$[c)]	$AlCuCl_4$ solid[d)]
0	100	100
1	102	59
2	103	54
3	99	—
4	101	—
5	100	—

a) Adsorbents were contacted with 5000 cm^3 of N_2 gas containing 2.0 mmol of water (water content: 9000 ppm) at 20 °C for 10 min. b) The ratios in percent of the amounts of CO adsorbed after the contacts with water vapor to the value for the adsorbent without the contacts. c) $AlCuCl_4$, 17.2 mmol; active carbon 10 g. d) $AlCuCl_4$, 20.0 mmol.

Discussion

Preparation of Active Carbon-Supported $AlCuCl_4$. Significant decrease (360 m^2 g^{-1}) of the BET surface area of active carbon on the formation of the adsorbent from active carbon and $AlCuCl_4$ (Table 1) shows that the double salt is supported on the surface of the pores in the active carbon. $AlCuCl_4$ largely exists in the pores with radii smaller than 15 Å, as clearly seen by the decrease of number of these small pores on the formation of the adsorbent (Fig. 2). Thus, the double salts in the adsorbents are mostly in their monomeric or dimeric forms. A possibility of formation of large aggregates of the salts is ruled out, since they are too large to be accommodated in these small pores.

Rough estimation, based on the decrease (360 m^2 g^{-1}) of the BET surface area and the amount (17.2 mmol) of $AlCuCl_4$ supported to 10 g of active carbon, indicates that one molecule of the double salt occupies around 35 Å^2 of the surface area of the active carbon. The double salts are separated from each other by about 6 Å on the surface.

Presence of $AlCuCl_4$ in such a close proximity without mutual aggregation is attributable to specific and strong interactions between the double salt and the condensed aromatic rings of active carbon. $AlCuCl_4$ forms charge-transfer complexes with various aromatic compounds such as benzene,[15)] toluene,[16)] and mesitylene,[16)] and thus easily dissolves in these aromatic solvents.

Adsorption and Desorption of CO by the Active Carbon-Supported $AlCuCl_4$. The adsorption of CO by the adsorbent is ascribed to complex formation of $AlCuCl_4$ with CO. Active carbon alone exhibits a small adsorption of CO (Table 3). Physical adsorption of CO by the adsorbent is ruled out, since the adsorptions of gases other than CO, e.g. methane, nitrogen, and argon, by the present adsorbent are, in contrast with promotion of CO adsorption, less efficient than the adsorptions by the original active carbon (Table 5).

High selectivity of CO adsorption for the present adsorbent (Table 5) is attributable to effective coverage of the surface of active carbon by $AlCuCl_4$. CO is sufficiently adsorbed by coordination to the double salt (vide infra), whereas physical adsorptions of other gases by the active carbon is suppressed by the $AlCuCl_4$.

The rate of adsorption of CO by the present adsorbent is almost identical with the value for the toluene solution of $AlCuCl_4$ (Figs. 3 and 4). This is ascribed to high and virtually molecular dispersion of $AlCuCl_4$ on the surface of the active carbon. In addition, CO can effectively diffuse to the double metal salt through the pores in the active carbon. The adsorption by solid $AlCuCl_4$ (Fig. 4), which has not a high dispersion, is much slower than that by the active carbon-supported $AlCuCl_4$.

Larger amount of the adsorbed CO for the active carbon-supported $AlCuCl_4$ (103 mol% with respect to $AlCuCl_4$: Table 3) than that (84 mol%) for the toluene solution of $AlCuCl_4$ is associated with absence of competition between CO and toluene in the complex formation with $AlCuCl_4$. On the CO absorption by the toluene solution, CO coordinates to $AlCuCl_4$ by replacing a toluene molecule which is originally complexing with the double salt.[16)]

The adsorption of CO by the adsorbent takes place by the coordination of CO to the vacant coordination site at copper(I) ion in $AlCuCl_4$. The vacant coordination site is produced during the process of the preparation of the adsorbent. Here, $AlCuCl_4$, in which the copper(I) ion is complexing with toluene, is first supported on the surface of the active carbon, and then the toluene is removed by evaporation. By the coordination of CO to the vacant site, the copper(I) ion takes the most stable tetrahedral and four-coordinate state.[17)]

Desorption of the adsorbed CO is accompanied by the structural change of the copper(I) ion from the stable four-coordinate state to less stable three-coordinate state. This process requires a considerable activation energy and thus rather severe conditions (180 °C, 0.4 mmHg) are required to desorb all the adsorbed CO during the desorption period 10 min employed in the present study (Table 4). The amount (50 mol% with respect to $AlCuCl_4$) of CO desorbed at 20 °C, 6 mmHg for 10 min (Table 4) is considerably smaller than the value (90 mol%) estimated for milder desorption conditions (20 °C, 152 mmHg) under the assumption that an equilibrium is attained in 10 min for desorption. If this assumption were valid, the desorbed amount at 20 °C, 152 mmHg should be the difference (90 mol%) between the amount (103 mol%) adsorbed at 20 °C, 684 mmHg (the CO partial pressure in 9:1 $CO-N_2$ mixture at 1 atm) and the value (13 mol%) adsorbed at 20 °C, 152 mmHg (see Table 2).

A prolonged desorption (3 h) at 20 °C, 6 mmHg increased the amount of desorbed CO from the value (50 mol%) for the 10 min desorption to 57 mol%.

With the present solid adsorbent, pressure-swing separation, which takes advantage of change in partial pressure of CO and is not possible with the use of liquid absorbents, is successfully carried out (Fig. 3 (a)) in addition to thermal-swing separation using change in temperature (Fig. 3 (b)). By use of adsorption-desorption cycles composed of the adsorption at 20 °C, 1 atm from 9:1 $CO-N_2$ mixture and the desorption at 20 °C, 6 mmHg, 8.8 mmol of CO is separated. Each of the cycles involving the adsorption at 20 °C, 1 atm and the desorption at 180 °C, 0.4 mmHg separates 17.7 mmol of CO (Table 4).

Water-Resistivity of Active Carbon-Supported $AlCuCl_4$. Stability of the present adsorbent against water vapor, clearly shown in Fig. 5 and Table 6, is attributable to protection of the double metal salt by active carbon, since the solid of $AlCuCl_4$ without active carbon is rapidly deactivated with water vapor (Table 6). Toluene solutions of $AlCuCl_4$ are also easily deactivated by water vapor.[5-8)] In the present adsorbent, $AlCuCl_4$ is almost molecularly dispersed and is located in the micropores with radii smaller than 15 Å (Fig. 2). The inside of the micropores is rather hydrophobic, since the pores are surrounded by the walls of fused aromatic rings. Thus, $AlCuCl_4$ can be shielded from water vapor in the micropores. In addition, diffusion of water vapor to the inside of quite small micropores through hydrophobic pores should be less efficient, which is also favorable for the stability of the double metal salt.

The argument is consistent with the previous result[12)] that cross-linked polystyrene-supported $AlCuCl_4$ is also a water-resistant CO adsorbent. There, $AlCuCl_4$ is located in the micropores of the polystyrene resin, and is protected by the hydrophobic aromatic rings.

Water-resistivity of the present adsorbent is quite important from the viewpoints of practical applications, since the sources of CO in industry are usually saturated with water. With this adsorbent, separation of CO from the gas mixtures containing water can be achieved without severe dehydration of the feed gases by pretreatments.

The authors would like to thank Dr. Toshio Osawa at the University of Tokyo for his assistance in the measurements of the BET surface area and pore size distribution.

References

1) "New Syntheses with Carbon Monoxide," ed by J. Falbe, Springer-Verlag, Berlin (1980).

2) "Kirk-Othmer Encyclopedia of Chemical Technology," 3rd ed, ed by H. F. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, John-Wiley & Sons, New York (1978), p. 772.

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

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

5) D. J. Haase and D. G. Walker, *Chem. Eng. Prog.*, **70**, 74 (1974).

6) D. J. Haase, *Chem. Eng.*, August 4, 52 (1975).

7) H. Hirai, M. Komiyama, and S. Hara, *Makromol. Chem., Rapid Commun.*, **2**, 495 (1981).

8) H. Hirai, M. Komiyama, and S. Hara, *Chem. Lett.*, **1981**, 1447.

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

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

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

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

13) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," 2nd ed., Pergamon Press (1980), p. 486.

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

15) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).

16) H. Hirai, M. Nakamura, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **56**, 2519 (1983).

17) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 4th ed., John Wiley & Sons, New York (1980), p. 804.