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Carbon Monoxide Adsorbent Composed of Copper(I) Chloride and Polystyrene Resin Having Amino Groups

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A novel adsorbent of carbon monoxide (CO) is prepared by stirring copper(I) chloride and a macroreticular type polystyrene resin having amino groups in acetonitrile, followed by removal of the liquid phase at 5 mmHg, 80 °C. The adsorbent rapidly adsorbs carbon monoxide from 9 : 1 carbon monoxide-nitrogen mixture at 20 °C under 1 atm. The adsorbed carbon monoxide is readily desorbed by heating the adsorbent to 80 °C under 1 atm or by reducing the partial pressure of carbon monoxide to 5 mmHg at 20 °C. The CO adsorbing capacity (15.9 mmol) of the adsorbent composed of 10.0 g of the resin and 70 mmol of copper(I) chloride is 5.7 times as large as the carbon dioxide adsorbing capacity (2.8 mmol). The efficient adsorption of carbon monoxide by the present adsorbents is attributed to coordination of carbon monoxide to the copper(I) ions which coordinate the amino residues in the resin. The carbon dioxide adsorbing capacity (2.8 mmol) of the adsorbent is much smaller than that (8.3 mmol) of the resin without copper(I) chloride. The present adsorbent exhibits no measurable adsorptions of methane, nitrogen, and hydrogen at 20 °C under 1 atm, and thus is applicable to selective separation of carbon monoxide from gas mixtures containing these gases and carbon dioxide.

Carbon monoxide (CO), an important raw material in industry, is usually obtained as gas mixtures with carbon dioxide (CO_2), methane, nitrogen, and hydrogen.[1] Thus, separation of CO from gas mixtures is required for efficient utilization of CO. Considerable number of liquid absorbents of CO have been proposed.[2] However, solid adsorbents of CO have been rather few.

Active carbon exhibits adsorbing ability of CO. The adsorbing capacity for CO, however, is smaller than those for CO_2 and methane.[3] As a result, selective separation of CO from gas mixtures containing CO_2 and methane is difficult by using active carbon as adsorbent. Zeolite-supported copper(I) ions adsorbed both CO and CO_2.[4,5]

Previously, the authors reported that polystyrene resin-supported aluminium copper(I) chloride,[6,7] active carbon-supported aluminium copper(I) chloride,[8,9] and active carbon-supported copper(I) chloride[10] adsorbed CO reversibly and selectively under mild conditions.

This paper describes preparation of solid CO adsorbents composed of copper(I) chloride (CuCl) and a macroreticular type polystyrene resin having amino groups. The CO adsorbing and desorbing abilities of the adsorbents are reported. The selectivity of CO adsorption with respect to adsorptions of CO_2, methane, hydrogen, and nitrogen is presented. In addition, the results of X-ray photoelectron spectroscopy on the adsorbents are shown. The mechanism of selective adsorption of CO by the present adsorbents is discussed in terms of these results.

Experimental

Materials. A macroreticular type polystyrene resin having primary and secondary amino groups was purchased from Mitsubishi Chemical Industries (DIAION WA20; pale yellow beads of diameter 0.35—0.55 mm; ion-exchange capacity 2.5 equiv dm^{-3}; apparent density 650 g dm^{-3}). A macroreticular type polystyrene resin having carboxylate residues, a macroreticular type polystyrene resin having sulfonate residues, and a macroreticular type polystyrene resin having no functional groups were obtained also from Mitsubishi Chemical Industries: DIAION WK20 (white beads of diameter 0.35—0.55 mm; ion-exchange capacity 3.5 equiv dm^{-3}; apparent density 690 g dm^{-3}), DIAION PK208 (pale yellow beads of diameter 0.40—0.55 mm; ion-exchange capacity 1.2 equiv dm^{-3}; apparent density 745 g dm^{-3}), and DIAION HP30 (white beads of diameter 0.20—0.30 mm; surface area 570 m^2 g^{-1}), respectively.

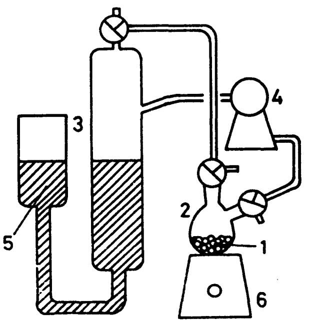

Fig. 1. Apparatus for measuring the amount of CO adsorbed by the adsorbents or desorbed from them; 1: Adsorbent, 2: flask, 3: gas burette, 4: gas pump, 5: leveling liquid (water), 6: magnetic stirrer.

Preparation of Adsorbent. 10.0 g of the polystyrene resin having amino groups and various amounts of CuCl were stirred in 80 cm^3 of solvents at 20° C for 5 h, and then the liquid phase was removed at 5 mmHg (1 mmHg=1.33×10^2 Pa), 80° C. In the present study, acetonitrile was used as a preparation solvent unless otherwise noted.

Adsorption and Desorption of Carbon Monoxide by the Adsorbent. Adsorption of CO by the adsorbents was carried out at 20° C under 1 atm using the apparatus depicted in Fig. 1. A flask (2) containing the adsorbent (1) under nitrogen (N_2) was connected with CO in the gas burette (3), and the adsorption was initiated by circulating the CO–N_2 mixture with the use of a gas pump (4). The uptake of CO was followed by the gas burette (3) using water as leveling liquid (5). The desorption of adsorbed CO was effected either by heating the adsorbents to 80° C under 1 atm for 10 min or by subjecting the adsorbents to a reduced pressure (5 mmHg) at

20° C for 10 min.

Adsorbing abilities of the adsorbents on carbon dioxide, methane, nitrogen, and hydrogen were measured in similar ways.

Determination of the Amounts of Copper(I) Chloride in the Adsorbents. The adsorbents were thoroughly washed with 100 cm^3 of aqueous nitric acid solution (11.8 mol dm^{-3}). The amounts of copper atoms in the resultant solutions were determined by atomic absorption spectroscopy (Shimadzu Model AA-646 spectrometer).

X-Ray Photoelectron Spectroscopy. X-Ray photoelectron spectra of the adsorbents were measured on a Shimadzu Electron Spectrometer ESCA 750 with Mg X-ray anode (8 kV, 30 mA) under a pressure smaller than 1.5×10^{-7} mmHg. Chemical shifts were determined using the $4f_{7/2}$ band of metallic gold at 84.0 eV as reference.

Results

Preparation of Carbon Monoxide Adsorbents Composed of Copper(I) Chloride and Polystyrene Resin Having Amino Groups. The adsorbents composed of CuCl and the macroreticular type polystyrene resin having amino groups were obtained as green beads. The amount of CuCl supported on the resin was 64 mmol, when the charged amounts of the resin and CuCl, respectively, were 10.0 g and 9.9 g (100 mmol), and acetonitrile was used as a preparation solvent.

Figure 2 shows a plot of the amount of CuCl supported on the polystyrene resin against the charged amount of CuCl. The charged amount of the resin is kept constant at 10.0 g. The supported amount of CuCl increases proportionally with increasing charged amount of CuCl up to the charged amount 50 mmol. Here almost all of the charged CuCl is supported on the resin. Above the charged amount 50 mmol, the supported amount is considerably smaller than the charged amount, being almost constant irrespective of the charged amount.

Adsorption and Desorption of Carbon Monoxide by the Adsorbents Composed of Copper(I) Chloride and Polystyrene Resin Having Amino Groups. Figures 3 and 4 show repeated adsorptions of CO by the adsorbents, which have been prepared from 10.0 g of the resin and 9.9 g (100 mmol) of CuCl, containing 64 mmol of CuCl. In Fig. 3 the desorption of adsorbed CO is carried out by heating the adsorbent to 80° C under 1 atm for 10 min, whereas in Fig. 4 it is achieved by subjecting the adsorbent to a reduced pressure (5 mmHg) at 20° C for 10 min.

The open circles in Fig. 3 depict the first adsorption of CO by the adsorbent from 9:1 CO–N_2 mixture at 20° C under 1 atm. The adsorption is rapid and the equilibrium amount of adsorbed CO is 15.2 mmol. Thus, 21 cm^3 (standard temperature and pressure) of CO is adsorbed by 1 g of the adsorbent.

The adsorbed CO is desorbed by heating the adsorbent to 80° C under 1 atm for 10 min. In the second adsorption (the closed circles), the adsorption of CO is rapid and the equilibrium amount of adsorbed CO is 9.1 mmol. In the third and the fourth adsorptions, both the rate of adsorption and the equilibrium amount of adsorbed CO are almost identical with the corresponding values in the second adsorption.

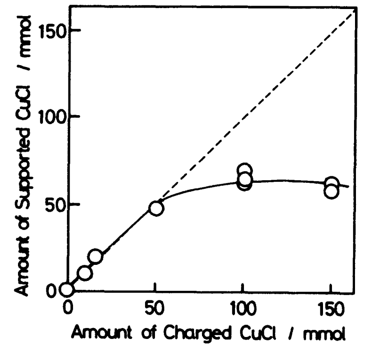

Fig. 2. Plot of the amount of CuCl supported on the polystyrene resin having amino groups against the charged amount of CuCl for the adsorbent prepared from CuCl and the resin by use of 80 cm^3 of acetonitrile as solvent: The charged amount of the resin was kept constant at 10.0 g.

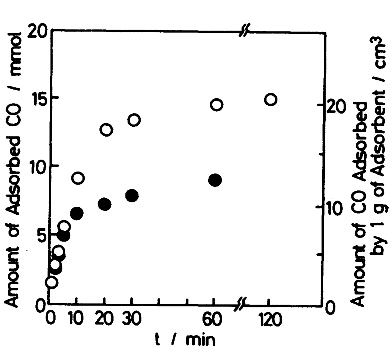

Fig. 3. Repeated adsorptions of CO from 9:1 CO–N_2 mixtures at 20 °C under 1 atm by the adsorbent composed of 64 mmol of CuCl and 10.0 g of the polystyrene resin having amino groups: The desorption of adsorbed CO was carried out at 80 °C under 1 atm for 10 min; the first (○) and the second (●) adsorptions.

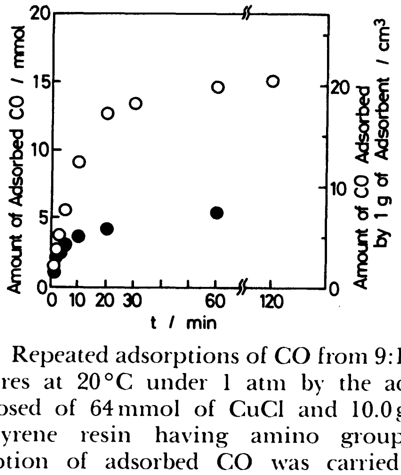

Fig. 4. Repeated adsorptions of CO from 9:1 CO–N_2 mixtures at 20 °C under 1 atm by the adsorbent composed of 64 mmol of CuCl and 10.0 g of the polystyrene resin having amino groups: The desorption of adsorbed CO was carried out at 5 mmHg, 20 °C; the first (○) and the second (●) adsorptions.

Table 1. Adsorbing Capacities of the CO Adsorbents Prepared from Copper(I) Chloride and Macroreticular Type Polystyrene Resins Having Various Functional Groups[a,b)]

Functional group in the polystyrene resin	CO adsorbing capacity mmol
Amino residue	15.9
Carboxylate residue	1.2
Sulfonate residue	0.8
None	2.2

a) Adsorption from 9:1 CO–N_2 mixture was carried out at 20 °C under 1 atm. b) The adsorbents were prepared from 9.9 g (100 mmol) of CuCl and 10.0 g of the resins by use of 80 cm^3 of acetonitrile as solvent.

Table 2. Adsorbing Capacities on Various Gases for the Adsorbent Composed of 70 mmol of Copper(I) Chloride and 10.0 g of the Polystyrene Resin having Amino Groups[a)]

Gas	Capacity/mmol	Amount of gas adsorbed by 1 g of adsorbent/cm^3[b)]
CO	15.9	21.0
CO_2	2.8	3.7
Methane	0.0	0.0
Hydrogen	0.0	0.0
Nitrogen	0.0	0.0

a) Adsorption from 9:1 CO–N_2 mixture was carried out at 20 °C under 1 atm. b) Standard temperature and pressure.

The open circles in Fig. 4 show the first adsorption of CO by the adsorbent, which is separately prepared. The equilibrium amount of adsorbed CO is 15.2 mmol. The adsorbed CO is desorbed by subjecting the adsorbent to a reduced pressure (5 mmHg) at 20° C for 10 min. In the second adsorption (the closed circles), the adsorption is rapid and the equilibrium amount of adsorbed CO is 5.4 mmol. Both the time courses and the equilibrium amounts of adsorbed CO in the third and the fourth adsorptions are identical with those in the second adsorption.

Adsorbing Capacities of Carbon Monoxide Adsorbents Composed of Copper(I) Chloride and Polystyrene Resins Having Various Functional Groups. Table 1 shows the CO adsorbing capacities of the adsorbents prepared from 100 mmol of CuCl and 10.0 g of the polystyrene resins having various functional groups. The capacity (15.9 mmol) of the adsorbent prepared with the use of the polystyrene resin having amino groups is much larger than the value (1.2 mmol) for the adsorbent with the resin having carboxylate residues, that (0.8 mmol) for the adsorbent with the resin having sulfonate residues, and that (2.2 mmol) for the adsorbent with the resin having no functional groups.

Selectivity of Carbon Monoxide Adsorption. Table 2 lists the adsorbing capacities of the adsorbent, composed of 10.0 g of the polystyrene resin having amino groups and 70 mmol of CuCl for various gases. The capacity (15.9 mmol) of the adsorbent for CO is 5.7 times as large as the value (2.8 mmol) for CO_2. The adsorbent exhibits no measurable adsorbing ability for methane, hydrogen, and nitrogen.

Figure 5 shows the plots of the adsorbing capacity for CO (the open circles) and the adsorbing capacity for CO_2 (the closed circles) against the amount of CuCl supported on 10.0 g of the polystyrene resin having amino groups. At the amount 0.0 mmol of supported CuCl, the resin does not adsorb CO in a measurable amount, and the adsorbing capacity for CO_2 is 8.3 mmol. The adsorbing capacity for CO largely increases with increasing amount of the supported CuCl, whereas the adsorbing capacity for CO_2 monotonously decreases. Consequently, the selectivity of CO adsorption, which is defined by the ratio of the adsorbing capacity for CO to the value for CO_2, significantly increases with increase in the supported amount of CuCl, as shown by the open squares. A selectivity 5.7 is attained at the supported amount 70 mmol of CuCl.

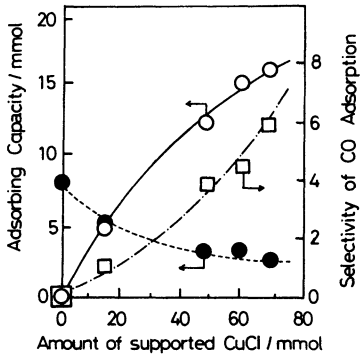

Fig. 5. Plots of adsorbing capacity (○) for CO, adsorbing capacity (●) for CO_2, and the selectivity (□) of CO adsorption against the amount of CuCl supported on the polystyrene resin having amino groups for the adsorbent prepared from CuCl and the resin by use of acetonitrile as preparation solvent: The selectivity of CO adsorption is defined by the ratio of the capacity for CO to the value for CO_2; the amount of the resin is kept constant at 10.0 g.

Effect of Preparation Solvent on the Adsorbing Capacity of the Adsorbent. Table 3 lists the CO adsorbing capacities of the adsorbents prepared with the use of various solvents. The adsorbent prepared using acetonitrile exhibits much larger capacity than the ones prepared using acetone, water, and the aqueous hydrochloric acid solution.

X-Ray Photoelectron Spectroscopy. Figure 6 shows the X-ray photoelectron spectra in the Cu_{2p} region of (a) the adsorbent composed of 65 mmol of CuCl and 10.0 g of the polystyrene resin having amino groups, (b) solid of CuCl, and (c) solid of $CuCl_2$. For the adsorbent, two bands are observed at 933 and 953 eV. The solid of CuCl also exhibits two bands at 933 and 953 eV. The spectrum for the solid of $CuCl_2$ con-

Table 3. CO Adsorbing Capacities of the Adsorbents Prepared by Use of Various Solvents[a,b)]

Preparation solvent	Adsorbing capacity/mmol
Acetonitrile	15.9
Acetone	7.2
Water	6.3
Aqueous hydrochloric acid solution (1 mol dm^{-3})	5.6

a) Adsorbents were prepared from 9.9 g (100 mmol) of CuCl and 10.0 g of the polystyrene resin having amino groups with the use of 80 cm^3 of solvents. b) Adsorption from 9:1 CO–N_2 mixture was carried out at 20 °C under 1 atm.

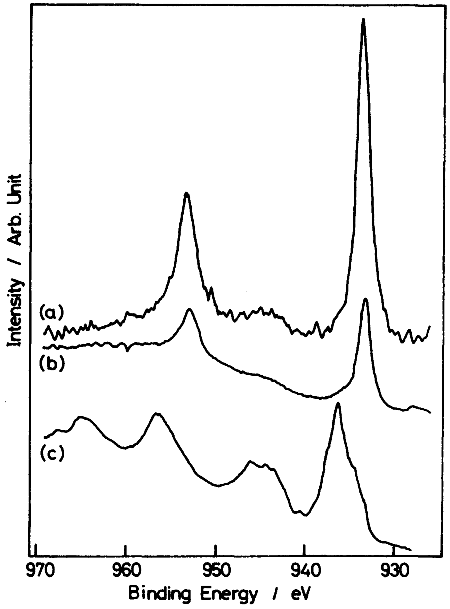

Fig. 6. X-Ray photoelectron spectra in the Cu_{2p} region for (a) the adsorbent composed of 65 mmol of CuCl and 10.0 g of the polystyrene resin having amino groups, (b) solid of CuCl, and (c) solid of $CuCl_2$.

sists of four bands at 937, 944, 957, and 964 eV.

Figure 7 depicts the X-ray photoelectron spectra in the Cl_{2p} region for (a) the adsorbent and (b) solid of CuCl. Both spectra are almost identical with each other, and are composed of a band at 200 eV and a shoulder peak around 201 eV.

Discussion

Adsorption and Desorption of Carbon Monoxide by the Adsorbents Composed of Copper(I) Chloride and Polystyrene Resin Having Amino Groups. The adsorptions of CO by the present adsorbents are ascribed to coordinations of CO to the copper(I) ions, which are complexing with the amino residues of the resin. Thus, the amount of adsorbed CO increases with increasing amount of the CuCl supported on the resin, as shown by open circles in Fig. 5.

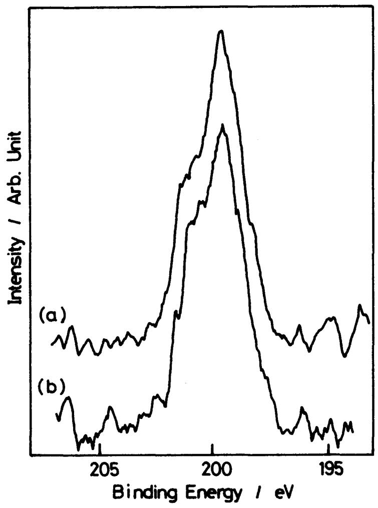

Fig. 7. X-Ray photoelectron spectra in the Cl_{2p} region for (a) the adsorbent composed of 65 mmol of CuCl and 10.0 g of the polystyrene resin having amino groups, and (b) solid of CuCl.

Significance of the complexes between CuCl and the amino residues of the resin as the active species for the CO adsorption by the present adsorbents is definitely shown by the fact that the adsorbing capacity (15.9 mmol) of the adsorbent, prepared by use of the macroreticular type polystyrene resin having amino groups, is much larger than those (0.8—2.2 mmol) of the adsorbents prepared by use of the macroreticular type polystyrene resin having carboxylate residues, the polystyrene resin having sulfonate residues, and the polystyrene resin having no functional groups (Table 1). A methanol solution of CuCl–ethylenediamine complex absorbs CO,[11)] whereas a solid of CuCl shows no measurable adsorption of CO at 20° C under 1 atm.[12)]

Larger adsorbing capacity (15.9 mmol) of the adsorbent prepared by use of acetonitrile as solvent than the values (7.2 and 6.3 mmol) of the ones prepared by use of acetone and water (Table 3) is also consistent with the important role of the CuCl–amine complexes for the CO adsorption. The solubility of CuCl in acetonitrile is larger than that in acetone or in water, due to complex formation between copper(I) ion and acetonitrile.[13)] Consequently, the formation of complex between CuCl and the amino residues of the resin proceeds more efficiently in acetonitrile than in acetone or in water. The small capacity (5.6 mmol) of the adsorbent obtained with the use of aqueous hydrochloric acid solution is associated with poor complex formation between CuCl and the amino residues of the polystyrene resin. In the aqueous hydrochloric acid solution, CuCl molecules dissolve in forms of $CuCl_2^-$[14)] and the amino residues are present in their protonated forms. Both of these ionic species are highly stabilized by solvation with water molecules, which is unfavorable for the formations of the CuCl–amine complexes in the adsorbents.

Univalent states of virtually all the copper atoms in the adsorbents are confirmed by the fact that the

X-ray photoelectron spectrum in the Cu_{2p} region (Fig. 6 (a)) showing two bands at 953 and 933 eV is almost identical with that (Fig. 6 (b)) for the solid of CuCl. The solid of $CuCl_2$, however, exhibits satellite bands at 964 and 944 eV in addition to main bands at 937 and 957 eV (Fig. 6 (c)). Spectra in the Cu_{2p} region can be used for distinction between copper(I) species and copper(II) species.[15]

The differences (6.1 mmol and 9.8 mmol, respectively, for Figs. 3 and 4) between the equilibrium amounts of adsorbed CO in the first adsorption by the adsorbent and the values in the second and the later adsorptions correspond to the amounts of CO, which are not desorbed under the desorption conditions employed (80° C under 1 atm for 10 min and 5 mmHg at 20° C for 10 min, respectively).

When cycles involving adsorption of CO at 20° C under 1 atm and desorption of CO at 80° C under 1 atm for 10 min are repeated using the adsorbent composed of 10.0 g of the resin and 64 mmol of CuCl, 9.1 mmol of CO is separated for each of the cycles. For the cycles involving adsorption of CO at 20° C under 1 atm and desorption of CO at 5 mmHg, 20° C for 10 min, the amount of CO separated by one cycle is 5.4 mmol. In these repeated cycles, the amounts of CO separated by 1 g of the adsorbent for one cycle are 12 and 7.4 cm^3 (standard temperature and pressure), respectively.

Selectivity of Carbon Monoxide Adsorption for the Adsorbent Composed of Copper(I) Chloride and Polystyrene Resin Having Amino Groups. Much larger adsorbing capacity (15.9 mmol) on CO for the adsorbent composed of 10.0 g of the resin having amino groups and 70 mmol of CuCl than that (2.8 mmol) on CO_2 (Table 2) is highly in contrast with the adsorbing abilities of the resin itself: The adsorbing capacities of the resin on CO and on CO_2, respectively, are 0.0 and 8.3 mmol. The CuCl molecules supported on the resin are predominantly important for high selectivities of the present CO adsorbents. The adsorbents show no measurable adsorption on methane, hydrogen, and nitrogen.

The amounts of CuCl supported on the polystyrene resin having amino groups in the present adsorbents are larger than the ion-exchange capacity (38 mmol) of 10.0 g of the resin. The capacity is estimated by use of both the ion-exchange capacity per volume (2.5 equiv dm^{-3}) and the apparent density (650 g dm^{-3}) of the resin. Thus, considerable amounts of CuCl are supported on the resin without formation of complexes with the amino residues of the resin. These CuCl molecules are connected by chloride bridges with each other and with the CuCl molecules, which are complexing with the amino residues of the resin. In solids of CuCl, tetrahedrally coordinated copper(I) ions are bound by chloride bridges.[16] Consequently, layers composed of CuCl molecules are probably formed on the surface of the micropores of the resin. Even within the ion-exchange capacity of the resin, some portion of the supported CuCl is probably bound to the resin without complex formation with the amino groups, resulting in monotonous increase of adsorbing capacity with increasing amount of supported CuCl up to the amount 70 mmol (Fig. 5).

The present adsorbents efficiently adsorb CO by coordination of CO to the copper(I) ions in the complexes between CuCl and the amino residues of the polystyrene resin. In contrast, physical adsorption of CO_2 to the surface of the resin is suppressed by the layers of CuCl formed on the surface of the micropores. Chemical adsorption of CO_2 due to interactions with the amino groups of the resin is also inhibited by the complex formation between the amino groups and CuCl.

The arguments are confirmed both by the increase in the adsorbing capacity on CO and by the decrease in the adsorbing capacity on CO_2 with increasing amount of CuCl supported on the resin (Fig. 5). For the resin without CuCl, chemical and physical adsorptions of CO_2 to the resin are predominant, and the amount of adsorbed CO is zero.

The X-ray photoelectron spectroscopy on the adsorbent (Fig. 7) is consistent with formation of layers of CuCl in the adsorbents. The spectrum (a) for the chlorine atoms in the adsorbent is similar to the one (b) for a solid of CuCl. The CuCl molecules, which form layers on the surface of micropores of the resin by mutual chloride bridges, are arranged in almost the same way as those in a solid of CuCl.

The proposed mechanism of the selective adsorption of CO by the present adsorbents is supported by the fact that the adsorbents selectively adsorb ethylene with minimal adsorption of ethane.[17] There, ethylene is effectively adsorbed by the coordination to the copper(I) ions complexing with the amino groups of the macroreticular type polystyrene resin. In contrast, physical adsorption of ethane to the resin is suppressed by the layer of CuCl formed on the surface of the micropores.

In conclusion, selective carbon monoxide adsorbents are prepared from copper(I) chloride and a macroreticular type polystyrene resin having amino groups. The adsorbents are applicable to selective separation of carbon monoxide from gas mixtures containing carbon dioxide, methane, hydrogen, and nitrogen.

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