January, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***60***, *385—390 (1987)* 385

Polymer-Protected Metal Complex for Gas Separation. III. Water-Resistivity of Polystyrene Resin-Supported Aluminium Copper(I) Chloride as Solid Carbon Monoxide Adsorbent[1)]

Hidefumi Hirai,* Susumu Hara, and Makoto Komiyama
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

(Received July 14, 1986)

Solid adsorbents of carbon monoxide are prepared from aluminium chloride, copper(I) chloride, and a macroreticular type polystyrene resin by use of various solvents, and their resistivities against water vapor are investigated. The adsorbing capacities of the adsorbents prepared by use of carbon disulfide and dichloromethane remain virtually unchanged even after repeated (3—5 times) contacts of the adsorbents with nitrogen gas containing 10 mol% water with respect to the charged copper(I) chloride (water contents: 5600 and 4600 ppm). The adsorbents obtained with the use of benzene and toluene as preparation solvents, however, exhibit small but gradual decreases in the adsorbing capacities on the repeated contacts with nitrogen gas containing water. Scanning electron microscopy and energy dispersive X-ray microanalysis on the water-resistant adsorbents, prepared with the use of carbon disulfide and dichloromethane, show that the active species for the adsorption, aluminium copper(I) chloride, uniformly distributes in the beads of the polystyrene resin without formation of aggregates. Almost all of aluminium copper(I) chloride is located in the apolar microporosities of the polystyrene resin here, and is effectively protected from water vapor.

Carbon monoxide (CO), which is one of the most important raw materials in chemical industry,[2)] is usually obtained as gas mixtures with hydrogen, nitrogen, oxygen, methane, carbon dioxide, and water vapor.[3)] Thus, CO must be separated from the gas mixtures prior to effective utilization.

In previous papers,[4,5)] the authors reported that toluene solutions of polystyrene-protected aluminium copper(I) chloride ($AlCuCl_4$) reversibly absorbed CO under mild conditions. These absorbents were stable against water vapor, and thus were applicable to separation of CO from gas mixtures containing considerable amounts of water vapor. In the absence of the polystyrene, however, $AlCuCl_4$ in toluene was rapidly deactivated by water vapor due to irreversible reaction of $AlCuCl_4$ with water.[6)]

Furthermore, the authors succeeded in the preparation of the macroreticular type cross-linked polystyrene resin-supported $AlCuCl_4$ as solid adsorbents for CO.[1,7,8)] With the use of them, separations of CO from gas mixtures were successfully achieved both by pressure-swing method and by thermal-swing method.

This paper reports on the resistivities against water vapor for the macroreticular type polystyrene resin-supported $AlCuCl_4$. Effects of preparation solvents on the water-resistivities of the adsorbents are described. Furthermore, the results of scanning electron microscopy and energy dispersive X-ray microanalysis on the surface and the cross-section of the adsorbents are shown. The mechanism of water-resistivities is discussed in terms of the microstructures of the adsorbents.

Experimental

Materials. A macroreticular type cross-linked polystyrene resin (8:2 styrene–divinylbenzene copolymer; 20—50 mesh; 296—740 μm in diameter; average pore diameter 9 nm; surface area 300 $m^2\,g^{-1}$)[9)] was obtained from Bio-Rad Laboratories (Bio-Beads SM-2). The resin was successively washed with 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.

Aluminium chloride was purified by sublimation. Copper(I) chloride was reprecipitated from a concentrated aqueous hydrochloric acid solution by the addition of distilled water, followed by washing successively with ethanol and diethyl ether, and then dried overnight in vacuo at 100 °C.

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 and nitrogen, 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. The solid CO adsorbents were prepared by refluxing aluminium chloride, copper(I) chloride, and the macroreticular type polystyrene resin in various solvents under dry nitrogen.[8)] Charged molar ratios of aluminium chloride and styryl residue in the resin, respectively, to copper(I) chloride were 1.0 and 1.2. After 6 h, the solvents were removed from the mixtures by evaporation at 4 mmHg (1 mmHg=133.3 Pa) for 4—6 h. Evaporation temperature was gradually elevated from room temperature to 80 °C, as the evaporation proceeded.

Adsorption and Desorption of CO. The adsorption of CO by the adsorbent, continuously stirred by use of a magnetic stirrer, was carried out at 25 °C, 1 atm, and was followed by measuring the uptake of CO with the use of a gas burette.[8)]

The desorption of adsorbed CO was achieved by subjecting the adsorbent to a reduced pressure (7 mmHg) at 25 °C for 10 min.

Contacts of CO Adsorbents with Water Vapor. The contacts of the adsorbents with water vapor were effected by circulating 10 dm^3 of nitrogen gas, which contained 10 mol% water to the charged CuCl, over the adsorbents at 25 °C for 10 min by use of a gas-circulating pump. The contents of water were in the range of 4600—6100 ppm. During the contacts, the adsorbents were stirred using a magnetic stirrer. The nitrogen containing water vapor was prepared by the introduction of distilled water into 10 dm^3 of evacuated vessel using a microsyringe, followed by the addition of dry nitrogen in an amount required to make the total pressure atmospheric.

Effects of contacts of the adsorbents with dry nitrogen, in place of nitrogen containing water vapor, were investigated in similar ways in order to evaluate precisely the effects of water vapor on the capacities of the adsorbents.

Scanning Electron Microscopy and Energy Dispersive X-Ray Microanalysis on CO Adsorbents. Scanning electron microscopy and the energy dispersive X-ray microanalysis were simultaneously carried out by use of a system composed of a Hitachi model S-550 scanning electron microscope and a KEVEX model 7000-75 energy dispersive X-ray spectrometer.[10)] Data analysis was made on a DEC type PDP 11/34 mini computer.

The specimens for the analysis of the cross-sections of the beads of the adsorbents were prepared by embedding the beads in an epoxy resin. The resultant composites were scraped with sand paper so that the cross-sections of the beads could be analyzed. Alternatively, the beads of the adsorbents were divided into two parts by using a stainless steel blade, and were used for the analysis.

Results

Effect of Water Vapor on Adsorbing Ability of Macroreticular Type Polystyrene Resin-Supported Aluminium Copper(I) Chloride Prepared Using Carbon Disulfide As Solvent. Open circles in Fig. 1 show the adsorption of CO at 25 °C, 1 atm by the adsorbent prepared from 3.03 g (22.7 mmol) of aluminium chloride ($AlCl_3$), 2.25 g (22.7 mmol) of copper(I) chloride (CuCl), and 2.84 g (26.1 mequiv. of styryl residue) of the macroreticular type cross-linked polystyrene resin (divinylbenzene content 20%) by use of 20 cm^3 of carbon disulfide as solvent. The adsorption is rapid and the equilibrium molar ratio of the adsorbed CO to the charged CuCl is 1.07. The amount of adsorbed CO per 1 g of the adsorbent is 67 cm^3 (standard temperature and pressure).

After the first adsorption, the adsorbent is contacted with 10 dm^3 of dry nitrogen at 25 °C for 10 min, and then is subjected to a reduced pressure (7 mmHg) at 25 °C for 10 min. In the second adsorption, the adsorbent promptly adsorbs CO and the equilibrium molar ratio of adsorbed CO to the charged CuCl is 0.54, as shown by the solid circles in Fig. 1.

The open triangles in Fig. 1 depict the third adsorption of CO. Before the adsorption, the adsorbent is contacted with nitrogen containing 10 mol% water to the charged CuCl (water content: 5600 ppm) for 10 min, and is kept at 7 mmHg, 25 °C for 10 min. The equilibrium molar ratio of the adsorbed CO to the charged CuCl is 0.54, which is identical with the value in the second adsorption. In the fourth, the fifth, the sixth, and the seventh adsorptions, the time courses of CO adsorptions are virtually the same as those for the second and the third adsorptions. Prior to each of these adsorptions, the adsorbent is contacted with nitrogen containing 10 mol% water (water content: 5600 ppm).

Water Resistivities of CO Adsorbents Prepared by Use of Various Solvents. Figure 2 depicts the plots of the CO adsorbing capacities of the adsorbents as functions of numbers of repeated adsorptions of CO. Prior to each of the third and the later adsorptions, the adsorbents are contacted with nitrogen containing 10 mol% water with respect to the charged CuCl, as indicated by the arrows. Before the second adsorptions the adsorbents are contacted with dry nitrogen.

In the first adsorptions, all the adsorbents, prepared by use of carbon disulfide, dichloromethane, toluene, and benzene, adsorb CO approximately equimolar to the charged CuCl.

The adsorbing capacity of the adsorbent prepared by use of carbon disulfide remains constant at 0.54 in the second to the seventh adsorption (see the open circles). Thus, no measurable decrease in the capacity

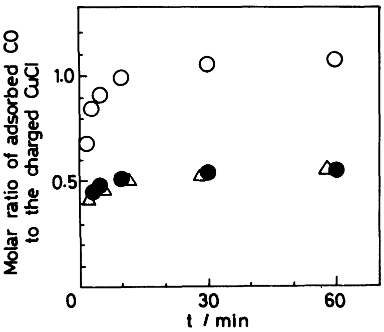

Fig. 1. Adsorption of CO at 25 °C, 1 atm by the adsorbent prepared from the macroreticular type (divinylbenzene content 20%) polystyrene resin, $AlCl_3$, and CuCl by use of carbon disulfide as solvent: the first adsorption (○), the second adsorption (●), and the third adsorption (△); the desorptions of CO were carried out by subjecting the adsorbent to a reduced pressure (7 mmHg) at 25 °C for 10 min; prior to the third adsorption, the adsorbent was contacted with 10 dm^3 of nitrogen containing 10 mol% water to the charged CuCl (water content 5600 ppm) at 25 °C for 10 min; the adsorbent was prepared from 3.03 g (22.7 mmol) of $AlCl_3$, 2.25 g (22.7 mmol) of CuCl, and 2.84 g (26.1 mequiv. in styryl residue) of the polystyrene resin with the use of 20 cm^3 of carbon disulfide.

is perceived even after five times of the contacts of the adsorbent with nitrogen containing water vapor. The capacity of the adsorbent prepared using dichloromethane is also unchanged after three times of the contacts with nitrogen containing water vapor (the closed circles). In contrast, the CO adsorbing capacities of the adsorbents prepared by use of toluene and benzene as solvents gradually decrease on the contacts with water vapor, as depicted by the open triangles and the closed triangles, respectively.

The differences between the adsorbing capacities in the first adsorptions and those in the second adsorptions are ascribed to the amounts of CO adsorbed in equilibria under the desorption conditions employed (7 mmHg at 25 °C for 10 min), as described in the previous paper.[8] When the CO adsorption-desorption cycles are repeated without the contacts of the adsorbents with water vapor, the adsorbing capacities of all the four adsorbents in the third and the later adsorptions are identical with the values in the corresponding second adsorptions.[8]

Scanning Electron Microscopy (SEM) on Surface of CO Adsorbents. Figure 3 depicts the SEM photographs of the surface of the adsorbents. The surface of the adsorbent prepared using carbon disulfide as solvent is smooth and deposition of metal salts is hardly detected, as exhibited by the photograph (a). On the surface of the adsorbent prepared with the use of toluene as solvent, however, depositions of considerable amount of metal salts are clearly observed (the photograph (b)).

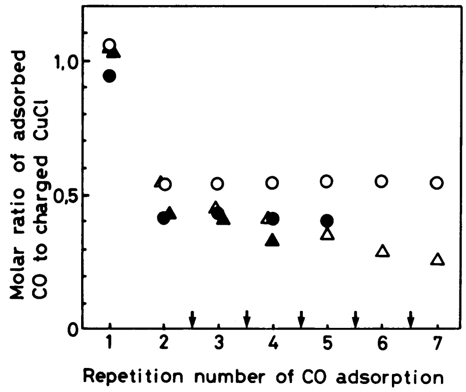

Fig. 2. Effects of water vapor on the CO adsorbing capacities at 25 °C, 1 atm for the adsorbents prepared from the macroreticular type polystyrene resin, $AlCl_3$, and CuCl by use of carbon disulfide (○), dichloromethane (●), toluene (△), and benzene (▲) as solvents: the arrows refer to the contacts of the adsorbents with nitrogen containing 10 mol% water to the charged CuCl at 25 °C for 10 min; the desorptions of CO were carried out by subjecting the adsorbents to a reduced pressure (7 mmHg) at 25 °C for 10 min.

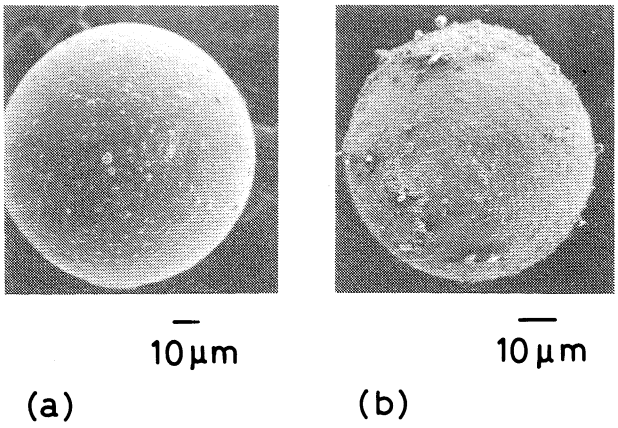

Fig. 3. SEM photographs of the surface of the CO adsorbents prepared from the macroreticular type polystyrene resin, $AlCl_3$, and CuCl by use of (a) carbon disulfide and (b) toluene as solvents.

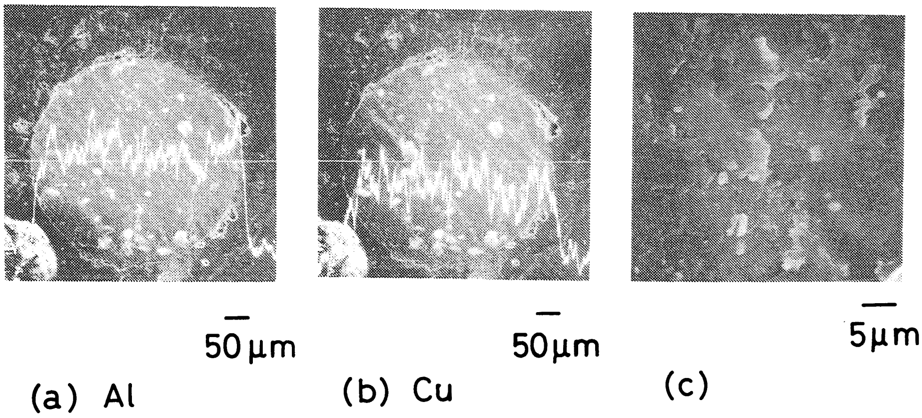

Fig. 4. SEM photographs as well as distributions of Al and Cu atoms for the cross-section of the CO adsorbent prepared from the macroreticular type polystyrene resin, $AlCl_3$, and CuCl by use of carbon disulfide as solvent: the waved lines show the distributions of (a) Al atoms and (b) Cu atoms along the corresponding white straight lines.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Microanalysis on Cross-Sections of Beads of CO Adsorbents. Figures 4—6 depict SEM photographs of the cross-sections of the beads of the adsorbents. The waved lines refer to the distributions of Al and Cu atoms along the corresponding white straight lines on the cross-sections of the beads.

For the adsorbent prepared by use of carbon disulfide, both Al atoms and Cu atoms uniformly distribute in the cross-section of the bead, as shown by the waved lines in the photographs (a) and (b) in Fig. 4. Even at a larger magnitude of magnification (the photograph (c) in Fig. 4), no depositions of metal salts are detected.

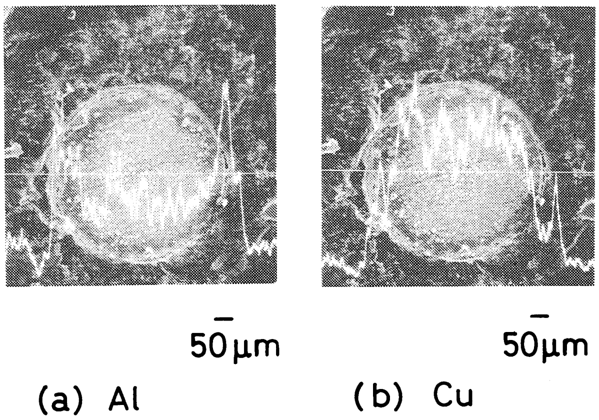

Fig. 5. SEM photographs as well as distributions of Al and Cu atoms for the cross section of the CO adsorbent prepared from the macroreticular type polystyrene resin, $AlCl_3$, and CuCl by use of toluene as solvent: The waved lines show the distributions of (a) Al atoms and (b) Cu atoms along the corresponding white straight lines.

In the adsorbent obtained with the use of toluene, Al atoms exist largely on or near the surface of the bead, as depicted in the photograph (a) in Fig. 5. The Cu atoms, however, are abundantly present in the inner portion of the bead with small population near the surface of the bead (the photograph (b) in Fig. 5). Thus, the distributions of Al and Cu atoms are different from each other. In addition, many granules are perceived mostly in the inner portion of the bead.

Figure 6 shows SEM photographs of the inner portion of the bead prepared with the use of toluene. Here, the middle parts of the cross-section of the bead in Fig. 5 (a) and (b) are analyzed at larger magnitudes of magnification. A number of crystalline deposits are observed in the photographs (a) and (b), while highly grown columnar crystals are seen in the photograph (c).

As depicted by the waved line in Fig. 6 (b), the distribution of the Cu atoms exhibits maxima at the positions where the crystalline deposits are present on the white straight line. In contrast, the distribution of the Al atoms shows minima at the positions of the deposits (Fig. 6 (a)). Thus, most of the Al atoms are located in the portions where no deposits exist. The X-ray microanalysis on one of the deposits, which involves signals from the region of diameter around 1—2 μm, has showed that the atomic ratio of Cu, Cl, and Al is 37.5:57.6:4.9.

Discussion

Water-Resistivity of Macroreticular Type Polystyrene Resin-Supported $AlCuCl_4$ As CO Adsorbent. The macroreticular type polystyrene resin-supported

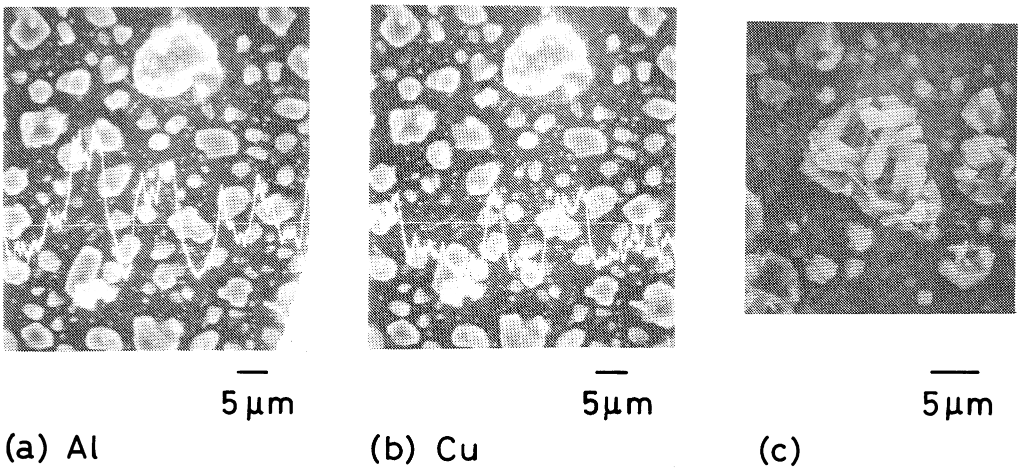

Fig. 6. SEM photographs as well as distributions of Al and Cu atoms for the inner portions of the bead of the CO adsorbent prepared from the macroreticular type polystyrene resin, $AlCl_3$, and CuCl by use of toluene as solvent: The middle parts of the cross-section of the bead in Fig. 5 (a) and (b), where many fine deposits of metal salts are observed, are analyzed at larger magnitudes of magnification; the waved lines refer to the distributions of (a) Al and (b) Cu atoms along the corresponding white straight lines.

$AlCuCl_4$ is stable against water vapor, as shown in Fig. 2, when carbon disulfide and dichloromethane are used as preparation solvents. No measurable decreases in the adsorbing capacities are observed after five and three repeated contacts of the adsorbents (total periods of contacts 50 and 30 min) with nitrogen containing 5600 and 4600 ppm of water, respectively. The water-resistivities of these adsorbents are quite important from the viewpoints of practical applications, since almost all of the CO sources in industry contain considerable amounts of water vapor.

These results are highly in contrast with the fact that the CO absorbing abilities of toluene solutions of $AlCuCl_4$ rapidly and significantly decrease on the contacts with water vapor.[4-6] Thus, CO separation processes using these liquid absorbents require pretreatments of feed gas to reduce the amount of water vapor to 1 ppm or smaller.[6] The water-resistivities of the present solid CO adsorbents are definitely attributable to protection of $AlCuCl_4$ by the polystyrene resin. As shown previously,[4,5] linear polystyrene exhibits effective protection of $AlCuCl_4$ from water vapor in toluene, resulting in water-resistant liquid CO absorbents.

In contrast to the water-resistivities of the adsorbents prepared by use of carbon disulfide and dichloromethane, the capacities of the adsorbents prepared by using toluene and benzene gradually decrease on the repeated contacts with water vapor (Fig. 2). The CO adsorbing and desorbing abilities of solid of $AlCuCl_4$ without the polystyrene resin are small.[8]

Microstructures of CO Adsorbents Prepared by Use of Various Solvents. In the polystyrene-supported $AlCuCl_4$ prepared by use of carbon disulfide as solvent, $AlCuCl_4$ uniformly disperses without formation of aggregates in the beads of the polystyrene resins (Fig. 4).

With the use of toluene as preparation solvent, however, the distribution of Cu atoms and that of Al atoms in the adsorbents are different from each other, and many deposits are formed in the beads (Fig. 5). The deposits are assignable to solid of CuCl on the basis of the atomic ratio (37.5:57.6:4.9) of Cu, Cl, and Al atoms. Both the deviation of the ratio (1.54) of Cl to Cu from the theoretical value (1.0) for CuCl and the presence of small amount of Al atoms are associated with the fact that the ratio has been determined by the analysis on a region of diameter around 1—2 μm. Thus the analysis involves signals from the parts other than the deposit, which are abundant in $AlCl_3$ (see Fig. 6 (a)), in addition to the signals from the deposit. Subtraction of three times (14.7) of the observed value (4.9) for Al atom from that (57.6) for Cl atom results in an estimated value (42.9) for Cl atom which exists in fact in the deposit. This subtraction is based on the assumption that all the Al atoms are present in the forms of $AlCl_3$. The ratio of the estimated value (42.9) for Cl atom to the observed value (37.5) for Cu atom is 1.14, which is close to the theoretical value (1.0) for CuCl.

The significant dependence of the distributions of the metal salts in the CO adsorbents on the preparation solvents is attributable to differences in the solubilities of the salts in the solvents. All the four solvents used, carbon disulfide, dichloromethane, benzene, and toluene, are good solvents for polystyrene.

When CuCl, $AlCl_3$, and the polystyrene resin are refluxed in carbon disulfide or dichloromethane, $AlCuCl_4$, formed in situ in the reaction mixtures, promptly penetrates into the polystyrene beads due to formation of molecular complexes between the double salt and the aromatic rings of the polystyrene resin. The amounts of $AlCuCl_4$ in the liquid phase after refluxing are virtually none.[8] Both carbon disulfide and dichloromethane are poor solvents for $AlCuCl_4$, $AlCl_3$, and CuCl. In the resin, $AlCuCl_4$ is located in the microporosities, and interacts with multiple aromatic rings there. Location of the $AlCuCl_4$ on the surface of the macroporosities of the resin in the adsorbents is energetically less favorable, since the number of the aromatic rings which can interact with one molecule of the double salt is smaller. On the subsequent evaporation of the liquid phase, homogeneous and molecular dispersion of $AlCuCl_4$ in the microporosities of the beads is achieved.

These arguments are supported by the finding[11] of strong charge-transfer bands having absorption maxima around 460 nm for the toluene solutions of $AlCuCl_4$ containing linear polystyrene. In the absence of the polystyrene, such charge-transfer bands were not detected at all.

On refluxing CuCl, $AlCl_3$, and the polystyrene resin in toluene or benzene, however, the $AlCuCl_4$ is present both in the polystyrene beads and in the liquid phase, since $AlCuCl_4$ effectively dissolves in benzene and toluene due to molecular complex formations with the aromatic solvents.[12,13] On the evaporation, most of the $AlCuCl_4$ in the liquid phase precipitates either on the surface of the macroporosities or on the surface of the beads.

The formation of deposits of CuCl in the beads of the adsorbents prepared with these aromatic solvents (Figs. 5 and 6) is probably associated with decomposition of some portion of $AlCuCl_4$ in the liquid phase to $AlCl_3$ and CuCl on the evaporation. Here, the CuCl aggregates each other to crystalline solids, and the $AlCl_3$ forms molecular complexes[14] with the aromatic rings around the macroporosities. As the evaporation proceeds still more, a part of the $AlCl_3$ dissolves in the solvents which are subsequently drawn out of the innermore parts of the beads. These $AlCl_3$ molecules gradually move towards the outside of the beads together with the solvents, and at the final stage of the evaporation they precipitate either on the surface of the polystyrene beads or in the vicinity of their surface. The CuCl, which shows virtually no solubility in the solvents, retains the crystalline forms. These arguments are consistent with the large population of Al atoms on and near the surface of the beads (Fig. 5 (a)) and with the large population of Cu atoms in the inner portion of the beads (Fig. 5 (b)).

Mechanism of Water-Resistivities of CO Adsorbents. For the adsorbents prepared by use of carbon disulfide and dichloromethane as solvents, most of the $AlCuCl_4$ is located in the microporosities of the polystyrene resin. Inside of the microporosities, composed of aromatic rings and methylene residues, is highly apolar and the concentration of water vapor there is quite small even when the adsorbents are present under the atmosphere containing considerable amounts of water vapor. In addition, the aromatic rings interacting with the $AlCuCl_4$ in the microporosities prevent the access of water vapor to the double salt by steric hindrance. These effects, both of which suppress the irreversible reaction between the $AlCuCl_4$ and water, function cooperatively, giving rise to the water-resistivities of the adsorbents.

Rather small water-resistivities of the adsorbents prepared with the use of toluene and benzene are ascribed to location of some of $AlCuCl_4$ on the surface of the beads of the polystyrene resin and on the surface of macroporosities. These $AlCuCl_4$ molecules without sufficient protection by the aromatic rings of the polystyrene are rapidly deactivated with water vapor due to irreversible reaction.5,6)

The above arguments are supported by the fact that the catalytic activity of $AlCl_3$ incorporated in a gel type polystyrene resin remains intact even after the resin–$AlCl_3$ composites are washed with water.15) Porosity of gel type polystyrene resin exists only in swollen states in good solvents.16)

The proposed mechanism for the water-resistivities of the present adsorbents is consistent with that for the water-resistivities of the toluene solutions of the linear polystyrene-protected $AlCuCl_4$ as liquid CO absorbents.5) There, $AlCuCl_4$ is effectively protected by the adjacent aromatic rings of linear polystyrenes from water vapor.

In conclusion, water-resistant solid adsorbents for carbon monoxide, the macroreticular type polystyrene resin-supported aluminium copper(I) chloride, are prepared from copper(I) chloride, aluminium chloride, and the resin. The use of solvents such as carbon disulfide and dichloromethane, which are good solvents for the resin and poor solvents for the double salt, is essential for the adsorbents to be sufficiently stable against water vapor.

The authors wish to express their thanks to Mr. Shigeru Ohtsuka and Mr. Mitsuhiro Adachi at the University of Tokyo for the assistance in the scanning electron microscopy and the energy dispersive X-ray microanalysis.

References

1) A preliminary communication: H. Hirai, S. Hara, and M. Komiyama, *Chem. Lett.*, **1982**, 1685.

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

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

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

5) H. Hirai, S. Hara, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **59**, 109 (1986).

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

7) H. Hirai, M. Komiyama, and S. Hara, *Makromol. Chem., Rapid Commun.*, **3**, 95 (1982).

8) H. Hirai, S. Hara, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **59**, 1051 (1986).

9) "Materials, Equipment and Systems for Chromatography Electrophoresis Immunochemistry and HPLC," Catalog G, Bio-Rad Laboratories Ltd., (1981), p. 28.

10) S. Ohtsuka, K. Okaya, and T. Inoue, *Funtai Kogaku Kaishi*, **17**(12), 709 (1980).

11) H. Hirai, K. Kanaka, and M. Komiyama, *Polym. Prep. Jpn.*, **34(3)**, 484 (1985).

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

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

14) S. J. Costanzo and N. B. Jurinski, *Tetrahedron*, **23**, 2571 (1967).

15) D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Am. Chem. Soc.*, **94**, 9284 (1972).

16) W. L. Sederel and G. J. Dejang, *J. Appl. Polym. Sci.*, **17**, 2815 (1973).