Adsorption of Carbon Monoxide on Activated Carbon Impregnated with Metal Halide

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Activated carbon was impregnated with a metal halide, and adsorption and desorption characteristics of CO on the carbon were measured by fixed-bed runs. It was found that the impregnation of $PdCl_2$ or CuCl effectively increases CO absorption. $PdCl_2$/CuCl-impregnated carbons were characterized by N_2 adsorption, SEM, EPMA, and XPS. Adsorption isotherms of CO were also measured on these carbons, and the influence of the loading of impregnant on CO adsorption was experimentally elucidated. A selection procedure of impregnant was proposed based on the frontier orbital theory. The perturbation energy for molecular orbital mixing was estimated by the HOMO - LUMO interaction. CO adsorption on impregnated carbons was qualitatively interpreted using the perturbation energy, and the energy was regarded as an index of impregnant selection.

Introduction

Carbon monoxide (CO) removal is important in the purification of ammonia-synthesis gas produced by the partial oxidation of hydrocarbons, the water-gas reaction, or the steam reforming of hydrocarbons. The gas contains 2 ~ 4% CO that must be removed to prevent poisoning of the catalyst. A coke-oven gas, a blast-furnace gas, and a converter gas also contain 8 ~ 89% CO. In order to protect air pollution and save the energy, it is very important to recover CO from these process gases. Many methods to separate CO from the gas mixture have been proposed. The following methods are representative: absorption, adsorption, membrane separation, cryogenic separation. Of the methods, CO removals by absorption with a complex formation and by the cryogenic process have been used in real plants. In the cryogenic process, mixed gases are liquefied, and CO is separated by the distillation at $-165 \sim -210$°C. As the boiling point of CO is -191.5°C and near to the boiling point of N_2 (-195.8°C), the separation of CO from the gas containing N_2 is economically disadvantageous.

Many liquid absorbents for CO have been reported (Larson and Teitsworth, 1922; Kohl and Riesenfeld, 1979). The copper-ammonium-salt process has retained a position of importance for many years (Kohl and Riesenfeld, 1979). In this process, CO at high pressure is absorbed by an aqueous solution of a copper-ammonium-salt in a countercurrent contactor with the formation of a copper-ammonium-carbon monoxide complex. This process is explained in detail in the reference (Kohl and Riesenfeld, 1979). The famous COSORB process (Haase and Walker, 1973) has been often used to recover CO from the process gas. In the COSORB method, the toluene solution containing aluminium copper(I) chloride ($AlCuCl_4$) selectively absorbs CO under mild conditions. Haase and Walker (1974) have reported that the COSORB process has substantial capital and operating advantages over two other major viable alternates, the ammonia-copper liquor process and the cryogenic process.

On the other hand, solid adsorbents have the following advantage compared with liquid absorbents. CO can be easily recovered by simple methods such as the pressure swing adsorption (PSA) and the temperature swing adsorption (TSA), and CO separated from the process gas contains no liquid vapor. Some solid adsorbents for CO have been reported (Huang, 1973; Rabo et al., 1977; Hirai et al., 1982, 1986; Kitagawa and Katsuragi, 1987). It has been reported that Y-type-zeolite-supported copper(I) ion adsorbs CO, and that the interaction between CO and the copper(I) ion is too strong to desorb CO (Huang, 1973; Rabo et al., 1977). Hirai et al. (1982, 1986) have prepared a polystyrene-supported copper-aluminum complex and an activated carbon-supported copper(I) chloride (CuCl), and reported that the effective CO adsorption was attributed to the formation of the complex between CO and CuCl, which is highly dispersed on the surface of adsorbents.

It is well known that activated carbon is impregnated with a transition metal to increase its adsorption ability for the gas whose molecular weight is small and boiling point is low (Hassler, 1963). In order to develop excellent adsorbents, it is very important what impregnant should be selected. If the adsorption mechanism is elucidated by taking into account the interaction between adsorbate and adsorbent, the selection method of impregnant can be proposed. However, this method hasn't been established. The impregnated carbon is empirically developed under present conditions.

The electronic state of adsorbent and adsorbate is very important to interpret adsorptive interaction in the gas phase. We consider that a molecular orbital (MO) calculation is a powerful tool to study the adsorptive interaction. Representative MO calculations are as follows: (1) empirical method, (2) semiempirical method, and (3) nonempirical method (*ab initio* method). MO calculations are described in the literature (Náray-Szabó et al., 1979). Many attempts at quantum-chemistry calculations of chemisorption of metals will be found in the literature (Clark, 1970; Ponĉec et al., 1974; Bortolani et al., 1990). Although the empirical MO calculation is easy, it is impossible to obtain the quantitative result by the calculation. The *ab initio* calculation is necessary to make clear the adsorptive interaction quantitatively. In the past several years some theoretical studies have been done, and the microscopic information has been obtained on the adsorption phenomena on a silica surface, such as adsorption energies and orientations of absorbates to adsorption sites (Sauer et al., 1984; Ugliengo et al., 1989a,b, 1990; Pelmenschikov et al., 1992; Suzuki et al., 1994). On the other hand, we must execute the *ab initio* calculation of activated carbon with a limited sum of calculation time because its surface is complex. An adsorption model is necessary to overcome the difficulty in the MO calculation. When we regard CO adsorption as the complex formation on the impregnated carbon, the frontier orbital theory proposed by Fukui et al. (1952), which is a famous theory giving a reactivity index, may be useful to study the adsorptive interaction. According to the frontier orbital theory, adsorptive interaction is attributed to the mixing of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Refer to the reference on the frontier orbital theory (Fukui et al., 1952; Fukui, 1964; Fleming, 1976). Hence, the purpose of the present work is to estimate adsorptive interaction of CO on the impregnated carbon based on the frontier orbital theory, and to propose a procedure to select the impregnant.

In this article, we prepare activated carbon impregnated with a metal halide, and determine adsorption and desorption characteristics of CO on the prepared carbon by fixed-bed runs. It is shown that the impregnation of $PdCl_2$ or CuCl is effective to increase the adsorption ability of CO. Then, we characterize $PdCl_2$/CuCl-impregnated carbons by N_2 adsorption, a scanning electron microscopy (SEM), an electron probe microanalysis (EPMA), and an X-ray photoelectron spectroscopy (XPS). We also measure adsorption isotherms of CO on these carbons, and elucidate the influence of loading of impregnant on CO adsorption. The perturbation energy for MO mixing is estimated by the HOMO–LUMO interaction, and adsorption characteristics of CO on impregnated carbons are qualitatively interpreted by the perturbation energy. We regard the energy as an index of the impregnant selection, and propose a selection procedure of impregnant based on the frontier orbital theory.

Table 1. Amount of CO Adsorbed on Impregnated Activated Carbon

Impregnant	w kg/kg	q 10^{-3} kg/kg	q' 10^{-3} kg/kg
AgCl	0.086	0.95	0.88
CuCl	0.242	7.06	7.81
CuBr	0.188	3.55	3.45
CuI	0.260	1.31	1.21
$FeCl_2$	0.187	0.74	0.64
$FeCl_3$	0.171	0.74	0.65
$NiCl_2$	0.158	0.82	0.73
$PdCl_2$	0.306	18.01	13.96
$ZnCl_2$	0.468	0.27	0.27
Unimpreg.	0.000	0.85	0.87

Note: Mole fraction of CO: 0.05; pressure: 101 kPa; temperature: 323 K; desorption temperature: 323 K ($PdCl_2$-carbon: 423 K).

Preparation and Characterization of Impregnated Carbon

Preparation of impregnated carbon

Activated carbon is impregnated with a metal halide to remove CO from a process gas by PSA or TSA. The coconut-activated carbon (WH_2C, 16–24 mesh) supplied by Takeda Chemical Industries, Ltd. was used as the support. A known amount of metal halide was magnetically stirred in 1 N HCl aqueous solution of 15 cm^3 under dry nitrogen (N_2) surroundings at room temperature, and then 4×10^{-3} kg activated carbon was added to the mixture. The carbon was impregnated with the solution for a day. It was washed by the distilled water until the pH of the water became around 5.0, and was dried by nitrogen at 403 K. Prepared adsorbents and their loading of impregnant are listed in Table 1.

Adsorption and desorption characteristics of impregnated carbon

Fixed-bed runs were carried out to determine breakthrough curves and desorption curves of CO on the prepared adsorbents. An experimental apparatus is shown in Figure 1. A stainless column (6.0 mm ID and 10 cm long) was filled with the prepared adsorbent particles of 1.0×10^{-3} kg. CO was diluted by helium (He) and was introduced to the adsorption column. The outlet concentration of CO was continually measured by a TCD detector of gas chromatograph

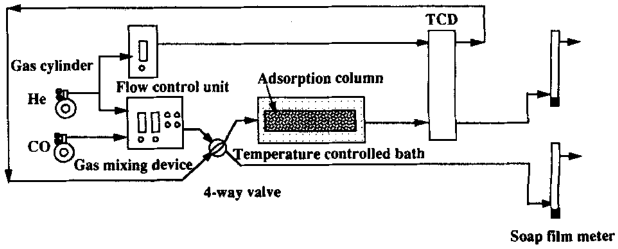

Figure 1. Experimental apparatus to measure breakthrough curve and desorption curve of CO on impregnated carbon.

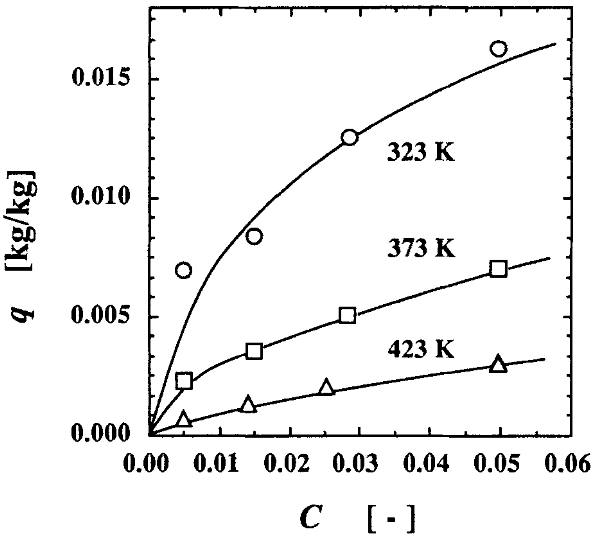

Figure 2. Adsorption isotherms of CO on $PdCl_2$-impregnated carbon.

Loading of $PdCl_2$ is 18.8 wt. %.

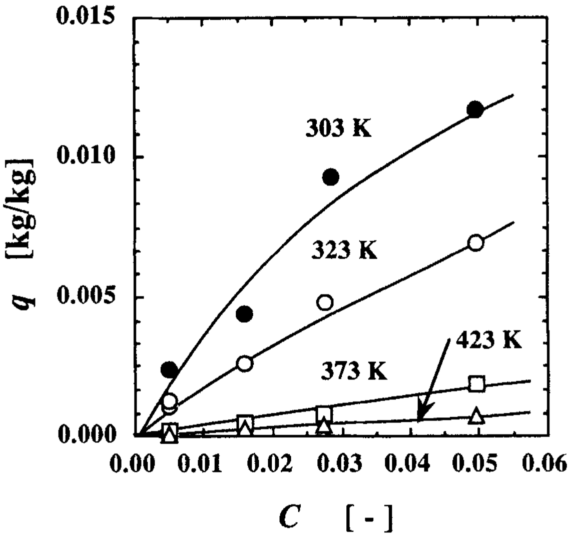

Figure 3. Adsorption isotherms of CO on CuCl-impregnated carbon.

Loading of CuCl is 24.4 wt. %.

(Shimadzu Corp., GC-8A). When the outlet concentration became equal to the inlet one, the equilibrium amount of CO adsorbed was calculated from the breakthrough curve. The breakthrough curve was obtained under the following conditions. The temperatures of adsorption were 303, 323, 373 and 423 K, the gas flow rate was 6.67×10^{-7} m^3/s, and the mole fractions of CO ranged from 0.005 to 0.05. After reaching the adsorption equilibrium, CO adsorbed on the adsorbent was desorbed by He. The gas phase was analyzed during CO adsorption on impregnated carbons by the gas chromatograph. It was found that CO didn't convert to other compounds when it was reacted with the impregnated metal halide.

Table 1 shows the amounts of CO adsorbed and desorbed on the carbons impregnated with metal halides. In this table, the mole fraction of CO is 0.05, the pressure is 101 kPa, and the temperature of adsorption or desorption is 323 K. Since a part of CO adsorbed on the $PdCl_2$-impregnated carbon was not desorbed at 323 K, the desorption temperature was set as 423 K for the carbon. The carbons impregnated with AgCl, $FeCl_2$, $FeCl_3$, $NiCl_2$, and $ZnCl_2$ give the same or the smaller amount adsorbed compared with the unimpregnated carbon (WH_2C). Although the loading of impregnant on each impregnated carbon is not constant, it can be seen that the carbons impregnated with CuCl, CuBr, CuI, and $PdCl_2$ give the large adsorption capacity of CO. Especially, the amounts of CO adsorbed on the carbons impregnated with CuCl and $PdCl_2$ are around eight and twenty times that on the unimpregnated carbon, respectively. As seen from Table 1, the amount of CO adsorbed is almost equal to that desorbed. Adsorption of CO on the prepared adsorbents seems to be reversible, and CO can be easily desorbed by PSA or TSA.

Since $PdCl_2$ and CuCl were especially excellent as the impregnant for CO removal as shown in Table 1, we elucidated the adsorption characteristics of CO on the carbons impregnated with these metal halides. Figures 2 and 3 show adsorption isotherms of CO on the carbons impregnated with $PdCl_2$ and CuCl, respectively. As seen from these figures, the amount of CO adsorbed increases with the increase of CO concentration and the decrease of adsorption temperature. CO adsorption seems to be attributed to a reversible complex formation between CO and impregnant.

Figures 4 to 7 show the influence of impregnant loading on CO adsorption. The ordinate in Figures 6 and 7 means the molar amount of CO adsorbed per unit molar amount of impregnant loaded q^*. Figures 4 and 5 show that the amount of CO adsorbed, q, increases with the loading of impregnant, w, and that the increase gradually becomes small with w. On the other hand, one can see that the amount adsorbed q^* decreases as w increases from Figures 6 and 7. From the present results, we suppose that the impregnant highly disperses in the carbon at low loading, and that the high dispersion cannot be held as the loading increases.

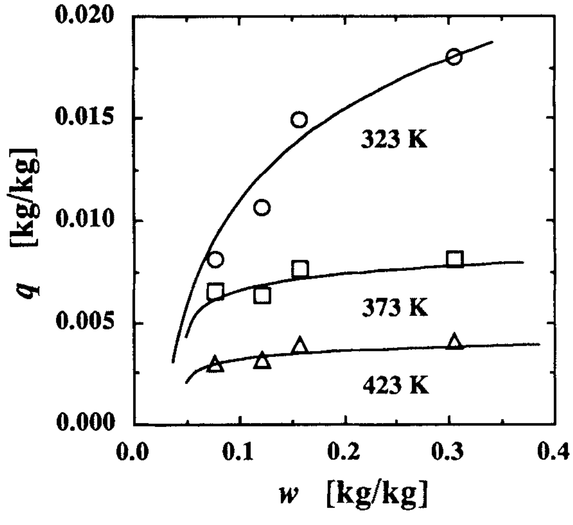

Figure 4. Influence of loading of $PdCl_2$ on amount of CO adsorbed.

Mole fraction of CO in gas phase is 0.05.

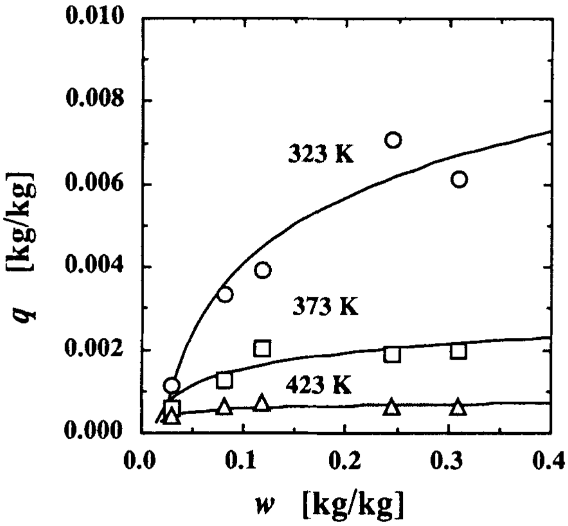

Figure 5. Influence of loading of CuCl on amount of CO adsorbed.

Mole fraction of CO in gas phase is 0.05.

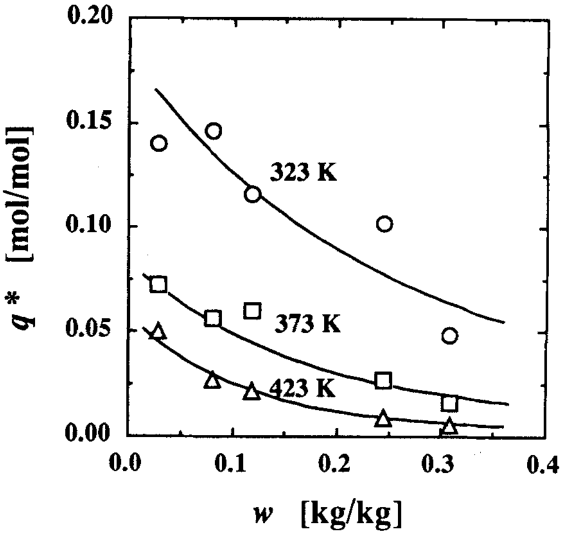

Figure 7. Influence of loading of CuCl on amount of CO adsorbed.

Mole fraction of CO in gas phase is 0.05.

Characterization of impregnated carbon

Since the carbon impregnated with CuCl or $PdCl_2$ is excellent for CO adsorption, it is characterized by N_2 adsorption, SEM, EPMA, and XPS.

N_2 adsorption isotherms were measured on the carbons impregnated with CuCl or $PdCl_2$ at 77 K. The *t*-plot analysis is available to estimate a micropore structure of activated carbon from the isotherm. Since the surface property of carbon may be changed by the impregnation of metal halide, the standard isotherm necessary to conduct this analysis is different from that on the unimpregnated carbon. In the present stage of investigation, we have no standard isotherms on the impregnated carbons. Therefore, we used the standard isotherm of N_2 on the carbon and applied the *t*-plot method to the measured isotherm. Then we determined the specific surface area S and the micropore volume V, and estimated the average slit width of micropores δ by a geometrical consideration. The values of S, V, and δ of the prepared adsorbent are presented in Table 2. It can be seen that S and V greatly decrease with the impregnation. On the other hand, it is very interesting that the amount of CO adsorbed is increased by the impregnation. These results show that the impregnation is effective to increase the adsorption capacity of CO. It is very interesting to elucidate the impregnation position of metal halide on activated carbon. It is found that δ is independent of the loading of impregnant as shown in Table 2. Consequently, we suppose that metal halide deposits at the entrance of micropores and blockages are part of micropores under present conditions. A detailed analysis, however, will be needed in the future.

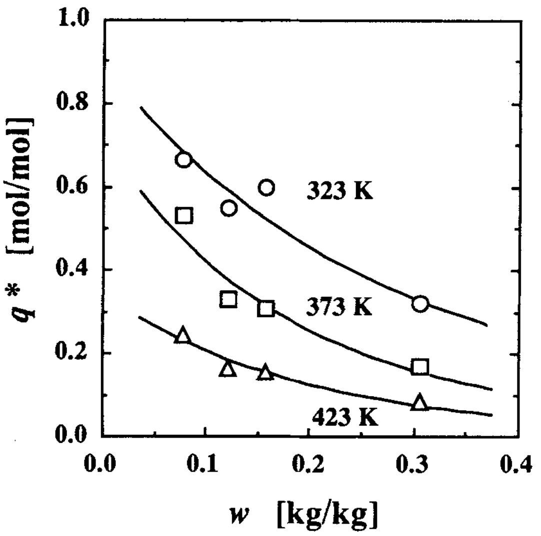

Figure 6. Influence of loading of $PdCl_2$ on amount of CO adsorbed.

Mole fraction of CO in gas phase is 0.05.

Distributions of metal halide in the prepared adsorbent were measured by EPMA. An X-ray microanalyzer (Horiba, Ltd., EMAX-2200S) was used for this analysis. Figure 8 shows the image of a cross section of a carbon particle impregnated with $PdCl_2$ by a scanning electron microscope (Hitachi, Ltd., S-510). Here, the loading of impregnant is 15.8 wt%. White waved lines indicate the distributions of Pd and Cl atoms along the white straight lines at the center. Both atoms don't deposit at the outer surface of the particle, but uniformly distribute in the cross section. Figure 9 shows the image of a

Table 2. Pore Structure of Carbons Impregnated with $PdCl_2$ and CuCl

Impregnant	w kg/kg	S 10^5 m^2/kg	V 10^{-4} m^3/kg	δ nm
Unimpreg.	0.0	11.94	4.36	0.74
$PdCl_2$	0.077	10.38	3.92	0.76
	0.158	3.52	1.11	0.64
	0.306	2.13	0.72	0.68
CuCl	0.029	9.95	3.54	0.72
	0.119	9.36	3.31	0.70
	0.224	6.36	2.10	0.66

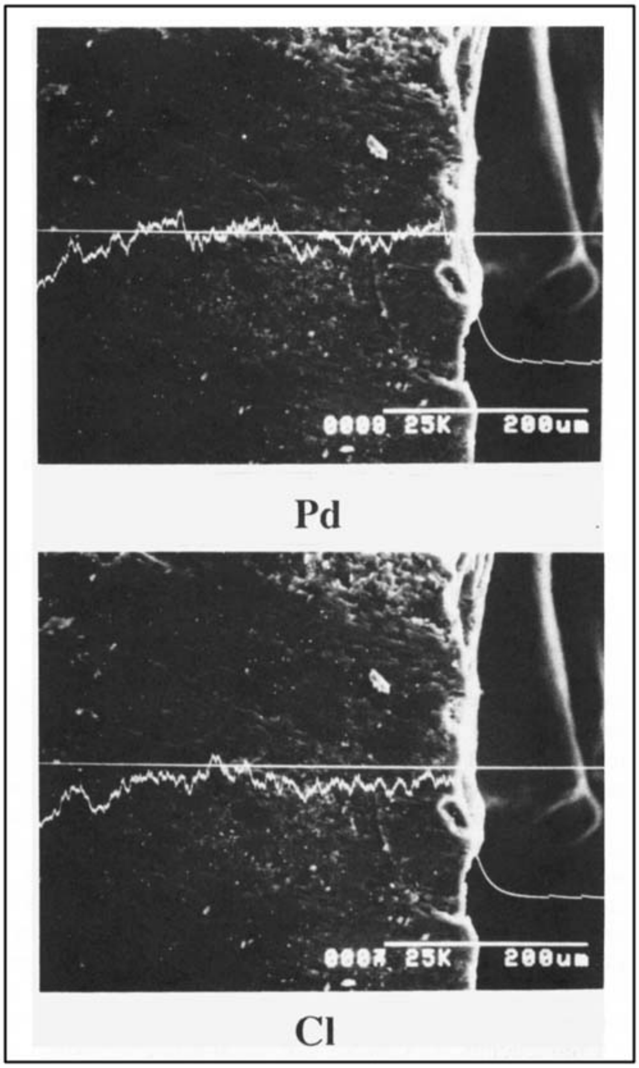

Figure 8. Distribution of impregnant on cross section of $\mathrm{PdCl_2}$-impregnated carbon.

Loading of $\mathrm{PdCl_2}$ is 15.8 wt. %.

cross section of a carbon particle impregnated with CuCl. Here, the loading of impregnant is 11.9 wt%. As for CuCl-impregnated carbon, one can see that the impregnant uniformly distributes in the cross section of carbon.

$\mathrm{PdCl_2}$ or CuCl loaded on the carbon was characterized by XPS. An X-ray photoelectron spectroscope (Shimadzu Corporation, ESCA-750) was used for this measurement. Figure 10 shows $\mathrm{Pd3d_{3/2}}$ and $\mathrm{Pd3d_{5/2}}$ spectra of $\mathrm{PdCl_2}$-carbon by XPS. Figure 11 shows $\mathrm{Cu2p_{3/2}}$ spectrum of CuCl-carbon by XPS. On the other hand, the bonding energies for $\mathrm{Pd3d_{3/2}}$, $\mathrm{Pd3d_{5/2}}$, and $\mathrm{Cu2p_{3/2}}$ of reduced metals are 340, 345, and 931 eV. It can be seen that XPS spectra for Pd and Cu chemically shift to the higher bonding energy from these figures. If the metal is oxidized, the bonding energy shifts to a higher energy side. Hence, we consider that the Pd and Cu on the carbon are metal cations. Figures 10 and 11 also give XPS spectra of $\mathrm{PdCl_2}$ and CuCl powder. It is found that the XPS spectra of metal halide-impregnated carbon are almost equal to those of metal halide powder. This result also suggests that the palladium cation loaded on the carbon is bivalent, and that the copper cation is univalent.

Selection of Impregnant Based on Frontier Orbital Theory

Procedure to estimate interaction energy

We consider that CO adsorption is attributed to the charge transfer between the electron donor and the electron acceptor. If we suppose that the adsorption site is the metal cation on the impregnated carbon, the donor is CO and the acceptor is the metal cation. Figure 12 shows a procedure to estimate the interaction energy. First, the adsorbent surface is modeled, and MO calculations of adsorbent and adsorbate are executed. Then, we obtain the information on energy levels and MO coefficients. According to the frontier orbital theory (Fukui et al., 1952; Fukui, 1964; Fleming, 1976), the charge transfer between the donor and the acceptor is regarded as the HOMO–LUMO interaction. The perturbation

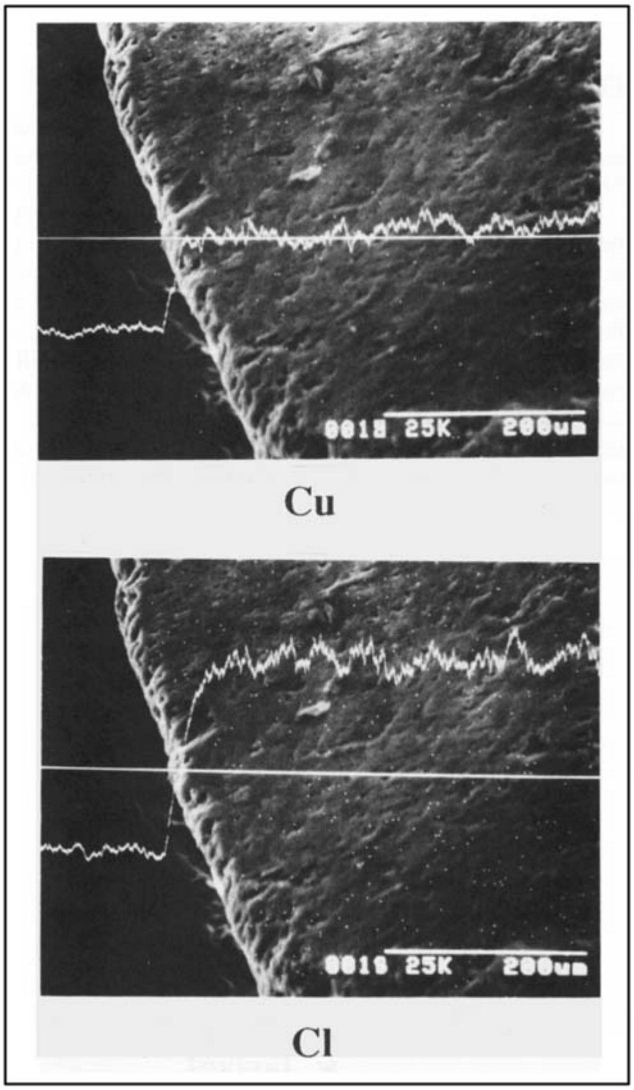

Figure 9. Distribution of impregnant on cross section of CuCl-impregnated carbon.

Loading of CuCl is 11.9 wt. %.

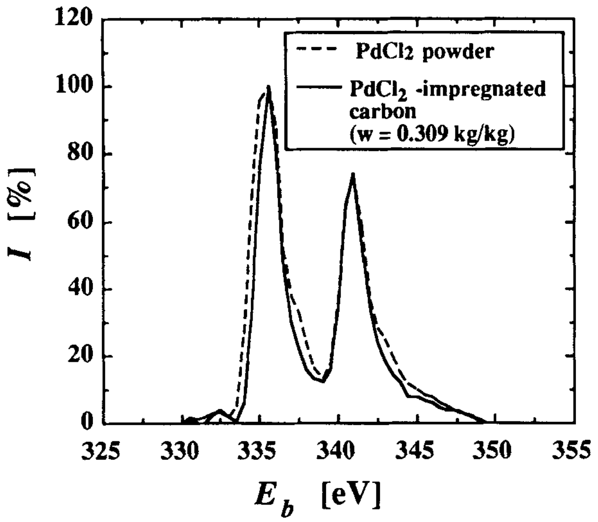

Figure 10. Pd3d$_{3/2}$ and Pd3d$_{5/2}$ spectra of PdCl$_2$-impregnated carbon and PdCl$_2$ powder by XPS.

energy for orbital mixing (HOMO–LUMO interaction) can be calculated. The energy is regarded as an index of the selection of impregnant.

Model of adsorption site

The experimental results suggest that the adsorption site is the metal cation on the impregnated carbon. We discuss the role of the activated carbon. As seen from Table 1, the unimpregnated carbon has very small adsorption capacity of CO, and the carbon surface seems to be inactive in CO adsorption. Thus, we suppose that the carbon surface acts as a kind of solvent in CO adsorption. Although we should use the dielectric constant ϵ of graphite to estimate LUMO energy of metal cation, we have no information on the constant. Hence, we assumed $\epsilon = 5.0$ as a first approximation.

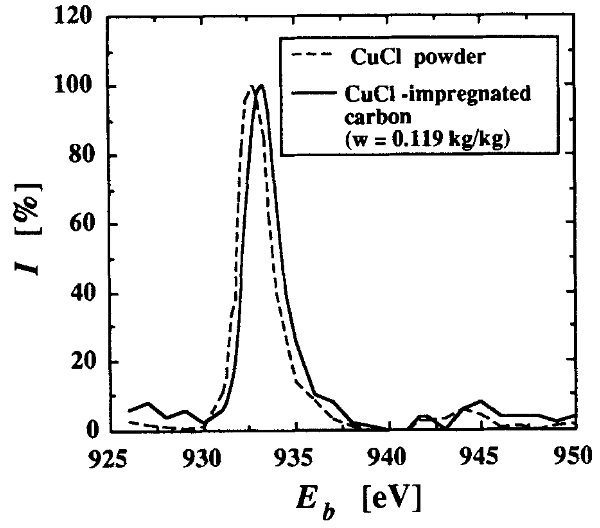

Figure 11. Cu2p$_{3/2}$ spectra of CuCl-impregnated carbon and CuCl powder by XPS.

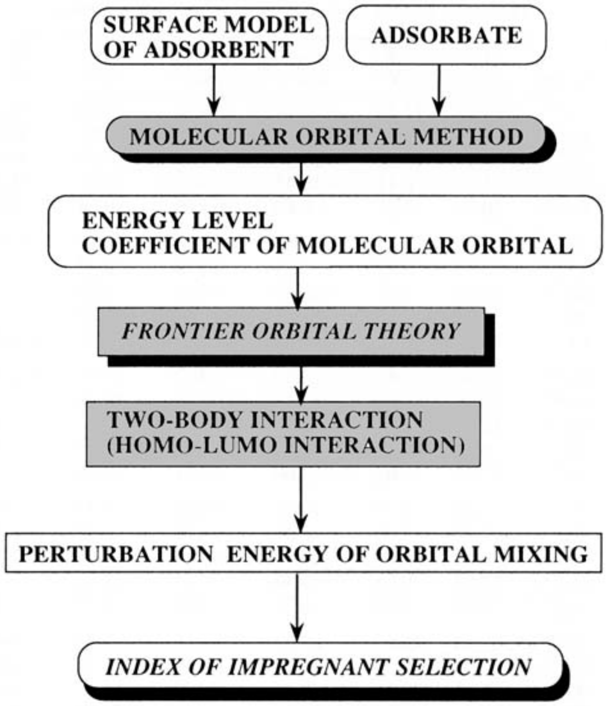

Figure 12. Procedure to estimate adsorptive interaction on impregnated carbon.

LUMO energy of metal cation on activated carbon

In the present work, we assumed that the metal cation is solvated by the carbon surface. As Klopman (1968) has proposed a method to estimate the electronic state of metal cations in solvent, we modified his method to estimate the MO energy of metal cation. The LUMO energy of cation E_B is given by Eq. 1 according to the Klopman's method:

$$E_B = -(3IP + EA)/4, \tag{1}$$

where IP and EA are the ionization potential and the electron affinity of the cation, respectively. These values are reported in the literature (Moore, 1949). The LUMO energy in solvent E_B^* can be estimated by Eq. 2 by taking into account the solvent effect:

$$E_B^* = E_B + E_S \tag{2}$$

$$E_S = 1.4388(Q - 0.5x)x(1 - 1/\epsilon)/(r + 0.082), \tag{3}$$

where Q is the charge of cation, and r is the ion radius given in the literature (Pauling, 1960). The dielectric constant of activated carbon is ϵ; it is assumed to be 5.0 in this article. The value of x is empirically given by the following equation (Klopman, 1968).

$$x = Q - (Q - 1)\sqrt{3/4}. \tag{4}$$

Table 3 shows LUMO energies of many metal cations. One can see that the LUMO energy is low for soft cations.

Table 3. LUMO Energy of Cations on Carbon

Cation	IP eV	EA eV	E_B eV	$r+0.082$ nm	E_S eV	E_B^* eV
La^{3+}	19.17	11.43	−17.24	0.196	17.64	0.40
Be^{2+}	18.21	9.32	−15.98	0.117	15.95	−0.03
Al^{3+}	28.44	18.82	−26.04	0.133	25.99	−0.05
Ca^{2+}	11.87	6.11	−10.43	0.181	10.31	−0.12
Ba^{2+}	10.00	5.21	−8.80	0.216	8.64	−0.16
Sr^{2+}	11.03	5.69	−9.69	0.194	9.52	−0.17
Li^{2+}	5.39	0.82	−4.25	0.150	3.84	−0.41
Mg^{2+}	15.03	7.64	−13.18	0.148	12.61	−0.57
Na^{+}	5.14	0.47	−3.97	0.179	3.22	−0.75
Cr^{2+}	15.01	7.28	−13.08	0.165	11.31	−1.77
Mn^{2+}	15.64	7.43	−13.59	0.162	11.52	−2.07
Fe^{2+}	16.18	7.90	−14.11	0.156	11.96	−2.15
Co^{2+}	16.49	8.42	−14.47	0.154	12.12	−2.35
Tl^{+}	6.10	2.00	−5.08	0.222	2.59	−2.49
Ni^{2+}	17.11	8.67	−15.00	0.151	12.36	−2.64
H^{+}	13.60	0.75	−10.38	0.078	7.37	−3.01
Cu^{+}	7.72	2.00	−6.29	0.178	3.23	−3.06
Fe^{3+}	30.64	15.96	−26.97	0.146	23.68	−3.29
Cu^{2+}	17.57	9.05	−15.44	0.154	12.12	−3.32
Ag^{+}	7.57	2.20	−6.23	0.208	2.77	−3.46
Cr^{3+}	30.95	16.49	−27.33	0.145	23.84	−3.48
Zn^{2+}	17.96	9.39	−15.82	0.156	11.96	−3.86
Ti^{4+}	43.24	28.14	−39.46	0.150	35.45	−4.01
Ga^{3+}	30.70	20.51	−28.15	0.144	24.01	−4.14
Cd^{2+}	16.90	8.99	−14.93	0.179	10.43	−4.50
Au^{+}	9.22	2.70	−7.59	0.219	2.63	−4.96
Pd^{2+}	19.43	8.34	−16.65	0.182	10.26	−6.39
Hg^{2+}	18.75	10.43	−16.67	0.192	9.72	−6.95
Tl^{3+}	29.30	20.42	−27.45	0.177	19.53	−7.92

Table 4. Amount of CO Adsorbed and Perturbation Energy

Impregnant	E_B^* eV	ΔE eV	w kg/kg	q 10^{-3} kg/kg	q^* mol/mol
$PdCl_2$	−6.39	0.390	0.306	18.01	0.373
AgCl	−3.46	0.163	0.086	0.95	0.057
CuCl	−3.06	0.151	0.244	7.06	0.102
$NiCl_2$	−2.64	0.140	0.158	0.82	0.018
$FeCl_2$	−2.15	0.130	0.187	0.74	0.013
$FeCl_3$	−3.29	0.079	0.171	0.74	0.019

Perturbation energy by HOMO–LUMO interaction

Figure 13 shows the concept of the MO mixing. The energy level of HOMO of CO changes to the more stable level by interacting with LUMO of metal cation. On the other hand, the energy level of LUMO becomes to the more unstable level. This energy difference is called the perturbation energy ΔE. The second-order perturbation expression for the energy that accompanies the interaction can be derived, and ΔE can be calculated by the HOMO–LUMO interaction (Klopman, 1968; Salem, 1968; Fleming, 1976)

$$\Delta E = n(C_r^* C_s^* \Delta\beta)^2 / |E_A^* - E_B^*|, \qquad (5)$$

where E_A^* and C_r^* are the energy and the coefficient of HOMO of CO. They can be estimated by the MO calculation. Johnson and Klemper (1975) have reported the HOMO energy of CO. CO orbitals are described in the literature (Fujimoto et al., 1986). $E_A^* = -8.5$ eV and $C_r^* = 0.916$ were used in this article. E_B^* and C_s^* are the energy and the coefficient of LUMO of metal cation on the carbon. As the adsorption site is the metal cation, C_s^* can be regarded as 1.0. E_B^* calculated by Eq. 2 is listed in Table 3. The value of n denotes the number of electron stabilized by the MO mixing. $\Delta\beta$ is the interorbital interaction integral and assumed to be −0.7 eV in this work. Equation 5 means that ΔE is large in the case where $|E_A^* - E_B^*|$ is small.

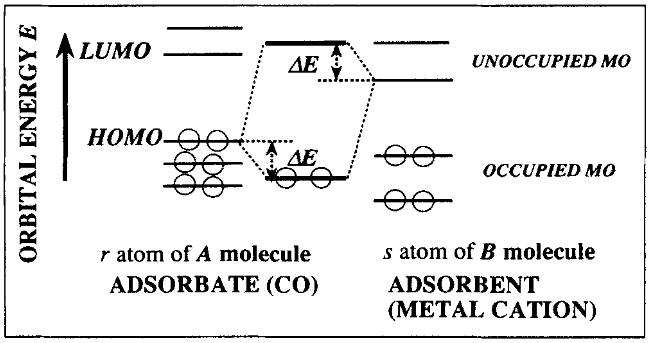

Figure 13. Concept of molecular orbital mixing.

Selection of impregnant based on perturbation energy

Table 4 shows the LUMO energy of metal cation, E_B^*, the amount of CO adsorbed, q^* (323 K, concentration of CO: 5 vol. %), and the perturbation energy, ΔE. The order of ΔE is as follows: $PdCl_2 > AgCl > CuCl > NiCl_2 > FeCl_2 > FeCl_3$. On the other hand, the order of the amount of q^* is as follows: $PdCl_2 > CuCl > AgCl$, $NiCl_2$, $FeCl_2$, $FeCl_3$. Both orders qualitatively coincide except AgCl. Accordingly, it can be seen that the metal chloride, of which cation has the low LUMO energy, should be selected as the impregnant.

We consider that cations with the low LUMO energy, which belong to soft bases, are suitable to the adsorption site for CO. Because CO is soft acid, it is reasonable to select soft bases as the adsorption site of CO according to the theory of hard and soft acids and bases (HSAB) proposed by Pearson (1963, 1968a,b).

Influence of ligand of copper halide on CO adsorption

In the adsorption of CO on the activated carbon impregnated with CuCl, CuBr, or CuI, the order of adsorption ability is CuCl > CuBr > CuI, as shown in Table 1. In order to explain the influence of ligand on CO adsorption, the HOMO energy of Cl^-, Br^-, or I^- was estimated using Klopman's method (Klopman, 1968). The HOMO energy of anion E_A is given by Eq. 6:

$$E_A = -(IP + 3EA)/4, \qquad (6)$$

where IP and EA are the ionization potential and the electron affinity of the anion, respectively. These values are reported in the literature (Moore, 1949). The HOMO energy in solvent E_A^* is estimated by Eq. 7 by taking into account the solvent effect:

$$E_A^* = E_A + E_S \qquad (7)$$

Table 5. HOMO Energy of Anions on Carbon

Anion	IP eV	E_A eV	E_A eV	r nm	E_S eV	E_A^* eV
Cl^-	13.01	3.69	−6.02	0.181	−3.18	−9.20
Br^-	11.84	3.49	−5.58	0.195	−2.95	−8.53
I^-	10.45	3.21	−5.02	0.216	−2.66	−7.68

$$E_S = 1.4388(Q + 0.5)(1 - 1/\epsilon)/(r + 0.082), \qquad (8)$$

where Q is the charge of cation, ϵ is the dielectric constant of activated carbon and assumed to be $\epsilon = 5.0$. Table 5 shows the HOMO energy of Cl^-, Br^-, and I^- calculated by Eq. 7. Since the LUMO energy of Cu^+ is −3.06 eV as shown in Table 4, the HOMO energy of I^- is nearest to the LUMO energy of Cu^+. The HOMO energy of Cl^- is farthest from the LUMO energy of Cu^+.

In the case of CuI, the HOMO energy of I^- is −7.68 eV, and is higher than the HOMO energy of CO. Cu^+ greatly perturbs with I^- more than CO. As seen from Figure 13, the energy level of LUMO is made unstable by the HOMO–LUMO interaction. Since the LUMO energy of Cu^+ becomes high by interacting with I^-, the perturbation energy ΔE for CO adsorption becomes small according to Eq. 5. On the other hand, in case of CuCl, the HOMO energy of Cl^- is lower than that of CO, and the influence of Cl^- on ΔE is small. Accordingly, one can see that the influence of ligand on the perturbation energy ΔE is as follows: $Cl^- > Br^- > I^-$. This result coincides with the CO adsorption ability of impregnated carbon as shown in Table 1.

General selection procedure of metal cation

Table 3 presents the values of LUMO energy for many cations on the carbon surface. Cations with low LUMO energy are considered to be suitable adsorption sites for CO. This is because these cations belong to soft bases, and CO is the soft acid. Thus, it is reasonable to select soft bases as the adsorption site for CO according to the HSAB theory.

The general selection procedure for metal cations for the other adsorbates is shown in Figure 14. First, the HOMO energy of adsorbate is determined by the MO calculation. When the HOMO energy is high and the polarizability of adsorbate is small, soft metal cations with low LUMO energy should be selected. When the HOMO energy of adsorbate is low and its polarizability is large, hard metal cations, with a small ion radius and large polarizability, are effective for adsorption. However, the charge transfer and van der Waals interactions should be taken into account in the following cases, and a detailed study will be needed in the future: (1) the HOMO energy of adsorbate is high and its polarizability is large; and (2) the HOMO energy of adsorbate is low and its polarizability is small.

Conclusions

Activated carbons impregnated with nine kinds of metal halides were prepared. Adsorption and desorption characteristics of CO were determined on prepared adsorbents by fixed-bed runs. The carbons impregnated with CuCl, CuBr, CuI, and $PdCl_2$ yielded a large adsorption capacity compared with the unimpregnated carbon. Especially, the amounts of CO adsorbed on $PdCl_2$/CuCl-impregnated carbons were around eight and twenty times that on the unimpregnated carbon, respectively. The amount of CO adsorbed was almost equal to that desorbed, and CO can be easily recovered by PSA or TSA.

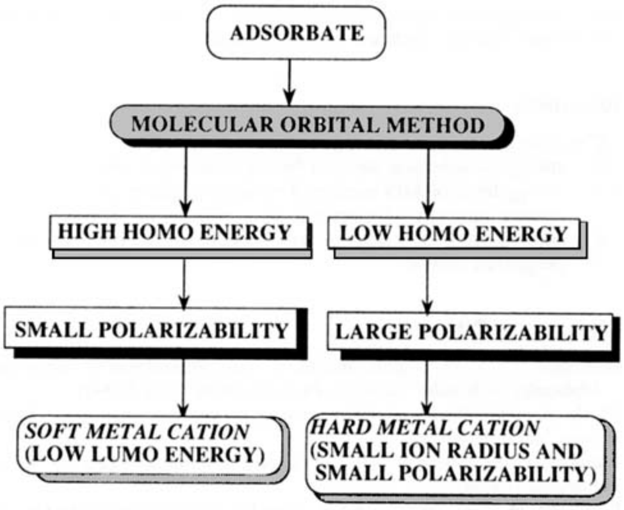

Figure 14. Selection procedure of metal cation in preparing impregnated carbon.

Adsorption isotherms of CO were measured on the carbons impregnated with CuCl and $PdCl_2$. The amount of CO adsorbed increased with the increase of CO concentration and the decrease of adsorption temperature. The experimental results suggest that $PdCl_2$ or CuCl give reversible adsorption sites. Then the influence of the loading of impregnant on CO adsorption was elucidated. Although the amount of CO adsorbed increased with the amount of impregnant loaded, the dispersion of impregnant on the carbon surface became low in the range of large loading.

The carbon impregnated with CuCl or $PdCl_2$ was characterized by N_2 adsorption, SEM, EPMA, and XPS. Although the micropore volume and specific surface area were greatly decreased by the impregnation, the amount of CO adsorbed was increased. It was found that the impregnation of metal halide is effective in increasing the adsorption ability of CO. The results obtained by EPMA measurements showed that the impregnant uniformly distributed in the carbon. XPS measurements suggested that the palladium cation loaded on the carbon was bivalent, and that the copper cation was univalent.

Adsorption of CO on the impregnated carbon was regarded as the charge transfer between CO and the metal cation. The charge transfer interaction was interpreted by the frontier orbital theory. The perturbation energy was estimated by the HOMO–LUMO interaction, and the energy was adopted as the index of impregnant selection. CO adsorption on the impregnated carbons was qualitatively interpreted using the perturbation energy. Consequently, a selection procedure of impregnant was proposed.

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Notation

C = mole fraction of CO in gas phase
E_S = energy by solvation defined by Eq. 3 or Eq. 8, eV
E^* = energy level of MO corrected by solvent effect, eV
I = relative intensity of spectrum, %
q' = amount of CO desorbed on impregnated carbon, kg/kg-impregnated carbon

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