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Studies of the Properties of the Basic Sites on the Silica-alumina Surface through the Reaction of the Basic Sites with Copper(II) Complexes Containing 2,2′-Bipyridine

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The substitution reactions of complexes with basic sites on the surfaces of silica-alumina and alumina and the properties of the basic sites were studied through the adsorption of the complexes onto the surfaces. The hydroxyl groups with basic strengths of two kinds, $H_0>9.3$ and $7.2<H_0<9.3$, exist on the silica-alumina surface pretreated at 300°C. They are present in a cluster state. The basic strength becomes higher as the outgassing temperature becomes lower. The complexes predominantly interact with the O^{2-} ions on the surface pretreated at a relatively high temperature, resulting in new chemical species. The basic strength of the O^{2-} ions is lower than that of the hydroxyl groups on the surface pretreated at a lower temperature. The hydroxyl groups on the alumina surface outgassed at 300°C are distributed, on the whole, homogeneously in comparison with those of the silica-alumina surface, and their basic strength is $H_0>9.3$. The nature of the basic sites on the alumina surface tends to vary with the outgassing temperature, similarly to those on the silica-alumina surface. These analyses were performed on the basis of the ESR spectra for complexes in basic solutions.

The acidic properties of the silica-alumina surface have been extensively studied by various techniques[1-4] because the catalytic action of silica-alumina is closely correlated with its acidic properties.[5,6] The nature and the structure of the acidic sites and such reactions as isomerization and polymerization on the surface have been reviewed by Tanabe and Takeshita.[7]

On the other hand, Krylov *et al.* have found, by the phenol-vapor adsorption method, that the basic sites are present on the surface of silica-alumina.[8] It is of great interest from the viewpoint of acid-base bifunctional catalysis that the basic sites as well as the acidic sites exist on the surface. The basic properties of the silica-alumina surface have been investigated by several means,[8,9] but the nature and structure of the basic sites have scarcely been revealed. However, the basic properties of alumina[10] as well as those of calcium oxide [11] and magnesium oxide[12] have been fairly well elucidated in comparison with those of silica-alumina. It has been reported that weakly basic sites are present on the surface of silica gel on the basis of the measurement of the amounts of phenol vapor retained on this surface at various elevated temperatures.[8] Peri[13] and Yamadaya[14] have proposed a mechanism of the formation of the basic sites which include hydroxyl groups and/or negatively-charged oxygen ions, O^{2-}.

We found, from our ESR measurements, that the coordinated water molecules in the copper(II) complexes with 2,2′-bipyridine were replaced by one or two hydroxyl ions in aqueous solutions at pH values higher than 8.[15] Such a phenomenon was also observed in basic methanol solutions. Thus, these complexes were adsorbed as so-called indicators in order to elucidate the basic properties of the hydroxyl groups on the surfaces of silica-alumina and alumina. The ESR spectra for the complexes adsorbed on the surfaces were quite similar to those in the basic solutions; the hydroxyl groups contribute to the formation of the chemical species on the surfaces. However, in

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[1] O. Johnson, *J. Phys. Chem.*, **59**, 827 (1955).

[2] H. Uchida and M. Temma, *Shokubai*, **4**, 353 (1962).

[3] W. K. Hall, *J. Catal.*, **1**, 53 (1962).

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[5] K. Tarama, S. Teranishi, H. Honda, and S. Yoshida, *Shokubai*, **6**, 268 (1964).

[6] J. W. Ward and R. C. Hansford, *J. Catal.*, **13**, 154 (1969).

[7] K. Tanabe and T. Takeshita, "San Enki Shokubai (Acid-Base Catalysis)," Sangyo Tosho, Tokyo (1966).

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[9] K. Tanabe and T. Yamaguchi, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **14**, 93 (1966).

[10] G. M. Schwab and H. Kral, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam*, **1**, 433 (1964).

[11] K. Saito and K. Tanabe, *Shokubai*, **11**, (25th Symp. Catalysis, Preprints of Paper), 206 (1969).

[12] J. Take, N. Kikuchi, and Y. Yoneda, *ibid.*, **10**, (23rd Symp. Catalysis, Preprints of Papers), 127 (1968).

[13] J. B. Peri, *J. Phys. Chem.*, **69**, 220 (1965).

[14] M. Yamadaya, K. Shimomura, T. Konoshita, and H. Uchida, *Shokubai*, **7**, 313 (1965).

[15] K. Takimoto and M. Miura, This Bulletin, in press.

addition to these hydroxyl groups, it is also necessary to take negatively-charged oxygen ions into consideration as basic sites when the samples are treated at relatively high temperatures; α sites which contain a negatively-charged oxygen ion in close proximity to an exposed aluminum ion are formed by the condensation of Al-OH groups in the course of the dehydration of the surface.[16] These sites are acid-base rather than Lewis-acid sites. This method can differentiate to some extent which of the basic sites is mainly bound to these complexes, as will be discussed later. In this paper, the substitution reaction of the complexes with the basic sites on the surfaces of silica-alumina and alumina, and the properties of the basic sites, as estimated from an analysis of the chemical species which are generated by these reactions, will be reported.

Experimental

Materials. The cupric sulfate, methanol, and 2,2′-bipyridine, all obtained from the Wako Pure Chemical Co., were of a guaranteed reagent grade and were used without further purification. The indicators,[17] bromothymol blue ($pK_a=7.2$), and phenolphthalein ($pK_a=9.3$) from the Yoneyama Co., were also of a guaranteed reagent grade. The copper(II) complexes with 2,2′-bipyridine, the 1 : 1 complex (or $[Cu(bip)(H_2O)_4]SO_4$) and the 1 : 2 complex (or $[Cu(bip)_2(H_2O)_2]SO_4$), were synthesized in methanol and were recrystallized repeatedly from methanol. The alumina, 50% silica-alumina, and silica gel were the same as those used in our preceding work.[18]

Procedures. These complexes were adsorbed from water-free methanol solutions onto surfaces which had previously been treated at 100, 300, 500, and 800°C for 3 hr. After the methanol had been eliminated, the ESR spectra were measured at 77°K. These experiments were carried out in a dark room because these complexes are photosensitive.

Apparatus. The ESR spectra were obtained by using a spectrometer described elsewhere.[19] The chemical species were determined from the ESR spectra of the 1st and 2nd derivatives.

Results and Discussion

Chemical Species in the Solutions. The ESR spectra in methanol solutions were measured in order to be compared with those obtained on the surfaces. The ESR spectrum for the 1:1 complex is shown in Fig. 1. The spin Hamiltonian can be described as:

$$\begin{aligned}\mathscr{H} &= \beta[g_{/\!/}H_zS_z+g_\perp(H_xS_x+H_yS_y)]\\ &\quad + A_{/\!/}S_zI_z + A_\perp(S_xI_x+S_yI_y)\end{aligned}$$

where β is the electron Bohr magneton, where $g_{/\!/}$ and $g_\perp$ are the components of the axial g tensor, and where $A_{/\!/}$ and $A_\perp$ are the components of the copper nuclear hyperfine (hf) interaction. This spectrum is axially symmetrical. Four peaks were observed in the lower magnetic field. These are ascribed to the parallel component of the hf interaction due to the nuclear spin of copper, $I=3/2$. The superhyperfine (shf) structure was observed in the perpendicular component in the higher magnetic field. When the 1:1 complex is prepared in methanol, the following chemical equilibrium may be established:

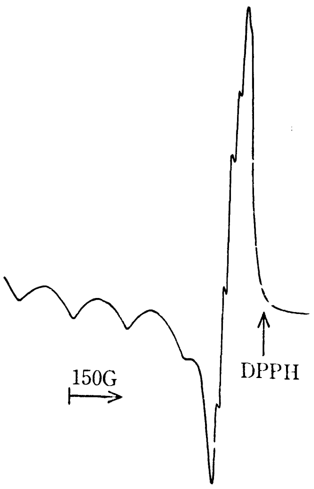

Fig. 1. ESR spectrum for the 1 : 1 complex in methanol at 77°K.

$$Cu^{2+} + bip + 4H_2O \rightleftarrows \underset{\text{I}}{[Cu(bip)(H_2O)_4]^{2+}} \qquad (1)$$

Only the I species was observed, probably because the equilibrium lies almost completely to the right. According to the Jahn-Teller effect, the long or distortion axis is frozen in different orientations at low temperatures. The stable state is the one in which the distorted z axis is perpendicular to the plane containing ligands. Thus, two nitrogen atoms in a bipyridine molecule predominantly coordinate with the copper ion in the xy plane.[20,21]

The ESR parameters for the 1:1 complex are plotted against the concentration of sodium hydroxide in a methanol solution in Fig. 2. With an increase in the basic concentration, three sets of $g_{/\!/}$ and $A_{/\!/}$ values were observed. The reactions of this complex with the hydroxyl ion may be represented as:[22]

$$\begin{aligned}&\underset{\text{I}}{[Cu(bip)(H_2O)_4]^{2+}} + OH^-\\ &\rightleftarrows \underset{\text{II}}{[Cu(OH)(bip)(H_2O)_3]^{1+}} + H_2O \qquad (2)\end{aligned}$$

$$\begin{aligned}&2\underset{\text{II}}{[Cu(OH)(bip)(H_2O)_3]^{1+}}\\ &\rightleftarrows \underset{\text{II}'}{[(H_2O)_2(bip)Cu\langle{}^{OH}_{OH}\rangle Cu(bip)(H_2O)_2]^{2+}} + 2H_2O \qquad (3)\end{aligned}$$

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[16] J. B. Peri, *J. Phys. Chem.*, **70**, 3168 (1966).

[17] K. Tanabe and T. Yamaguchi, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **11**, 179 (1964).

[18] M. Miura, Y. Kubota, T. Iwaki, K. Takimoto, and Y. Muraoka, This Bulletin, **42**, 1476 (1969).

[19] A. Hasegawa and M. Miura, *ibid.*, **40**, 2553 (1967).

[20] W. B. Lewis, M. Alei, and L. O. Morgan, *J. Chem. Phys.*, **45**, 4003 (1966).

[21] M. Noack and G. Gordon, *J. Chem. Phys.*, **48**, 2689 (1968).

[22] R. B. Ryland, G. S. Ronay, and F. M. Fowkes, *ibid.*, **62**, 798, 867 (1958).

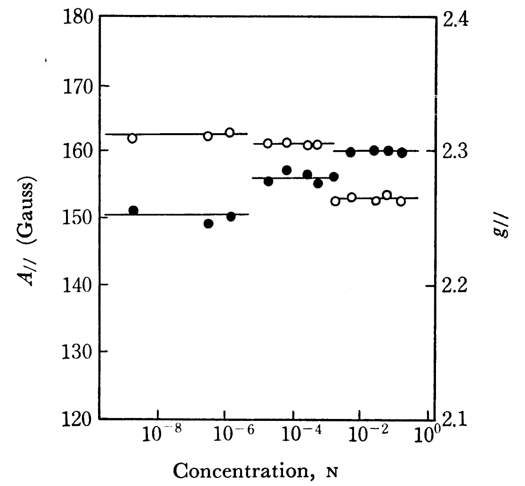

Fig. 2. Variations of the ESR parameters for the 1 : 1 complex with the concentration of sodium hydroxide in methanol solution.

●: $A_{//}$; ○: $g_{//}$

$$\frac{1}{2}[(H_2O)_2(bip)Cu\begin{smallmatrix}OH\\OH\end{smallmatrix}Cu(bip)(H_2O)_2]^{2+} + OH^-$$
$$\text{II}'$$
$$\rightleftarrows [Cu(OH)_2(bip)(H_2O)_2]^0 \quad (4)$$
$$\text{III}$$

$$[Cu(OH)(bip)(H_2O)_3]^{1+} + OH^-$$
$$\text{II}$$
$$\rightleftarrows [Cu(OH)_2(bip)(H_2O)_2]^0 + H_2O \quad (5)$$
$$\text{III}$$

It is well known that the value of $g_{//}$ decreases, and that of $A_{//}$ increases, with an increase in the ability of eletron donation of a ligand, which can be represented by pK_a;[23] the covalency of the bonding of the copper ion with the ligand increases. The covalency depends mainly upon the value of $g_{//}$, as has been reported by Maki and McGarvey[24] and by Kivelson and Neiman.[25] When the ligand is replaced by a more basic one, the values of $g_{//}$ and $A_{//}$ change with the number of the latter ligands.[26] Thus, the species with the highest value of $g_{//}$ (2.313) corresponds to I. On the other hand, the species with the middle and lowest values of $g_{//}$ (2.306 and 2.263) correspond to II and III respectively. However, the dimer species II′ could not be observed in the methanol solution; the coupling constant of the hf interaction was not one-half of that of the II species, and furthermore the signal due to the $\Delta M_s = \pm 2$ transitions could not be detected in a much lower field, *ca.* 1600 gauss. On the contrary, the formation of the dimer species was confirmed in a basic aqueous solution by Ryland[22] and by Harris.[27]

When the 1:2 complex is prepared in methanol, the chemical equilibrium may be established as follows:

$$[Cu(bip)(H_2O)_4]^{2+} + bip$$
$$\text{I}$$
$$\rightleftarrows [Cu(bip)_2(H_2O)_2]^{2+}\ 2H_2O \quad (6)$$
$$\text{IV}$$

The IV species was overwhelmingly observed, probably because the equilibrium lies almost to the right. Figure 3 shows the ESR parameters for the 1:2 complex, also with the basic concentration of the methanol solution. The following chemical equilibria for the 1:2 complex in the basic methanol solution are considered to be established by taking those in the basic aqueous solutions into account:[28]

$$[Cu(bip)_2(H_2O)_2]^{2+} + OH^-$$
$$\text{IV}$$
$$\rightleftarrows [Cu(OH)(bip)(H_2O)_3]^{1+} + bip \quad (7)$$
$$\text{II}$$

$$2[Cu(OH)(bip)(H_2O)_3]^{1+}$$
$$\text{II}$$
$$\rightleftarrows [(H_2O)_2(bip)Cu\begin{smallmatrix}OH\\OH\end{smallmatrix}Cu(bip)(H_2O)_2{}^{2+} + 2H_2O$$
$$\text{II}' \quad (8)$$

$$[Cu(OH)(bip)(H_2O)_3]^{1+} + OH^-$$
$$\text{II}$$
$$\rightleftarrows [Cu(OH)_2(bip)(H_2O)_2)]^0 + H_2O \quad (9)$$
$$\text{III}$$

$$\frac{1}{2}[(H_2O)_2(bip)Cu\begin{smallmatrix}OH\\OH\end{smallmatrix}Cu(bip)(H_2O)_2]^{2+} + OH^-$$
$$\text{II}'$$
$$\rightleftarrows [Cu(OH)_2(bip)(H_2O)_2]^0 \quad (10)$$
$$\text{III}$$

Two sets of ESR parameters were observed, as can be seen in Fig. 3. The species with the higher value

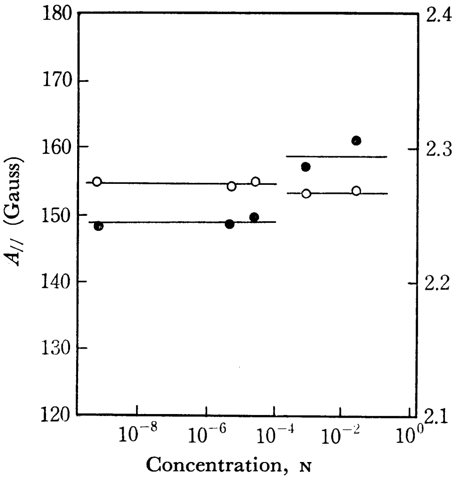

Fig. 3. Variations of the ESR parameters for the 1 : 2 complex with the concentration of sodium hydroxide in methanol solution.

●: $A_{//}$; ○: $g_{//}$

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[23] H. Yokoi, U. Otagiri, M. Sai, and T. Isobe, Symp. ESR, 10th, Tokyo, Preprints of Papers, 62 (1971).

[24] A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).

[25] D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961).

[26] K. Takimoto, A. Hasegawa, and M. Miura, in press.

[27] C. M. Harris, E. Sinn, W. R. Walker, and P. R. Woolliams, *Aust. J. Chem.*, **21**, 631 (1968).

[28] H. Ojima, *Nippon Kagaku Zasshi*, **84**, 787 (1963).

of $g_{//}$ corresponds to IV. The II species in Eq. (7) could not be observed, although that in Eq. (2) could be detected. This may indicate that the equilibrium of Eq. (7) lies almost completely to the left. On the contrary, the II species in Eq. (7) could be observed in the aqueous solution. The dimer species II′ could not be observed either, as in the case of the 1:1 complex.

When the 1:2 complex was dissolved in 40% ethanol-60% water and measured at 77°K, two chemical species were observed by Noack and his co-worker.[21] One is a *trans* isomer which is the same as the IV species observed in methanol at 77°K. The other species, with a much lower value of $g_{//}$ and a smaller value of $A_{//}$, is the *cis* isomer (Species V). Two bipyridine molecules coordinate with the copper ion, on the *xy* and *xz* or *yz* planes respectively. The *cis* isomer is predominant at room temperature.

The ESR spectra were also measured in the basic aqueous solution, since the chemical species in the aqueous solution had been determined by means of the absorption-spectra and conductometric-titration methods.[22,28] The $g_{//}$ value in a methanol solution was almost the same as that in an aqueous solution, while the $A_{//}$ value varied somewhat; the chemical species of the former are the same as the latter. However, the perpendicular component of the ESR spectra obtained in the methanol solution was a single line, while that in the aqueous solution was split. This may be ascribed to the effect of the linewidth. The over-all spectra obtained on the surface are rather similar to those in methanol solutions

Chemical Species on the Surfaces. Since the acitve sites on the surface are largely influenced by water molecules, an adsorbate is usually adsorbed on the surface from a solution of a nonpolar solvent. In this study, however, these complexes were adsorbed on the surface from water-free methanol solutions because they scarcely dissolved at all in any nonpolar solvent. The complex and methanol competitively react with surface hydroxyl groups, so that an ester may be formed by the reaction of methanol with the hydroxyl groups. If the 1:1 complex is present on the esterified surface, the values of $g_{//}$ and $A_{//}$ may be similar to those of the I species, since the electron-donation ability of the $-OCH_3$ group is much lower than that of the hydroxyl group. Such a species, however, could not be observed on the surfaces. Thus, the basic hydroxyl group on the surfaces may be considered to react with the complexes in preference to methanol. The comparison of the ESR parameters in the solutions with those obtained on the surfaces is reasonable, since the axial symmetry of the latter is also approximately maintained.

The properties of the basic sites on the surfaces, the distribution and the strengths of the basic sites, were determined in the following way. The qualitative distribution of the basic sites was estimated from the distance between the neighboring ligands replaced by two hydroxyl ions or hydroxyl groups, which can be calculated from the data of the X-ray analysis of the 1:2 complex;[29,30] the complex is a measure for determining the distribution of the basic sites. It is presumed that the distance is about 3 Å. The distance between the neighboring ligands of the 1:1 complex may be slightly different from that of the 1:2 complex.[21] On the other hand, the strengths of the basic sites on the surfaces were deduced from the pK_a value corresponding to the pH value of the aqueous solution, in which the complexes begin to react with hydroxyl ions. For the 1:1 complex, the coordinated water molecule begins to be replaced by the hydroxyl ion at $\mathrm{pH} \fallingdotseq 8$. The color of bromothymol blue ($pK_a = 7.2$) begins to change from yellow to green at $\mathrm{pH} \fallingdotseq 8$. Thus, the basic strength of the aqueous solution at $\mathrm{pH} \fallingdotseq 8$ appreximately corresponds to $H_0 = 7.2$.[31] The basic strength of the aqueous solution at $\mathrm{pH} \fallingdotseq 9.6$ corresponds to $H_0 = 9.3$, since the color of phenolphthalein ($pK_a = 9.3$) begins to change at $\mathrm{pH} \fallingdotseq 9.7$. The coordinated water molecule in the 1:2 complex begins to be replaced by the hydroxyl ion at $\mathrm{pH} \fallingdotseq 9.6$; it resists the substitution reaction more than the 1:1 complex. This tendency becomes larger with an increase in the number of the bipyridine molecule coordinated to the copper ion.[28] Thus,

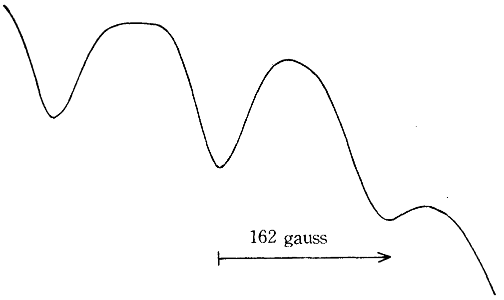

Fig. 4. Parallel component of the ESR spectra for the 1 : 1 complex adsorbed on the surface of 50% silica-alumina pretreated at 300°C.

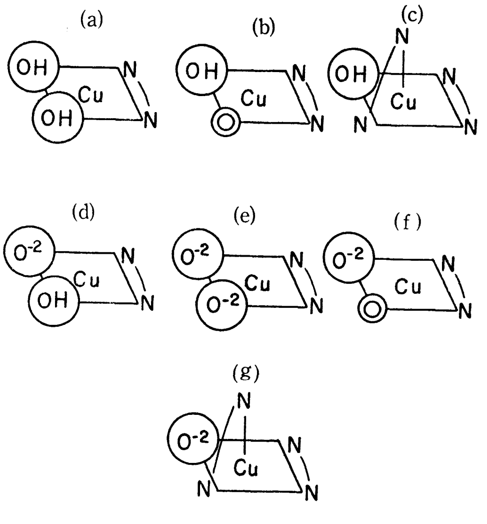

Fig. 5. Chemical species which are possibly generated by the interaction between the complexes and the basic sites of the surfaces.

◎: solvent molecule

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[29] H. Nakai, S. Ooi, and H. Kuroya, This Bulletin, **43**, 577 (1970).

[30] I. M. Procter and F. S. Stephens, *J. Chem. Soc., A*, **1969**, 1248.

[31] Reference 7, p. 73—76.

the formation of the II or III species by the adsorption of the 1:1 and 1:2 complexes suggests that basic sites with at least $H_0>7.2$ and $H_0>9.3$ exist on the surfaces.

Figure 4 shows the parallel component of the ESR spectrum for the 1:1 complex adsorbed on the surface of 50% silica-alumina treated at 300°C for 3 hr. By comparison with the values of $g_{//}$ and $A_{//}$ in the solutions, only one species formed on this surface was determined to be III. The chemical species which are possibly generated by the interaction between the complexes and the surfaces are represented in Fig. 5. The III species can be illustrated by (a) in the figure. The basic strength of the hydroxyl groups participating in the formation of the (a) type is at least $H_0>7.2$. The distance between the neighboring hydroxyl groups on the surface is estimated to be about 3 Å.[29,30] Thus, the (a) type is generated on only two contacted hydroxyl groups. The maximum number of hydroxyl groups which can be present on the surface is calculated to be 11 OH's per 100 Å. On the other hand, Morimoto *et al.*[32] have reported that the number of hydroxyl groups on the 50% silica-alumina surface pretreated at 300°C is 3.5 OH's per 100 Å. These facts may indicate that the hydroxyl groups exist in a cluster rather than homogeneously.

Figure 6 shows the parallel components of the ESR spectrum for the 1:2 complex adsorbed on the surface of 50% silica-alumina which had previously treated at 300°C for 3 hr. This spectrum indicates that another type exists in addition to the (a) type. The spectrum with the values of $g_{//}=2.224$ and $A_{//}=138$ gauss is the *cis* isomer, represented as the (c) type; only the hydroxyl groups of $H_0>9.3$ can expel one bipyridine molecule from the 1:2 complex, while those of $7.2<H_0<9.3$ can not, as can be understood from the substitution reaction in the basic aqueous solution. The (b) type could not be observed, either. Certainly, then, basic sites with basic strengths of two kinds are present on the 50% silica-alumina.

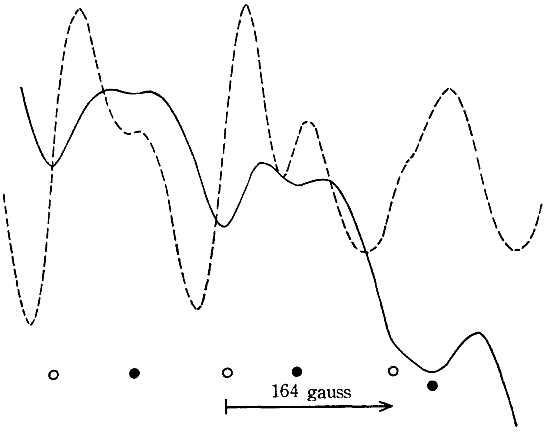

Fig. 6. Parallel component of the ESR spectra for the 1:2 complex adsorbed on the surface of 50% silica-alumina pretreated at 300°C.
——: the 1st derivative, ----: the 2nd derivative;
○: type (a), ●: type (c)

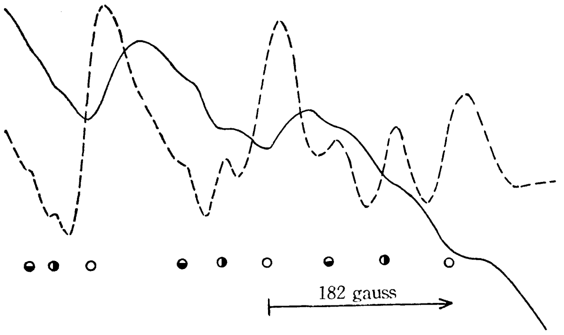

Fig. 7. Parallel component of the ESR spectra for the 1:1 complex adsorbed on the surface of alumina pretreated at 300°C.
——: the 1st derivative, ----: the 2nd derivative;
○: type (a), ◑: type (b), ◒: unknown

Figure 7 shows the parallel components of the ESR spectrum for the 1:1 complex adsorbed on the surface of alumina pretreated at 300°C for 3 hr. Three chemical species were observed. The species with the lowest value of $g_{//}$ (2.265) corresponds to the (a) type, while that of the middle value of $g_{//}$ (2.306) is assigned to the (b) type by comparison with those in the solutions. In additon to these two species, a third species ($g_{//}=2.340$) exists. Its structure is still uncertain. It is necessary for the formation of the (a) type that the distance between the neighboring basic hydroxyl groups of $H_0>7.2$ is at least 3 Å, as has been described previously. Furthermore, the presence of the (b) type suggests that the distance between the neighboring hydroxyl groups of $H_0>7.2$ is larger than 3 Å. That is, the basic hydroxyl groups may, as a whole, be distributed homogeneously without forming a cluster, unlike the case of 50% silica-alumina. When the 1:2 complex was adsorbed on the alumina surface, the ESR spectrum was exactly the same as that for the 1:1 complex. Three types are present on this surface, while the (c) type could not be observed. This suggests that the basic hydroxyl groups of $H_0>9.3$ predominate over those of $7.2<H_9<9.3$.

The ESR parameters on the surface of 50% silica-alumina are plotted against the outgassing temperature in Fig. 8. When the 1:2 complex was adsorbed on a surface pretreated at 100°C for 3 hr, the (c) type could hardly be detected. This probably reflects the lack of basic hydroxyl groups of $7.2<H_0<9.3$. The basic strength of the hydroxyl groups became higher as the outgassing temperature was lowered; the value of $g_{//}$ increased and that of $A_{//}$ decreased with a rise in the outgassing temperature from 100 to 300°C. O'Reilley *et al.* have indicated, from their NMR studies, that the majority of protons are present as Si-OH groups on the surface.[33] Basila has reported that the isolated Si-OH groups on the silica-alumina surface increase as the outgassing temperature is raised.[34] The appearance of the stronger hydroxyl groups, with a decrease in the outgassing temperature seems, therefore, to be due to the weakly-bonded hydroxyl group attached to the aluminum atom. This me-

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[32] T. Morimoto, M. Nagao, and J. Imai, This Bulletin, **44**, 1282 (1971).

[33] D. E. O'Reilley, H. P. Leftin, and W. K. Hall, *J. Chem. Phys.*, **29**, 970 (1958).

[34] M. R. Basila, *J. Phys. Chem.*, **66**, 2223 (1962).

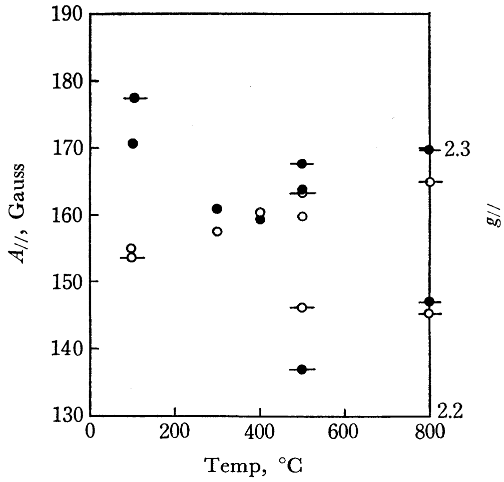

Fig. 8. Variations of the ESR parameters for the complexes adsorbed on the surface of 50% silica-alumina with the outgassing temperature.
●: $g_{//}$, ○: $A_{//}$ for the 1:1 complex;
-●-: $g_{//}$, -○-: $A_{//}$ for the 1:2 complex

chanism is similar to that for the alumina surface, as will be described later. When the surface is pretreated at a relatively high temperature, it is considered that the negatively-charged oxygen ions play an important role in the substitution reaction. It has been reported that α sites which contain a negatively-charged oxygen ion in close proximity to an exposed aluminum atom are present on the surface pretreated between 300 and 500°C at a concentration of less than 10^{13} sites/cm^2.[16] Above this outgassing temperature, the O^{2-} ions are closely connected with the formation of the chemical species of the (d)-(g) types.

The 1:2 complex was adsorbed on the surface pretreated at a much higher temperature, 800°C, in order to investigate whether or not the O^{2-} ions reacted with the complex. Two chemical species were observed on this surface. However, they were different from the two types, (a) and (c), generated on the surface pretreated at 300°C. The value of $g_{//}$ for one species was somewhat higher than that of the (a) type. The other was slightly different from that of the (c) type. The absorption band at 3745 cm^{-1} which is due to an isolated Si-OH group appears on the surface pretreated at 500°C and is quite similar to that on the the silica gel surface.[34] Linear relationships have been found between the electronegativities of elements bonded to the hydroxyl groups and the vibrational frequencies of the hydroxyl groups;[35] the charge density of the hydroxyl groups becomes larger and the wave number shifts upward as the electronegativities of the elements decrease. The wave number of the Si-OH group on the surface of silica-alumina is approximately the same as that on silica gel. Thus, the hydroxyl groups on the silica-alumina surface pretreated at higher temperatures are not basic, since the silica gel sufrace is not basic, as will be discussed later. The (e) and (g) types, therefore, seem to be present on the surface pretreated at 800°C. Judging from the $g_{//}$ value, the basic strength of the O^{2-} ions formed at relatively high temperatures is rather weaker than that of the hydroxyl groups retained on the surface pretreated at a lower temperature. The values of $g_{//}$ for the complex adsorbed on the surface pretreated at 400–800°C were approximately constant. This may indicate that the O^{2-} ions predominantly react as basic sites on the surface, while the hydroxyl groups mainly react as basic sites on the surface pretreated below 300°C.

In order to compare them with those of the silica-alumina surface, the ESR spectra were also measured on the calcium oxide surface since the basic properties of the latter surface have been fairly well established. The basic strength of the hydroxyl groups on the surface of calcium hydroxide is quite different from that of the O^{2-} ions on the surface of calcium oxide. When the 1:2 complex was adsorbed on the surface of calcuim hydroxide pretreated at 100°C for 3 hr, the (a) type was observed. On the other hand, when the 1:2 complex was adsorbed on the surface of calcium oxide pretreated at 600°C for 3 hr, the observed species was quite different from the (a) type. The O^{2-} ions are responsible for the formation of this species, since scarcely no hydroxyl groups exist on this surface.[36] The parallel components of the ESR spectrum consist of four peaks. This spectrum is rather similar to that of cupric sulfate in methanol. All the bipyridine molecules in the 1:2 complex, therefore, seem to be expelled through the reaction with the surface. However, no such phenomenon was observed in the basic solutions These facts suggest that the basic strength of the O^{2-} ions is much higher than that of hydroxyl ions or hydroxyl groups. This is aslo in good agreement with the fact that the basic strength of the O^{2-} ions on the surface of calcium oxide is quite great, as determined by the phenol-vapor adsorption method.[8,12]

The ESR parameters for the surface of alumina are plotted against the outgassing temperature in Fig. 9. When the complexes were adsorbed on the surface of alumina pretreated at 100°C, the (a) and (b) types were observed. The value of $g_{//}$ for the (a) type was low in comparison with that on the alumina surface pretreated at 300°C. This supports the mechanism of the formation of the basic sites proposed by Yamadaya *et al.*; [14] they attributed the basic property of alumina to weakly-adsorbed hydroxyl groups rather than to strongly-adsorbed ones. The 1:2 complex was adsorbed on the surface of alumina pretreated at 800°C in order to determine whether the complex reacts with the hydroxyl groups or with O^{2-} ions. Two chemical species were observed. The $g_{//}$ values for these two species ($g_{//}$=2.270 and 2.316) were somewhat higher than those of the (a) and (b) types respectively. The α sites which contain negatively-charged oxygen ions begin to appear at about 400°C.[24] Thus, the O^{2-} ions are considered to be responsible for the formation of three chemical species, the (d), (e), and (f) types. The surface of alumina pretreated at 800°C has well-defined absorption maxima at 3700, 3733,

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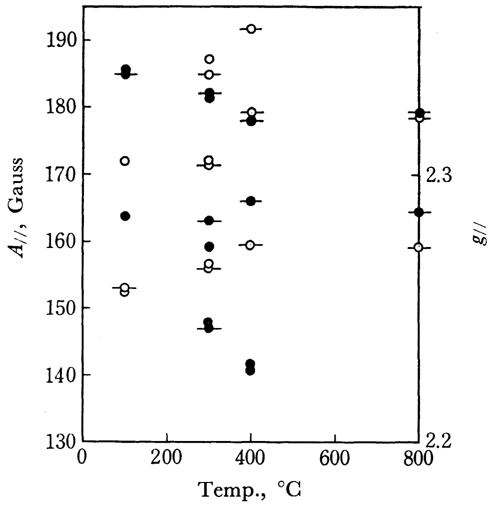

Fig. 9. Variations of the ESR parameters for the complexes adsorbed on the surface of alumina with the outgassing temperature.
●: $g_{//}$, ○: $A_{//}$ for the 1:1 complex;
-●-: $g_{//}$, -○-: $A_{//}$ for the 1:2 complex

3744, 3780, and 3800 cm^{-1}.[13] These correspond to the isolated hydroxyl groups. Peri has reported that the basic strength of the hydroxyl group becomes higher as the number of negatively-charged oxygen ions surrounding its hydroxyl group increases;[13] some of these isolated hydroxyl groups can act as basic sites. The species with the value of $g_{//}$ (2.270) may be ascribed to the (d) or (e) type, and that with the value of $g_{//}$ (2.316) may correspond to the (b) or (f) type. On the whole, the basic strengths of both the hydroxyl groups and O^{2-} ions on this surface are lower than those of hydroxyl groups on the surface pretreated at a very low temperature, as can be seen in Fig. 9. The value of $g_{//}$ increased to 400°C and thereafter was approximately constant. This may indicate that the strengths of the basic sites on the surface of alumina pretreated below 400°C mainly depend on the hydroxyl groups, while those of sites on the surface evacuated above this temperature predominantly depend upon the the hydroxyl groups and/or the O^{2-} ions.

When the 1:1 complex was adsorbed on the surface of silica gel pretreated at 300°C for 3 hr, only one species was observed. The shf structure at the higher magnetic field coincided in position with that observed in the acidic methanol solution. The hydroxyl groups on the surface of silica gel, therefore, seem to be acidic rather than basic, though it has been reported, on the basis of the phenol-vapor adsorption method,[8] that those on the surface are weakly basic.

Conclusion. Hydroxyl groups with basic strengths of two kinds, $H_0>9.3$ and $7.2<H_0<9.3$, are present on the 50% silica-alumina surface pretreated at 300°C for 3 hr. They exist in a cluster state on the surface. The negatively-charged oxygen ions play an important role as basic sites on the silica-alumina surfaces pretreated at relatively high temperatures. The basic strengths of the hydroxyl groups become higher as the outgassing temperature is lowered. This seems to be due to the weakly-bonded Al-OH groups on the silica-alumina surface. The hydroxyl groups of $H_0>9.3$ are present on the alumina surface pretreated at 300°C, and they are distributed, as a whole, homogeneously in comparison with those on the silica-alumina surface. The basic strengths of the hydroxyl groups get higher as the outgassing temperature is lowered. This seems to be ascribable to the weakly-bonded hydroxyl groups rather than to the strongly-bonded ones. The negatively-charged oxygen ions and/or the hydroxyl groups act as basic sites on the alumina surface pretreated above 400°C. The hydroxyl groups on the silica gel surface are acidic rather than basic.

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