# Studies of the Basic Sites of the Silica-Alumina Surface by Means of the Adsorption of Copper(II) Complexes with 2,2′-Bipyridine

Kazuto Takimoto and Masaji Miura
*Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima*

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The basic properties of the silica-alumina surface have been studied by means of the calorimetric titration and phenol-vapor adsorption methods,[1,2] but the nature and structure of its basic sites have not yet been revealed. On the other hand, the basic properties of alumina have been elucidated fairly well in comparison with those of silica-alumina.[3] We have found, from ESR measurements, that one or two $OH^-$ ions coordinate to the copper (II) complex with 2,2′-bipyridine in the aqueous solution of the complex at pH values higher than 8. Such a phenomenon has also been observed in a basic methanol solution. In this paper, the properties of the basic OH groups on the silica-alumina and alumina surfaces will be presented and compared with the ESR spectra in these solutions.

Alumina, 50% silica-alumina, and silica gel were treated *in vacuo* at 300°C for 3 hr. The copper(II) complexes with 2,2′-bipyridine, $[Cu(bip)(OH_2)_4]SO_4$, $[Cu(bip)_2(OH_2)_2]SO_4$, were synthesized in methanol and recrystallized repeatedly from methanol. The water-free methanol solutions of these complexes were evacuated and introduced to the solids through a breakable seal. After the methanol had been eliminated, the ESR spectra were measured at 77°K. The chemical species were determined from the ESR spectra of the 1st and 2nd derivatives.

Figure 1 shows the ESR spectrum for the 1 : 1 complex adsorbed on the surface of 50% silica-alumina. This spectrum suggests the presence of only one chemical species. The $g_{//}$ and $A_{//}$ values of the spectrum were 2.268 and $-172\times10^{-4}$ cm$^{-1}$ respectively. This chemical species is identified to that in which two basic OH groups on the surface coordinate to the 1 : 1 complex by means of a comparison with the ESR spectrum of the complex in an aqueous solution at pH>12.5. This is considered to be reasonable, since the axial symmetry of this spectrum is approximately maintained, much as in the solution. On the other hand, when the 1 : 2 complex was adsorbed on the surface, two chemical species were observed; one is the same as that described above, while the other possesses lower values of $g_{//}$ and $A_{//}$, 2.224 and $-143\times10^{-4}$ cm$^{-1}$ respectively, than the former. Noack *et al.* have found the species corresponding to these values in 40% ethanol - 60% water and identified it as the *cis* isomer of the 1 : 2 complex.[4]

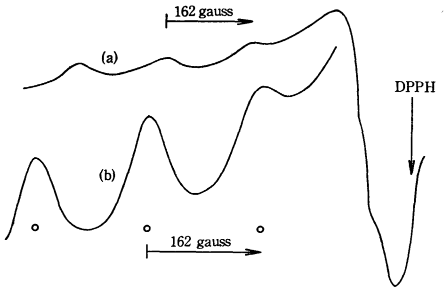

Fig. 1. ESR spectrum of the 1 : 1 complex adsorbed on the surface of 50% silica-alumina; (a) over-all spectrum, (b) parallel components of the spectrum magnified in the lower field region. ○: $g_{//}=2.268$.

The ESR spectrum for the 1 : 1 complex adsorbed on the surface of alumina is represented in Fig. 2. Three chemical species were observed. The species with the lowest value of $g_{//}$ (2.265) is the same as that of the 1 : 1 complex adsorbed on 50% silica-alumina. On the other hand, the species with the middle value of $g_{//}$ (2.306) is identified as that in which one basic OH group coordinates to the 1 : 1 complex by means of a comparison with the ESR spectrum of its aqueous solution in the 8—11 pH range, while the species corresponding to the highest value of $g_{//}$ (2.340) is still uncertain. It is of interest to note that the ESR spectrum of the 1 : 2 complex adsorbed on the surface of alumina was quite the same as in the case of the 1 : 1 complex.

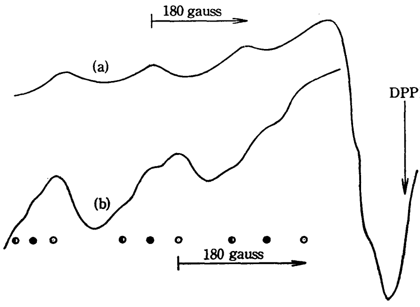

Fig. 2. ESR spectrum of the 1 : 1 complex adsorbed on the surface of alumina; (a) over-all spectrum, (b) parallel components of the spectrum magnified in the lower field region. ○: $g_{//}=2.265$, ●: $g_{//}=2.306$, ◐: $g_{//}=2.340$.

Though the negatively-charged oxygen ion and the OH group are present as basic sites, the effects of these sites on the ESR spectra are quite different; the OH group on $Ca(OH)_2$ and the $O^{2-}$ group on CaO gave rise to different species. It was also found that the $O^{2-}$ on the silica-alumina has a much smaller electron-donating ability than the OH group. The basic sites were thus clarified to exist on the surfaces of 50% silica-alumina and alumina, but they were not observed on the silica gel surface. The basic strength of the sites on the surfaces could also be revealed; the $g_{//}$ value decreases, and that of $A_{//}$ increases, with the electron-donating ability of the ligands. Thus, the adsorption of these complexes on the solid surfaces may be useful means for the elucidation of the basic properties.

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