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SUBSTITUTION REACTION OF THE COPPER(II) COMPLEXES WITH 2,2'-BIPYRIDINE AND WITH PYRIDINE BY THE BASIC SITES ON THE CALCIUM OXIDE SURFACE

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A substitution reaction of the copper(II) complexes quite different from those in the basic solutions and on the silica-alumina surface was found on the calcium oxide surface. The reaction is due to the highly basic site, O^{2-} ion on the surface.

In previous papers$^{1)}$ we have reported that the copper(II) complexes with 2,2'-bipyridine react with the basic sites on the silica-alumina and alumina surfaces, hydroxyl groups and O^{2-} ions, similarly to the substitution reaction in the basic solutions. Here, we found that these complexes react with the basic sites on the calcium oxide surface, O^{2-} ions, in a way quite different from the above-mentioned reaction.

Calcium hydroxide used as a adsorbent was prepared from calcium nitrate and potassium hydroxide. The calcium hydroxide was pretreated at 100, 200, 250, 300, 500, and 800°C for 3 hr in vacuo. The copper(II) complexes with 2,2'-bipyridine (1:1) and with pyridine (1:2) were synthesized in methanol and repeatedly recrystallized from methanol. These complexes were adsorbed on the adsorbent from their water-free methanol solutions through a breakable seal. After the methanol had been eliminated, the ESR spectra were measured at 77°K.

When these complexes were adsorbed on the calcium hydroxide surface pretreated below 250°C, the chemical species, in which one or two coordinated water molecules were substituted by hydroxyl groups, were observed. These species were similar to those on the silica-alumina and alumina surfaces.$^{1)}$ On the contrary, when these complexes were adsorbed on the surfaces pretreated at 300°C, the ESR spectrum shown in Fig. 1(a) was obtained for both complexes. The $g_{/\!/}$ and $|A_{/\!/}|$ values of the species were 2.402 and 136.8×10^{-4} cm^{-1} respectively. It was rather similar to that of cupric sulfate in methanol which is shown in Fig. 1(b). The intensity of the spectrum became larger as the outgassing temperature was raised. In place of the complexes, cupric sulfate was adsorbed on the surface pretreated above 300°C in order to confirm whether the complexes adsorbed on the surface contain 2,2'-bipyridine or pyridine or not. The spectrum was quite the same as the spectrum(a); the complexes on the surface have no these ligands.

These complexes have a square planar structure. According to Kivelson's approach, the $g_{/\!/}$ value decreases and the $|A_{/\!/}|$ value increases as the electron-donating ability of the ligand increases.2) On the other hand, it has been reported that the electron-donating ability of the O^{2-} ion on the calcium oxide surface is much higher than that of the hydroxyl groups on the calcium hydroxide surface.3) If the coordinated water molecules of the 1:1 or 1:2 complex are substituted by one or two O^{2-} ions, the $g_{/\!/}$ value should decrease and $|A_{/\!/}|$ value should increase in comparison with those of the original complex. The observed spectra, however, had the larger $g_{/\!/}$ and smaller $|A_{/\!/}|$ values than the expected ones. It is also known that the $g_{/\!/}$ value increases and $|A_{/\!/}|$ value decreases as the complexes are distorted from the square planar structure to a tetrahedral one.4) Thus, when the complexes were adsorbed on the calcium oxides, their ligands, the 2,2'-bipyridine and pyridine, were expelled from the complexes, as a result of the distortion of the complexes caused by the strong bonding with the highly basic O^{2-} ion.

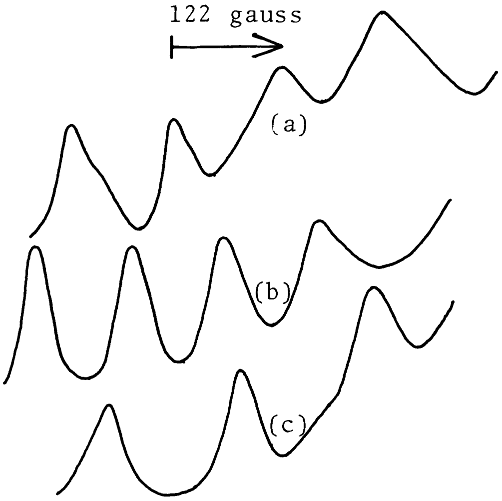

Fig. 1(a): Parallel component of the ESR spectrum for the 1:1 complex adsorbed on calcium oxide pretreated at 300°C. (b): ESR spectrum of cupric sulfate in methanol. (c): ESR spectrum of the 1:1 complex in methanol.

References

1) K.Takimoto and M.Miura, Bull. Chem. Soc. Jap., 45, 653 (1972); K.Takimoto, ibid., to be published.
2) D.Kivelson and R.Neiman, J. Chem. Phys., 35, 149 (1961).
3) T.Iizuka, H.Hattori, Y.Ohno, J. Sohma and K.Tanabe, J. Catalysis, 22, 130 (1971).
4) Y.Murakami, Y.Matsuda, and K.Sakata, Inorg. Chem., 10, 1734 (1971).

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