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# Spectroscopic Study of Cu(II) Ions Supported on Silica Gel by Cation Exchange Method

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The ESR and the electronic spectra of cupric ions introduced on silica gel by cation exchange between surface hydroxyl groups of silica gel and tetrammine cupric ions were investigated. The cupric ions in the initial state had the distorted octahedral configuration, of which coordinated ammonia molecules were less than four. The evacuation treatment at temperatures over 200°C led to desorption of ammonia and to change in configuration of copper ion to tetrahedral. For samples treated below 400°C, the subsequent exposure to ammonia restored the original coordinate environment. Two different ESR parameters were observed with the water adsorption, and one was assigned to the distorted octahedral and the other to the tetrahedral configuration. The former disappeared by evacuation at room temperature. The electronic spectrum also suggested the existence of the tetrahedral cupric ions. The ESR parameters of cupric ions depended on the adsorption temperature of pyridine. At lower temperature, the configuration of cupric ions was similar to that of the ammoniated cupric ions. When the adsorption temperature was raised to 200–300°C, the marked decrease of the hyperfine splitting of cupric ion was observed indicating the distortion of the configuration of cupric ion from octahedral towards tetrahedral.

## INTRODUCTION

Catalytic activity of the solid catalysts depends on the physical and chemical structures of the solid and these, in turn, are determined by the method of the preparation of the catalysts. For example, the nature of the supported catalyst depends strongly on the method of supporting the active components. Benesi and Curtis (*1*) found that finely dispersed platinum particles were obtained when tetrammine platinum ions were introduced on silica gel. Morikawa *et al.* (*2*) and Furuoya and coworkers (*3,4*) carried out the exchange between surface protons and metal ammine complexes (cation exchange method), and then extensively studied the catalytic activity and the selectivity for various reactions with use of the supported metal catalyst prepared by this method. The introduction of metal complexes onto surfaces were described by Burwell *et al.* (*5*). But the nature of the metal cations introduced at the first stage of the catalyst preparation, ion exchange, has not been fully understood.

The knowledge of the behavior of metal cations on surfaces is important also in respect to the heterogenization of homogeneous complex catalysts, which is one of the major subjects in the catalytic research at present days (*6*).

In this work, we have studied the nature of cupric cations supported on silica gel with electron spin resonance and electronic spectroscopy. Cupric ions are introduced by the ion exchange of surface hydroxyl groups of silica gel with tetrammine cupric ions $Cu(NH_3)_4^{2+}$. We have found that ion exchange with $Cu(NH_3)_4^{2+}$ is much easier than the direct exchange with $Cu^{2+}$ ions in acidic pH region. The ion exchange with the former species proceeds quantitatively and very readily, but the ion exchange by the latter needs several days before the ion exchange equilibrium is established and the degree of the exchange is low (7).

Among metal cations, cupric ion is one of the most convenient metal cations to be studied by the spectroscopic method, since the spectroscopic information on the nature of the cations in solution and in crystals is so abundantly accumulated in the literature that one can easily compare the spectra obtained from the cations on the surfaces with those in the literature.

The purpose of this study is to characterize the cupric ions introduced on silica gel by the ion exchange of the surface hydroxyl groups with $Cu(NH_3)_4^{2+}$ and their interactions with adsorbed molecules, such as water, ammonia and pyridine.

## EXPERIMENTAL METHODS

### *Preparation of Catalyst*

Silica gel used (Mizusawa Chemicals) has physical properties as follows; BET surface area = 460 m$^2$/g, mean pore radius = 25.2 Å, surface hydroxyl groups concentration = 3.5 mmole/g which was determined by gravimetric analysis.

Tetrammine cupric nitrate solution was obtained by the direct mixing of an aqueous solution of cupric nitrate with excess aqueous ammonia and diluted to 0.05 mole/liter. The quantitative analysis of cupric ion was carried out by the EDTA titration. Tetrammine cupric nitrate solution (25 ml) was added to 200 ml of 1 *N* ammonium nitrate solution with pH 11.0 and 5 g of silica gel were immersed in this solution. The mixture was allowed to stand for 24 hr at 25°C, then filtered and dried at 90°C overnight. The amount of the supported cupric ion was 0.15 mmole/g silica gel.

### *ESR Measurement*

Sample was placed in a quartz tube (4 mm o.d.) and evacuated at room temperature for 3 hr ($10^{-4}$ Torr), and then evacuated at a prescribed temperature for 3 hr. The ESR measurement was performed by Japan Electron Optics JES-PE-1X in X-band (9.5 GHz) at room temperature and at liquid nitrogen temperature. The experimental error of the ESR parameters was as follows; $g$-values = $\pm 0.005$ and hyperfine splitting constant = $\pm 5 \times 10^{-4}$ cm$^{-1}$. Adsorption of ammonia, water and pyridine was performed by the conventional vacuum system.

### *Electronic Spectroscopy Measurement*

The measurement was carried out with a spectrophotometer, Shimazu MPS-5000 with reflectance method, with use of attachment available from the manufacturer.

## RESULTS AND DISCUSSION

### *Evacuation Treatment*

The copper-supported silica gel exchanged with tetrammine complex was evacuated at various temperatures and the changes in the ESR and the electronic spectra were followed.

When the silica gel was evacuated at room temperature for 3 hr, ESR spectra shown in Fig. 1 were obtained. No remarkable change was observed between

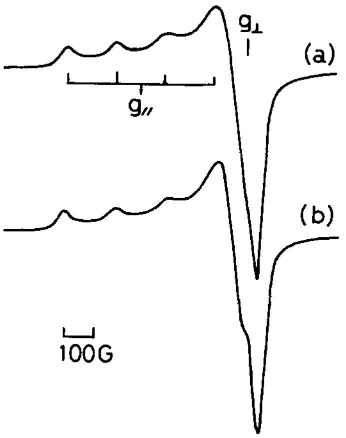

FIG. 1. ESR spectra of copper-supported silica gel measured at room temperature (a) and at −196°C (b).

the spectrum taken at room temperature and the one taken at liquid nitrogen temperature. The anisotropic nature of the spectrum indicates that the motion of the cupric ion is restricted even at room temperature.

The observed ESR parameters are $g_{/\!/} = 2.277$, $g_{\perp} = 2.033$ and $A_{/\!/} = 171 \times 10^{-4}$ cm$^{-1}$. The values of these ESR parameters indicate that cupric ions on silica gel surface are in the distorted octahedral (probably tetragonal) crystal field (*8,9*). Since the ion exchange was carried out the tetrammine cupric nitrate solution, the cupric ions supported on silica gel would be expected to exist as tetrammine complexes. A complex $Cu(NH_3)_4(NO_3)_2$ in solution gives the ESR absorption with parameters of $g_{/\!/} = 2.245$, $g_{\perp} = 2.061$, $A_{/\!/} = 192 \times 10^{-4}$ cm$^{-1}$ and $A_{\perp} = 23.2 \times 10^{-4}$ cm$^{-1}$ (*10*). These values do not completely agree with those for cupric ions on silica gel. This may suggest that all of the four ligand positions in the tetragonal copper complex on the surface may not be occupied solely by ammonia molecules, but the part of the four positions may be occupied by the oxygen species such as $H_2O$ or lattice oxygen of silica gel.

The above supposition is confirmed from the electronic spectrum of the supported cupric ion. The *d–d* transition of the supported cupric ion shows the broad band with adsorption maximum at 700 nm as shown in Fig. 2a. A tetrammine cupric ion $Cu(NH_3)_4^{2+}$ in an aqueous solution gives the absorption maximum at 610 nm (Fig. 2b), while a hexaquo-cupric ion $Cu(H_2O)_6^{2+}$ in an acidic solution gives the absorption maximum at 810 nm (Fig. 2c). It is known that the complexes $Cu(NH_3)_n(H_2O)_{4-n}^{2+}$ $(1 < n < 3)$ show the absorption maxima between two extremes (*11*). For example, *cis*-$Cu(NH_3)_2(H_2O)_2^{2+}$ exhibits the absorption maximum at 680 nm (*11*). Thus, the broad band at 700 nm for cupric ions on silica gel suggests that there exists the series of ammine complexes, differing in the number of the coordinated ammonia molecules.

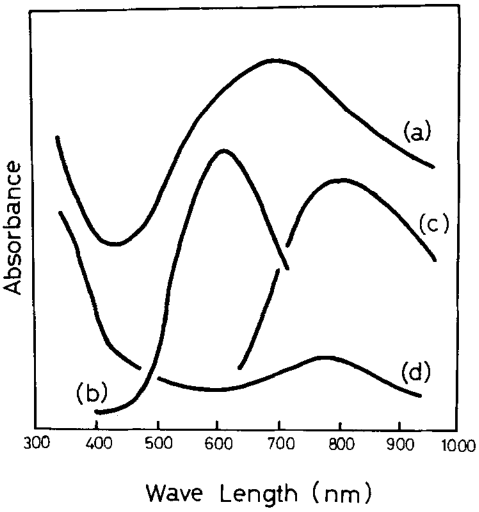

FIG. 2. Electronic spectra of copper–silica gel (a), $Cu(NH_3)_4^{2+}$ ion in an aqueous solution (b), $Cu^{2+}$ ion in an acidic solution (c), and copper–silica gel evacuated at 300°C for 3 hr (d).

The ESR spectrum does not change by rising the evacuation temperature to 100°C. When the sample was evacuated over 200°C, the color changed from blue to colorless and it has no absorption band in the visible region (Fig. 2d). Figure 3 show the change in the ESR spectra of cupric ions with the temperature of the evacuation treatment in the range of 200–500°C. After the evacuation treatment over 200°C, the ESR spectrum became broader and lost the hyperfine splitting. The ESR parameters are listed in Table 1.

When the treated sample was exposed to ammonia at room temperature, these spectra soon changed to the original one and the intensity was also same as that of the sample before the evacuation treatment if it was done below 400°C. When the sample was treated at 500°C and exposed to ammonia, the line shape returned to that of the sample before the evacuation treatment, but the intensity of the signal

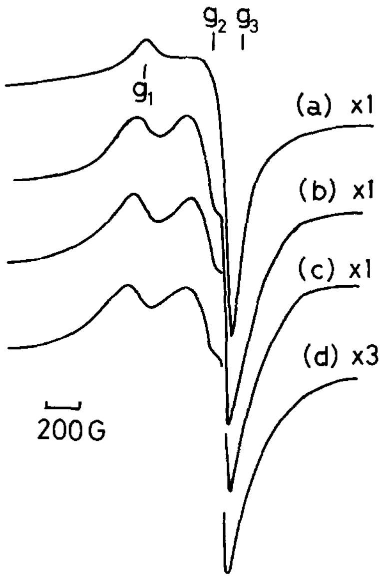

FIG. 3. ESR spectra of copper–silica gel after evacuation treatment at various temperatures (°C): (a) 200; (b) 300; (c) 400; and (d) 500.

was about 30% of the original signal. It is uncertain if the decrease in the intensity is caused by the reduction of cupric ions or by their transformation into ESR insensitive compound, in which copper remains divalent. It is clear that the evacuation treatment between 200 and 400°C leads to the desorption of ammonia, but that the original coordination environment is recovered by exposing the treated sample to ammonia.

The disappearance of the hyperfine structure suggests that the coordination environment of the cupric ion changes from the distorted octahedral to the distorted tetrahedral, for the cupric ions in the tetrahedral crystal field are known to have a small hyperfine splitting constant (*12–15*). It is also supported by the fact that cupric ions in tetrahedral environment have a relatively large *g*-value, though this is not an exact criterion (*13*). This is in accord with the fact that no bands are in the visible region of the electronic spectra, since cupric ions in tetrahedral environment have their *d–d* transition band in the near infrared region (*16,17*).

TABLE 1
THE ESR PARAMETERS OF THE COPPER-SUPPORTED SILICA GEL AFTER EVACUATION TREATMENT AT VARIOUS TEMPERATURES

| Evacuation temp (°C) | $g_1$ | $g_2$ | $g_3$ |
|---|---|---|---|
| 200 | 2.447 | — | 2.043 |
| 300 | 2.471 | 2.165 | 2.048 |
| 400 | 2.500 | 2.155 | 2.051 |
| 500 | 2.516 | 2.155 | 2.044 |

### *Adsorption of Water*

When the copper–ammine complex supported on silica gel was evacuated at 300°C for 3 hr and then exposed to water vapor at room temperature for 30 min, the ESR spectrum shown in Fig. 4a was obtained. It has two resolved hyperfine structures in the low field region; $g_{\parallel}^{(1)} = 2.334$, $A_{\parallel}^{(1)} = 142 \times 10^{-4}$ $\mathrm{cm}^{-1}$ and $g_{\parallel}^{(2)} = 2.373$,

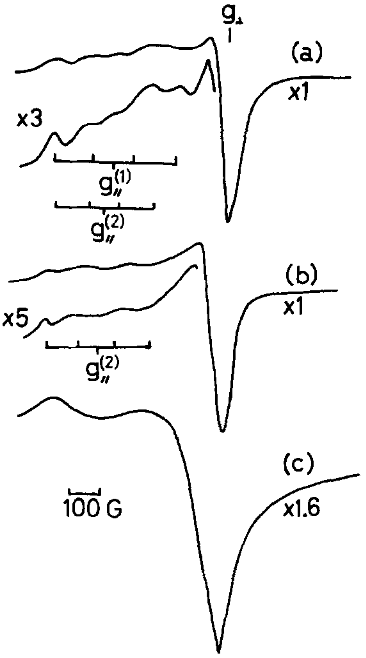

FIG. 4. ESR spectra of copper–silica gel with adsorbed water (a) and after evacuation treatment at room temperature for 30 min (b), at 100°C for 3 hr (c).

$A_{\parallel}^{(2)} = 109 \times 10^{-4}$ cm$^{-1}$ with unresolved $g_{\perp} = 2.071$. Upon adsorption of water, the color of the sample turned yellow. The electronic spectrum of this yellow sample has the absorption maximum at 460 nm as shown in Fig. 5a. The presence of two different ESR signals means the existance of two different cupric ion species. The first copper species with $g_{\parallel}^{(1)} = 2.334$ and $A_{\parallel}^{(1)} = 142 \times 10^{-4}$ cm$^{-1}$ is considered to be in the distorted octahedral field, because the $g_{\parallel}$-value and $A_{\parallel}$-value are close to those of cupric ions on hydrated ion-exchange resins (*18*) or hydrated layer silicates (*19*). The absorption band at 740 nm is close to that of the cupric ions in an aqueous solution.

Rather small hyperfine splitting of the second species with $g_{\parallel}^{(2)} = 2.373$ and $A_{\parallel}^{(2)} = 109 \times 10^{-4}$ cm$^{-1}$ suggests that this complex has probably the configuration intermediate between in the planar and the tetragonal. The number of the coordinated water in this complex is probably smaller than that in the distorted octahedral complex, since, when the sample was evacuated at room temperature for 30 min, the first species disappeared, and only the second species was observed (Fig. 4b). When the sample was evacuated at 100°C for 3 hr, the line shape of ESR spectrum returned to that of the spectrum observed before water adsorption (Fig. 4c), but the color of this sample remained yellow. Thus, the yellow color (absorption band at 460 nm) is ascribed to the species in the tetrahedral environment, and the band may be caused by the charge-transfer between cupric ion and one of the ligand atoms, since the *d–d* transition bands of the cupric ion in the tetragonal environment usually appear in the near-infrared region (*16,17*).

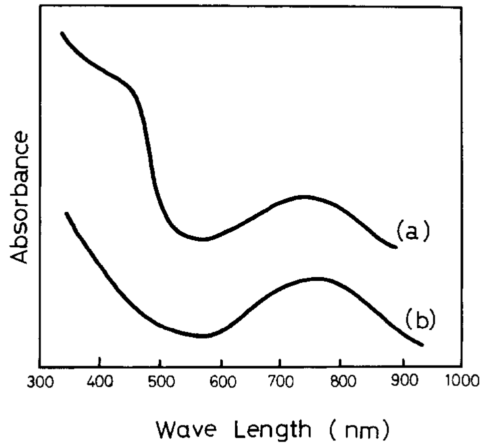

FIG. 5. Electronic spectra of copper–silica gel: (a) after water adsorption with evacuation treatment at room temperature for 30 min, (b) after adsorption of pyridine for 24 hr.

### *Adsorption of Pyridine*

The silica gel ion exchanged with copper–ammine complex was evacuated at 300°C, the sample showed the ESR spectrum of Fig. 3b and no absorption peak was observed in the visible region, as described above. Then, the sample was exposed to pyridine vapor of 25 Torr at various temperatures for 24 hr. Figure 6 shows the ESR spectra after the pyridine adsorption. When pyridine was adsorbed at room temperature, the ESR spectrum with following parameters were ob-

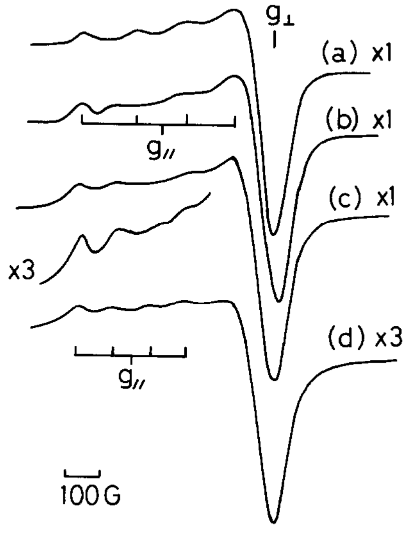

FIG. 6. ESR spectra after adsorption of pyridine; adsorbed at: room temperature (a); 100°C (b); 200°C (c); 300°C (d).

tained: $g_{//} = 2.276$, $g_{\perp} = 2.037$ and $A_{//} = 170 \times 10^{-4}$ cm$^{-1}$. These parameters are close to those of the ammoniated complex and the configuration of both surface complexes are considered to be similar. The cupric ions are in the distorted octahedral (or tetragonal) configuration and the number of pyridine coordinated to cupric ion may be less than four, which is the most probable number of coordination for the $Cu^{2+}$-pyridine complex in solution. The electronic spectrum supports this supposition since the sample shows a single peak at 770 nm (Fig. 5b). The position of this peak is far apart from the position of $Cu(pyridine)_4^{2+}$ complex (*20*) and indicated that the number of pyridine molecules coordinated to a cupric ion is probably one or at most two.

When the adsorption of pyridine was carried out at 100°C, the situation remained almost same (Fig. 6b). When the adsorption temperature was raised to 200–300°C, the ESR spectrum with the parameters of $g_{//} = 2.327$, $g_{\perp} = 2.051$, and $A_{//} = 120 \times 10^{-4}$ cm$^{-1}$ were observed as shown in Fig. 6c and d. Comparing the ESR spectra obtained after the adsorption of pyridine at 200–300°C, with those obtained after the adsorption at lower temperatures, the former has a much smaller $A_{//}$-value and a larger $g_{//}$-value. This marked change in the ESR parameters is explained in terms of a distortion of the surface complex from a tetragonal structure towards a tetrahedral structure.

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