JOURNAL OF CATALYSIS 50, 400–406 (1977)

Cation Exchange of Surface Protons on Silica Gel with Cupric Ions

HIDEMITSU TOMINAGA, MASAMICHI KANEKO, AND YOSHIO ONO

Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo, Japan 152

Received March 15, 1977; revised August 15, 1977

The exchange of surface protons on silica gel with cupric ions was investigated under two different conditions. The equilibrium constant was determined and the mechanism of the exchange was suggested. In ammonia water, two protons exchange with one tetrammine cupric ion and formed two ammonium ions. In acidic solution, where one proton exchanges with one cupric ion, the apparent equilibrium constant increases with an increase in the amount of copper loading. The structure of surface species on silica gel was suggested from the mechanism of the exchange and from ESR study. The surface species prepared in acidic solution is changed into the one prepared in ammonia water by exposure to ammonia. The change in the structure of surface species by the adsorption of foreign molecules was also studied.

INTRODUCTION

Surface protons of silica gel can be replaced by metal cations or complex ions (*1–6*). In view of the catalyst preparation, cation exchange provides a useful method for preparing the catalyst with finely dispersed metals or metal cations (*6–8*). In order to obtain well-defined catalysts, it seems of importance to establish the mechanisms of the cation exchange and to characterize the nature of metal cations introduced by this method.

Here, we have studied the cation exchange of surface protons on silica gel with cupric ions. The equilibrium constant of the exchange is determined and the mechanism of the exchange is suggested. The cation exchange was carried out under two different conditions: (a) cation exchange with tetrammine cupric ions, $Cu(NH_3)_4^{2+}$, in ammonia water (pH = 10.0–11.0); and (b) cation exchange with cupric ions, Cu^{2+}, in acidic solution (pH = 5.6–6.4). Moreover, ESR studies were made to characterize the cupric ions introduced by the second method and the results are compared with those for the cupric ions introduced by the first method, which has been reported previously (*9*).

EXPERIMENTAL METHOD

Silica gel. Silica gel was obtained from Mizusawa Chemicals and has a BET area of 460 m^2/g. The amount of surface hydroxyl groups was determined as 3.5 mmole/g by gravimetric analysis.

Cation exchange in ammonia water. A 1-g sample was mixed with 30 ml of ammonia water solution containing cupric nitrate (0.002–0.08 *M*). The pH of the solution was adjusted by ammonium nitrate and ammonia water to 10.0–11.0. The mixture was allowed to stand at 30°C with occasional stirring until establishment of the equilibrium, which took about 24 hr. The supported amount of cupric ions was calcu-

ISSN 0021-9517

lated from the decrease of cupric ion concentration determined by EDTA titration.

Cation exchange in acidic solution. A 1-g sample was mixed with 30 ml of cupric nitrate aqueous solution (0.03–0.08 *M*). The ionic strength and the pH of the solution were varied by sodium acetate and acetic acid with the ranges of 0.5–1.5 and 5.6–6.4 *M*, respectively.

ESR measurement. The ESR spectra were measured by Japan Electron Optics JES-PE-1X in X-band at liquid nitrogen temperature. The evacuation of the sample and the adsorption of water or ammonia were performed by a conventional vacuum system. The experimental errors of the ESR parameters were as follows; g values = ± 0.005 and hyperfine splitting constants = $\pm 5 \times 10^{-4}$ cm^{-1}.

RESULTS AND DISCUSSION

Cation Exchange with $Cu(NH_3)_4^{2+}$

Two mechanisms are proposed for the cation exchange.

(i) Surface protons are exchanged with $Cu(NH_3)_4^{2+}$ ions,

$$Cu(NH_3)_4^{2+} + n\mathrm{SiOH} \overset{K_1}{\rightleftarrows} Cu(NH_3)_4\text{–}(\mathrm{OSi})_n^{(2-n)+} + nH^+, \quad (1)$$

where n is the number of hydroxyl groups involved.

(ii) Surface protons react with ligand ammonia molecules to form NH_4^+,

$$Cu(NH_3)_4^{2+} + n\mathrm{SiOH} \overset{K_2}{\rightleftarrows} Cu(NH_3)_{4-n}\text{–}(\mathrm{OSi})_n^{(2-n)+} + nNH_4^+. \quad (2)$$

According to the first mechanism, the equilibrium constant should be given by the following equation,

$$K_1 = \frac{[Q][H^+]^n}{[A - Q]^n[Cu(NH_3)_4^{2+}]}, \quad (3)$$

where A is the initial concentration of surface hydroxyl groups (3.5 mmole/30 ml), and Q is the concentration of the groups exchanged with metal cations.

According to the second mechanism, the equilibrium constant should be expressed as

$$K_2 = \frac{[Q][NH_4^+]^n}{[A - Q]^n[Cu(NH_3)_4^{2+}]}. \quad (4)$$

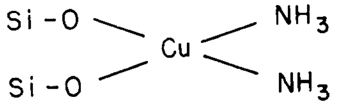
The cation exchange was carried out at various concentrations of cupric ions and at various ammonia concentrations. Then, the values of K_1 and K_2 were calculated according to Eqs. (3) and (4) with n values of 1 and 2.

Mechanism (1) can be refuted since the calculated values of K_1 with $n = 1$ or 2 did not give the constant value. Mechanism (2) with $n = 1$ was also refuted by the same reason. Only Mechanism (2) with $n = 2$ gave a constant value for the equilibrium constant independent of cupric ion concentrations and ammonia concentrations. Thus, rearrangement of Eq. (4) with $n = 2$ yields Eq. (5).

$$\frac{[Q]}{[A - Q]^2} = K_2 \frac{[Cu(NH_3)_4^{2+}]}{[NH_4^+]^2}. \quad (5)$$

In Fig. 1, $[Q]/[A - Q]^2$ was plotted against $[Cu(NH_3)_4^{2+}]/[NH_4^+]^2$. A good straight line through the origin was obtained and the equilibrium constant K_2 was calculated as $(2.3 \pm 0.4) \times 10^{-6}$ at 30°C.

Thus, the mechanism of the cation exchange of surface protons with tetrammine cupric ions in ammonia water is expressed as Eq. (2) with $n = 2$. The supported state of cupric ions probably has the following structure.



(6)

This is exactly what we expected from the spectroscopic study of the cupric ions introduced on silica gel by this method (*9*). Both ESR and electronic spectra suggested that the surface species is $Cu(NH_3)_n^{2+}$

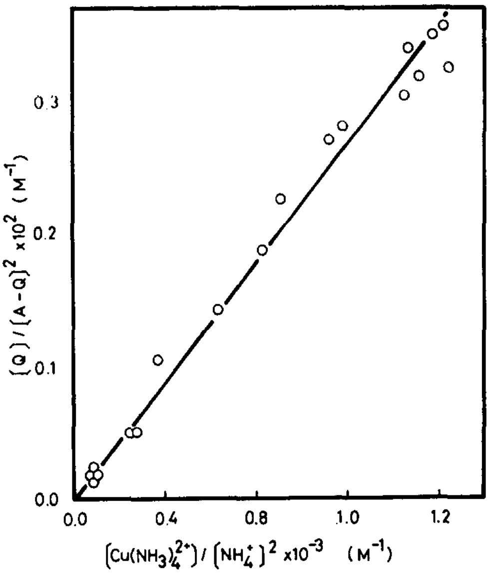


FIG. 1. The plot of $[Q]/[A - Q]^2$ against $[Cu(NH_3)_4^{2+}]/[NH_4^+]^2$ for the exchange in ammonia water at 30°C.

(n = 1–3) and not Cu^{2+} nor $Cu(NH_3)_4^{2+}$. Burwell also predicted the same surface species of the supported cupric ions (*8*).

Cation Exchange in Acidic Solution

It takes about 8 days until the exchange equilibrium is established in acidic solution (pH = 5.6–6.4). This was much longer than the cation exchange in the basic solution.

The exchange reaction between surface protons and cupric ions in the acidic solution could be predicted as follows:

$$Cu^{2+} + nSiOH \overset{K_3}{\rightleftarrows} Cu\text{-}(OSi)_n{}^{(2-n)+} + nH^+. \quad (7)$$

Thus, the equilibrium constant K_3 could be expressed as

$$K_3 = ([Q][H^+]^n)/([A - Q]^n[Cu^{2+}]). \quad (8)$$

When the value of K_3 was calculated from experimental results by assuming that $n = 2$, they were so scattered that no trends were found; for example, the K_3 value ($n = 2$) does not show any systematic change with the change in ionic strength of the solution. Thus, it is concluded that mechanism (7) with $n = 2$ is not operative for the cation exchange in acidic solution.

Equation (8) with $n = 1$ can be rearranged to yield the following expression:

$$Q = AKp/(1 + Kp), \quad (9)$$

where $p = [Cu^{2+}]/[H^+]$.

When the supported amount of cupric ions Q was plotted against p, the Q/p curve showed a clear dependence on the ionic strength of the solution (Fig. 2). At a constant ionic strength, a clear dependence of Q on p is observed irrespective of pH or cupric ion concentration. Therefore, one may assume that the exchange mechanism with $n = 1$ is operative for the cation exchange in acidic solution. However, the calculated equilibrium constant K_3 ($n = 1$) increases with increasing copper loading on silica gel, Q, as shown in Fig. 3. The increase of the "equilibrium constant" with in-

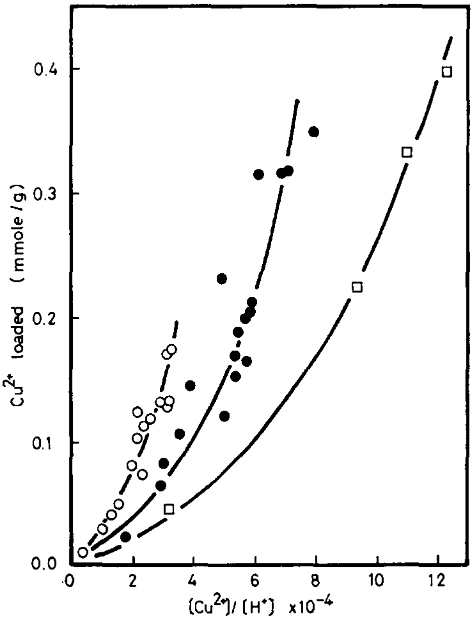


FIG. 2. The dependence of the supported mount of cupric ions on p ($[Cu^{2+}]/[H^+]$) for the exchange in acidic solution at 30°C with ionic strength 0.5 (○), 1.0 (●), and 1.5 M (□).

creasing extent of cation exchange has also been observed in the case of the exchange of surface protons of silica gel with UO_2^{2+} and Th^{4+} ions (*2*).

The increase in K_3 with increasing degree of cation exchange suggests that the cation exchange reaction is facilitated by the presence of the preloaded cupric ions. Suppose that the free energy change accompanied by the cation exchange (ΔG) varies with the extent of the cation exchange.

$$\Delta G = \Delta G^\circ + u\theta. \qquad (10)$$

Here, ΔG° is the free energy change in the initial stage of the cation exchange, θ is defined as $[Q]/[A]$ and expresses the extent of the cation exchange, and u is the increase of the free energy change with the extent of the cation exchange. Thus, the dependence of apparent equilibrium constant K on θ is given by

$$K = K_0 \exp(u\theta/RT), \qquad (11)$$

where K_0 is the equilibrium constant at the initial stage of the cation exchange. Taking the logarithm of Eq. (11), one obtains

$$\log K = \log K_0 + u\theta/RT. \qquad (12)$$

The relation found in Eq. (12) is exactly the observation in Fig. 3; the logarithm of the equilibrium constant increases linearly with the amount of loaded cupric ions. So, the K_0 values and the attraction energy u were calculated and listed in Table 1. It should be noted that the K_0 value decreases with ionic strength of the solution, while u is independent on the ionic strength. The dependence of the K_0 value on the ionic strength may be due to the change in the activity coefficients of cations with ionic strength. The independence of the attraction energy, u, on the ionic strength give a definite evidence that the change in the equilibrium constant with copper loading is entirely caused by the surface phenomenon, not by the solid–liquid interaction, though the origin of the attractive force is not clear at this moment.

TABLE 1

The K_0 values and the Attraction Energy u

Ionic strength (M)	K_0	u (kcal/mole)
0.5	7.6×10^{-7}	9
1.0	4.5×10^{-7}	9
1.5	2.6×10^{-7}	9

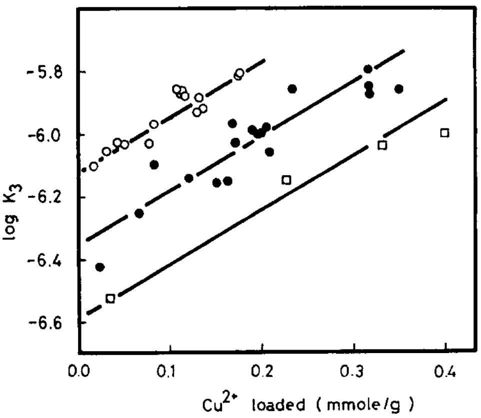


FIG. 3. The dependence of the apparent equilibrium constant on the amount of copper loading on silica gel for the exchange in acidic solution with ionic strength 0.5 (○), 1.0 (●), and 1.5 M (□).

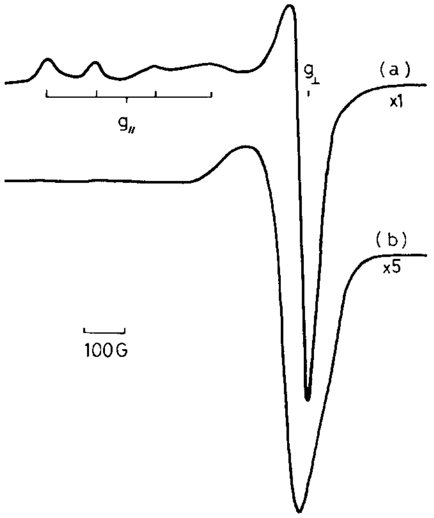


FIG. 4. ESR spectra of copper–silica gel prepared in acidic solution; (a) moist sample and (b) after evacuation at 300°C for 3 hr.

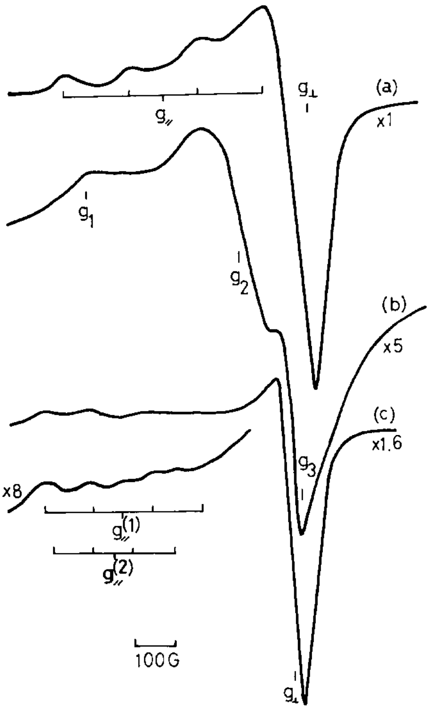


FIG. 5. ESR spectra of copper–silica gel prepared in acidic solution; (a) after adsorption of ammonia, (b) after the subsequent evacuation at 300°C for 3 hr, and (c) after the readsorption of water vapor.

In conclusion, the cation exchange in acidic solution is expressed by the following equation.

$$Cu^{2+} + SiOH \rightleftarrows Cu\text{-}(OSi)^{+} + H^{+}. \qquad (13)$$

The surface cupric ions should bear anions to maintain the neutrality of the solid. Thus, the surface species may be drawn as

$$SiO\text{-}Cu(H_2O)_nNO_3.$$

ESR Study

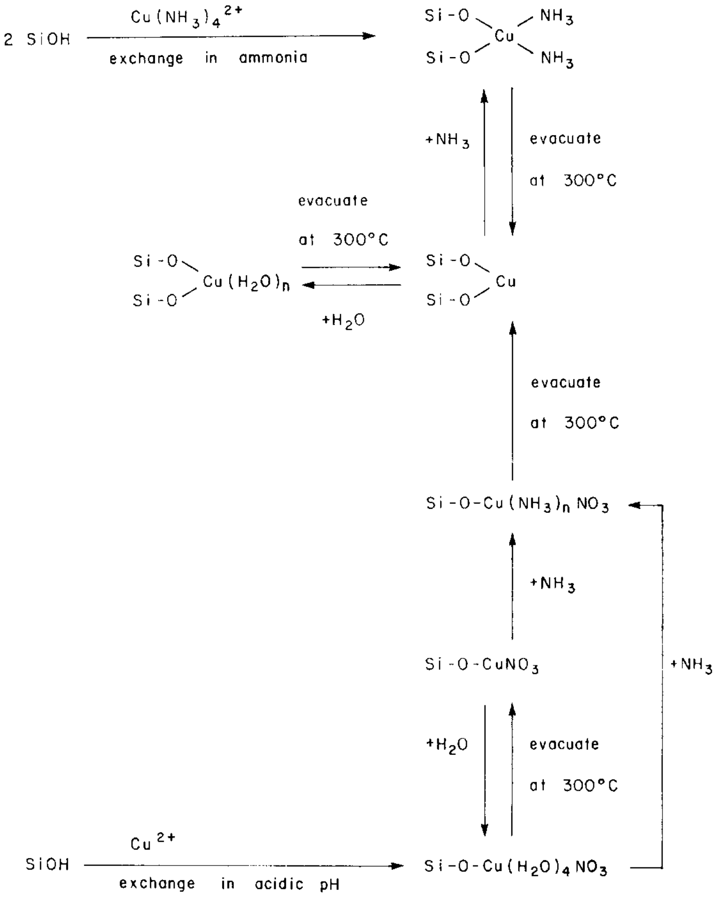
The ESR spectrum of the cupric ions introduced onto silica gel by cation exchange with tetrammine cupric ions and their change by interaction with adsorbed molecules have been reported previously (*9*). Here, we report the same kind of investigation on the cupric ions introduced by cation exchange with cupric ions in acidic solution.

The moist sample gives the ESR spectrum with parameters $g_{\parallel} = 2.345$, $g_{\perp} = 2.060$, and $A_{\parallel} = 133 \times 10^{-4}$ cm^{-1}, as shown in Fig. 4a. These parameters are close to those of cupric ions on hydrated ion-exchange resins (*10*) or hydrated layer silicates (*11*), on which cupric ions have six aqua ligands with tetragonal configuration. Thus, the surface species may be in the form of $SiO\text{-}Cu(H_2O)_4NO_3$ with tetragonal structure. The spin density calculated from the intensity of the ESR spectrum agreed with the number of cupric ions loaded by ion exchange within experimental error.

The evacuation of the moist sample at 300°C for 3 hr changed the spectrum to an asymmetric single peak as shown in Fig. 4b. It is difficult to tell the surface structure of this species. But, it should be noted that the spectrum is quite different from the one observed when silica gel exchanged with $Cu(NH_3)_4^{2+}$ is evacuated at the same temperature (*9*), indicating that the structure of the surface species depends on the method of cation exchange. The readsorption of water vapor onto the evacuated sample restored the spectrum to the one of the original moist sample, indicating that the process is reversible.

When a moist or evacuated sample was exposed to ammonia at room temperature, the spectrum with $g_{\parallel} = 2.273$, $g_{\perp} = 2.038$, and $A_{\parallel} = 175 \times 10^{-4}$ cm^{-1} was observed (Fig. 5a). The large A value clearly shows the coordination of ammonia to cupric ion. Evacuation of the sample at 300°C did not restore the spectrum to the one observed before ammonia adsorption, but changed to a new spectrum with g values of $g_1 = 2.453$, $g_2 = 2.165$, and $g_3 = 2.050$ (Fig. 5b). The disappearance of the hyperfine structure suggests that the coordination environment of the cupric ions is close to 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*). The sample was then exposed to water vapor. The color of the sample changed from colorless to yellow. The ESR spectrum observed was shown in Fig. 5c, which again is the almost same as the spectrum of the silica gel exchanged with $Cu(NH_3)_4^{2+}$, evacuated at 300°C, and then exposed to water vapor; two different surface species were observed: One has parameters of $g_{\parallel} = 2.336$ and $A_{\parallel} = 145 \times 10^{-4}$ cm^{-1}, and the other has $g_{\parallel} = 2.376$ and $A_{\parallel} = 114 \times 10^{-4}$ cm^{-1}, with unresolved $g_{\perp} = 2.050$. The assignment of the both species was given in the previous paper (*9*).

The whole change is expressed by the following scheme.



REFERENCES

1. Kozawa, A., *J. Inorg. Nucl. Chem.* **21**, 315 (1961).

2. (a) Stanton, J., and Maatman, R. W., *J. Colloid Sci.* **18**, 132 (1963); (b) Stanton, J., and Maatman, R. W., *J. Colloid Sci.*, **18**, 878 (1963).

3. Dugger, D. L., Stanton, J. H., Irby, B. N., McConnell, B. L., Cummings, W. W., and Maatman, R. W., *J. Phys. Chem.* **63**, 757 (1964).

4. Burwell, R. L., Jr., Peason, R. G., Haller, G.L., Tjok, P. B., and Chock, S. P., *Inorg. Chem.* **4**, 1123 (1965).

5. Tarama, K., Yoshida, S., Taniguchi, K., and Osaka, S., *Nippon Kagaku Zasshi* **91**, 575 (1968).

6. Benesi, H. A., and Curtis, R. M., *J. Catal.* **10**, 328 (1968).

7. Morikawa, K., Shirasaki, T., and Okada, M., *in* "Advances in Catalysis" (E. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 97. Academic Press, New York, 1969.
8. Burwell, R. L., Jr., *Chemtech*, 370 (1974).
9. Tominaga, H., Ono, Y., and Keii, T., *J. Catal.* **40**, 197 (1975).
10. Umezawa, K., and Yamabe, T., *Bull. Chem. Soc. Japan* **45**, 56 (1972).
11. Clementz, D. M., Pinnavia, T. J., and Mortland, M. M., *J. Phys. Chem.* **77**, 196 (1973).
12. Sharnoff, M., *J. Chem. Phys.* **42**, 3383 (1965).
13. Bates, C. A., Moore, W. S., Standley, K. J., and Stevens, L. W. H., *Proc. Phys. Soc.* **79**, 73 (1962).
14. Foster, D., and Weiss, V. W., *J. Phys. Chem.* **72**, 2669 (1968).
15. Gould, D. C., and Ehrenberg, A., *Eur. J. Biochem.* **5**, 451 (1968).