ESR Study of the Impregnation Process of Silica Gels with $Cu(NO_3)_2 \cdot 6H_2O$

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The use of electron spin resonance in the study of the different steps in the impregnation process of hydrated $Cu(NO_3)_2$ onto silica gels with pore size of 20, 50 and 100 nm is described. The desolvation step with concomitant beginning of the salt decomposition step occurred at ~ 100 °C in silica with pores of 50 and 100 nm while a temperature higher than 200 °C were necessary for 20 nm pores. In the range 300 to 500 °C the decomposition step was completed and the adsorption of Cu(II) on $\equiv SiO^-$ surface sites started. Well-defined localization was completed after heating at 650 °C. The bond features of the surface adsorbed Cu(II) species are also described.

Introduction

Interest in the chemistry of transition metal oxide catalysts for the total oxidation of hydrocarbons and CO and for the reduction of NO derives mainly from attempts to reduce air pollution. It is widely accepted that the activity of solid catalysts containing metal ions largely depends on the previous history of the sample and on the distribution of the metal ions on the surface and into the bulk. Thus, detailed knowledge of the mechanism of metal incorporation is, in principle, relevant for the characterization of the catalyst. When paramagnetic ions are involved in the preparation of active catalysts, electron spin resonance (ESR) spectroscopy has proved to be a powerful tool in the study of the nature, the mobility, and the localization of the paramagnets in the various steps of the preparation process. Several ESR studies of Cu(II) ions dispersed on various media have appeared in the past literature [1–6]. However, no particular attention seems to have been devoted to the detailed mechanism of adsorption.

This paper describes a method by which ESR spectroscopy may be employed to study the single steps of the impregnation process in which Cu(II) ion is desolvated and transferred to the solid surface of homoporous silica gels.

Experimental

A stock water solution of 0.01 M $Cu(NO_3)_2$ was used for all the experiments, and the pH was varied over the range 3.6–1.1 by adding appropriate amounts of nitric acid. Homoporous silica gels were Merck adsorbents for chromatography with pore diameter 20 nm (henceforth called S 20; surface area 150 m^2/g; pore volume 0.65 ml/g; data as given by the manufacturer), 50 nm (S 50; surface area 50 m^2/g; pore volume 0.65 ml/g), and 100 nm (S 100; surface area 25 m^2/g; pore volume 0.65 ml/g). The silica gels (1 g) were impregnated with the 0.01 M Cu(II) water solution (5 ml) and kept at room temperature for 24 h. After filtering, the samples were gently dried on a filter paper until an apparently dry powder was obtained. This powder was stored in a water-vapor-saturated box to maintain full hydration. As previously observed in the same systems [7], the adsorbed solution retains its initial concentration: thus 6.5×10^{-3} mmol of Cu(II) per g of silica gel is calculated in the samples used in this work.

The ESR spectra were registered with a Bruker model 200 tt spectrometer operating in the X-band, equipped with the Bruker S 100/700 variable temperature accessory. Modulation amplitude was kept of the order of 1–2 gauss, to avoid signal overmodulation; power ~ 2 dB was used since Cu^{2+} signals do not show appreciable saturation. Optical measurements were carried out with a Perkin-Elmer UV-VIS model 200 spectrophotometer equipped

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with an internal reflection accessory. MgO was used as a standard. Thermal treatments were carried out by heating the samples in a furnace at the air and at controlled temperature in the range 120 to 650 °C. Finally the samples were calcined at 800 °C.

Results and Discussion

Silica gel samples containing 0.01 M $Cu(H_2O)_6^{2+}$ water solution before thermal treatment (*i.e.* in the conditions of full hydration) gave rise at room temperature to a symmetrical unstructured signal centered at $\langle g \rangle \sim 2.2$ and $\Delta H \sim 140$ gauss. This spectrum is identical to the one observed in unadsorbed solutions of equal concentration, and is clearly due to $Cu(H_2O)_6^{2+}$ ions in free motion in the liquid inside the pores. In fact, it has been reported that $Cu(H_2O)_6^{2+}$ ions inside pores with diameter $\geqq 20$ nm showed over the range 0 to 90 °C the same correlation times for the motion as in a bulk solution [7], *i.e.* the liquid had the same mobility in both situations, and no surface adsorption was detected at this stage. Different results were obtained with silica gels with pore diameter lower than 20 nm [7].

The removal of water from the pores (*dehydration step*) starts above 100 °C. After heating at 120 °C for 6 h, the ESR spectra of Cu(II) onto S 20 consisted in a broad signal with partially resolved $A_\parallel$ components (approximately $A_\parallel = 125$ gauss) (Figure 1). Immobilized species are responsible for this signal. All of the coordinated water molecules are retained by the Cu(II) ions since almost the same ESR parameters as those of $Cu(H_2O)_6^{2+}$ in a glassy matrix are calculated. Only a fraction of the water filling the pores has been removed by the thermal treatment at 120 °C as determined from weight loss in comparison with samples heated at higher temperature. It is known that secondary interactions with the hydrophilic silica surface propagate in the water layers outside the surface [8]. Although these interactions are poorly defined in molecular details, they are accepted to give rise to changes in many properties, because of surface-induced effects of both chemical and physical nature. The distance from the surface over which secondary interactions are effective has been evaluated by several techniques to be ~2–3 nm, *i.e.* 10–15 water layers. ESR of Cu(II) and Mn(II) as paramagnetic probes confirmed these figures [7, 9]. It is therefore conceivable that in S 20 samples the large fraction of water involved in these differently structured layers will be harder to remove with respect to free water. Thus, we suggest that $Cu(H_2O)_6^{2+}$ ions responsible for this signal reside near the surface in the first ten-fifteen layers.

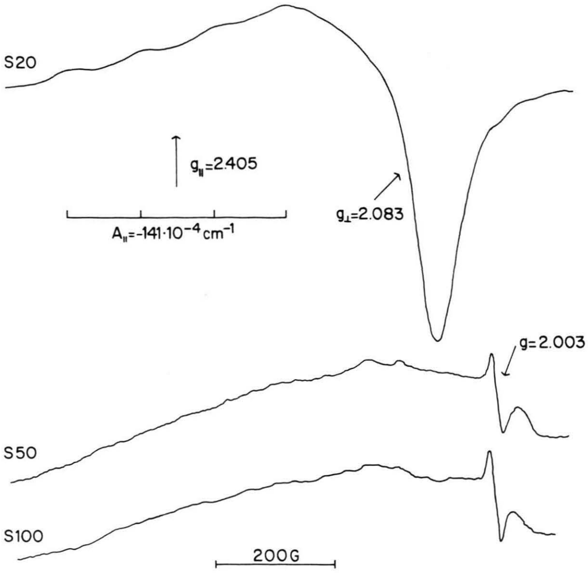

Fig. 1. ESR spectra at 25 °C of Cu(II) adsorbed on silica gels with different pore size after heating at 120 °C for 6 h. (Same instrumental settings for the three spectra.)

The fraction of water involved in these partially immobilized layers with respect to the total water inside pores of different diameters decreases with increasing pore size, and an increasing amount of pore filling water will be removed at a given temperature and for an equal duration of thermal treatment in S 50 and S 100 samples. Indeed, smeared-out spectra were obtained from S 50 and S 100 samples heated at 120 °C for 6 h (Figure 1). The extensive signal height decrease in these samples indicates that partially desolvated surface species with a variable number of coordinated water molecules were formed under heating (*desolvation step*). The magnetic parameters, in these cases, are expected to be spread over a wide range of values. The resulting ESR absorptions were therefore randomly distributed over a wide field range. In addition, a narrow signal centered at $g = 2.003$ appeared from S 50 and S 100 samples heated at 120 °C for 6 h, which may be due to a nitrogen free radical adsorbed on the surface. This

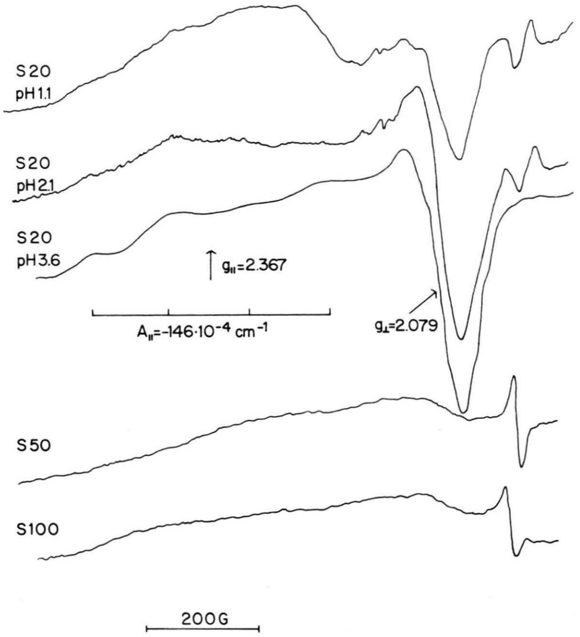

Fig. 2. ESR spectra at 25 °C of Cu(II) adsorbed on S20 (at three different pH values), on S50 and on S100 after heating at 200 °C for 6 h.

fact could suggest that the decomposition of the nitrate salt began on S50 and S100 samples at 120 °C with formation of oxidic Cu(II) material on the surface (*decomposition step*). It is noteworthy that the appearance of the adsorbed radical is related to the disappearance of the axial spectrum due to immobilized $Cu(H_2O)_6^{2+}$. However, the possibility that the $g = 2.003$ signal may be attributed to carbon radical cannot be ruled out. It is quite usual for organic material from several sources to be adsorbed on solid surfaces and to give rise to carbonaceous material after burning at moderate temperature. In fact, S50 and S100 samples treated at 120 °C for 2 h showed an axial spectrum apparently similar to that observed on S20 samples heated at 120 °C for 6 h, superimposed on the liquid-like spectrum given by unheated samples. No narrow signal was observed in these conditions.

There is therefore a lower limit for the start of the desolvation and decomposition steps which depends on the temperature and on the time of heating treatment as well as on the pore size.

Figure 2 shows the spectra of silica gel samples heated at 200 °C for 6 h. A partial resolution of the $A_{\parallel}$ components was again observed from the S20 samples. In the case of S50 and S100 samples heated at 200 °C for 6 h, no large variations were observed with respect to those heated at 120 °C for 6 h, except an increase in the relative intensity of the radical signal. The parameters of the S20 spectrum significantly differ from those of $Cu(H_2O)_6^{2+}$ in a glassy solution (Table 1). We suggest that in this case the largest fraction of hydrated Cu(II) ions were adsorbed on the surface with at least a $\equiv SiO^-$ group acting as a ligand after replacement of water molecules from $Cu(H_2O)_6^{2+}$. This strongly adsorbed copper-silanoxy complex was prevented from further dehydration at 200 °C. As a contrast, further dehydration was possible for the more labile, not surface adsorbed $Cu(H_2O)_6^{2+}$ in the water layers outside the surface. The large differences in the $-OH$ group number per gram from S20 to S50 and S100 samples may be the reason for the different behavior of the three supports. Indeed, assuming [10, 11] 8 OH groups/1 nm^2, about 12×10^{20}, 4×10^{20}, and 2×10^{20} OH/g are present on S20, S50, and S100 samples respectively. In conditions of full hydration, 0.65 cm^3 of the 0.01 M Cu(II) solution, *i.e.* 4×10^{18} Cu(II) ions, was adsorbed in each gram of solid support, with Cu/OH ratios of 1/300, 1/100, and 1/50 respectively. From the ESR

Table 1. ESR Parameters of Cu(II) Species Adsorbed on Silica Gels.

System	Temperature °C	$g_{\parallel}$ (±0.002)	$g_{\perp}$ (±0.002)	$A_{\parallel}$ (cm^{-1}, $\times 10^4$) (±2)	α^2
Cu(II)−S20	120	2.405	2.083	−141	−
Cu(II)−S20 (pH 3.6)	200	2.367	2.079	−146	−
Cu(II)−S50	650	2.348	2.073	−135	0.79
Cu(II)−S100	650	2.359	2.073	−133	0.78
$Cu(H_2O)_6^{2+}$-glycerol	−177[a]	2.409	2.082	−144	0.88

[a] Temperature of ESR spectrum registration.

data it was apparent that only a minor fraction of the total OH groups acted as a ligand towards Cu(II) ions (significantly lower than 1/100, since in the S 50 sample the axial spectrum due to the adsorbed species was completely masked under the resolved spectrum). Higher values of the Cu/OH ratio (1/10 – 1/12) were previously found for the adsorption of copper-ammonia complexes at room temperature [12, 13].

The above suggestion was supported by additional runs carried out by using Cu(II) solutions at pH lower than that of the starting solution (pH = 3.6), obtained by simple adding of diluted nitric acid. Adsorption of solution at pH 1.1 and 2.1 in the case of S 20 samples gave rise to spectra that came closer to those from S 50 and S 100 the more acidic was the pH. The decrease of the solution pH decreased the degree of the $=\mathrm{Si-OH}$ dissociation, with consequent decrease of the $\mathrm{Cu-O-Si}$ complex concentration. Similar pH effects on the degree of surface adsorption of copper complexes were previously observed in adsorption of water-ammonia solutions with different ammonia contents on the same supports [12, 13].

At temperatures in the range 300 to 500 °C, the ESR spectra showed an increasing recovery of the high field component with increasing temperature (Figure 3). This indicates a trend towards more definite symmetries. The fact that the increase was at its maximum for the S 20 samples at 500 °C is well in agreement with the higher availability of ligand sites in this support with respect to S 50 and S 100 samples. On S 20 samples an additional absorption was observed superimposed on the narrower $g_\perp$ component (Figure 3 b). This large, unstructured signal, although not well characterized, had $g \sim 2.2$ and $\Delta H \sim 800$ gauss. The assignment of this signal on the basis of ESR data only is very difficult. A possible source of this signal will be discussed below.

The ESR spectra from all samples in the range 300 to 500 °C are again attributable to Cu(II) ions still belonging to sites with ill defined symmetry, although a trend was observed with increasing temperature and decreasing pore size towards a localization on more characterized sites on the support surface.

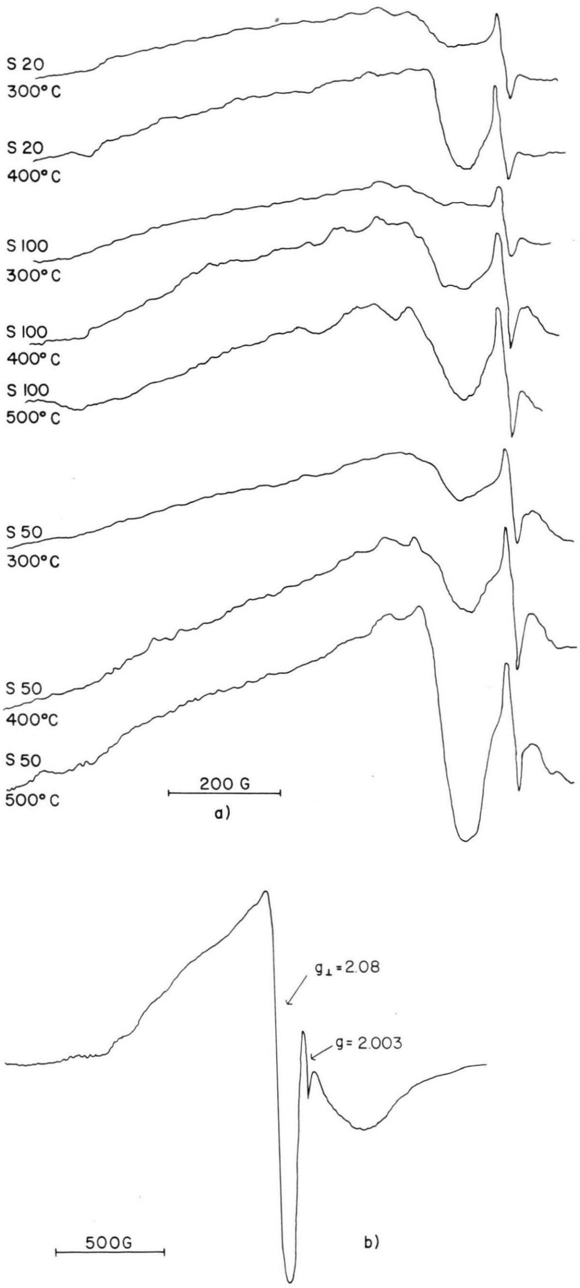

Fig. 3. In a) ESR spectra at 25 °C of Cu(II) on S 20, S 50, and S 100 samples after heating in the range 300 to 500 °C. In b) the Cu(II) spectrum from S 20 sample heated at 500 °C.

Internal reflection spectra aid the above suggestion. An absorption maximum at $\sim 13.500\ \mathrm{cm}^{-1}$ (almost the same value reported for the hexaaquo-complex of copper [14]) was shown by S 20 samples heated at 120 °C for 6 h and by S 50 and S 100 samples heated at 120 °C for 2 h, while a progressive shift to $\sim 15.000\ \mathrm{cm}^{-1}$ was shown by samples heated up to 500 °C, with an almost regular increase

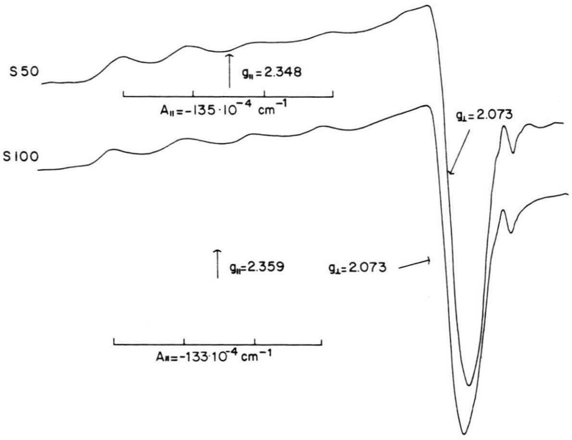

Fig. 4. ESR spectra at 25 °C of Cu(II) on S50 and S100 samples after heating at 650 °C.

of the smearing out of the absorption width, as expected from progressive dehydration of $Cu(H_2O)_6^{2+}$.

After heating S50 and S100 samples at 650 °C, the signals turned to well-defined axial spectra with the ESR parameters reported in the Table 1 (Figure 4). From these spectra the presence of bulky crystalline phases of Cu(II) oxides cannot be inferred because owing to spin pairing such species escape ESR detection. Thus, at temperatures above 500 °C, the final step of the impregnation process leads to single and well-localized surface-adsorbed and/or bulk-migrated species (*adsorption and diffusion steps*). The amount of bulk-diffused Cu(II) ions cannot be easily evaluated in these particular cases. Other systems have been investigated in the past, in which fast and irreversible bulk diffusion occurred even at room temperature [15, 16].

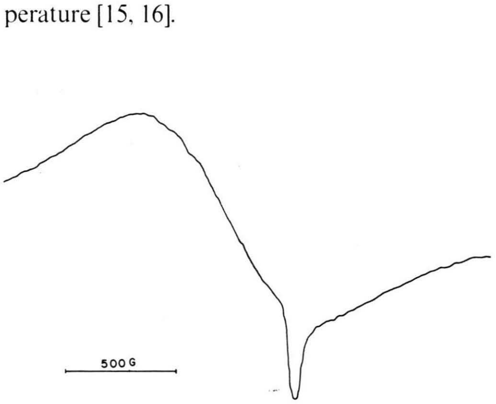

Fig. 5. ESR spectrum at 25 °C of Cu(II) on S20 sample after heating at 650 °C.

S20 samples heated at 650 °C for 6 h gave a more complex spectrum (Fig. 5) consisting on an axial signal with features similar to those of the spectra obtained from S50 and S100 superimposed on an intense, broad ($\Delta H \sim 800$ gauss) absorption centered at $g \sim 2.2$. This second signal cannot be unambigously attributed on the basis of the ESR data only. Similar absorption (but narrower) were observed by Derouane et al. [17] and by Walters [18] after adsorption of Cu(II) on magnesium oxide. From their apparent isotropic lineshape, these spectra were attributed to Cu(II) ions in a regular octahedral environment. We therefore suggest that in S20 samples, a large fraction of dehydrated Cu(II) ions are able to migrate into almost regular sites of the silica skeleton and occupy quite close positions since their ESR absorptions are clearly broadened via dipolar interaction. The reasons why this large apparently isotropic signal was not observed on S50 and S100 are not clear at the moment.

The ESR spectra from all samples investigated maintained their features even after calcination at 800 °C for 6 h, thus indicating that the different steps of the impregnation process have taken place over the temperature range 25 – 650 °C.

In conclusion it follows from the data presented here that the various steps of the incorporation of Cu(II) onto silica gel supports are mainly affected by the pore size in the sense that: i) the lower the pore size the higher was the temperature of complete desolvation and of salt decomposition; ii) the lower the pore size the lower was the temperature of Cu(II) adsorption at definite sites.

Several authors have interpreted the spin hamiltonian parameters of copper complexes in frozen solution [18 – 21] and in the adsorbed state [2] in terms of molecular orbitals. An approximate evaluation of the covalency, α^2, of the in-plane σ-bond between a 3d copper orbital and the ligand orbitals can be obtained from the magnetic parameters by using the equation (19):

$$\alpha^2 = -A_\parallel/P + (g_\parallel - 2) + 3/7\,(g_\perp - 2) + 0.4\,,$$

where P is the free-ion dipole term, to which the value 0.036 cm^{-1} was given. The values of α^2 obtained for Cu(II) adsorbed on silica gels are reported in Table 1. They indicate an appreciable degree of covalency of the in-plane σ-bond. This suggests that $\equiv Si-O^-$ groups from the surface may act as coordinating ligands for the adsorbed species. A relatively high portion of covalent in-plane σ-bond was previously reported for other surface copper complexes with oxygen ligands [2, 22].

It is possible that the degree of covalency of Cu(II) may have a role in determining the activity and selectivity of copper-containing catalysts. A thorough comparison involving the degree of dispersion on surface and/or in bulk, the covalency of Cu(II), and the catalyst activity should be of interest.

Acknowledgements

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