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ESR Investigations of Copper Oxide on Alumina

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In situ ESR investigations of copper oxide supported on alumina during a reduction–oxidation cycle are reported. Four different ESR signals have been clearly distinguished. A tentative interpretation is given by using our own measurements and the results of other authors.

INTRODUCTION

The mechanism of the oxidation of copper to CuO and the reduction of CuO to copper has been investigated with different methods in recent years. Nevertheless, no unequivocal model exists. The ideas of O'Keeffe and Stone (*1*) suggest that ESR measurements might be of some value for elucidation of this problem. These authors postulate the formation of copper vacancies and defect electrons during oxidation.

Furthermore, the state of dispersion of a supported catalyst is undoubtedly important for catalytic reactions. By means of susceptibility measurements Jacobson *et al.* (*2*) found that even at very low copper concentrations of 1 wt % copper on alumina only a very small part of the copper ions are in an "atomically" dispersed state. ESR investigations should lead to some clarification on these points.

EXPERIMENTAL

1. Samples. Spherical particles of a high-surface-area δ-alumina, P110C1/6, obtained from Degussa Hanau (specific surface area 98 m^2/g), were impregnated in an excess aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$, Merck p.a. They were subsequently dried at 100°C for several hours and finally calcined in air at 600°C for 5 hrs. The catalysts thus formed were green. The copper concentration of the samples was about 1 wt % copper.

Highly purified H_2 and CO gases were used for the reduction. The catalysts were oxidized by exposure to the air.

2. Apparatus. The ESR measurements were performed with a Varian X-band spectrometer. For the determination of spin densities an apparatus similar to that described by Thompson and Waugh (*3*), who used a ruby crystal as intensity standard, was constructed. The ruby mount allowed measurements to be made even at high temperatures. In all experiments the crystal had the same fixed orientation, giving two signals of nearly equal intensity with estimated g factors of 1.5 and 2.8. The spectrum of the ruby crystal together with the signal of the Varian Standard No. 904450-01 is shown in Fig. 1, spectrum 1. Spectrum 2 of Fig. 1 displays simultaneously the ruby signals and the hyperfine lines of the solution of vanadyl ions. Using the known distance of the vanadyl lines the distance of the ruby signals is estimated to be about 1800 gauss. The depth of insertion of the ruby crystal into the cavity was so chosen as to allow the determination of the relative intensities of very strong as well as rather weak signals with sufficient accuracy.

The different gases were allowed to flow successively or simultaneously through the *in situ* reaction tube. Figure 2(a) shows a cross-sectional view of the reaction tube with a surrounding heat isolation tube. Figure 2(b) displays the cross section of the

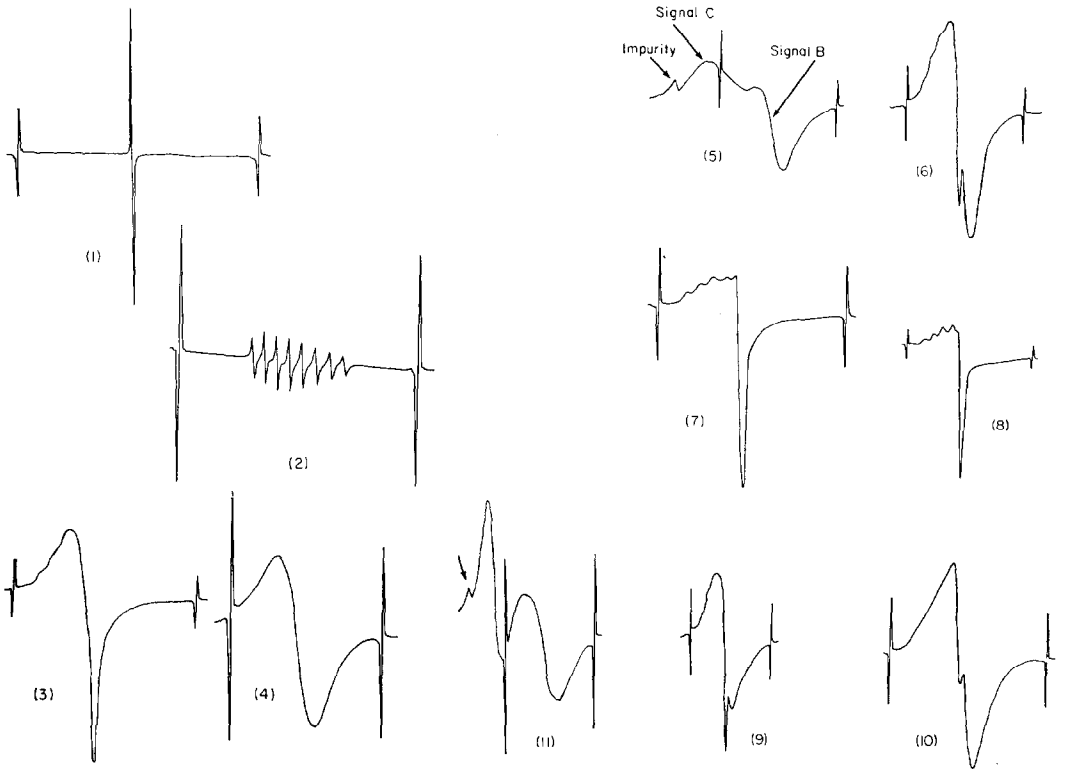

FIG. 1. Spectra of the different samples. (The two ruby lines are given for reference.) (1) Signal of the VARIAN Standard No. 904450-01. (2) Spectrum of a solution of vanadyl ions. (3) Signal A. (4) Signal B. (5) Signals B and C. An impurity line is indicated by an arrow. (6) Signals A and D. (7) Signal A immediately after the beginning of the reduction period. (8) Signal A after a slow reoxidation at room temperature. (9, 10) Signals A and D, originating from different samples. (11) Signals B and C during reduction with CO, together with the impurity signal of the support mentioned in the legend of spectrum 5. Spectra 4–6 and 9–11 were recorded during measurements at the temperature of 400°C.

inner tube near the sintered glass disk. To heat the samples up to temperatures of 500°C two platinum film strips were painted on opposite sides of the inner tube according to the method of Singer *et al.* (*4*). Both tubes were made of quartz.

EXPERIMENTAL RESULTS

1. Signal of the Oxidized Catalyst (Fig. 1, spectrum 3)

The line parameters of all signals, as obtained by graphical evaluation of the spectra, are collected in Table 1. The determination of the spin density of the oxidized catalyst signal with the help of the Varian standard resulted in 1.93×10^{18} spins/g. This measurement considers the g-factor dependency of the transition probability (*5*) and the effective length of the sample tube in the cavity. Sample and standard tubes had the same dimensions.* The estimated total error should be lower than 50%. The total copper content of the catalyst was equivalent to $(0.95 \pm 0.01) \times 10^{20}$ spins/g. A measurement of the static susceptibility resulted in $(1.04 \pm 0.17) \times 10^{20}$ spins/g. This means that nearly all Cu^{2+} ions contribute to the susceptibility, in good agreement with the results of Selwood and Dallas (*6*), but only 2% contribute to the ESR signal.

Five days sintering at 900°C resulted in an evident intensity increase, but no appreciable change in line shape. Considering

* Operating instructions of the AEG spectrometer 12X, No. 1816.201 A24FR/0165.

TABLE 1
LINE PARAMETERS OF THE DIFFERENT SIGNALS

	Signal A	Signal B	Signal C	Signal D
g Factor	$g_\perp = 2.05$ $g_\parallel = 2.33$	$g = 2.08$	$g = 2.27$	$g = 2.05$(450°C)
ΔH(linewidth)	—	0.55 kG(400°C)	0.94 kG(400°C)	1.7 kG(175°C) 0.51 kG(360°C) 0.26 kG(450°C)
$\lvert A_\parallel \rvert$	0.015 cm^{-1}	—	—	—

the ESR signal, there is no clear evidence of spinel formation. On evacuating the sample one finds an obvious decrease of the linewidth, showing that an appreciable part of the paramagnetic ions contributing to the signal lie on the surface and interact with the adsorbed oxygen.

There was no evident temperature dependency of the linewidth in the temperature range from 25° to 470°C. The ESR intensity as a function of temperature showed a fairly good $1/T$ dependency.

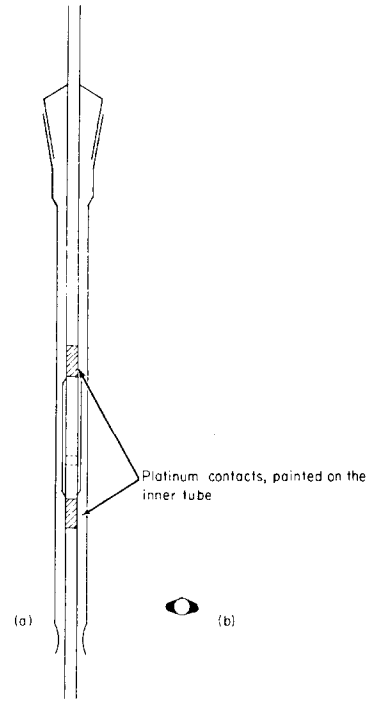

FIG. 2. (a) Cross-sectional view of the apparatus for *in situ* measurements, consisting of two quartz tubes, the inner one being the reaction tube. (b) Cross section of the inner reaction tube near the sintered quartz disc.

2. Spectra of the Catalyst during Reduction with H_2 and Reoxidation

During a reduction and reoxidation cycle four different signals are found. At the beginning of the reduction period the signal of the oxidized catalyst previously described (Fig. 1, spectrum 3) disappears. This occurs quickly (15 min) at about 400°C and very slowly (several hours) at room temperature. Simultaneously a first (Fig. 1, spectrum 4) and sometimes a second new line (Fig. 1, spectrum 5), which gradually disappear during further reduction, emerge. On reoxidation these lines appear in the inverse sequence with one difference: together with the above-described line of the oxidized catalyst a fourth signal (Fig. 1, spectrum 6) emerges. We call these four lines, according to the above enumeraction, signals A, B, C, and D. Figure 3 shows the intensity of the lines A–C during an average cycle.

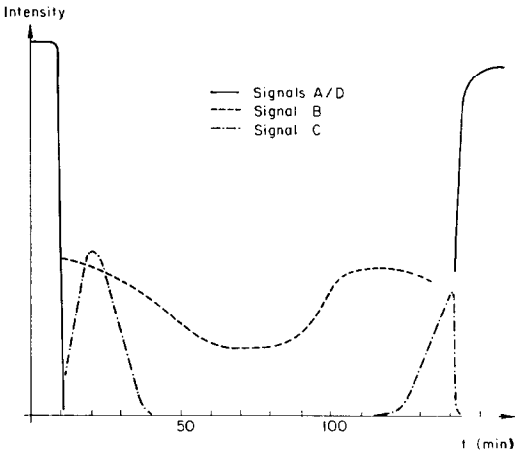

FIG. 3. Intensities of signals A–C during a reduction and reoxidation cycle. Signal D behaves like signal A. The intensity scales for the three signals are only approximately equal.

Signal A. At the beginning of the reduction a remarkable line-narrowing can be recognized (Fig. 1, spectrum 7); the hf structure of the copper ions gradually appears and the spectrum is very similar to those spectra calculated by Vänngård and Aasa (*7c*) and by Kneubühl (*7b*) powder samples of copper compounds. Equally slow reoxidation at room temperature leads to signal A with a well-resolved hf structure (Fig. 1, spectrum 8).

Signal B. This signal appears at every cycle. The intensity shows no dependence on the number of previous cycles, but varies strongly among different samples. Especially the density of the powder seems to be very important. There is a remarkable line-narrowing with rising temperature. The signal shows a weak anisotropy up to high temperatures.

Signal C. The appearance of this signal depends upon several parameters not clearly understood during this work. It seems that the density and the reaction temperature, and therefore the reaction velocity, are of some importance. There is an evident correlation with signal A. The intensity varies strongly among different samples, as does the intensity ratio between signals B and C. The linewidth temperature dependence is similar to that of signal B. At temperatures lower than 300°C the line disappears because of broadening.

Signal D. This signal appears regularly after the first cycle. The intensity ratio of signal A to signal D varies from sample to sample (Fig. 1, spectra 6, 9, 10). The reason for this is not clearly understood. Even after a 5-hr reoxidation period at 470°C line shape and intensity do not change. During reduction and reoxidation treatment the intensity ratio of signal A to signal D remained nearly constant. The linewidth increased markedly with decreasing temperature and the signal totally disappeared at room temperature.

Although the signals B and D at elevated temperatures are of similar line shape and *g*-factor, these lines do not seem to be identical, as the different temperature dependence of linewidth and velocity of appearance and disappearance indicates.

3. Spectra of the Catalyst during Reduction with CO and Reoxidation

Reduction with CO was mainly performed in order to eliminate the influence of water, which inevitably is developed by reduction with H_2. Apart from the lower reduction rate, signals A–D were found with the same characteristics already described in Section 2. The reaction velocity remained nearly constant during several cycles, contrary to the experiments of Garner *et al.* (*8*) on unsupported CuO. Only signal C showed a slight alteration of line shape (Fig. 1, spectrum 11) and a higher sensitivity to temperature. Contrary to our expectations, reoxidation gave the various ESR signals in exactly the reverse order to that which occurred on reduction. Wieder and Czanderna (*9*) found distinct differences between reduction and reoxidation according to their measurements of optical transmittance of films of copper and copper oxide. Regarding the change of line intensities with time, there is no direct correlation between our experiments and the resistivity measurements of Garner *et al.* on copper films. The reason may be that the mechanism of CuO reduction is different for highly dispersed samples, as was found by Voge and Atkins (*10*) in a study of the kinetics of the reduction.

Discussion

1. Spectrum of the Oxidized Catalyst

Like Matsunaga (*11*) and Berger and Roth (*12*) we assume signal A to be due to Cu^{2+} centers. Because all Cu^{2+} ions of our samples contribute to the magnetic susceptibility but only 2% to the ESR intensity, two different kinds of Cu^{2+} centers, the ESR signal being due to only one kind, must exist. Because of the rising portion of the copper ions, which contribute to the ESR signal, with increasing copper dispersion on the alumina surface (*12*), signal A will not be due to bulk CuO. Our interpretation is based on the ideas of Selwood *et al.* (*2, 6*). These authors assume the formation of CuO microcrystals on the alumina surface. With higher dispersion the volume of the microcrystals decreases; this

is accompanied by an increase in the copper–copper distance.

The line-narrowing during evacuation of the samples further suggests that a considerable part of the ions contributing to the ESR signal lie on the surface. The assumption that the signal is merely due to surface ions implies the formation of unreasonably large microcrystals in order to explain the contribution of only 2% of the copper ions to the ESR signal. We believe that the signal results from Cu^{2+} ions near the surface of rather small microcrystals and/or those of complete microcrystals beneath a certain volume.

Matsunaga (*11*) assumes that the ESR signal is caused by nearly isolated magnetic centers. There are some arguments against this explanation. After a long reduction period all signals disappeared. Contrary to this—under the assumption of no ion movements—Cu^0 centers should show an ESR signal due to the unpaired 4*s* electron. Because of the unchanged distance of the centers no considerable dipolar interaction seems possible. In addition, considering the poor coupling of the *s* electrons with the lattice, the spin–lattice relaxation time cannot be drastically reduced. On the other hand a continuous increase of signal A from the beginning of the reoxidation would be expected. However, it is found that at high temperatures ($\sim$ 400°C) at first only line B can be observed with no trace of A. The latter appears suddenly near the end of the reoxidation period.

Berger and Roth (*12*) explain the absence of a Cu^0 signal by the following mechanism: during reduction oxygen is removed from the surface and copper atoms migrate to form diamagnetic clusters.

The poorer resolution of signal A as compared with the spectra of Berger and Roth (*12*) may be due to the higher surface of the alumina used by these authors, and to the fact that they evacuated the samples in order to eliminate the line broadening effect of the adsorbed oxygen. The same arguments will hold, if one considers the results of Nicula, Stamires, and Turkevich (*13*), who made ESR measurements on copper ions in the open porous lattice of crystalline zeolite. Apparently, the high dispersion of the copper ions and the evacuation of the samples resulted in a high resolution of their spectra, which enabled them to some detailed theoretical considerations.

The line parameters of signal A, as roughly estimated by graphical evaluation, are in good agreement with those calculated by Berger and Roth.

2. Signals B and C

Signals B and C can be found during reduction and reoxidation, apparently without changing line shape or linewidth. We therefore assume that these signals are due to bulk centers. Two further properties seem to be important: firstly, there is a strong line-narrowing with rising temperature and secondly we observed a correlation between signals A and C.

Our interpretation is based upon the oxidation model by O'Keeffe and Stone (*1*). They propose that the oxidation of copper at low temperatures proceeds by formation and diffusion of copper vacancies from the surface to the interior. For charge neutrality defect electrons are bound to the vacancies with an energy of 0.3 eV (*14*). The line-narrowing with rising temperature indicates that the holes are not localized at the copper vacancies themselves but preferentially on neighboring O^{2-} or Cu^+ ions. Thus it is possible that with rising temperature by a frequent hopping of the holes about the vacancy an averaging of the *g*-factor anisotropy and of the dipole broadening takes place. By combination of such centers several different ESR signals are imaginable. The O'Keeffe and Stone model gives a good understanding of the correlation between signals C and A.

No explanation has as yet been found for signal D.

Acknowledgments

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