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Electron Spin Resonance of Cu^{2+} in CuO–Silica–Alumina Catalyst, and the Effect of Acetone Adsorption

Copper oxide, supported or unsupported, is widely used in catalytic reactions, and it has been the subject of several electron spin resonance (ESR) studies, particularly in the CuO–alumina (*1–4*) and CuO–silica (*5*) systems. However, no such work has been reported for the CuO–silica–alumina system. In the present work the ESR spectrum of Cu^{2+} on silica–alumina is studied along with the change in the spectrum upon adsorption of acetone vapor. The formation of a new paramagnetic species on the surface of the catalytic system after adsorption of acetone is also studied.

The magnetic resonance was done at X-band microwave frequency (~9.4 GHz) and at room temperature. Cu^{2+} ($S = \frac{1}{2}$, $I = \frac{3}{2}$) produces a single fine-structure line which is split into four lines of nearly equal intensity and spacings due to hyperfine interaction. The Cu^{2+} ESR spectrum in solids, subjected to an external magnetic field H, is usually observed to be strongly anisotropic for both the Zeeman and hyperfine interactions. For the case of Cu^{2+} in an axially symmetric crystalline electric field the spectrum is described by the spin Hamiltonian

$$\mathcal{H}_S = g_{\|}\mu_B S_z H_z + g_{\perp}\mu_B(S_x H_x + S_y H_y) + A S_z I_z + B(S_x I_x + S_y I_y),$$

where the terms have their usual meaning.

Silica–alumina (STREM Chemical Company, USA, 87% SiO_2 + 13% AlO_3) was ground, and only 30–40 mesh size grains were used. The copper-doped silica–alumina was prepared by impregnating silica–alumina in a cupric nitrate (Fisher-certified) water solution, using measured quantities of the components. The mixture was then slowly heated over a hot water bath until dried, and then dried further for 3 hr at 110°C. It was finally calcined at 500°C for 18 hr. Fisher-certified acetone was used in the acetone adsorption studies.

Undoped silica–alumina produced no ESR signals with the exception of a low intensity hump at $g \simeq 4.0$, which is likely due to Fe^{3+} impurities. No change in the spectrum was observed after evacuation and heating for 3 hr at 400°C. Figure 1a shows the ESR spectrum obtained for 3% Cu-doped silica–alumina after the catalyst was evacuated and heated at 300°C for 3 hr. A broad asymmetric line due to Cu^{2+} is obtained with an average g value of 2.10. The observed lineshape is typical for a polycrystalline sample containing Cu^{2+} in a site of axial symmetry, but there is an absence of any well-resolved hyperfine structure in the spectrum. When the sample was evacuated but unheated a similar spectrum with lower intensity was obtained. The lack of resolution of the hyperfine structure can have different causes. Excessive Cu^{2+} concentration can cause line broadening due to ordinary dipole–dipole and exchange interactions. Since the hyperfine structure was not resolved even at the lowest concentrations (0.125% CuO), this

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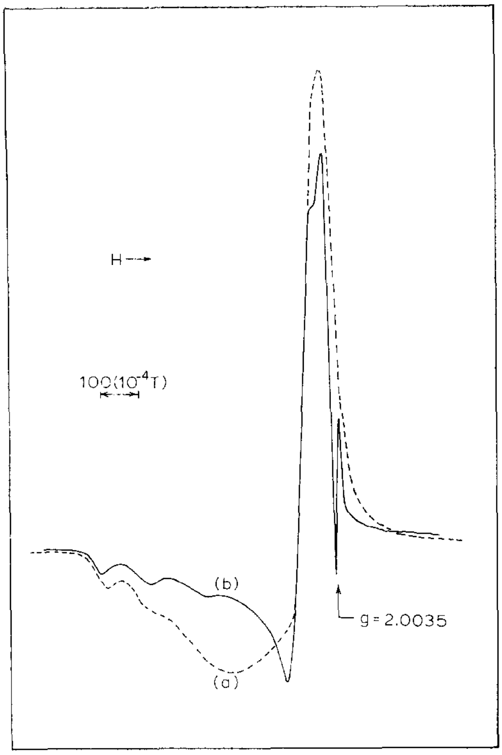

FIG. 1. (a) Electron spin resonance spectrum of Cu^{2+} in CuO–silica–alumina catalyst. (b) Spectrum obtained after the system was exposed to acetone vapor and heated at 300°C for 2 min.

suggests that the Cu^{2+} ion complexes are grouped into clusters on the support surface.

Figure 2 shows the relative intensity of the Cu^{2+} ESR line at different concentrations of CuO on silica–alumina. A maximum in signal intensity is observed at ~3% CuO. In the region of 0 to 3% CuO the color of the catalyst varies from white to green, and on upon increasing the concentration to 10% it becomes greenish black. The results of Fig. 2 indicate that the Cu^{2+} complexes which produce the ESR signals are in special types of sites on the support surface, possibly in open octahedra of the type $Cu^{2+}\cdot 5O^{2-}$. As the concentration of CuO is increased beyond 3% then the existence of ordinary CuO is favored and the number of special sites will decrease.

CuO powder does not produce any ESR lines (*6*). In the study of CuO on alumina Lumbeck *et al.* (*4*) reported that only about 2% of the Cu^{2+} ions produce an ESR signal whereas all the ions contribute to the magnetic susceptibility.

A typical sample of CuO–silica–alumina was exposed to a small amount of acetone vapor (10 Torr) at room temperature and only a slight change in the appearance of the Cu^{2+} ESR spectrum was observed. But after heating the system at 250°C for 2 min a significant change occurred (Fig. 1b). The Cu^{2+} spectrum showed a well-resolved hyperfine structure especially for the Z-axis spectrum, which is the lower field group of hyperfine lines, and the ESR line intensity decreased concurrently with the formation of a new paramagnetic species. The new species consists of a single sharp line at $g = 2.0035$ with a linewidth of 3.5 (10^{-4} T), and it is attributed to an acetone related radical on the surface of the catalyst. The

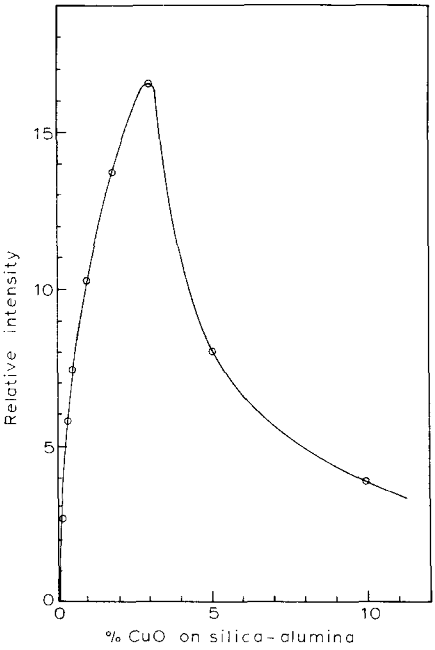

FIG. 2. Relative intensity of the Cu^{2+} ESR line for different concentrations of CuO on silica–alumina.

amount of resolution of the Cu^{2+} hyperfine structure depends on both the interaction time with the acetone vapor and the temperature at which the mixture is heated. The Cu^{2+} ESR line intensity continually decreased due to this process and the new species line increased with an approximately one-to-one correspondence. The Cu^{2+} spin Hamiltonian parameters were calculated to be $g_{\parallel} = 2.273$, $g_{\perp} = 2.068$, $A = 118.8$ (10^{-4}) cm^{-1}, and $B = 26.3$ (10^{-4}) cm^{-1}.

After heating the system in the presence of acetone vapor for 8 min at 250°C only a trace of the Cu^{2+} signal was observed and the single sharp line remained. After heating for 2 hr the Cu^{2+} spectrum disappeared completely, the sharp line increased further, and the color of the catalyst changed from grey to pitch black. When the heating was continued for 24 hr the sharp line increased appreciably and the color of the sample changed to reddish brown. The reddish brown color is typical of clustered copper metal, and may have formed on the catalyst surface. In order to confirm that the new paramagnetic species is related to the reaction of acetone with Cu^{2+}, undoped silica–alumina was heated in the presence of acetone vapor. It was observed that the color of the catalyst changed from white to pitch black, but no ESR line due to the new species was produced.

The new paramagnetic species is quite stable at temperatures $\leq 400°C$ under evacuation, and also there was no appreciable affect on it when heated at 300°C in the presence of CO or H_2. However, when oxygen was admitted to the system at room temperature the intensity of the sharp line decreased, with the amount of decrease being dependent on the oxygen pressure. When the oxygen was removed by evacuation the original sharp line reappeared with its initial intensity. The line disappeared completely when heated in the presence of oxygen for 24 hr. Since the oxygen adsorbed at room temperature interacts strongly and reversibly with the radical it must therefore be located on the surface of the catalyst. At no time during the oxidation process did the Cu^{2+} signal increase. In the reduction and reoxidation experiments of Berger *et al.* (*2*) on CuO–alumina it was found that the Cu^{2+} signal was reversibly dependent on whether or not oxygen was present.

Berger *et al.* (*2*) reported that the color of CuO–alumina catalyst changed from green to pitch black on heating alone, and also on mild reduction. No such color change was observed in the present work for the CuO–silica–alumina system on heating and evacuating, but the catalyst was very sensitive to such color changes in the presence of organic vapors. It was reported (*2*) that the continued reduction of CuO–alumina by H_2 or CO caused the Cu^{2+} spectral lines to decrease in intensity, but many hours were required to achieve a complete obliteration. In the present study it was found that on heating the CuO–silica–alumina catalyst with acetone vapor at 300°C the Cu^{2+} spectrum completely disappeared within 2 hr. The various color changes occurring in the catalyst suggests that an optical spectra study would provide useful additional information on the nature of the paramagnetic species formed due to acetone vapor adsorption.

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K. C. KHULBE,
A. MANOOGIAN,[1]
R. S. MANN, AND
P. D. GROVER[2]

Dept. of Chemical Engineering
University of Ottawa
Ottawa, Ontario, K1N 9B4

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[1] Dept. of Physics.

[2] Indian Institute of Technology, New Delhi, India.