Note on the Electron Spin Resonance of Cupric Oxide-Alumina Catalysts

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(Received February 20, 1961)

Cupric oxide-alumina is one of the supported catalyst systems examined by Selwood's susceptibility-composition isotherm method. The presence of a plateau of susceptibility of cupric ion at low concentrations is characteristic in this oxide system. The plateau found in the isotherm seemed to suggest that the cupric ions are effectively isolated from each other at low concentrations. However, the paramagnetism which is to be expected for isolated copper atoms in the reduced catalyst samples was not observed[1,2]. Here we wish to present the results of an electron spin resonance study of this oxide catalyst system.

Pure gamma-alumina was impregnated with cupric nitrate solution. The mixture was filtered after standing overnight, dried without washing, and heated in a stream of air at 400°C for six hours. The catalysts containing 0.44 to 16.6 per cent of copper were prepared. Using a Gouy balance as described previously, the magnetic susceptibility measurements were carried out at room temperature[3]. The alumina used in this study was found to have a value of -0.36×10^{-6} per gram. The gram susceptibility of the cupric ion was estimated on the assumption that the magnetic susceptibilities of cupric, aluminum, and oxide ions are additive and those of the latter two are independent of the composition of catalysts. Curve A in Fig. 1 shows the susceptibility of

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1) P. W. Selwood and N. S. Dallas, *J. Am. Chem. Soc.*, **70**, 2145 (1948).

2) P. E. Jacobson and P. W. Selwood, ibid., **76**, 2641 (1954).

3) Y. Matsunaga, This Bulletin, **30**, 868 (1957).

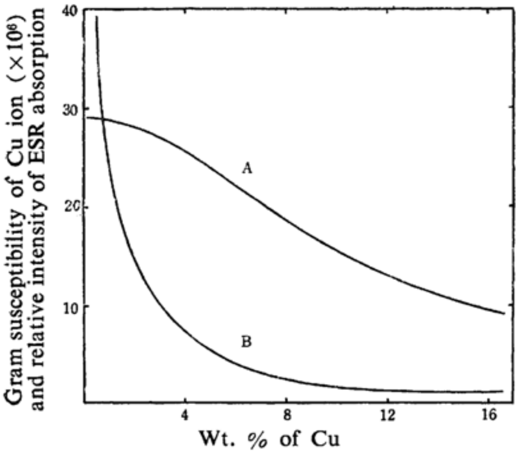

Fig. 1. Relation of susceptibility (curve A) and relative intensity of ESR absorption (curve B) of cupric ion supported on gamma-alumina to its concentration.

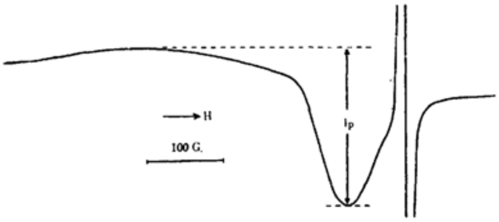

Fig. 2. Derivative of ESR of cupric oxide-alumina catalyst. The sharp peak on the right hand side is due to DPPH ($g=2.00$).

cupric ion plotted against the copper concentration. The value below three per cent of copper appears to be nearly constant. The general feature of curve A is quite similar to the curve reported by Jacobson and Selwood[2].

The electron spin resonance absorption was recorded on a spectrometer made by Japan Electron Optics Laboratory Ltd. at room temperature and at a frequency of 10 kMc./sec. No resonance absorption was found in massive cupric oxide with a field modulation of 15 gauss; on the other hand, the derivative of resonance absorption as shown in Fig. 2 was obtained from all of our catalysts. The spectrum seems to arise from the cupric ions with random orientation of tetragonal symmetry axes. The value of $g_{\perp}$ was estimated to be 2.05 using the method proposed by Kneubühl[4]. This absorption must be attributed to the cupric ions in the dispersed state and its intensity can be a measure of the amount of such cupric ions. The relative intensity was given by the ratio of the peak-to-peak intensity to the copper concentration, see I_p of the derivative curve of resonance absorption in Fig. 2. Curve B in Fig. 1 gives the plot of relative intensity to the copper concentration. If our supported cupric oxide consists of a mixture of massive crystalline oxide and the cupric ions which contribute to the resonance absorption, curve B must show a plateau at low concentrations. The relative intensity of resonance absorption was found in a sharp increase in the range where the susceptibility value was nearly constant. Therefore, we may conclude that the above view is incorrect. The presence of another kind of dispersed state, in which the cupric ions do not give resonance absorption but do contribute to the increase of susceptibility value observed at low concentrations, must be taken into consideration. We may assume that the decrease of copper concentration is accompanied by a continuous diminution in the average number of neighboring cupric ions surrounding each cupric ion. At low concentrations each cupric ion may have only a few paramagnetic neighbors, possibly separated farther than in massive crystalline oxide. The interaction between such dispersed cupric ions may be too weak to affect the susceptibility value of these cupric ions, but may contribute to the broadening of resonance absorption to some extent. It seems likely that the observed asymmetric resonance absorption arises from the completely isolated cupric ions, probably dissolved in alumina in the course of the preparation of catalysts, and the cupric ions dispersed on the surface of a carrier and under the weak interaction with neighboring cupric ions give too broad resonance absorption to be detected.

The author wishes to express his hearty thanks to Professor Shizuo Fujiwara for his interest and encouragement.

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[4] F. K. Kneubühl, *J. Chem. Phys.*, 33, 1074 (1960).