The Electron Spin Resonance Absorption of Vanadium Pentoxide Catalysts

By Kimio TARAMA, Shiichiro TERANISHI, Satohiro YOSHIDA and Hiroshi YOSHIDA

(Received June 2, 1961)

Kozyrev[1] and Pecherskaya et al.[2] studied the electron spin resonance (ESR) absorption of VO^{2+} in organic solvents at room temperature and observed that its spectrum consisted of eight hyperfine components, while Sands[3] reported the ESR absorption of V^{4+} ions in glass, and Faber et al.[4] observed the hyperfine structures of VO^{2+} ions on the ion exchangers. But no one has ever reported the ESR absorption of vanadium pentoxide.

The ESR method was used in order to study the magnetic properties of vanadium pentoxide and the binary system of vanadium pentoxide-potassium pyrosulfate.

Vanandium pentoxide was prepared by calcining ammonium metavanadate at 450°C, and vanadium pentoxide-potassium pyrosulfate

1) B. M. Kozyrev, *Discussions Faraday Soc.*, **19**, 135 (1955).
2) Y. I. Pecherskaya et al., International Congress on Catalysis, Paris, 1960.
3) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).
4) R. Faber and M. Rogers, *J. Am. Chem. Soc.*, **81**, 1849 (1959).

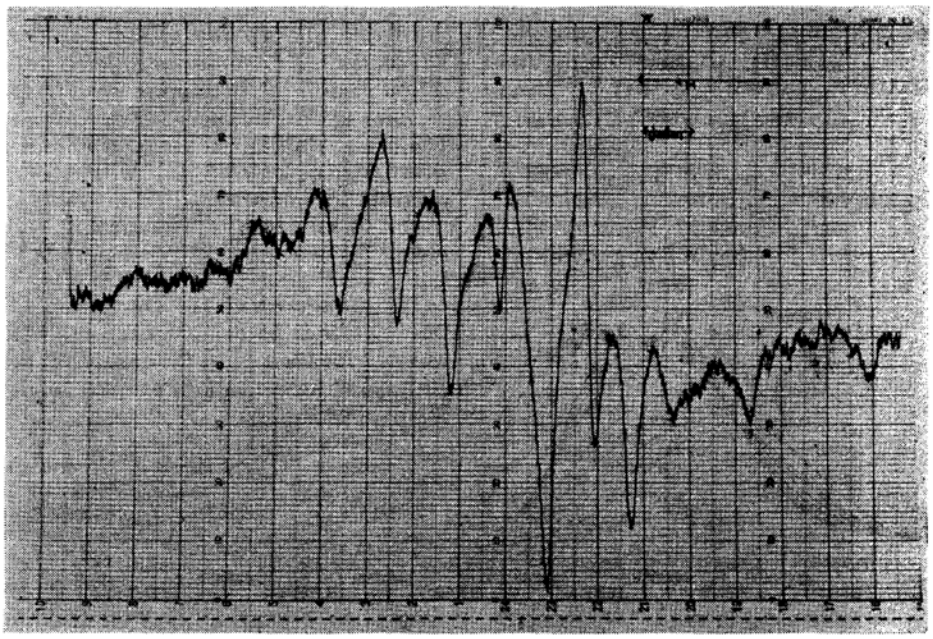

Fig. 1. ESR spectrum of the solid solution of vanadium pentoxide and potassium pyrosulfate.

samples were prepared by calcination of the mixture vanadium pentoxide and potassium pyrosulfate which contained vanadium pentoxide 10, 15, 25, 40, 50 and 70 mol. % respectively at 450°C, in closed glass vessels. Vanadium pentoxide-potassium pyrosulfate samples containing vanadium pentoxide less than 40 mol. % melted completely, and changed into amorphous substances of dark brownish color.

The spectrometer used in this research was of reflecting-type, and its resonance frequency was 9410 Mc. The observation were carried out at room temperature and also at liquid oxygen temperature.

In the case of vanadium pentoxide, an asymmetric ESR signal was observed and the *g*-value was 1.96. The line width ($\Delta Hmsl$) was 89 gauss at 16°C and 173 gauss at −183°C.

ESR signals of vanadium pentoxide-potassium pyrosulfate samples containing vanadium pentoxide less than 25 mol. %, showed the well-resolved hyperfine structures at room temperature. Fig. 1 shows the hyperfine structure of the sample consisting of vanadium pentoxide 15 mol. % and potassium pyrosulfate 85 mol. %. Eleven components are observed and its central eight components are stronger than the others.

In the case of the samples containing vanadium pentoxide more than 25 mol. %, the spectrum was not so well-resolved as Fig. 1.

The analysis of this spectrum according to Kozyrev's method shows that the *g*-value and the coupling constant for the central eight components are 1.98 and 98 gauss, and for the other three components are 1.92 and 320 gauss respectively.

The spectrum of vanadium pentoxide-potassium pyrosulfate is quite similar to that of VO^{2+} ions on the ion exchangers observed by Faber et al.[4] and this fact shows that the observed paramagnetic absorption results from VO^{2+} ions.

The authors wish to thank Professor Seizo Okamura, Kyoto University, for allowing one of the authors to use the ESR absorption apparatus.

Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto