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ESR Study of V_2O_5, MoO_3, and V_2O_5–MoO_3 Catalysts

R. S. MANN and K. C. KHULBE
Faculty of Science and Engineering, University of Ottawa, Ottawa, Canada

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Tarama and co-workers[1] and other investigators[2,3] have demonstrated the usefulness of electron spin resonance (ESR) in obtaining information about the local structure surrounding V^{4+} ion in V_2O_5 catalyst. Petcherskaya *et al.*[4] and Kazanskii and co-workers[5] could not observe any ESR signal in pure vanadium pentoxide, while Tarama *et al.*[1,5] reported a single broad ESR signal. This contrast may be due to the different methods employed for the preparation of the catalysts. In this note the results of ESR studies of the catalysts V_2O_5, MoO_3, and V_2O_5–MoO_3 system, have been compared with the results of the other investigators.

The mixed oxide catalyst was prepared by weighing ammonium molybdate (B. D. H., A. R. Grade) and ammonium metavanadate (Fisher) according to a desired ratio of the MoO_3 and V_2O_5. Ammonium molybdate dissolved in distilled water was mixed with ammonium metavanadate to make a paste. The paste was dried for 12 hr at 40°C and for 6 hr at 150°C. The temperature was increased stepwise and maintained successively for 2 hr at 200, 300, and 400°C. The catalyst was calcined at 500°C for 6 hr and activated at 600°C for 2 hr. Pure MoO_3 and V_2O_5 were obtained by thermal decomposition of ammonium molybdate and purified ammonium metavanadate. The catalysts were calcined at same temperature similar to their mixtures.

Recently Dosi[6] studied the oxidation of methanol over these catalysts and observed that 20: 80 vanadium pentoxide and molybdenum trioxide catalyst proved to be highly active and selective for the formaldehyde formation and gave nearly 99% conversion of methanol to formaldehyde for a feed ratio, (W/F), of 31.7 gm·hr/mol and 8 mol percent methanol in air.

The ESR measurements were carried out by a Varian E9, ESR spectrometer, in which the microwave frequency was in the X band and a 2G modulation was adopted. All measurements were made at room temperature unless otherwise noted.

Pure V_2O_5 showed an asymmetric broad ESR signal (Fig. 1) for which g value was 1.972. Pure MoO_3 gave no ESR signal. On addition of 10% V_2O_5 to MoO_3, strong signals were obtained (Fig. 2). Similar

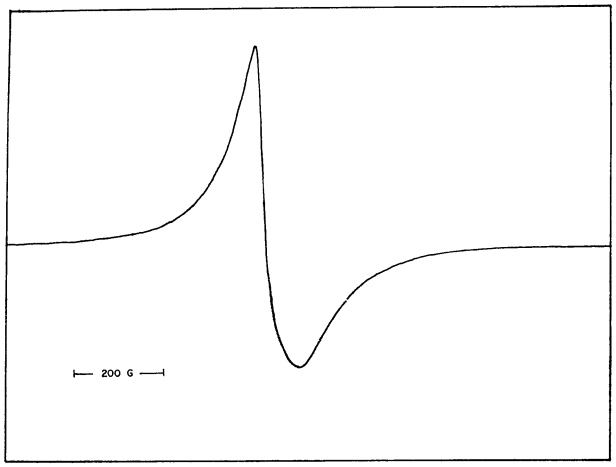

Fig. 1. 100% V_2O_5.

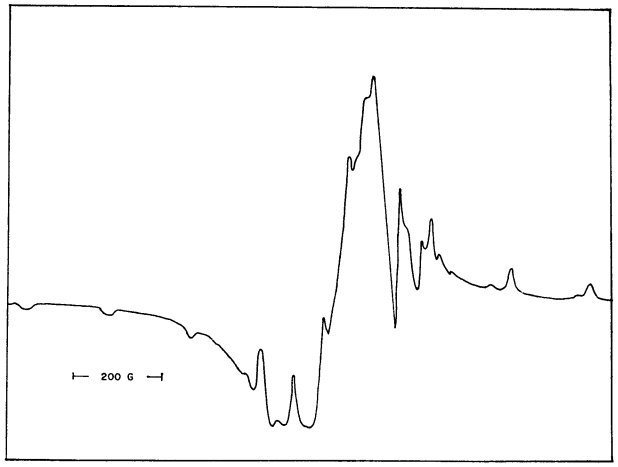

Fig. 2. 10% V_2O_5-90% MoO_3.

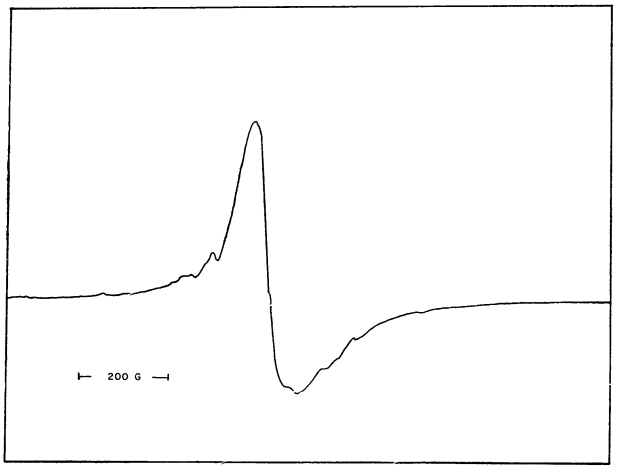

Fig. 3. 50% V_2O_5–50% MoO_3.

1) K. Tarama, S. Teranishi, S. Yoshida, and N. Tamura, Proc. Intern. Congr. Cat. 3rd Amsterdam, (1964), p. 202, North America Publ. Co. 1965.
2) V. B. Kazanskii, Z. I. Ezhkova, A. G. Lyubarskii, V. V. Voevodskii, and I. I. Ioffe, *Kinet. Katal.* **2**, 862 (1961).
3) K. Hirota and K. Kuwata, This Bulletin, **36**, 229 (1963).
4) V. I. Petcherskaya, V. B. Kazanskii, and V. V. Voevodskii, Proc. Intern. Cong. Cat. 2nd Paris, 1961, Edition Technip 2121.
5) K. Tarama, S. Teranishi, S. Yoshida, and H. Yoshida, This Bulletin, **34**, 1195 (1961).
6) M. K. Dosi, M. A. Sc. Thesis, University of Ottawa, Ottawa, 1971.

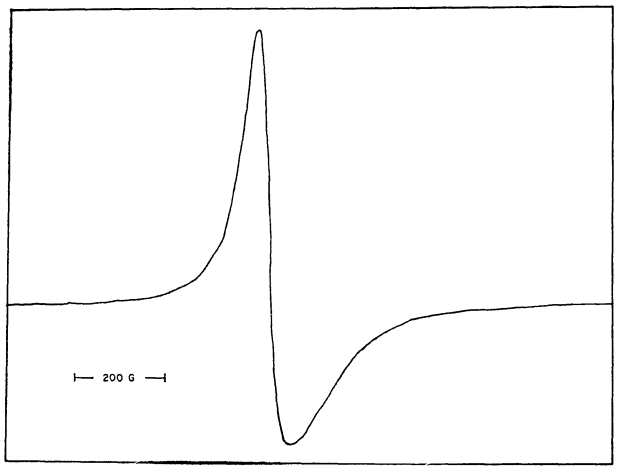

Fig. 4. 75% V_2O_5–25% MoO_3.

results were obtained by Tarama *et al.*[5] for the sample containing 15 mol% V_2O_5 and 8.5 mol% $K_2S_2O_7$. Tarama *et al.*[1] observed that every sample of the V_2O_5–MoO_3 system (5, 25, 50, 75, 95, and 100% V_2O_5) gave a single broad ESR spectrum and their shapes were similar to the pattern of the pure V_2O_5 sample. In the present study 10% V_2O_5–90% MoO_3 showed more than eleven components (Fig. 2). However, these components disappeared on further addition of V_2O_5 to MoO_3 (Figs. 3 and 4). Catalyst containing 75% V_2O_5 and pure V_2O_5 gave one broad signal. The intensity of ESR signal was highest for 10% V_2O_5–75% MoO_3 catalyst and decreased with increasing concentration of V_2O_5 in the system. The disparity between the shape of spectra observed by Tarama *et al.*[1] and in the present study in MoO_3–V_2O_5 system are atrributed to the dissimilarity in the methods of preparation of the two catalysts. The present work supports the views of Tarama *et al.*,[1] who suggested that the ESR spectrum of the system is not due to Mo^{5+} as proposed by Petcherskaya *et al.*,[4] but due to V^{4+}.

Kazanskii *et al.*,[2] found that pure MoO_3 and V_2O_5 do not give any ESR signals (at room temperature and at −196°C), but in freshly prepared mixed catalysts which have not been used in a reaction an ESR signal was observed whose width and intensity depended on the molybdenum content. With a molybdenum content less than 5% the signal has hyperfine structure (HFS) consisting of two groups of lines with a split between the 50 and 140G components in each group. But in the present study no such spectra were observed. It seems that the method for the preparation of the catalyst plays an important role to give ESR spectra.

For the purpose of comparison, the ESR spectrum of Analar Grade V_2O_5 (Fisher certified) was taken. The signal intensity observed with the sample (Fisher) was approximately 6 times less than the intensity of V_2O_5 catalyst prepared in our laboratory, confirming the dependence of the ESR spectrum on the method of the preparation and activation of the catalyst.

On raising the temperature of the catalyst, (upto 400°C) the intensity of ESR signals of V_2O_5 and V_2O_5–MoO_3 decreased.

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