

ESR INVESTIGATION OF VANADIUM-MOLYBDENUM OXIDE CATALYSTS

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Upon calcination of vanadium-molybdenum catalysts in air at 500 °C two ESR signals are observed. They are attributed to a solid solution of MoO_3 in V_2O_5 (a) and to the incorporation of VO^{2+} into the compound V_2MoO_8 (b).

В прокалённых на воздухе при 500 °C ванадий-молибденовых катализаторах наблюдается сигнал а, обусловленный образованием твёрдого раствора MoO_3 в V_2O_5 , и сигнал обусловленный внедрением VO^{2+} в соединение V_2MoO_8 .

The ESR method has been used to study the oxide system $\text{V}_2\text{O}_5-\text{MoO}_3$ /1-5/. The present communication reports on the ESR spectra of vanadium-molybdenum oxide catalysts over the total concentration range of V_2O_5 and MoO_3 .

EXPERIMENTAL

Samples were prepared via the evaporation of solutions of ammonium paramolybdate with ammonium metavanadate, vanadyl chloride and ammonium metavanadate in the presence of ethylenediamine and vanadyl oxalate referred to as series I, II, III and IV, respectively. The powders prepared were dried for 10-12 hrs at 110 °C, then calcined at 500 °C for 4 hrs in a stream of air.

ESR spectra were recorded on a JES-3BQ device in the temperature range from 77 to 300 K at two bands ($\lambda = 3$ cm and $\lambda = 8$ mm). The parameters of the ESR spectra were specified via simulation of the lineshapes.

Table 1
ESR parameters of V^{4+} ions

I.	$g_x = 1.979 \pm 0.003$	$A_x = 50.5 \pm 0.5$ G
	$g_y = 1.982 \pm 0.003$	$A_y = 51.9 \pm 0.5$ G
	$g_z = 1.909 \pm 0.003$	$A_z = 157 \pm 0.5$ G
II.	$g_x = 1.977 \pm 0.003$	$A_x = 64 \pm 0.5$ G
	$g_y = 1.973 \pm 0.003$	$A_y = 66 \pm 0.5$ G
	$g_z = 1.875 \pm 0.003$	$A_z = 206 \pm 0.5$ G
III.	$g_{\perp} = 1.972 \pm 0.003$	$B = 54 \pm 0.5$ G
	$g_{\parallel} = 1.927 \pm 0.003$	$A = 183 \pm 0.5$ G
IV.	$g_{\parallel} = 1.90 \pm 0.003$	$A = 185 \pm 0.5$ G
a	$g_{\perp} = 1.979 \pm 0.003$	b $g_{\perp} = 1.974 \pm 0.003$
	$g_{\parallel} = 1.906 \pm 0.003$	$g_{\parallel} = 1.875 \pm 0.003$

RESULTS AND DISCUSSION

In the system under consideration the ESR spectra detected are attributed to V^{4+} ions regardless of the chemical nature of the initial vanadium compounds, while Mo^{5+} and Mo^{3+} ions have not been observed. In the sample containing 0.1 mol% MoO_3 the spectrum of V^{4+} ions is detected (Table 1). The parameters of this spectrum (signal I) coincide with those of Refs /3, 4/. From the values of the g-factors it follows that this spectrum is due to V^{4+} ions with a short V = O bond. The small hyperfine splitting constant (HFS), however, does not correspond to V^{4+} complexes containing a vanadyl moiety. This might be explained by incomplete freezing of electron "tunneling" /4/ to the nearest V^{5+} cations, which is confirmed by the increase of the delocalization at elevated temperatures.

With increasing molybdenum content, the intensity of the ESR spectrum of isolated V^{4+} ions increases and the HFS components of the ^{51}V nuclei broaden.

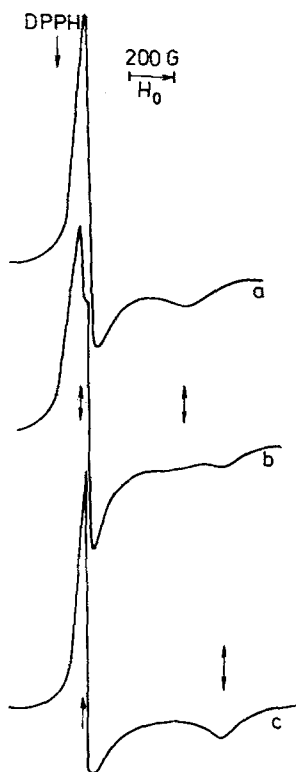


Fig. 1. ESR spectra of exchange coupled V^{4+} ions at MoO_3 contents of 5(a), 15(b) and 50(c) mol. % ($\lambda = 8$ mm)

At molybdenum contents above 1 mol% MoO_3 , the spectrum undergoes exchange-narrowing to a line with an axial anisotropy of the g-factor (Fig. 1a). The parameters of this signal (signal a) correspond to the g-factors of isolated V^{4+} ions in V_2O_5 (signal I) which points to stabilization of the nearest environment of V^{4+} ions with increasing molybdenum content.

At MoO_3 contents above 15 mol%, the ESR spectrum, along with signal a, exhibits signal b (an exchange-narrowed line of axial symmetry) (Fig. 1b). A further increase of the MoO_3 concentration leads to an increase of the intensity of signal b and a drop in the intensity of signal a (Fig. 2).

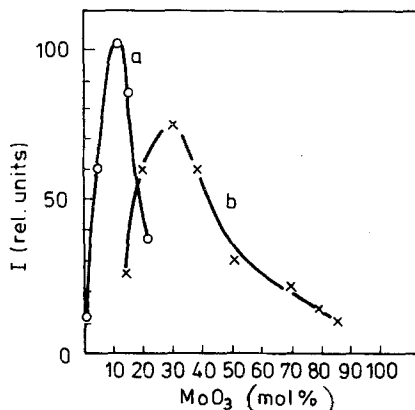


Fig. 2. Intensity of ESR signals a and b in relative units vs. the $\text{MoO}_3/\text{V}_2\text{O}_5$ ratio in the samples

The ESR spectra shown in Fig. 1 show a low-intensity singlet with a g -factor close to g_0 . This may be seen from the computer simulation of the lineshape. The appearance of this signal is probably the consequence of exchange interaction between noncorrelated spins of unpaired V^{4+} electrons located at the defect sites and primarily on the boundaries of microcrystallites.

The identity of the ESR parameters of the compound V_2MoO_8 [5] and of signal b permits to suppose that beyond the solubility limit of MoO_3 in V_2O_5 a compound of composition V_2MoO_8 is formed, which contains a significant number of defects. With increasing the MoO_3 content from 10 to 30 mol%, the content of V_2MoO_8 with an ordered defect structure also increases. This is supported by the unchanged signal shape of type b despite significant intensity variations. We attribute the defect structure to the stabilization of excess vanadium in the form of VO^{2+} in the interstitial positions of the V_2MoO_8 compound, the charge being compensated via the substitution of some of Mo^{6+} by V^{5+} ions.

If for the samples containing 30–40 mol% MoO_3 one assumes the distribution of excess vanadium in the interstitial positions (in the form of VO^{2+}) and the

substitution of V^{5+} by Mo^{6+} ions for charge compensation, then in this approximation the calculated number of paramagnetic centers (5%) is in good agreement with the experimental total vanadium content (7%).

The drop of signal intensity in the samples with MoO_3 contents above 30 mol% may be explained by the formation of low-defect V_2MoO_8 , which is confirmed by the appearance of the ESR spectrum of isolated ions of type II, coinciding with signal b.

The analysis of the parameters of ESR spectra II and b shows that, as compared to ions I and a, the axial component of the crystal field is insignificant. This case of coordination of the ions of type II and b is most probable for the interstitial positions in the compound V_2MoO_8 .

In addition, signals of type III and IV are detected for the samples with excess MoO_3 , probably as a result of VO^{2+} stabilization by residual decomposition products.

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