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# An ESR Study of Reduced $V_2O_5$ Catalyst on $\gamma\text{-Al}_2O_3$ Carrier<sup>†</sup>

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An electron spin resonance (ESR) study has been made with a number of reduced  $V_2O_5$  catalysts supported on  $\gamma\text{-Al}_2O_3$  with  $V_2O_5$  varying from 3.41 to 20.11 wt %. While the catalysts do not exhibit any ESR at 300 K, the spectra obtained at 109 K are characteristic of isolated  $V^{4+}$  or  $(V\cdots O)^{2+}$  species in a ligand field of axial symmetry provided by a distorted octahedron of oxygen ions. For  $V_2O_5$  contents equal to or in excess of 9.84%, the low-field parallel components of the axial ESR spectra show doublet structure, suggesting the presence of two chemically distinct  $V^{4+}$  species. The concentration of the second species attains a maximum when the  $V_2O_5$  content in the catalyst is 20.11%. The second weaker set of parallel components also due to  $V^{4+}$  probably arises from a relatively unstable intermediate whose ligands consist of adsorbed oxygens. The results are discussed in terms of the crystal structures of  $V_2O_5$  and  $\gamma\text{-Al}_2O_3$ .

## Introduction

The study of the mechanism of catalytic reactions requires detailed investigation of the active intermediates formed by transition-metal ions interacting with various molecules on the surface of a supported oxide catalyst. Electron spin resonance (ESR) offers a powerful and sensitive technique with which to investigate the oxidation states, surface and bulk coordination, and the physical form of a transition-metal oxide on a diamagnetic support.<sup>1</sup> The ESR technique has been applied to  $V_2O_5$  catalysts supported on  $SiO_2$ ,<sup>2-9</sup>  $Al_2O_3$ ,<sup>8-12</sup> and  $MgO$ <sup>13,14</sup> as well as  $MoO_3$ <sup>15,16</sup> and  $TiO_2$ <sup>17,18</sup> in order to obtain specific information about (i) the local structure surrounding  $V^{4+}$ , (ii) the difference in the microstructure arising from the distinct nature of the support, and (iii) the so-called "carrier effect" involving the support and active sites.<sup>19-21</sup> Results of such investigations enable definite conclusions to be drawn about the reactivity of  $V^{4+}$  with gaseous oxygen formed on the supported catalyst, which is the theme of the heterogeneous catalysis.

The  $V_2O_5/Al_2O_3$  catalyst has been used in a number of oxidation and ammoxidation reactions involving aromatic hydrocarbons<sup>22-24</sup> and also for the reduction of NO with  $NH_3$ .<sup>25-28</sup> In this paper the results of a detailed ESR study on various reduced  $V_2O_5$  catalysts supported on  $\gamma\text{-Al}_2O_3$  carrier are reported and discussed.

## Experimental Section

The unsupported  $V_2O_5$  was prepared by direct decomposition of ammonium metavanadate (SISCO, India) at 450 °C in air for 4 h.  $\gamma\text{-Al}_2O_3$  (ACC, India) with pore volume 0.4 cm<sup>3</sup> g<sup>-1</sup> and BET surface area 188 m<sup>2</sup> g<sup>-1</sup> was used as support. As received,  $\gamma\text{-Al}_2O_3$  was ground to 60-70-mesh particles.

Catalyst samples with different contents of  $V_2O_5$  were prepared by the wet impregnation method. Aqueous  $NH_4VO_3$  was added to  $\gamma\text{-Al}_2O_3$ , and the excess water was evaporated (365 K) on a hot plate. The impregnated samples were dried at 110 °C for 16 h and calcined at 500 °C for 4 h in air.

The samples used in the ESR study were prepared in glass tubes (25 cm long, 3-mm diameter) which formed part of the catalyst reduction apparatus. The reduction was carried out at 500 °C for 6 h in a continuous flow (35 cm<sup>3</sup>/min) of low-pressure hydrogen. The setup was subsequently evacuated at the same temperature for an hour, cooled to room temperature, and finally evacuated for an hour at 10<sup>-6</sup> torr. The catalyst thus prepared was transferred to the ESR sample tube and sealed off under vacuum.

The ESR spectra of reduced supported  $V_2O_5$  catalysts were recorded on a JEOL FE-3X X-band spectrometer (with 100-kHz modulation) at 109 K using the variable-temperature accessory.

The  $V_2O_5$  contents (Table I) in the catalysts were determined by atomic absorption spectrometry.

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<sup>†</sup> Forms part of the Ph.D. Thesis of K.V.R.C.

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TABLE I: Spin Hamiltonian Parameters of V<sup>4+</sup> in V<sub>2</sub>O<sub>5</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

V <sub>2</sub> O <sub>5</sub> content, wt %	color of catalyst	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ , G	$A_{\perp}$ , G	$K$ , cm <sup>-1</sup>	$\alpha^2$	parallel component		
								AM <sup>a</sup>	AS <sup>b</sup>	AM/AS
3.41	light green	1.940	2.000	194	71	0.0118	0.868			
6.96	light green	1.939	1.997	194	73	0.0119	0.847			
9.84	dark green	1.942	2.000	194	70	0.0118	0.876			
		1.983		175				20.00	7.75	2.60
11.89	light yellow	1.942	1.999	192	70	0.0117	0.857			
		1.983		170				20.25	6.25	3.25
13.64	dark yellow	1.938	1.995	194	71	0.0117	0.852			
		1.971		174				42.00	9.00	4.67
14.76	dark yellow	1.939	1.998	192	72	0.0118	0.843			
16.37	dark yellow	1.941	1.999	192	71	0.0117	0.852			
		1.977		175				20.00	6.00	3.33
18.46	dark yellow	1.939	1.999	193	71	0.0118	0.856			
		1.966		180				18.00	8.00	2.25
20.11	dark yellow	1.939	1.997	192	71	0.0117	0.846			
		1.960		180				31.50	5.25	6.00

<sup>a</sup> Area of main ( $m_I = -7/2$ ). <sup>b</sup> Area of satellite ( $m_I = -7/2$ ).

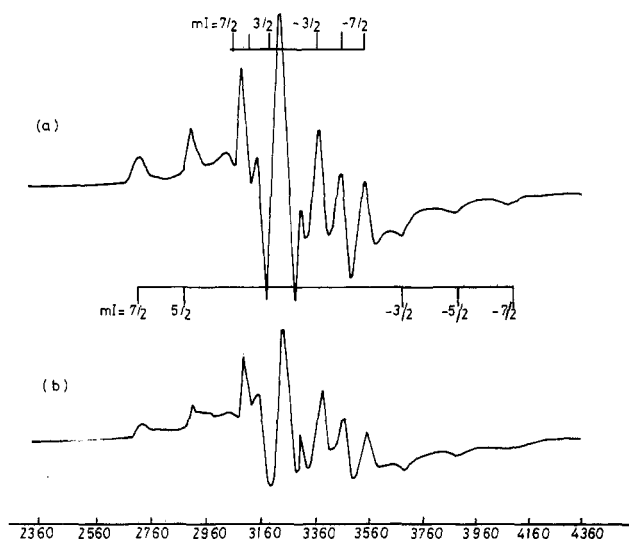


Figure 1. ESR spectra of reduced V<sub>2</sub>O<sub>5</sub> catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 109 K: (a) 3.41% V<sub>2</sub>O<sub>5</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) 18.46% V<sub>2</sub>O<sub>5</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

## Results and Discussion

Pure unsupported V<sub>2</sub>O<sub>5</sub> shows a singlet ESR spectrum at 300 K with a peak-to-peak width of 170 Oe, which reduces to 142 Oe at 109 K. However, upon reduction a very weak but hyperfine-resolved spectrum is obtained. Further, no ESR signal was detectable in the case of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The reduced V<sub>2</sub>O<sub>5</sub> catalysts stabilized on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier do not exhibit ESR spectra at 300 K. At 109 K, however, a well-resolved spectrum is obtained for all the catalysts studied. Figure 1 shows the typical spectra for two widely different concentrations of the catalyst. The absence of ESR at 300 K suggests that the spectrum represents V<sup>4+</sup> in a ligand field having axial symmetry such as would arise from a distorted octahedron or tetrahedron of oxygen ions surrounding a V<sup>4+</sup> ion. It is well-known that for both octahedral and tetrahedral ligand fields, there are excited states close to the ground state of V<sup>4+</sup>(d<sup>1</sup>), resulting in short spin-lattice relaxation times and undetectably broad ESR spectra at room temperature.<sup>29</sup> The tetragonal/trigonal distortion of the octahedron/tetrahedron usually responsible for the occurrence of the room-temperature ESR spectrum of V<sup>4+</sup> appears to be too small in the present case to permit its observation. Figure 1 which represents the spectrum for 18.46% V<sub>2</sub>O<sub>5</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst shows doublet structure in the outermost low-field components. This feature will be discussed later. The unpaired electron associated

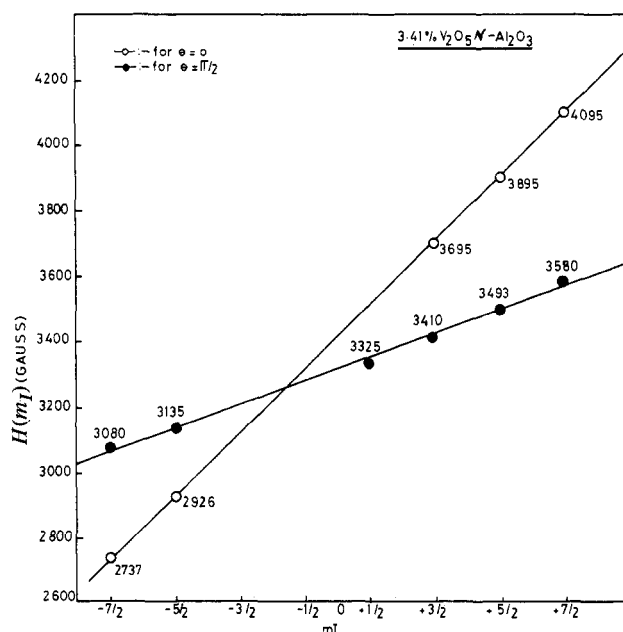


Figure 2. plots of  $H_{\parallel}(m_I)$  and  $H_{\perp}(m_I)$  vs.  $m_I$  to deduce  $g$  and  $A$  parameters (see text).

with V<sup>4+</sup>(3d<sup>1</sup>) interacts with the nuclear magnetic moment of <sup>51</sup>V ( $I = 7/2$ ) to give rise to eight parallel and eight perpendicular components in the ESR spectrum which may be described by the axially symmetric spin Hamiltonian<sup>30</sup>

$$\mathcal{H} = \beta g_{\parallel} H_z S_z + \beta g_{\perp} (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

where  $\beta$  is the Bohr magneton,  $g_{\parallel}$ ,  $A_{\parallel}$  and  $g_{\perp}$ ,  $A_{\perp}$  are the parallel and perpendicular components of the  $g$  and hyperfine coupling tensors, respectively. The observed ESR peaks are related to the  $2I + 1$  values of  $m_I$ , the nuclear magnetic quantum number, and their positions are given to the first order in energy by

$$H_{\parallel} = 2H_0^{\parallel}/g_{\parallel} - (A_{\parallel}/g_{\parallel}\beta)m_I \quad (2a)$$

$$H_{\perp} = 2H_0^{\perp}/g_{\perp} - (A_{\perp}/g_{\perp}\beta)m_I \quad (2b)$$

The linear relationship between  $H_{\parallel}$  (or  $H_{\perp}$ ) and  $m_I$  was utilized (Figure 2) to deduce the values of  $g_{\parallel}$ ,  $A_{\parallel}$ ,  $g_{\perp}$ , and  $A_{\perp}$ , which are presented in Table I. From the hyperfine coupling constants,  $A_{\parallel}$  and  $A_{\perp}$ , the isotropic constant term ( $K$ ) and the coefficient of

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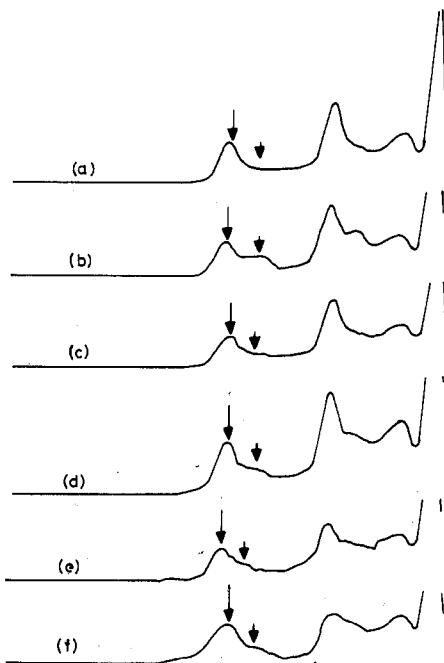


Figure 3. Evolution of the low-field ESR peaks as a function of  $V_2O_5$  content: (a) 6.96%, (b) 9.84%, (c) 11.89%, (d) 13.64%, (e) 16.37%, (f) 20.11%  $V_2O_5/\gamma-Al_2O_3$ . The lengths of the arrows indicate peak heights.

the  $V^{4+}$  ground state by the  $d_{xy}$  orbital are calculated by using the method outlined by McGarvey.<sup>31</sup> The  $\alpha^2$  values obtained (Table I) suggest that the unpaired electron is mostly confined to the metal d orbital. For  $VO^{2+}$  in  $Al_2O_3$ , Ueda<sup>21</sup> finds  $g_{\parallel} = 1.9490$ ,  $g_{\perp} = 1.9980$ ,  $A_{\parallel} = 158$ , and  $A_{\perp} = 63$  G. While  $g_{\parallel}$  of our catalysts are smaller than his, our  $A_{\parallel}$  values are greater, which suggests that we are dealing with a  $(V \cdots O)^{2+}$  species rather than  $VO^{2+}$ .

Figure 3 shows the evolution of the two outermost parallel components ( $m_I = -7/2, -5/2$ ) with an increase in the  $V_2O_5$  concentration in the catalyst. One could easily identify two sets of parallel components for the  $V_2O_5$  concentrations greater than or equal to 9.84%. As the "doublet structure" is rather well resolved, the peaks are analyzed for the area by resolving the two peaks by symmetrically removing the overlapping region. The  $g_{\parallel}$  and  $A_{\parallel}$  values for the second set of peaks (satellite) and the ratio of the area of the main peak to the satellite are included in Table I. It is interesting to compare the  $g_{\parallel}$  values for the main peaks with those for the satellite. The values for the satellite increase as the concentration decreases from the maximum value studied, namely 20.11%, and ultimately merges with the main peak at the lowest concentration of 3.41%. The area under the ESR absorption curve is a measure of the  $V^{4+}$  concentration, and thus the ratio of areas (Table I) represents the variation in the relative concentrations of the two chemically distinct  $V^{4+}$  ions in the catalyst. This ratio is maximum when the concentration of  $V_2O_5$  in the catalyst is 13.64%. The fact that  $g_{\parallel}$  is quite different for the two species suggests that the ligand field around the two  $V^{4+}$  species would be different. Interestingly, our  $g_{\parallel}$  and  $A_{\parallel}$  values resemble those of Inomata et al.<sup>18</sup> for  $V^{4+}$  in  $V_2O_5/Al_2O_3$  catalysts, suggesting that the satellite peaks represent  $V^{4+}$  ions formed on the catalyst surface.

Vanadium pentoxide catalyst is a redox system; i.e., the catalyst surface is both reduced and oxidized during the reactions. Thus, the catalyst is present in a reduced surface state. The orthorhombic crystal structure of  $V_2O_5$  is built up from distorted trigonal bipyramids with V—O<sub>5</sub> sharing edges to form zigzag chains along (001) (i.e.,  $c$  axis) and cross-linked chains along (100) (i.e.,  $a$  axis) through corner sharing, thus forming sheets in the  $ac$  plane (Figure 4).<sup>32</sup> The bulk has three different oxygen atoms, but

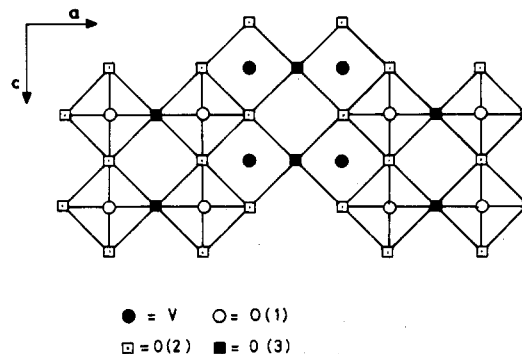


Figure 4. The schematic structure of  $V_2O_5$  in the  $ac$  plane with the  $VO_5$  polyhedra idealized to tetragonal pyramids. The O(1) oxygens forming the strongest bonds with V are shown as open circles.

all its V atoms are equivalent. From the catalytic point of view, however, it is the surface configuration that is of interest.

It is generally believed that for the  $V_2O_5$  catalyst for  $V=O$  bond connecting V with type 1 oxygen in the (010) (i.e.,  $ac$  plane) plane plays a significant role in catalytic oxidation reactions. In fact, two kinds of O(1) can be located on the catalytically active  $ac$  plane. The first type involves 50% of O(1) in the  $V-O(1)_I$  bond, 1.585 Å along with a strength of 1.93, while the second type is a much weaker  $V-O(1)_{II}$  bond, 2.785 Å, having a charge of 0.04 electron. However, in the present case, the observed ESR spectra cannot possibly arise from the bulk of  $V_2O_5$ . The absence of ESR spectra at 300 K just as in the case of  $V_2O_5/SiO_2$ <sup>33,34</sup> definitely indicates the important role played by the support ( $\gamma-Al_2O_3$ ) in stabilizing the active  $V^{4+}$  species on the surface of the catalyst at sites of square-planar and tetrahedral symmetry. According to Kazanskii,<sup>1</sup> the influence of the support becomes predominant when the catalyst concentrations are in excess of 1%. Thus, a consideration of the crystal structure of  $\gamma-Al_2O_3$ , in order to account for the observed ESR features in terms of the symmetry around  $V^{4+}$ , is in order.  $\gamma-Al_2O_3$  possesses the crystal structure of  $\gamma-Fe_2O_3$  which is a defect-ordered inverse spinel structure<sup>33</sup> with both oxygen vacancies and  $Al^{3+}$  in tetrahedral and octahedral sites and oxygen in only octahedral sites. Thus, the  $V^{4+}$  ions either could have the coordination of  $Al^{3+}$  or they could simply fill the octahedral and/or tetrahedral holes. While ionic-size consideration and preparative conditions make the direct replacement of  $Al^{3+}$  by  $V^{4+}$  rather difficult, the filling up of the octahedral and tetrahedral holes by the latter would be energetically more favorable. Thus, we could assign the two distinct sets of hyperfine peaks to  $V^{4+}$  occupying octahedral and tetrahedral vacant sites surrounded by oxygens in the  $\gamma-Al_2O_3$  lattice. Thus, on the surface of  $\gamma-Al_2O_3$  we could have  $V^{4+}$  dispersed uniformly as active sites with tetrahedral or square-pyramidal surroundings. However, the relative intensities of the two distinct spectra suggest that one type of sites—most probably octahedral—outnumber the other. Perhaps, there could be a dynamic equilibrium between the two, with the number of sites available for occupation depending upon the concentration of  $V_2O_5$  in the catalyst.

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