

## Structure of Monolayer Type Vanadium Pentoxide, Supported on $\gamma$ -Alumina

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### ABSTRACT

The structure of vanadium pentoxide supported on  $\gamma$ -alumina has been studied by high-resolution analytical microscopy and radial electron distribution (RED). The vanadium is found uniformly distributed over alumina. The interatomic distances obtained by RED indicate that the structure of vanadium pentoxide on alumina is different from bulk vanadium pentoxide. Its structure is described in terms of corner-sharing  $\text{VO}_4$  tetrahedra forming a flexible two dimensional array over the alumina surface.

### INTRODUCTION

A number of investigations have been devoted to the characterization of transition metal oxides such as vanadium pentoxide, molybdenum trioxide and tungsten trioxide spread over the surface of oxide supports. The supported oxides do not form three-dimensional crystal phases but rather patchy or continuous "monolayers" covering the support. Thus, vanadium pentoxide supported on  $\gamma$ -alumina has been studied by various techniques such as Raman [1, 2], IR [3, 4] and electron spin resonance spectroscopy [3, 5], temperature-programmed reduction (TPR) [1], and low-temperature oxygen chemisorption [5]. All these techniques suggest that the structure of vanadium pentoxide supported on alumina is different from that of bulk vanadium pentoxide provided the concentration of vanadium pentoxide is less than ca. 5 mole% on a high-surface ( $200\text{--}250\text{ m}^2\text{ g}^{-1}$ ) porous alumina. However, the precise structure of the so-called monolayer is still under debate. Kozlowski et al. [6] have con-

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cluded from an extended X-ray absorption fine structure (EXAFS) study of vanadium pentoxide supported on  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ , that vanadium is in a distorted tetrahedral coordination with two shorter bonds. However, the double bond character is less pronounced and the disorder is higher on vanadium pentoxide/alumina than on vanadium pentoxide/titania.

A tetrahedral coordination of vanadium at low vanadium pentoxide content was also invoked by Roozeboom et al. [1] on the basis of TPR data and by Inomata et al. [3]. The important point as far as catalysis is concerned is that V=O bonds which play a role in selective, mild-oxidation reactions [2, 7-9] depend upon the linkage of tetrahedrally coordinated vanadium.

The aim of this paper is to study the structure of vanadium pentoxide wetting the alumina surface. High-resolution analytical microscopy has been used to check the homogeneity of the vanadium pentoxide distribution on alumina and the radial electron distribution (RED) technique was applied to describe the coordination of vanadium.

## EXPERIMENTAL

Vanadium pentoxide supported on alumina was prepared by impregnating  $\gamma$ -alumina ( $180 \text{ m}^2 \text{ g}^{-1}$ ) with an aqueous solution of ammonium metavanadate and evaporating to near dryness as described previously [5]. The resulting paste was dried at  $110^\circ\text{C}$  and calcined in air at  $500^\circ\text{C}$  for 4 h. The vanadium pentoxide content of the final catalyst was 9.8 wt.-% and the BET area was  $173 \text{ m}^2 \text{ g}^{-1}$ .

The catalyst was analyzed by X-ray emission spectroscopy in dispersive mode (EDX) using a LINK (Si-Li) detector and a Tracor 5500 analyser. The detector was in the column of a scanning transmission electron microscope (STEM) equipped with a field-emission gun (FEG) (Vacuum Generator HB 501). The spatial resolution of EDX analysis was  $1 \times 1 \text{ nm}^2$ , a routine quantitative analysis gives the elemental ratio V/Al with an accuracy better than 5%.

The structure of vanadium pentoxide was studied by the radial electron distribution technique which is described in review papers [10, 11]. Let us recall that the Fourier transform of X-ray scattering data collected with a conventional diffractometer in a large domain of reciprocal space (1-140  $2\theta$  Bragg angle with Mo  $K\alpha$  wavelength) gives the distribution of interatomic distances present in the solid. The distribution of distances in vanadium pentoxide is obtained by subtracting the RED of the support from the RED of vanadium pentoxide/alumina.

## RESULTS AND DISCUSSION

A preliminary examination of vanadium pentoxide/alumina by conventional transmission electron microscopy (CTEM) was carried out to check the

absence of vanadium pentoxide particles on alumina. TEM photographs give the same images as for pure alumina with no extra-contrast which would indicate the presence of a crystalline vanadium pentoxide phase. However these observations do not rule out the possible presence of oxide clusters smaller than 1 nm which would escape detection. Therefore CTEM indicates that vanadium pentoxide is highly dispersed on the support but it does not tell us in which form it is dispersed.

The EDX analysis coupled with the FEG-STEM was performed to confirm the homogeneous dispersion of the vanadium on alumina. Different parts of the alumina support were examined with different analysis windows (scanned areas). Thus on a given alumina particle the analysis window was zoomed from  $10^2 \times 10^2 \text{ nm}^2$  to  $1 \times 1 \text{ nm}^2$ ; the smallest area was probed in spot mode, i.e. with the 0.5 nm diameter electron beam stopped on a given point of the sample.

About a hundred spectra were recorded from which V/Al ratios and vanadium pentoxide percentages were computed. All the measurements are within 8–12 wt.-% vanadium pentoxide. This is a narrow distribution given the difference of thickness of the alumina support at different places. However the values would be much more scattered if the alumina support was not porous and if the vanadium had not spread into the pores. Then thicker alumina parts would give very low V/Al ratios.

To sum up, conventional and analytical microscopy suggest that the vanadium is uniformly distributed over the surface of the alumina, like a skin even along the pore walls. This agrees with all previous reports [1–6] that concluded that monolayer-type vanadium pentoxide is formed over alumina. The structure of this monolayer has been solved by RED.

The RED of pure alumina was subtracted from the RED of vanadium pentoxide/alumina, and the resulting distribution given in Fig. 1a exhibits the interatomic distances in vanadium pentoxide/alumina which are not present in alumina, i.e. essentially the coordination of vanadium. Note that the V–Al distances should also be present but they are weighted less than the V–V distances because peak intensity is proportional to the product of the atomic numbers.

The experimental distribution can be compared to a radial distribution calculated from the known structure of vanadium pentoxide [12] using the program RADMOR [13] (Fig. 1b). The peaks on the calculated distribution are broadened with a gaussian profile to be more easily compared with the experimental distribution. The calculated distribution exhibits the characteristic distances of the vanadium pentoxide structure [12] thus the 1.87 and 2.82 Å peaks are the mean V–O and O–O distances in the  $\text{VO}_5$  square pyramid which is the building block of the vanadium pentoxide crystal. The 3.01 and 3.52 Å peaks are the two nearest V–V distances in the (010) plane: the former between vanadium in edge-sharing pyramids and the latter between vanadium in corner-sharing pyramids. The peak at 3.95 Å is the average distance between a vanadium atom and oxygen atoms belonging to two different  $\text{VO}_5$  pyramids.

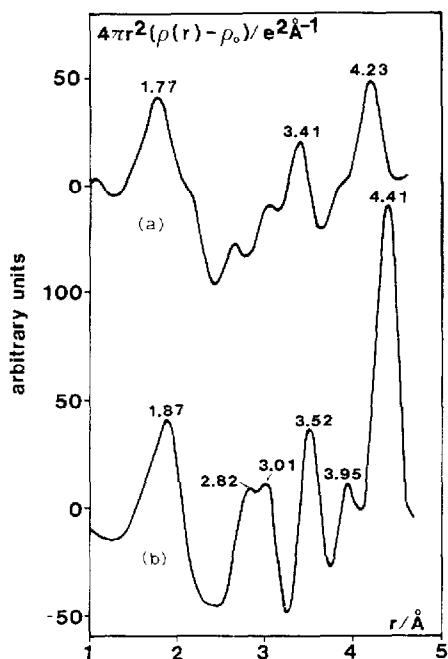


Fig. 1. (a) RED of vanadium pentoxide/alumina. The RED of pure alumina has been subtracted. (b) RED of vanadium pentoxide calculated from single crystal data [12].

Finally the 4.41 Å peak is the average distance separating nearest vanadium atoms in two superimposed (010) planes, i.e. it is characteristic of the piling of layers in the vanadium pentoxide crystal.

The RED of vanadium pentoxide given in Fig. 1a differs markedly from that of bulk vanadium pentoxide (Fig. 1b) since it does not exhibit the 3.01 and 3.52 Å distances characteristic of the arrangement in the (010) plane nor the 4.41 Å distance characteristic of the stacking of (010) planes. Furthermore, the coordination polyhedron of vanadium is no longer the square pyramid since both the V–O and the O–O distances contract from 1.87 to 1.77 Å and from 2.82 to 2.64 Å, respectively.

Putting together all the modifications of the RED mentioned above, it can be concluded that vanadium pentoxide spreading over alumina does not have the same building blocks and the same linkages between building blocks as in bulk vanadium pentoxide. Instead the distribution of distances is very similar to that found by Mosset et al. [14] for amorphous vanadium pentoxide prepared by ultrafast quenching from a melt. According to these authors the structure of amorphous vanadium pentoxide is based on  $\text{VO}_4$  tetrahedra sharing corners as shown in Fig. 2 where two tetrahedra forming the basic unit are represented with a third tetrahedron. The dotted line indicates the bonding with other tetrahedra; note that each tetrahedron is bonded to only three

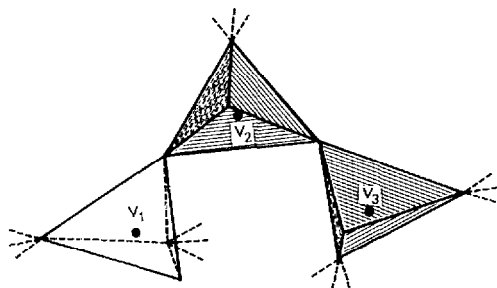


Fig. 2. Proposed structure of the so-called monolayer of vanadium pentoxide on alumina. Mean distances:  $V-O = 1.77 \text{ \AA}$ ,  $V_1-V_2 = 3.41 \text{ \AA}$ ,  $V_1-V_3 = 4.23 \text{ \AA}$  (each tetrahedron is connected to three other tetrahedra).

neighbours. This arrangement accounts for all the features observed on the distribution of vanadium pentoxide/alumina (Fig. 1a). Indeed, the first peak at  $1.77 \text{ \AA}$  is similar to the  $1.75 \text{ \AA}$  peak found in amorphous vanadium pentoxide [14] as well as in vanadium pentoxide melt [15], and is characteristic of tetrahedrally coordinated vanadium. The second main peak at  $3.41 \text{ \AA}$  is also very similar to the  $3.45 \text{ \AA}$  peak found on amorphous vanadium pentoxide and can be attributed to  $V-V$  distances in two corner sharing tetrahedra. Finally the third main peak at  $4.23 \text{ \AA}$  corresponds to the distance between vanadium atoms in second nearest neighbour tetrahedra.

From the analogy between the RED of amorphous vanadium pentoxide and of vanadium pentoxide spreading over alumina, we conclude that in the latter case, the corner sharing  $VO_4$  tetrahedra form interconnected chains resulting in a two-dimensional array. This arrangement is very flexible and can easily cover the tortuous surface of  $\gamma$ -alumina. As described by Mosset et al. [14] the change from amorphous to crystalline vanadium pentoxide could be relatively easy. Furthermore in  $K_2V_3O_8$  [16] the basic unit of vanadium pentoxide, namely the square pyramid, coexists with the basic unit of amorphous vanadium pentoxide, namely two corner-sharing tetrahedra.

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