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The Structure and Redox Properties of Vanadium Oxide Surface Compounds

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The redox properties of V—O layers supported on TiO_2, Al_2O_3, and SiO_2 have been examined and discussed in terms of structural models. On this basis monodispersed VO_4 units are postulated on the (001) plane of anatase (TiO_2), located at the cationic sites with two terminal and two bridging oxygens, one of the latter being removed on reduction. Dimeric, pyrovanadate-type species seem to be predominantly formed on γ-Al_2O_3, whereas grains of poorly crystalline V_2O_5 are observed on SiO_2. The structure of the vanadium–oxygen species determines the number of oxygens which can be removed per V atom.

INTRODUCTION

V_2O_5 supported on various oxide carriers is widely used as a catalyst in many different oxidation processes. Use of the appropriate carrier enables modification of the catalytic properties of the system to make it more selective in a given reaction. In particular, V_2O_5 supported on the anatase modification of TiO_2 is a catalyst of considerable commercial importance; for instance, the presence of anatase increases the selectivity of the oxidation of *o*-xylene to phthalic anhydride.

There have been several studies of the solid state chemistry of this system aimed at establishing the mode of interaction between the two components (*1–4*). It has been observed that the maximal yields and selectivities in *o*-xylene oxidation coincide with the composition 10–15 mole% V_2O_5 for which there is maximum contact between the components of the system (*1, 2*). Vejux and Courtine (*3*) pointed to a considerable match between the surface structure of the V_2O_5 plane (010) and the predominant morphological planes of the anatase support. This effect may give rise to an epitaxial growth of V_2O_5 in the form of platelets with increased exposure of the (010) plane. Gąsior and Machej (*4*) found a remarkable correlation between the abundance of the (010) plane in the V_2O_5 habit and the selectivity of V_2O_5 toward phthalic anhydride in *o*-xylene oxidation. They have also shown that the presence of faces other than (010) brings about the unselective total combustion of the hydrocarbon.

In line with these observations it has been shown that a thin layer of pentavalent vanadium oxide laid down in coherent contact with the support makes a remarkably selective and active catalyst for selective oxidation of *o*-xylene (*5, 6*). It seemed obvious that the structure of the layer must be different from that of the external faces of V_2O_5 and that the epitaxial model based on the bulk V_2O_5–anatase interaction cannot account for the superior catalytic properties of the monolayer systems. On the other hand, the phenomenon of wetting of anatase by V_2O_5 was recently described (*7*), in which vanadium oxides spread over the anatase grains, forming a thin surface layer. XPS analysis revealed that this layer is composed of two types of vanadium ions: there are those constituting the inner layer, which are linked directly to the TiO_2 sur-

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face, their electronic properties being strongly modified by the interaction with the support, and those forming the outer layer with properties resembling V_2O_5.

The structure of the vanadium oxide monolayer on γ-Al_2O_3 and TiO_2 was studied by Roozeboom *et al.* (*8, 9*) and Wachs *et al.* (*10*) with the use of Raman spectroscopy. Roozeboom *et al.* conclude from a comparison with the spectral data of VO_4^{3-} and $[V_{10}O_{28}]^{6-}$ ions as well as V_2O_5 that three types of species may be present at the surface, namely monomeric vanadate tetrahedra, two-dimensional polymeric octahedral clusters and V_2O_5. Wachs *et al.* ascribe a broad Raman feature to the disordered surface phase of vanadia. When the concentration of vanadium and the heating temperature increase, a well-defined spectrum of V_2O_5 appears.

The Raman data described are conclusive only in the respect that they point to a lack of the V_2O_5 crystallites in the monolayer systems. As to the attempts to assign definite types of coordination to the different surface structures, basing on single broad Raman features, they seem rather unconvincing due to the very irregular coordinations of vanadium with oxygen. To label, for example, the coordination of V in $[V_{10}O_{28}]^{6-}$ (*11*) as "octahedral," rather than "pyramidal" or "tetrahedral," is an arbitrary decision based on whether one includes or not the very long V—O bonds in the coordination sphere of vanadium.

In previous work (*12*) EXAFS characterization of vanadium oxide supported on titania (anatase) and γ-Al_2O_3 was reported, and this gave more detailed information on the bond lengths and coordination numbers of vanadium–oxygen surface compounds. It has been shown that supported layers of vanadium oxide are composed of isolated species of the vanadate type individually attached to a support surface. The basic structural unit, when supported on anatase, has two terminal (r = 1.65 Å) and two bridging (r = 1.90 Å) V—O bonds. When supported on γ-Al_2O_3, it also exhibits two terminal (r = 1.67 Å) and two bridging (1.82 Å) V—O bonds, the latter being shorter than for the TiO_2-supported phase. The disorder of the local structure appears to be larger with γ-Al_2O_3 than with the anatase support.

Roozeboom *et al.* investigated also the reducibility of the supported vanadia layers using TPR and TGA methods (*9, 13*). Since the redox properties of the V—O layers supported on TiO_2, Al_2O_3, and SiO_2 have also been examined in this report and discussed in terms of the structural models, we describe their data in detail later.

In this and previous studies we used an ultrafine anatase of surface area exceeding 100 m^2/g in order to increase the concentration of vanadium to a level which enables structural and redox studies to be made. The results of Bond and Brückman (*5*) as well as our own data clearly demonstrate that an increase in the surface area of the support leads to a decrease in the selectivity to phthalic anhydride, these catalysts being very active in the total oxidation of hydrocarbons to carbon oxides. This may be accounted for by changes in heat and mass transport properties of the system with growing dispersion. It has been found, however, that the structure of anatase does not change when the average grain size decreases (*14*). Thus we believe that structural models derived from the studies of ultrafine preparations may be at least useful in understanding the structure and properties of V—O layers in the real low-surface-area catalysts.

EXPERIMENTAL

1. *Materials*

Three materials were used as supports for vanadia: TiO_2, Al_2O_3, and SiO_2. The ultrafine anatase was prepared by hydrolysis of titanium(IV) butoxide in water giving a preparation of surface area 120 m^2/g. The γ-Al_2O_3 and SiO_2 were obtained from Degussa and were characterized by surface areas of 80 and 160 m^2/g, respectively. $VOCl_3$

TABLE 1

Surface Areas, Chemical Compositions, and Reducibility of Catalysts

Support	Surface coverage as a fraction of V—O monolayer	V content (mole × 10^{-3} g^{-1})	BET surface area (m^2 g^{-1})	Average surface coverage (V atoms nm^{-2})	Number of oxygens remover per V on reduction[a]
TiO_2	1	1.46	106	8.3	0.90
	0.6	1.03	127	4.9	0.85
	0.4	0.57	106	3.3	0.88
	0.15	0.22	105	1.3	0.88
γ-Al_2O_3	1	1.09	70	9.4	0.64
	0.8	0.96	75	7.7	0.59
	0.3	0.40	80	3.0	0.49
	0.15	0.18	83	1.3	0.51
SiO_2	1	1.34	165	4.9	0.54
	0.6	0.63	130	2.9	0.56
	0.15	0.22	159	0.8	0.56
	0.1	0.12	161	0.4	0.54

[a] In 200 Torr of H_2 at 400°C.

(reagent grade) from Ventron was used to produce the active phase.

2. *Catalyst Preparation*

An appropriate amount of $VOCl_3$ dissolved in CCl_4 under water-free conditions was added to a support suspended in CCl_4. Reaction with surface hydroxyls is visually apparent because the powder becomes orange and HCl appears in the gas phase. CCl_4 was then distilled off and the solid was dried on a water bath. The samples were then heated at 350°C for 5 h.

In order to obtain samples with a saturation coverage of the supports with vanadium, the reaction of $VOCl_3$ was carried out in an increasing excess of the reagent in respect to the OH concentration. It was found that the constant amount of vanadium was stabilized on the surface at the saturation coverage irrespectively of how much total vanadium was present in the solution. This amount was assumed to represent the monolayer coverage.

The following notation will be used to denote the samples: XmV-S, where X represents the surface coverage of the support with vanadium expressed in monolayers, and S represents the type of support; for example, 0.5mV-Ti describes a sample of anatase containing 0.5 monolayer of vanadium ions, and 1mV-Al a sample of γ-Al_2O_3 containing 1 monolayer of vanadium ions.

3. *Chemical Analysis*

To determine the vanadium content each sample was treated with hot H_2SO_4 diluted with water (1 : 4) and stirred for about 15 min. Samples containing TiO_2 were heated first in concentrated H_2SO_4 and then diluted with water. Under these conditions all vanadium was dissolved and was potentiometrically titrated with standardized Fe(II) solution. Surface areas were calculated from argon adsorption isotherms using the BET equation. Chemical compositions and surface areas of the samples studied are given in Table 1.

4. *Reduction–Oxidation studies*

Reduction–oxidation cycles were followed by monitoring mass changes of a sam-

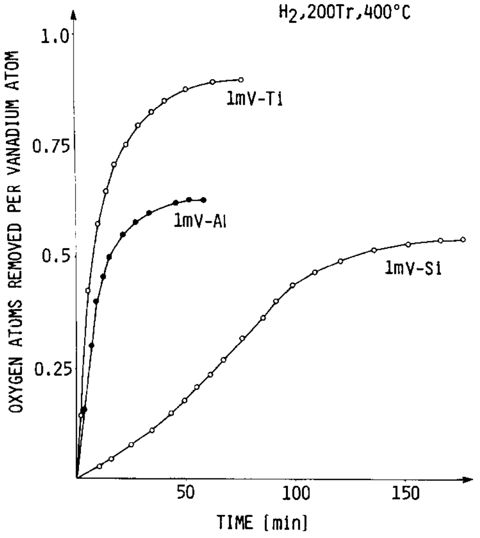


FIG. 1. Amount of oxygen removed from the monolayer samples as a function of time of reduction with H_2 at 400°C.

ple with the use of a Sartorius vacuum microbalance. The standard pretreatment of samples (0.1 g) prior to the reduction involved the evacuation at the temperature of the reduction for 1 h followed by oxidation in pure O_2 and subsequent degassing for 20 min.

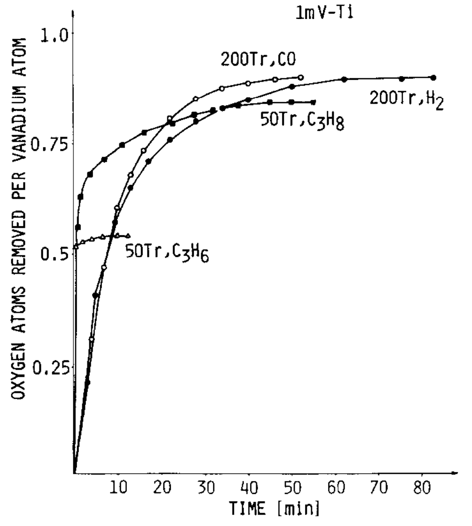


FIG. 2. Amount of oxygen removed from the 1mV-Ti sample as function of time of reduction at 400°C with H_2, CO, propane, and propylene.

The reducing agents were H_2,CO, propane, and olefins. In the first step of a cycle the sample was reduced by exposure to 200 Torr of the reducing gas for a period of time required to attain a constant mass of the sample. After completing the reduction the sample was degassed and oxidized in 50 Torr of pure oxygen.

5. *EXAFS*

EXAFS spectra were recorded in the absorption mode on the DORIS storage ring at HASYLAB, Hamburg. The specimen preparation and the crude data analysis have been described in detail in Ref. (*14*).

RESULTS AND DISCUSSION

1. *Reduction and Oxidation*

The pure supports TiO_2, SiO_2, and γ-Al_2O_3 when treated in any of the reducing agents do not undergo any reduction. Figure 1 shows the course of reduction of 1mV-Ti, 1mV-Al, and 1mV-Si samples in 200 Torr of hydrogen at 400°C. The degree of reduction is expressed in terms of the number of oxygen atoms removed per one vanadium atom present in the sample. The V—O polyhedra supported on different carriers show a very characteristic reactivity. The vanadia monolayer on anatase gives off stoichiometrically one oxygen atom for each vanadium polyhedron, whereas in the case of vanadium oxides supported on γ-Al_2O_3 and SiO_2 only about 0.5 oxygen atom per vanadium ion can be removed on reduction.

The number of oxygen atoms which can be removed from each V—O polyhedron is independent of the reducing agent. This is illustrated in Fig. 2 in which the number of oxygen atoms removed per vanadium ion in the 1 mV-Ti sample is plotted as function of the time for reductions with H_2, CO, propane, and propylene. In all cases except propylene the reduction stops after the same amount of oxygen has been removed from the layer.

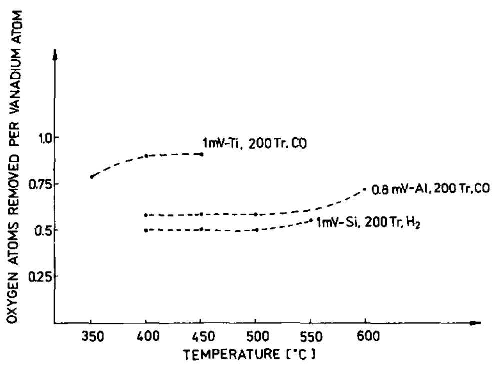


FIG. 3. Total amount of oxygen removed from 1mV-Ti, 0.8mV-Al, and 1mV-Si preparations on reduction in CO or H_2 at different temperatures.

The reduction in propene is accompanied by an extensive irreversible adsorption of the olefin itself and its oxidation products in the form of a coke deposit and/or hydrocarbon polymers. This renders the weight method unsuitable for the determination of the degree of reduction. When, however, CO or H_2 is admitted to a sample prereduced already in the olefin, no further reduction is observed. This proves indirectly that the level of reduction by the olefin is the same as that characteristic of H_2 or CO. When the samples were reduced in *o*-xylene the adsorption and polymerization of the hydrocarbon was even larger, rendering any assessment of the final degree of reduction impossible.

Figure 3 shows the total amount of oxygen removed from 1mV-Tr, 0.8mV-Al, and 1mV-Si preparations on reduction in CO or H_2 at different temperatures, ranging from 350 to 600°C. At temperatures lower than 350°C reduction is slow and even after a very long time a constant level is not yet attained. At higher temperatures the removal of oxygen stops after nearly one oxygen atom has been removed from each V—O polyhedron supported on anatase, but already after about 0.5 oxygen atom has been taken away per vanadium ion when they are supported on γ-Al_2O_3 and SiO_2.

The vanadia monolayer on titania is unstable above 450°C since the support shrinks and the system transforms to a physical mixture of the crystalline TiO_2 and V_2O_5, as has been assessed by X-ray diffraction and surface area measurements. The reduction of the layer could not thus be performed at temperatures exceeding 450°C. It has been checked by X-ray diffraction that the V—O layers on γ-Al_2O_3 and SiO_2 are stable when heated even to 600°C.

The results illustrated in Fig. 3, however, clearly indicate that for temperatures higher than about 400°C and within the temperature range of sample stability there exists a wide range of temperatures in which the final degree of reduction is constant and may be considered as an intrinsic property of the solid in question, characterizing a certain definite state of the system.

There are also distinct differences in the kinetics of the reduction depending on the support used (cf. Fig. 1). The process is fastest for TiO_2, only a little slower for γ-Al_2O_3 and considerably slower for SiO_2. No reduction of V-Si samples was observed in CO. The reduction in propane is very fast for TiO_2 and γ-Al_2O_3, and 400°C the process being completed in less than 10 s. It is much slower for SiO_2 and 15 min were necessary to attain the final degree of reduction.

The reoxidation is fast and complete already at low temperature and the redox cycles described may be repeated many times without any noticeable decrease in the amount of oxygen removed, as is illustrated in Fig. 4 for the case of 1mV-Ti catalyst.

It is noteworthy that the number of oxygen atoms which can be removed from each V—O polyhedron is independent of the surface coverage of the carrier with vanadium ions. This is shown in Table 1 and Fig. 5 in which the number of oxygen atoms removed per vanadium ion is plotted as a function of the time of reduction for samples of TiO_2 and SiO_2 containing different loadings of vanadium. The fact that the amounts of oxygen removed from partially covered supports are exactly proportional

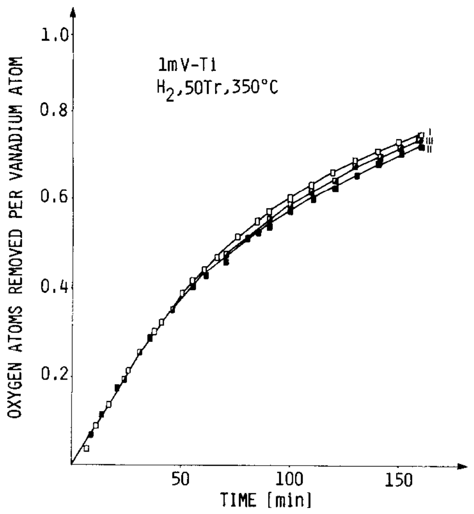


FIG. 4. Amount of oxygen removed on reduction at 350°C in H_2 from the 1mV-Ti sample in consecutive runs followed each time by reoxidation.

to the amount of vanadium present indicates that it is only the V—O species which become reduced.

The earlier EXAFS results for V—O monolayers on TiO_2 and γ-Al_2O_3 show that vanadium–oxygen units are dispersed on the surface structure of a support and that they do not form any three-dimensional particles. The reduction–oxidation study reveals now the composition of these units. The divanadate seems to be formed on γ-Al_2O_3 since the removal of 1 oxygen per 2 V atoms is consistent with the simplest reduction stoichiometry for a dimeric group. Along the same line of argument the monovanadate species should predominate on titania, since the removal of 1 oxygen per 1 V atom would be the simplest possible reduction of a monomeric group. In the case of SiO_2 the EXAFS analysis described later in this paper points to the existence of grains illustrated later in this paper points to the existence of grains of ill-defined V_2O_5 on its surface. The reduction stoichiometry must thus be related to a bulk V—O phase rather than to isolated surface species.

The results of a thermogravimetric study performed by Roozeboom *et al.* (*13*) for vanadia supported on TiO_2, ZrO_2, CeO_2, and γ-Al_2O_3 using H_2 as reducing agent are consistent with our data. The weight changes show that vanadium is reduced to the trivalent state for TiO_2, ZrO_2, and CeO_2 and to the quadrivalent state for γ-Al_2O_3, which corresponds to the removal of 1 and 0.5 oxygen per vanadium, respectively. However, different results were obtained by Roozeboom *et al.* (*9*) with the temperature-programmed reduction (TPR) method. Thus, when the Al_2O_3-supported sample was reduced in H_2 and the amount of H_2 consumed was determined, it turned out that it corresponded roughly to the reduction of V^{5+} to V^{3+}, i.e., to the removal of approximately 1 oxygen per 1 vanadium.

To elucidate this point we determined the average oxidation state of vanadium in 0.8 mV-Al samples prereduced in CO and H_2, using pulsed titrations with O_2, thereby reoxidizing the ion back to the pentavalent state. It turned out that the amount of oxygen consumed is consistently 1.5 times higher after the reduction in H_2 than after the reduction in CO. This seems to indicate that for each oxygen removed one hydrogen atom remains bound to the reduced site leading probably to the formation of a hydroxyl group.

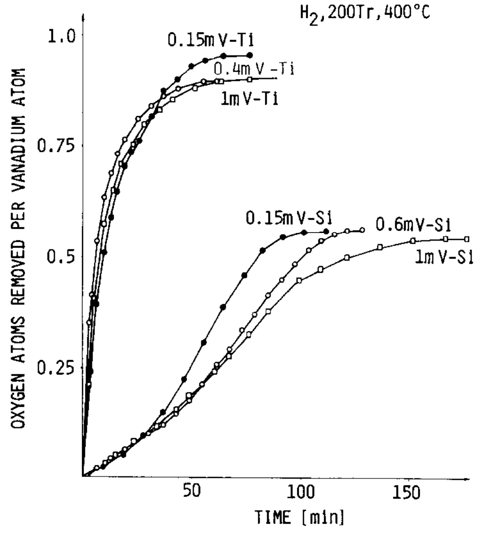


FIG. 5. Amount of oxygen removed on reduction at 400°C in H_2 from the samples of TiO_2 and SiO_2 containing varying loadings of vanadium.

These results have a more general significance, directly bearing upon the interpretation of the data obtained by the TPR method. For instance, in the TPR experiments it is generally assumed that the stoichiometry of the reaction can be described by a simple equation:

$$M^{+m}O_{m/2} + R \rightarrow M^{+m-2}\,O_{m/2-1} + RO$$

the amount of the reducing agent R consumed being a direct measure of the amount of oxygen removed from the oxide. This is indeed usually the case when CO is used as the reducing agent:

$$M^{+m}\,O_{m/2} + CO \rightarrow M^{+m-2}\,O_{m/2-1} + CO_2$$

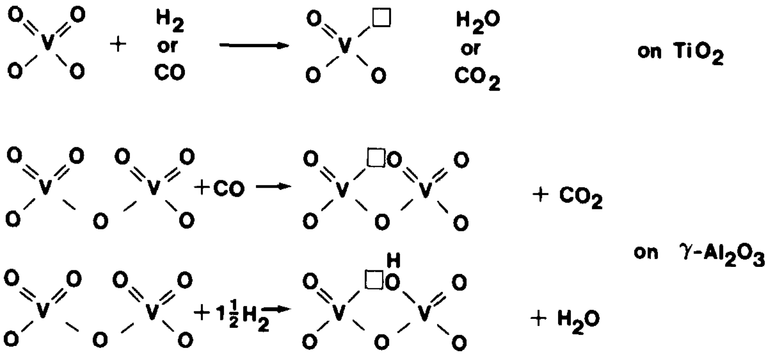
When, however, hydrogen is used, removal of oxygen may be sometimes followed by the chemisorption of hydrogen on the reduced sites, the resulting stoichiometry depending on the amounts of oxygen removed and hydrogen chemisorbed. When one hydrogen atom is used to remove oxygen and another one becomes attached to a site the process may be described by the equation

$$M^{+m}\,O_{m/2} + H_2 \rightarrow M^{+m-2}\,O_{m/2\,-\,1/2}\,H + 1/2\;H_2O$$

In our experiments we have found that 1.5 molecules of hydrogen as compared to one molecule of CO react per 2 vanadium ions. The straightforward explanation of these facts is to assume that dimeric vanadate units prevail at the surface, one oxygen per unit being removed on reduction and one hydrogen atom remaining chemisorbed.

The mass change due to the chemisorption of hydrogen is so small compared to the total mass change resulting from the reduction that the effect could not be detected by the gravimetric method, which accounts for the apparent discrepancy between the volumetric and gravimetric methods. The results for other systems, the detailed description of the experiments and the discussion of the nature of hydroxyl groups formed will be reported in a forthcoming paper (*15*).

It may thus be concluded that the reduction stoichiometry observed in the case of systems containing isolated V—O surface units permits conclusions to be drawn on the composition of these units. On the basis of the results discussed above one may postulate following schemes of the reduction:



We will attempt to substantiate this hypothesis by examining the surface structures of TiO_2 and γ-Al_2O_3 and the way they can attach mono- or divanadate groups of the structure determined with EXAFS. We shall show as well that the reduction data must be interpreted with caution since they may be similar for systems containing dispersed or bulk V—O phase.

2. *Structure of V—O Surface Sites*

a. TiO_2. The bulk structure of anatase is built up of TiO_6 octahedra edge-linked to form zig-zag ribbons running in *a* and *b* di-

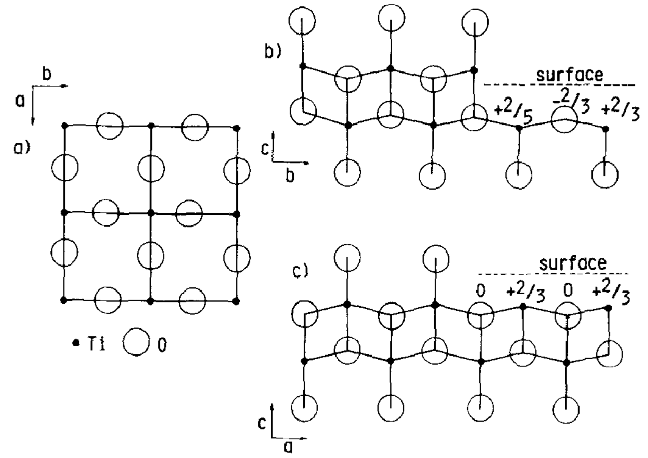


FIG. 6. The anatase structure projected on (a) (001), (b) (100), (c) (010), planes.

rections at different levels and coupled together in such a way that each O^{2-} ion has three Ti^{4+} neighbors. Boehm (*16*) advanced a simple structural model of the anatase surface. A clean (001) plane should contain unsaturated Ti^{4+} ions with one O^{2-} missing in their coordination and two types of O^{2-} bridging ions with half of the oxygens coordinating three Ti^{4+} and half bridging just two Ti^{4+} with the third Ti^{4+} missing (Fig. 6). Formally, therefore, the unbalanced charges would be +2/3 on Ti^{4+} and −2/3 on an unsaturated oxygen. A decrease of local charges could be achieved by dissociative chemisorption of water with a proton going to oxygen and a hydroxyl group being attached to Ti^{4+}. The resulting formal charges would be +1/3 and −1/3, respectively (Fig. 7); thus, the hydroxylation of the TiO_2 surface with two types of OH groups should be favored. Analogous deductions can be advanced for the other morphological planes of TiO_2 crystals.

The proposed model was fully confirmed by NMR (*17*). The OH groups occupy two different sites (Fig. 7). The (001) plane is the most prevalent. The water molecules are bound to every second "positive" OH group. The hydroxyl density on the fully hydrated (001) plane of titania should be about 14 OH/nm^2. A lower value of the OH density of 9.3 was found with NMR.

The amount of vanadium which can be bound to the surface was found to be 8 V/nm^2 (Table 1). The earlier assessments, based on a cross-sectional area of a simple V_2O_5 "molecule" in crystalline V_2O_5 lead to a higher value of 10 V/nm^2.

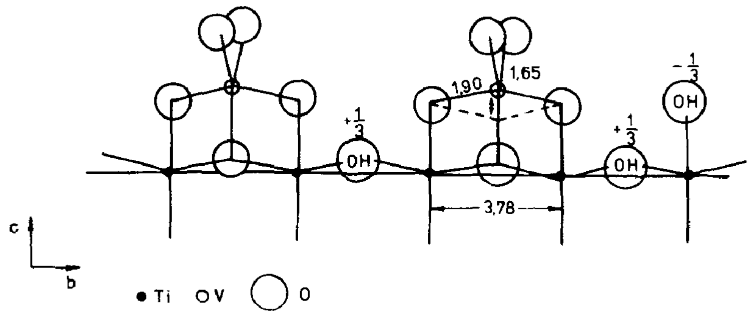


FIG. 7. VO_4 polyhedra located on the (001) plane of the anatase surface.

As to the geometry of the V—O species formed on the (001) plane of anatase, the simplest model would involve bonding of vanadium–oxygen ions to the surface through esterification with three hydroxyls as shown in Fig. 7. Vanadium would in this case occupy roughly a position which another Ti^{4+} would occupy, had the bulk structure continued. This should bring about almost perfect balance of the local charges rendering the vanadium complex particularly stable.

The EXAFS and XANES results seem to support this model. XANES, which is sensitive both to bond angles and lengths, is characteristic of distorted coordination with two kinds of bonds. V—O bridging bonds of 1.90 Å (±0.05 Å) established with EXAFS are very close to those of 1.93 Å found for crystalline anatase (Fig. 7). Moreover, one can suspect that the characteristic distortion of the TiO_6 octahedron in the bulk structure may not be present at the relaxed surface layer. In this case a linear O—V—O (2 × 1.90 Å) configuration will exactly match the Ti—Ti distance of 3.78 Å characteristic of the anatase. It was postulated in the EXAFS work that an additional oxygen may be coordinated by vanadium but which is not seen by EXAFS because of the high degree of disorder. This might be the bridging Ti—O—Ti oxygen and the disorder observed may be due to an enhanced vibration of vanadium perpendicularly to the surface.

In contrast to the (001) plane, pairs of edge-shared TiO_6 octahedra are present on the other possible morphological planes. They also possess sites for binding vanadium ions. It is impossible, however, to find sites which are similarly suitable for stabilizing a monovanadate group as those on the (001) plane. We postulate later that divanadate groups are formed on anatase faces other than (001). It thus seems plausible to assume along the lines of the NMR work that (001) is a dominating plane in TiO_2 grains and that it determines the structure of the V—O layer.

b. γ-Al_2O_3. γ-Al_2O_3 has a tetragonally distorted defect spinel structure (*18*). The distortion involves only the arrangement of cations in an approximately cubic close-packed oxygen array with $a = 7.91$ Å, if an ideally cubic lattice is assumed. Soled proposed recently (*19*) a simple formulation of γ-Al_2O_3 in its fully hydroxylated state as $Al_{2.5}\ \phi_{0.5}\ O_{3.5}\ (OH)_{0.5}$. In this model all hydroxyl groups populate the surface of oxide particles. Furthermore it postulates that the most densely packed (111) cubic face predominates on the particle surface. The concentration of OH ions on this face may be in the limit as high as 19 OH/nm^2.

A level of saturation amounting to 9.4 V/nm^2 was found in this work.

Undoubtedly other low index planes such as (110) or (100) may exist, as assumed by Knözinger and Ratnasamy (*20*) in their model of the surface structure of alumina.

The structural difference between V—O/TiO_2 and V—O/Al_2O_3 as revealed by EXAFS and XANES consists of a more regular tetrahedral coordination and shorter V—O bridging bond (1.82 Å) in the latter material. The stoichiometry of the reduction points to a divanadate group, as was discussed earlier. We could thus postulate formation of a surface dimeric group of the eclipsed conformation shown in Fig. 8 in which two VO_4 tetrahedra are bound to two surface oxygens and share another oxygen. The magnitude of the bridging bond falls well within the range characteristic of structures containing isolated or interlinked V_2O_7 groups, i.e., pyrovanadates (*21*) and alkali metal metavanadates (*22*) in which it varies between 1.76 and 1.85 Å. Since the V—O—V bond angle can vary from about 115° to 180° a divanadate group can easily be accommodated on the pairs of surface hydroxyls of O—O distance 4.8 Å present on the (111) surface of the alumina. It should be emphasized that the number of oxygen atoms removed per 1 vanadium ion amounts to 0.5 (cf. Fig. 4) independently of the surface coverage and does not change even in the case of samples whose surface is only sparsely populated with vanadium. Thus, formation of dimeric V—O species is

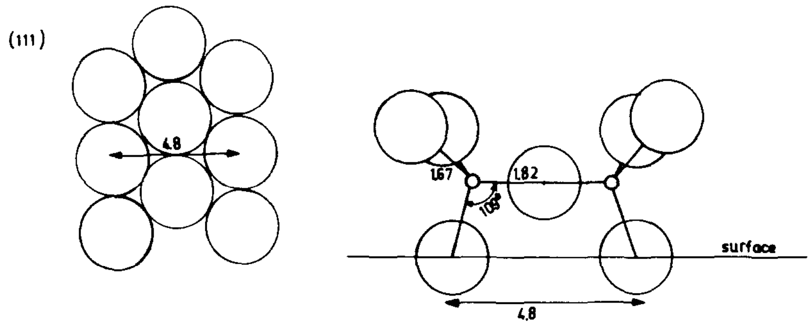


FIG. 8. V_2O_7 polyhedra located on the (111) plane of γ-Al_2O_3.

not forced by the too high surface concentration of vanadium, but apparently is inherent to the γ-alumina surface.

c. SiO_2. The structure both of crystalline modifications of silica and of amorphous silica can be visualized as a network of interlinked SiO_4 tetrahedra where each oxygen is shared by two silicon atoms. Hydroxyl groups are attached to the surface due to the tendency of silicon to complete tetrahedral coordination. The hydroxyl density on fully hydrated silica is usually about 5 OH/nm^2 (*16*). The saturation vanadium coverage found in this work is about 5 V/nm^2.

The EXAFS structure obtained for the V—O layer on SiO_2 is shown in Fig. 9 (spectrum a). It differs considerably from the spectra characteristic for the V—O layer supported on γ-Al_2O_3 (spectrum b) or TiO_2 (spectrum c), indicating important differences in the structures of these layers. In Fig. 10 this spectrum is compared with those of the crystalline V_2O_5 and amorphous V_2O_5 phases, the latter being obtained by hydrolysis of vanadium alcoxide in water, filtering and drying at 120°C. It may be noticed that the three spectra show distinct common features, but the spectrum of the V—O layer on SiO_2 resembles more that of the amorphous V_2O_5 phases, both differing from the spectrum of crystalline V_2O_5 by the lack of some finer structural details such as the peaks at 115, 135, 160, and 210 eV. Thus, if we consider the EXAFS spectra as finger-prints of the different structures of V—O layers we may conclude that grafting of the SiO_2 surface with vanadyl compounds and subsequent heat treatment does not result in the formation of isolated V—O units, but rather in the growth of clusters of amorphous V_2O_5 phase. This is consistent with the results of the studies of the phenomenon of wetting of

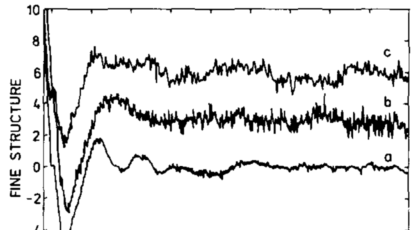


FIG. 9. EXAFS spectra for the vanadium edge of the V—O monolayer on SiO_2 (a), γ-Al_2O_3 (b), and TiO_2 (c).

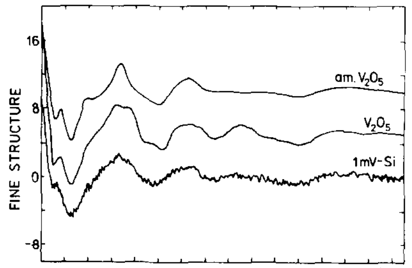


FIG. 10. EXAFS spectra for the vanadium edge of the V—O monolayer on SiO_2, crystalline and amorphous V_2O_5, respectively.

different oxides surfaces by V_2O_5 which show that V_2O_5 does not wet the surface of SiO_2 (*23*).

The reduction of bulk V_2O_5 to V_2O_3 is known to proceed in several steps, the intermediate species being V_6O_{13} and VO_2 (*24*). The fact that on reducing our SiO_2-supported samples we have observed in the temperature range 400–500°C the removal of 0.5 oxygen atoms per 1 V atom indicates that apparently the amorphous V_2O_5 supported on SiO_2 becomes reduced only to VO_2.

Results obtained with the V_2O_5/SiO_2 system clearly demonstrate that the redox characterization of the surface oxide phase cannot be unambiguously interpreted until the structure of the material in question is properly established.

A hypothesis emerging from the experimental data available would be that the structure of an anatase plane (001) offers a possibility of particularly favorable surface neutralization on incorporating monovanadate species into the cationic sites of the surface. We could speak about a specific interaction between this particular plane and vanadia. On the other hand a divanadate structure is stabilized on the surface of alumina and bulk vanadium oxide is formed on silica. It should be recalled at this point that even for TiO_2 the number of oxygen atoms removed during reduction does not attain the value of 1 O per 1 V. This might be explained by the presence of other morphological planes than (001), which can stabilize a divanadate structure or bulk V_2O_5.

CONCLUSIONS

All the experimental evidence discussed in this paper confirms the earlier EXAFS findings that for TiO_2 and γ-Al_2O_3 a vanadium–oxygen monolayer is composed of isolated vanadate-type units. Monodispersed VO_4 units are postulated on the (001) plane of anatase. They seem to form by locking vanadium ions into the cation surface sites. This brings about a nearly perfect neutralization of the surface. One is tempted to speak about "molecular epitaxy" in which half of the vanadium coordination, used to bind the VO_2 group to the surface, is determined by the structure of the support. This is a very stable arrangement, which explains why the layer is so resistant to treatments in strongly reducing agents.

Vanadia supported on γ-Al_2O_3 forms dimeric, pyrovanadate-type species, whereas bulk V_2O_5 exists on SiO_2.

The structure of the vandium–oxygen species determines in turn the number of oxygens which can be removed per V atom (the oxygen capacity of the layer).

The TiO_2-supported layer seems to be different from those on silica or alumina in several respects. It possesses a high concentration, 8 V/nm^2, of monovanadate species which gives a high overall oxygen capacity to the layer. The oxygen is readily removable from the sample and there is an effective reoxidation mechanism. These properties may be significant in understanding the unique activation property of anatase as a support. It engenders a structure capable of an effective transfer of oxygen from the gas phase to the surface and its insertion into the reacting molecule.

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