JOURNAL OF SOLID STATE CHEMISTRY **42**, 263–275 (1982)

# An Oxidized Surface State Model of Vanadium Oxides and Its Application to Catalysis

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Received October 2, 1981; in revised form January 15, 1982

The charge distribution around the V–O bonds in $V_2O_5$, $V_6O_{13}$, and $V_2O_4$ was calculated by using an empirical formula. The same expression was also used to calculate the oxygen bond strengths on the surface. The surfaces of lower oxides were treated as though they were in an oxidized state which is believed to correspond to the conditions in oxidation and ammoxidation processes. The result is that $O^{2-}$, in the form of V=O surface groups, is responsible for the catalytic oxidation of hydrocarbons. $O^-$ is hindered by the formation of stable $OH^-$ groups. The positions of lower valent oxygens are considered to be vacant because of a slow reoxidation rate. In $V_2O_5$ the V=O groups are located on the (010) plane, while in $V_6O_{13}$ they are mainly located on the (001) surface plane. But in this case the (100) and (010) surface planes also have some V=O groups. The catalytic activity of the rutile form of $V_2O_4$ is limited by sterical factors, but the (110) surface plane has oxygens pointing perpendicular out of the surface.

## 1. Introduction

Vanadium oxide catalysts have been used extensively in the oxidation and ammoxidation of aromatic hydrocarbons. It is well known that these systems can be considered as redox systems, i.e., the catalyst surface is both reduced and reoxidized during the reactions. This means that the catalyst is present in a reduced surface state. The composition at steady state is dependent on the reaction parameters (*1*, *2*).

Different opinions about active and selective species have appeared in the literature (*3*). In the oxidation of *o*-xylene to phthalic anhydride, Simard *et al.* (*1*) found that the reaction ceased when the catalyst, during the reaction, was reduced to $V_2O_4$ with a small amount of $V_2O_3$. The activity was considered to be limited to $V_2O_5$, $V_6O_{13}$, and to intermediate structures which may exist on the surface. Shaprinskaya *et al.* (*4*) studied the oxidation of naphthalene. They found that the catalytic activity on a per surface area basis in the range 380–415°C decreased in the order $V_6O_{13} > V_2O_3 > V_2O_4 > V_2O_5$. Contradictory results were obtained by Nishisaka *et al.* (*5*). According to these authors the activity decreased in the order $V_2O_5 > V_6O_{13} > V_2O_4$ (=0). In a study of the ammoxidation of 3-picoline (*6*) we found that the activity per surface area of $V_6O_{13}$ was greater than that of $V_2O_5$. $V_2O_4$ did not show any activity.

The origin of the differences in activity and selectivity of the various oxides is found in the structure. This work deals with the structure of $V_2O_5$, $V_6O_{13}$ and the rutile form of $V_2O_4$. $V_2O_3$ is not considered because it is not present at steady state under normal conditions (*4*). V–O bond strengths, charge distributions, and oxygen concentra-

0022-4596/82/060263-13$02.00/0

tions have been calculated for various crystal planes. Both bulk and surface conditions are treated. With reference to these basic data the differences in activity and selectivity are discussed.

## 2. Calculations and Discussion

### 2.1. The $V_2O_5$ Structure

The structure of $V_2O_5$ is schematically drawn in Fig. 1. The structure is built up from distorted trigonal bipyramids, $VO_5$, sharing edges to form zigzag chains along [001] and crossed-linked along [100] through shared corners, thus forming sheets in the *ac* plane. In Fig. 1 the $VO_5$ polyhedra are idealized to tetragonal pyramids.

The bulk of $V_2O_5$ has three different oxygen atoms and all its vanadium atoms are equal. The charge distribution or the localization of the *d* electrons was calculated by the empirical expression derived for vanadium oxides (*7*), $d = 1.791 - 0.722 \log s$, where *d* is the individual bond length and *s* is the electron delocalization around the individual bond. This expression is based on the logarithmic relationship given by Pauling (*8*), and includes refined values of previously published constants (*9*). The same method can be used to calculate cation–oxygen bond valences in other compounds. Brown and Wu (*10*) have given empirical parameters for 84 different cations. The *d* values used for $V_2O_5$ were from Bachmann *et al.* (*11*). The distribution thus obtained is given in Table I. The value obtained for the valence of vanadium is 5.00, which is in agreement with the theoretical value. It is also seen that O(3) is more negatively charged than O(1) and O(2). O(1) and O(3) are 2-coordinated while O(2) is 3-coordinated.

From a catalytic point of view it is the situation on the surface which is of interest. This matter will be treated in following sections.

### 2.2. The $V_6O_{13}$ Structure

The structure of $V_6O_{13}$ can be visualized as being composed of distorted octahedra connected by sharing corners and edges as illustrated in Fig. 2.

In $V_6O_{13}$ there are three different vanadium atoms and seven different oxygen atoms. The *d* electron localization was calculated by using the same expression as was used in the case of $V_2O_5$. The *d* values determined by Wilhelmi *et al.* (*9*) were used in the calculations. The resulting charge

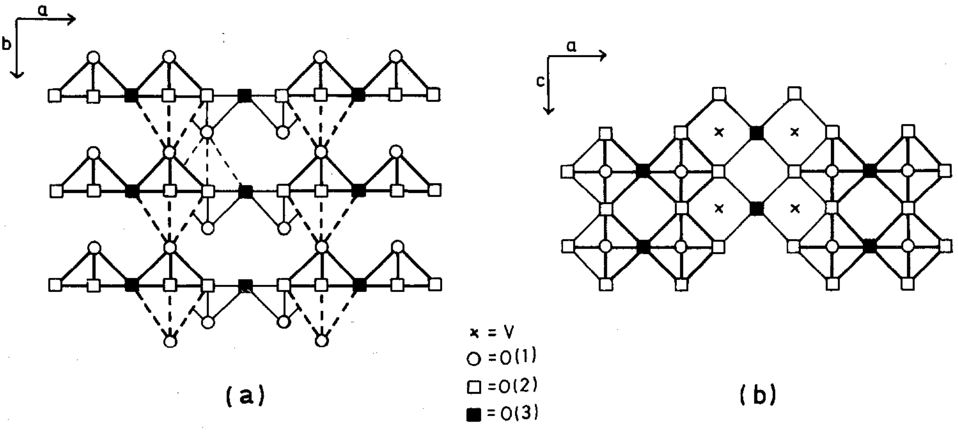


FIG. 1. Schematic presentation of the $V_2O_5$ structure. (a) (001) plane and (b) (010) plane.

TABLE I

CHARGE DISTRIBUTION AROUND V AND O IN $V_2O_5$

| Bond | $d$ (Å) | $s(e^-)$ for V | $s(e^-)$ for O(1) | O(2) | O(3) |
|---|---|---|---|---|---|
| V–O(1) | 1.585 | 1.93 | 1.93 | | |
| V–O(1) | 2.785 | 0.04 | 0.04 | | |
| V–O(2) | 2.021 | 0.48 | | 0.48 | |
| V–O(2) | 1.878 | 0.76 | | 0.76 | |
| V–O(2) | 1.878 | 0.76 | | 0.76 | |
| V–O(3) | 1.780 | 1.04 | | | 2 × 1.04 |
| | | $\Sigma = 5.00$ | $\Sigma = 1.97$ | $\Sigma = 2.00$ | $\Sigma = 2.07$ |

distribution is given in Table II. The result is that V(2) has more $V^{5+}$ character than V(1) and V(3). The mean value obtained for the valence of vanadium is 4.38. The error is 1.1%, which seems acceptable.

The values obtained will be used to calculate the charge distribution on various surface planes.

### 2.3. *The $V_2O_4$ Structure*

The rutile structure of $V_2O_4$ can be described as $VO_6$ octahedra joined at the edges to form rows. The rows are connected to each other by octahedra sharing corners. This is illustrated in Fig. 3, where projections of the structure along the [010], [001], and [110] directions of the unit cell are outlined. The (010) and (100) planes are equivalent.

All the oxygen atoms in $V_2O_4$ are equivalent. No single-crystal study of the rutile-type $V_2O_4$ structure seems to have been made. Marezio *et al.* (*12*) have carried out a refinement of the rutile structure of $V_{0.976}Cr_{0.024}O_2$. The interatomic distances obtained by these authors were used to calculate the charge distribution. The result is given in Table III. The value obtained for the valence of vanadium is 3.92, which corresponds to an error of 1.9%. The same expression has been used (*7*) to calculate

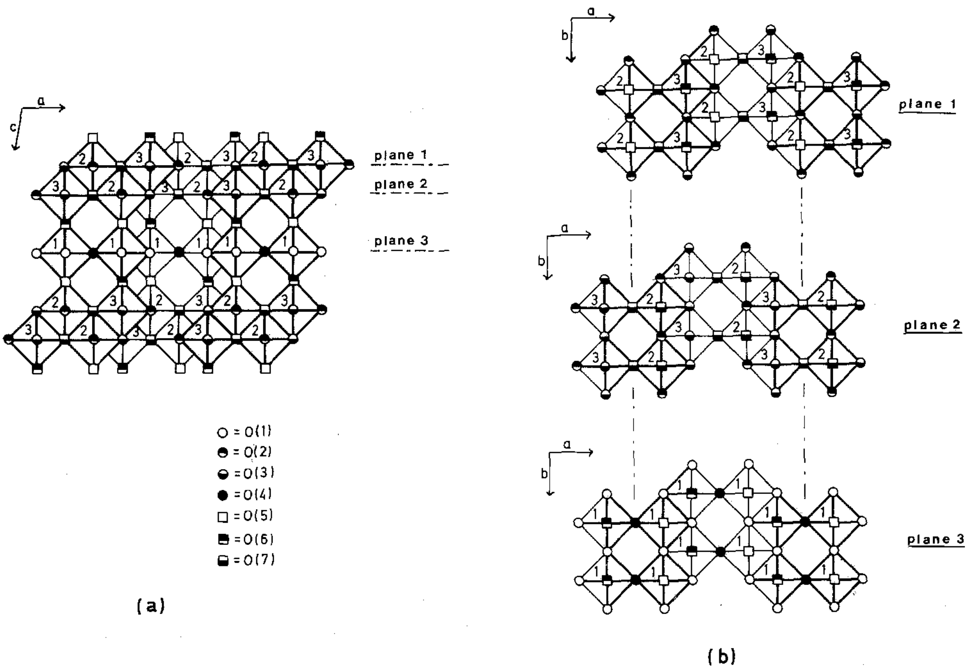


FIG. 2. Schematic presentation of the $V_6O_{13}$ structure. (a) (010) plane and (b) view along the [001] direction. The indices indicate the three different $VO_6$ octahedra.

TABLE II

CHARGE DISTRIBUTION AROUND V AND O IN $V_6O_{13}$

| Bond | $d$ (Å) | $s(e^-)$ for V | $s(e^-)$ for O(1) | O(2) | O(3) | O(4) | O(5) | O(6) | O(7) |
|---|---|---|---|---|---|---|---|---|---|
| V(1)–O(1) | 1.876 | 0.76 | 0.76 | | | | | | |
| V(1)–O(1) | 1.876 | 0.76 | 0.76 | | | | | | |
| V(1)–O(1) | 2.064 | 0.42 | 0.42 | | | | | | |
| V(1)–O(4) | 1.766 | 1.08 | | | | 2 × 1.08 | | | |
| V(1)–O(5) | 1.964 | 0.58 | | | | | 0.58 | | |
| V(1)–O(6) | 1.993 | 0.53 | | | | | | 0.53 | |
| | $\Sigma$V(1) = | 4.13 | | | | | | | |
| V(2)–O(2) | 1.902 | 0.70 | | 0.70 | | | | | |
| V(2)–O(2) | 1.902 | 0.70 | | 0.70 | | | | | |
| V(2)–O(3) | 2.084 | 0.39 | | | 0.39 | | | | |
| V(2)–O(5) | 1.655 | 1.54 | | | | | 1.54 | | |
| V(2)–O(7) | 1.761 | 1.10 | | | | | | | 1.10 |
| V(2)–O(7) | 2.277 | 0.21 | | | | | | | 0.21 |
| | $\Sigma$V(2) = | 4.65 | | | | | | | |
| V(3)–O(2) | 1.981 | 0.55 | | 0.55 | | | | | |
| V(3)–O(3) | 1.919 | 0.66 | | | 0.66 | | | | |
| V(3)–O(3) | 1.919 | 0.66 | | | 0.66 | | | | |
| V(3)–O(3) | 2.261 | 0.22 | | | 0.22 | | | | |
| V(3)–O(6) | 1.641 | 1.61 | | | | | | 1.61 | |
| V(3)–O(7) | 1.928 | 0.65 | | | | | | | 0.65 |
| | $\Sigma$V(3) = | 4.36 | | | | | | | |
| | $\Sigma$O = | | 1.94 | 1.95 | 1.95 | 2.17 | 2.12 | 2.14 | 1.96 |

the valence of vanadium in the monoclinic form of $V_2O_4$. The value obtained was 3.99. The larger discrepancy in the rutile case is probably due to the uncertainty of the *d* values.

### 2.4. *The $V_2O_5$ Surface*

Although the crystal structures of vanadium oxides are well known, there seems to be no method to fully characterize the microstructure of any solid surface. In the treatment of surfaces it is necessary to make assumptions. The *d* electron delocalization around a V–O bond can be considered to be a measure of the bond strength. The more electrons transferred from the vanadium atom to the oxygen atom, the stronger is the bond. The treatment of surfaces will be limited to 1-coordinated anions. Furthermore, only $VO_6$ units with one undercoordinated anion will be considered. This means that corners and edges of the crystals will not be discussed. It is anticipated that the equation used to calculate the charge distribution between vanadium and oxygen in the bulk is still valid at a solid surface. The assumption is valid, in this treatment, if the equation is applicable to a 1-coordinated anion. This seems reasonable because it can be used to calculate the charge distribution around 2-, 3-, and 4-coordinated anions in the bulk of vanadium oxides. In these cases, the electron delocalization around each V–O bond is in prac-

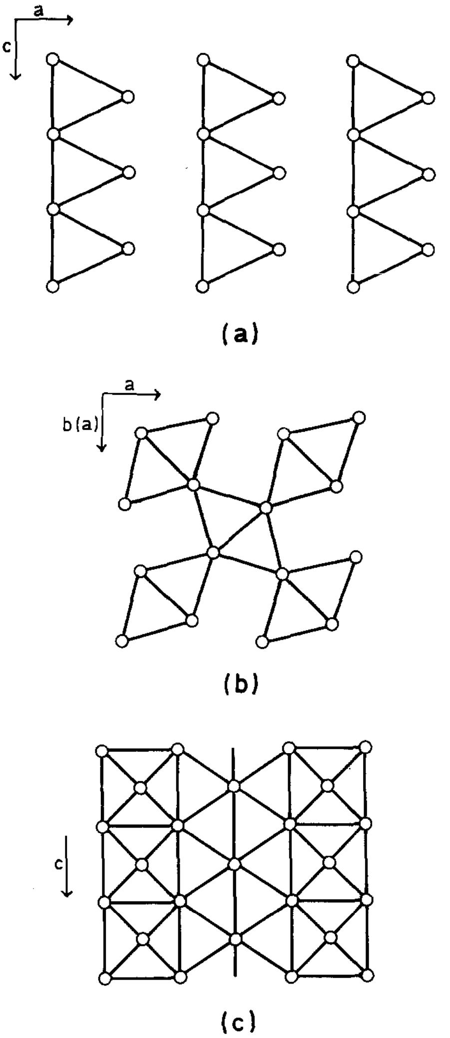


FIG. 3. Schematic presentation of the $V_2O_4$ rutile structure. (a) (010) plane, (b) (001) plane, and (c) (110) plane.

TABLE III

CHARGE DISTRIBUTION AROUND V AND O IN $V_2O_4$

| Bond | $d$ (Å) | $s(e^-)$ for V | $s(e^-)$ for O |
|---|---|---|---|
| V–O | 1.920 | 0.66 | 0.66 |
| V–O | 1.920 | 0.66 | 0.66 |
| V–O | 1.920 | 0.66 | |
| V–O | 1.920 | 0.66 | |
| V–O | 1.933 | 0.64 | 0.64 |
| V–O | 1.933 | 0.64 | |
| | | $\Sigma = 3.92$ | $\Sigma = 1.96$ |

tice calculated as though the anion may be considered to be 1-coordinated. The V–O bond lengths at the $V_2O_5$ surface can be approximated with the values valid for the bulk because the $V^{5+}$ ions at the surface cannot donate any further electrons. They are already in the highest possible oxidation state, and have only one undercoordinated anion. The rest of the anions are bonded to the lattice and cannot change their positions relative to vanadium. The conditions at various surface planes are given in Table IV.

It is generally accepted that for $V_2O_5$ catalysts the double-bonded oxygen, V–O(1), in the (010) plane plays a role in catalytic oxidation reactions. It has been found that the activity can be correlated to the strength of the V═O bond (*13*). Infrared investigations showed that the V═O bond participated in the exchange of $^{18}O$ between $CO_2$ and $V_2O_5$ (*14*). ESR measurements, combined with ir studies, revealed that CO, $SO_2$, and $C_2H_4$ are adsorbed on the double-bonded oxygen (*15*). In a study of the exchange of gaseous oxygen with $V_2O_5$ (*16*), it was found that the exchange begins mainly at V═O groups. Therefore, it is of interest to locate such groups at surfaces.

In Table IV, two kinds of O(1) in the catalytically active (010) plane are seen. Fifty percent of O(1) is of the double-bonded type, while the other 50% only has

TABLE IV

SURFACE BOND STRENGTHS IN $V_2O_5$

| Bond | Plane | $d$ (Å) | $\Sigma s(e^-)$ for V | $s(e^-)$ for O (bond strength) |
|---|---|---|---|---|
| V–O(2) | 100 | 2.021 | 5 | 0.48 |
| V–O(3) | 100 | 1.780 | 5 | 1.04 |
| V–O(1) | 010 | 1.585 | 5 | 1.93 |
| V–O(1) | 010 | 2.785 | 5 | 0.04 |
| V–O(2) | 001 | 1.878 | 5 | 0.76 |

a charge of 0.04 electrons, which indicates that they are very weakly bonded. These oxygens are probably absent at the high temperatures which are used in catalytic oxidation and ammoxidation of aromatic hydrocarbons. In the drawing of the $V_2O_5$ structure in Fig. 1, these oxygens were also considered to be absent. However, it is possible that the resulting naked $V^{5+}$ ions in the (010) surface plane can act as adsorption sites for electron-donating species. It was found (*17*) that the infrared spectrum of $V_2O_5$ after adsorption of $NH_3$, except for the band due to $NH_4^+$ (*ad*), also had bands showing the presence of $NH_3$ coordinatively linked to Lewis centers.

It was proposed (*16*) that even if the exchange of gaseous oxygen with $V_2O_5$ started mainly at V═O groups, participation of oxygens on the (100) and (001) surfaces in reactions could not be excluded. However, the results given in Table IV show that O(2) and O(3) on the (100) surface and O(2) on the (001) surface are strongly undersaturated, having valences of −0.48, −1.04, and −0.76, respectively. Therefore, it seems reasonable to suggest that O(2) and O(3) on surface planes correspond preferentially to stable $OH^-$ groups. In the literature (*7, 18, 19*), similar calculations have been made to localize and discuss the presence of $OH^-$ groups. A step in the oxidation and ammoxidation mechanism of an alkyl aromatic hydrocarbon is an abstraction of hydrogen from the alkyl group, followed by adsorption of the hydrocarbon via the alkyl radical on an adjacent site (*6, 20*). This process is illustrated in Fig. 4. Thus, if $OH^-$ groups on $V_2O_5$ crystals are mainly localized on the (100) and (001) surface planes, it does not seem reasonable that these planes can possess high catalytic activity, since they cannot coordinate the alkyl group to an oxygen. Furthermore, the (100) and (001) planes have a layer structure (see Fig. 1) with a long distance between the 1-coordinated surface oxygens positioned at adjacent layers. This limits the activity of these planes. Both the abstracted hydrogen and the hydrocarbon radical have to be adsorbed on the same layer. However, the proposal (*16*) that the (100) and (001) planes can exchange oxygen with the atmosphere can be true to some extent. This mechanism does not include a hydrogen abstraction. The existence of $OH^-$ groups at the $V_2O_5$ surface can be revealed by infrared studies of the adsorption of $NH_3$. It was found (*21*) that the amount of $NH_3$ adsorbed on $OH^-$ groups corresponded to about one-half of the surface vanadium atoms. This clearly shows the existence of planes with a high concentration of $OH^-$ groups. These planes can be the (100) and (001) planes.

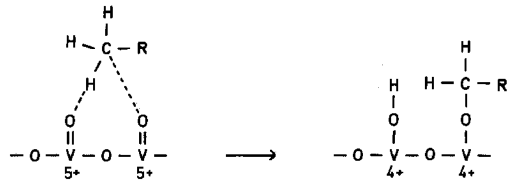


FIG. 4. Adsorption of an alkyl aromatic hydrocarbon on $V_2O_5$. R = Benzene or pyridine ring.

There is another argument in favor of the activity being concentrated to the (010) surface plane. After the double-bonded surface oxygen on this plane has reacted, the oxygen vacancy will be situated on a $V^{3+}$ ion. On the other hand, if an oxygen on the (100) or (001) plane participates in an oxidation reaction, the resulting vacancy will be situated on a vanadium ion with mainly $V^{4+}$ character. A $V^{4+}$ ion probably reoxidizes slower than a $V^{3+}$ ion. Bielański *et al.* (*22*) found that the reoxidation step was greatly enhanced by the presence of $V^{3+}$ ions. In view of this, it seems possible that the position of the loosely bonded O(2) on the (100) surface is vacant to some extent. Then the resulting vacancy on the vanadium ion can act as an adsorption site for oxygen at lower temperatures. In an ESR study (*23*) of oxygen adsorption on $V_2O_5$ supported on silica gel, both $O_2^-$ and $O^-$ radicals could be identified. $O_2^-$ was obtained at liquid $N_2$ temperature. At room temperature $O_2^-$ was partly transformed into $O^-$. These radicals could be observed up to 300°C.

### 2.5. The $V_6O_{13}$ Surface

In the treatment of this surface only 1-coordinated anions bonded to a $VO_6$ octahedron with one undercoordinated anion will be considered. In contrast to the situation in $V_2O_5$, the V–O bond lengths on the surface of $V_6O_{13}$ differ considerably from those in the bulk. The reason for this is that the vanadium ions in $V_6O_{13}$ are not in the highest possible oxidation state. Therefore, they can donate more electrons to the oxygen species, which leads to a shortening of the V–O surface bonds. The 1-coordinated surface anion is the object for this donation, since the fully coordinated anions cannot accept any more electrons and their positions are determined by the lattice. The result is that the surface of $V_6O_{13}$ is in an oxidized state. This nonstoichiometric surface of $V_6O_{13}$ can exist in an oxygen-rich atmosphere. If a $V_6O_{13}$ crystal is cleaved under vacuum, the situation will be different. The surface will partly be covered with vacancies. ESCA investigations of $V_6O_{13}$ and other lower oxides (*24*) have shown that these oxides contain $V^{5+}$ on the surface. Only a combination of a high vacuum and a high temperature gave surfaces in close agreement with the stoichiometry. These findings support the assumption made in the calculations. The bond distances and the charge distributions calculated are presented in Table V, where the change of state compared to the bulk is indicated by arrows. The formal valence of vanadium is +5.00, except in the case of V(3) bonded to O(6), which has a formal valence between +4.74 and +5.00.

TABLE V

SURFACE BOND STRENGTHS IN $V_6O_{13}$

| Bond | Plane | $\Sigma s(e^-)$ for V | $s(e^-)$ for O (bond strength) | $d$ (Å) |
|---|---|---|---|---|
| V(1)–O(1) | 100 | 4.13 → 5.00 | 0.42 → 1.29 | 2.064 → 1.71 |
| V(1)–O(4) | 100 | 4.13 → 5.00 | 1.08 → 1.95 | 1.766 → 1.58 |
| V(2)–O(3) | 100 | 4.65 → 5.00 | 0.39 → 0.74 | 2.084 → 1.88 |
| V(2)–O(7) | 100 | 4.65 → 5.00 | 1.10 → 1.45 | 1.761 → 1.67 |
| V(3)–O(2) | 100 | 4.36 → 5.00 | 0.55 → 1.19 | 1.981 → 1.74 |
| V(3)–O(7) | 100 | 4.36 → 5.00 | 0.65 → 1.29 | 1.928 → 1.71 |
| V(1)–O(1) | 010 | 4.13 → 5.00 | 0.76 → 1.63 | 1.876 → 1.64 |
| V(2)–O(2) | 010 | 4.65 → 5.00 | 0.70 → 1.05 | 1.902 → 1.78 |
| V(3)–O(3) | 010 | 4.36 → 5.00 | 0.66 → 1.31 | 1.919 → 1.71 |
| V(1)–O(5) | 001 | 4.13 → 5.00 | 0.58 → 1.45 | 1.964 → 1.67 |
| V(1)–O(6) | 001 | 4.13 → 5.00 | 0.53 → 1.40 | 1.993 → 1.69 |
| V(2)–O(5) | 001 | 4.65 → 5.00 | 1.54 → 1.89 | 1.655 → 1.59 |
| V(2)–O(7) | 001 | 4.65 → 5.00 | 0.21 → 0.56 | 2.277 → 1.97 |
| V(3)–O(3) | 001 | 4.36 → 5.00 | 0.22 → 0.86 | 2.261 → 1.84 |
| V(3)–O(6) | 001 | 4.36 → 4.74 | 1.61 → 2.00 | 1.641 → 1.57 |
|  |  | 4.36 → 5.00 | 1.61 → 2.25 | 1.641 → 1.54 |

In an investigation (*6*) of the catalytic activity of $V_6O_{13}$, this oxide was prepared by reduction of cleaved $V_2O_5$ crystals. In these $V_2O_5$ crystals the (010) plane is a major surface plane (*25*). During the reduction of $V_2O_5$, these planes are replaced by the $V_6O_{13}$ (001) plane. It has been shown (*26*) that structural coherence exist at $V_2O_5$ (010)/$V_6O_{13}$ (001) boundaries because of the small lattice misfit between these planes. By considering the structure in Fig. 2 and the values in Table V, it can be seen that there are three possibilities. Either O(5) and O(6), or O(3) and O(7) can be 1-coordinated. O(5) and O(6) can either be bonded to V(2) and V(3), respectively, or to V(1). During reduction it is most probable that the surface layer formed includes oxygens with the highest possible coordination. O(1), O(2), and O(7) are 3-coordinated, O(3) is 4-coordinated, while the others are 2-coordinated. Thus it seems most likely that the surface plane formed contains 1-coordinated O(5) and O(6) bonded to V(2) and V(3), respectively. With this configuration V(2) and V(3) will be surrounded in the surface plane by 3-coordinated O(2) and O(7), and 4-coordinated O(3). As can be seen in Table V, O(5) and O(6) will in this case be double bonded, having formal valences of −1.89 and −2.25, respectively. This means that the liability of O(5) and O(6) to form stable $OH^-$ groups, which prevent hydrogen abstraction, is small. Also, the concentration of oxygen vacancies on these sites will be small because of the rapid reoxidation of a $V^{3+}$ ion. Another factor is that one of the O(5)–O(6) distances is extremely short. This improves the possibility of hydrogen abstraction and adsorption of the hydrocarbon radical. The arguments given show that the $V_6O_{13}$ phase produced by reduction of $V_2O_5$ should be active in oxidation and ammoxidation of hydrocarbons. The activity of $V_6O_{13}$ formed by reduction is well documented in the literature (*1*, *6*). Another possibility concerning O(5) and O(6) in the (001) plane is that these are bonded to V(1) (see Fig. 2). In this case the valence of O(5) and O(6) is −1.45 and −1.40, respectively. Because they are underbonded, these sites can have a relatively high concentration of $OH^-$ groups. But it is possible that some of these oxygens participate in catalytic reactions because the $OH^-$ group formation may be far from complete. The (001) plane has also the possibility to exhibit V(2)–O(7) and V(3)–O(3) bonds. The data in Table V indicate that these bonds are weak and probably represent vacancies. After desorption of these oxygens the formal valence of vanadium is +4.44 and +4.14, which concludes that the rate of reoxidation is low. If any concentration of $OH^-$ groups exists, these are localized to O(3).

If the (100) plane is considered, the data in Table V show that V(1)–O(4) is a double bond. This site represents a catalytically active oxygen because the double bond indicates a fast reoxidation rate and a low concentration of vacancies and stable $OH^-$ groups. Also O(7) bonded to V(2) can be active, even though some $OH^-$ groups seem to be localized to this site. In Fig. 2 it can be seen that the V(1)–O(4) bonds lie within a layer, which is only about 3.6 Å from the V(2)–O(7) layer (*9*). These arguments strongly suggest that the catalytic activity is concentrated to O(7)–V(2)–O(5)–V(1)–O(4) configurations. The V(1)–O(1), V(3)–O(2), and V(3)–O(7) sites, in agreement with the previous discussion, are covered with a high concentration of $OH^-$ groups. V(1)–O(1) and V(3)–O(2) are positioned in adjacent layers. Thus the O(2)–V(3)–O(6)–V(1)–O(1) configuration on the (100) plane represents surface sites not taking part in catalytic reactions. The vacancies in the (100) plane are concentrated to the V(2)–O(3) position because of the low localization of *d* electrons to O(3).

When the (010) plane constitutes a surface there are three kinds of 1-coordinated oxygens being exposed. These are O(1), O(2), and O(3). According to Table V the valences of these are −1.63, −1.05, and −1.31, respectively. These values show that the concentration of $OH^-$ groups on this plane is high. The catalytic activity should be localized to the V(1)–O(1) position, even though the activity is limited by $OH^-$ groups surrounding these sites.

### 2.6. A Catalytic Comparison of $V_2O_5$ and $V_6O_{13}$

So far a localization of V=O species, $OH^-$ groups, and oxygen vacancies has been carried out. In comparing the catalytic activity of $V_2O_5$ to $V_6O_{13}$, it is useful to calculate the surface concentrations of the active species as well as the bond energies. The concentrations can be obtained from the structure and the unit cell dimensions (*9*, *11*). The bond energies were calculated by using the heat of formation values of the oxides (*27*). From the $\Delta H^\circ_{f,298}$ values an average bond energy can be obtained by dividing the value with the number of oxygens in a formula unit. This value was considered applicable for oxygen with a formal valence of −2.00. Bond energies of surface oxygens were calculated relative to this value using

$$\text{bond energy, } V_2O_5 = \frac{1553}{5} \times \frac{S}{2.00}\ (\text{kJ}),$$

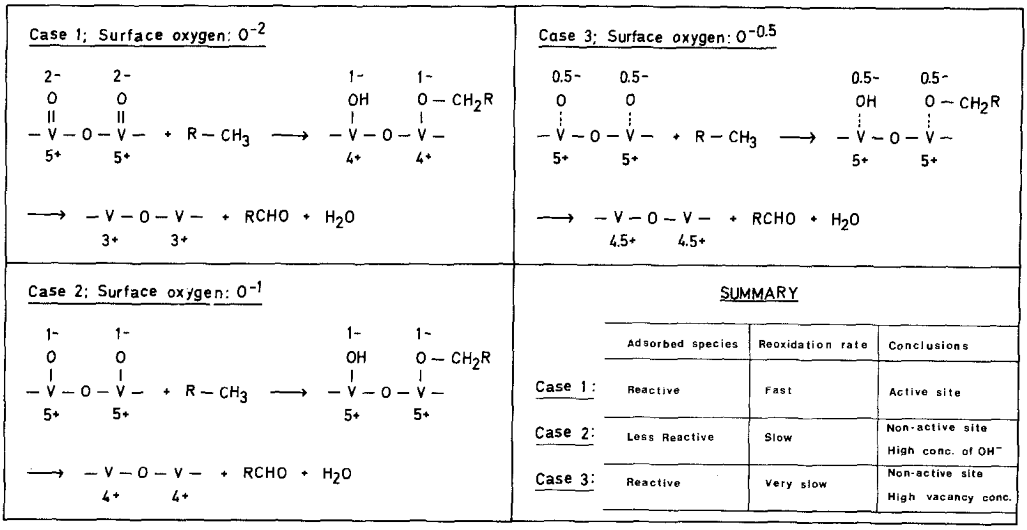
$$\text{bond energy, } V_6O_{13} = \frac{4440}{13} \times \frac{S}{2.00} \text{ (kJ),}$$

where $S$ is the formal charge of the oxygen. The results of these calculations are given in Table VI. The bond energies given cannot be used directly to correlate catalytic activity. The reason for this is that the situation on the surface changes during the reaction. This is illustrated in Fig. 5. Three cases have been considered. If the valence of the surface oxygen is $-2$, the adsorbed species, having a formal valence of $-1$, will be bonded to a $V^{4+}$ ion. This attraction is relatively weaker than that in the case when the surface oxygen has a valence of $-1$, where the adsorbed species will be attracted to a $V^{5+}$ ion. When the valence of the surface oxygen falls below $-1$, the attraction between the adsorbed species and the vanadium ion will again diminish. This means that in case 2 in Fig. 5, the adsorbed species are less reactive, and that the concentration of nonreactive $OH^-$ groups are localized to $O^-$ positions. The reoxidation rate decreases when the valence of the vanadium at the oxygen vacancy increases (*22*). Therefore, positions which correspond to an oxygen with a valence less than $-1$ can be considered to be vacant. The conclusion must be that double-bonded surface oxygens are the active species in oxidation and ammoxidation of hydrocarbons. When these oxygens have been localized, the values of the bond energies might be used as a measure of their relative activity. If a measure of the activity per surface area is desired, it is also necessary to consider their concentration.

TABLE VI

OXYGEN CONCENTRATION AND BOND ENERGIES ON $V_2O_5$ AND $V_6O_{13}$ SURFACES

| Bond | Plane | Concentration ($\mu$mole/m$^2$) | Bond energy (kJ) |
|---|---|---|---|
| | | $V_2O_5$ | |
| V–O(1) | 010 | 8.10 | 300 |
| | | $V_6O_{13}$ | |
| V(1)–O(4) | 100 | ≤4.45 | 334 |
| V(2)–O(7) | 100 | <4.45 | 247 |
| V(1)–O(1) | 010 | <2.75 | 279 |
| V(1)–O(5) | 001 | <7.57 | 247 |
| V(1)–O(6) | 001 | <7.57 | 238 |
| V(2)–O(5) | 001 | ≤7.57 | 323 |
| V(3)–O(6) | 001 | ≤7.57 | 341–384 |



| | Adsorbed species | Reoxidation rate | Conclusions |
|---|---|---|---|
| Case 1: | Reactive | Fast | Active site |
| Case 2: | Less Reactive | Slow | Non-active site<br>High conc. of OH$^-$ |
| Case 3: | Reactive | Very slow | Non-active site<br>High vacancy conc. |

FIG. 5. Formal changes of the vanadium valence during a catalytic reaction and its influence on the catalytic activity. R = benzene or pyridine ring.

In the oxidation of naphthalene (*4*) and in the ammoxidation of 3-picoline (*6*), it was found that a $V_6O_{13}$ catalyst had a higher specific activity (activity/surface area) than a $V_2O_5$ catalyst. Table VI shows that the concentration of active V–O(1) species on the (010) plane of $V_2O_5$ is 8.10 $\mu$mole/m$^2$. In $V_6O_{13}$ the combined amount of active V(2)–O(5) and V(3)–O(6) species on the (001) plane is about 15 $\mu$mole/m$^2$. Additionally, in $V_6O_{13}$ each active double-bonded oxygen belongs to a $VO_6$ octahedron which shares edges with two other octahedra having double-bonded oxygens. This gives extremely short distances between the active species, which is not the case on $V_2O_5$. In $V_6O_{13}$ the (100) and (010) planes, according to the model, also can possess catalytic activity. The activity of $V_2O_5$ seems to be concentrated to the (010) plane. All these facts together can explain the greater activity of $V_6O_{13}$. The analysis performed shows that the relative activity per surface area between $V_2O_5$ and $V_6O_{13}$ must depend upon the planes that are being exposed on the surface. This may be why Nishisaka *et al.* (*5*) reported that the activity of $V_2O_5$ was greater than that of $V_6O_{13}$ in the oxidation of naphthalene.

The oxidation of 2-picoline and 3-picoline to pyridinecarboxylic acids has been studied over a $V_2O_5/SnO_2$ catalyst (*20*). ESCA investigations of the catalyst after use showed that the catalyst was partly reduced. The vanadium was reduced from $V^{5+}$ to a state between $V^{5+}$ and $V^{4+}$. From ESCA data it is not possible to conclude what phases are present, but according to the literature it is known that $V_6O_{13}$ can be formed (*1, 2*). An important contradiction should be noted. In spite of a reduction of the vanadium, the percentage of oxygen was increasing in the surface layer. The authors interpreted this as an increase of active centers having the ability to adsorb more oxygen than the original catalyst surface. As already mentioned and in agreement with the literature (*26*), the most probable change during a reduction of $V_2O_5$ is that the (010) plane in $V_2O_5$ transforms to a (001) plane in $V_6O_{13}$ with V(2)–O(5) and V(3)–O(6) species on the surface. Thus, the increase observed in the concentration of oxygen on the surface can well be explained in accordance with the data in Table VI. It shows that the concentration of surface oxygens on the (001) plane of $V_6O_{13}$ is about twice that on the (010) plane in $V_2O_5$. In another article (*24*) it was reported that $V_6O_{13}$ obtained by heating a stoichiometric mixture of $V_2O_3$ and $V_2O_5$ was nonstoichiometric on the surface with respect to the quantitative analysis. The percentage of oxygen was too high. A pure $V_6O_{13}$ surface, with a surface composition close to the theoretical one, could only be obtained by heating a $V_2O_5$ sample in the spectrometer to a temperature of 400°C. The vacuum was $10^{-8}$–$10^{-10}$ Torr. These results also support the theory that $V_6O_{13}$ is capable of having a high surface concentration of oxygen during the conditions of catalytic reactions.

The fact that the concentration of surface oxygen on $V_6O_{13}$ can be greater than that on $V_2O_5$ might imply that $V_6O_{13}$ can be expected to be less selective than $V_2O_5$ toward partial oxidation products. In opposition to this, some of the double-bonded oxygens on the $V_6O_{13}$ surface are more strongly bonded than those in $V_2O_5$ (Table VI). The latter fact favors selectivity toward partial oxidation products, at least at lower temperatures. Therefore, it seems reasonable that the selectivity has been observed to have the same magnitude on $V_2O_5$ and $V_6O_{13}$ (*4, 6*). However, the concentration of oxygen vacancies on $V^{5+}$ ions is high for $V_2O_5$ (Fig. 1). This should lead to a greater possibility for $V_2O_5$ to activate double bonds which is in agreement with observations. Colpaert (*28*) studied the oxidation of butenes on $V_2O_5$ single crystals exposing the (010) plane. The first reaction which appeared was an isomerization of the butenes.

### 2.7. *The $V_2O_4$ Surface and Its Catalytic Activity*

The situation concerning the bond lengths on the $V_2O_4$ surface differs from that in the bulk. The reason is the same as in the $V_6O_{13}$ case, namely, that the vanadium ions on the surface layer can be considered to be oxidized to $V^{5+}$. This assumption seems reasonable as ESCA investigations showed (*24*) that $V_2O_4$ does contain $V^{5+}$ on the surface. Only by combining vacuum with a high temperature does the $V_2O_4$ phase became stoichiometric. Such conditions do not, however, prevail in catalytic oxidation and ammoxidation processes, where an excess of oxygen is generally used. The treatment is limited to 1-coordinated anions on surfaces, which was also the case for $V_2O_5$ and $V_6O_{13}$. Because of the structure, this results in the following limitations: (i) on the (100) or (010) plane only $VO_6$ octahedra with one 1-coordinated and two 2-coordinated anions are considered; (ii) on the (001) plane only $VO_6$ octahedra with two 1-coordinated anions are considered; and (iii) on the (110) plane only $VO_6$ octahedra with one 1-coordinated anion are considered. The V–O distances and the charge distribution on $V_2O_4$ surfaces were calculated and are given in Table VII. On the crystallographically equal (100) and (010) planes there are no V–O bonds pointing perpendicular out of the surface, which was the case for $V_2O_5$ and $V_6O_{13}$ surfaces. Both the 1- and 2-coordinated oxygens lie practically in the same plane, which is illustrated in Fig. 3a. The vanadium ions on the surface can be oxidized from +4 to +5 by donating a formal electron to the surface oxygens, and thereby binding them closer. It is, however, not probable that the 2-coordinated oxygens are closer bonded. If this was the case, the 2-coordinated oxygen has to move on a straight line toward a 3-coordinated oxygen lying below. This process is prevented by repulsion forces between the negatively charged oxygen ions. The most probable situation on the (100) and (010) planes is that the electron from the vanadium ion is donated to the 1-coordinated oxygen. The formal charge of this surface oxygen will thus be −1.71, and the 2-coordinated oxygen will have a formal charge of −1.33 (Table VII). This indicates that $OH^-$ groups are preferentially located on the 2-coordinated oxygens. By the formation of $OH^-$ groups, electrons can be located closer to the 1-coordinated oxygens which can then be considered to be double bonded. This means that the catalytic activity should be located to these oxygens. However, their activity is probably severely limited by a steric hindrance, because they are practically lying in the plane and are not pointing out of the surface.

TABLE VII

SURFACE BOND STRENGTHS IN $V_2O_4$

| Bond | Plane | $\Sigma s(e^-)$ for V | $s(e^-)$ for O (bond strength) | $d$ (Å) |
|---|---|---|---|---|
| V–O | 100 | 3.92 → 5.00 | 0.64 → 1.71 | 1.933 → 1.62 |
| V–O–V | 100 | 3.92 → 5.00 | 1.33 → 1.33 | 1.920 → 1.92 |
| V–O | 010 | 3.92 → 5.00 | 0.64 → 1.71 | 1.933 → 1.62 |
| V–O–V | 010 | 3.92 → 5.00 | 1.33 → 1.33 | 1.920 → 1.92 |
| V–O | 001 | 3.92 → 5.00 | 0.66 → 1.20 | 1.920 → 1.73 |
| V–O | 110 | 3.92 → 5.00 | 0.64 → 1.71 | 1.933 → 1.62 |

TABLE VIII

OXYGEN CONCENTRATION AND BOND ENERGIES ON $V_2O_4$ SURFACES

| Bond | Plane | Concentration ($\mu$mole/m$^2$) | Bond energy (kJ) |
|---|---|---|---|
| V–O | 100 | 12.78 | 306 |
| V–O | 010 | 12.78 | 306 |
| V–O | 110 | <9.03 | 306 |

When considering the (001) plane there are two 1-coordinated oxygens belonging to each $VO_6$ surface octahedron. These oxygens have a formal valence of $-1.20$, indicating that $OH^-$ groups are located on these positions. The rate of reoxidation of vacancies is also relatively slow. These facts, in combination with some steric hindrance, lead to the conclusion that the (001) plane is not active in catalytic processes involving hydrocarbons. If the rutile structure is viewed along the [110] direction, it is seen that the (110) plane contains oxygens pointing perpendicular out of the surface. This is the same situation as that in $V_2O_5$ and $V_6O_{13}$. The valence of these 1-coordinated oxygens is $-1.71$ (Table VII). These oxygens can take part in oxidation and ammoxidation of hydrocarbons. This is because of the relatively small concentration of $OH^-$ groups, and the rapid reoxidation rate of vacancies being localized to these sites. A limitation of the activity is the fact that the 1-coordinated oxygens lie in rows with a long distance of 6.4 Å between the rows.

The bond energies of the presumably active oxygens were calculated by the same method which was used for $V_2O_5$ and $V_6O_{13}$. The value being used for the heat of formation was $\Delta H^{\circ}_{f,298} = -1428$ kJ/mole (*27*). The surface concentration of these oxygens was calculated from the dimensions of the unit cell (*29*). The data calculated are given in Table VIII.

In the literature there are both reports on $V_2O_4$ being not active in catalytic reactions involving aromatic hydrocarbons (*1, 5, 6*), as well as a report on $V_2O_4$ having a high activity (*4*). In all these investigations, though not always mentioned, it is probably the rutile form of $V_2O_4$ which has been investigated or observed. The inactivity can be explained by assuming that the major planes on the $V_2O_4$ surface were either (100), (010), or (001). The (001) plane does not exhibit any double-bonded oxygens, and (100) and (010) have such oxygens, but the steric hindrance is great. The activity of $V_2O_4$ can be ascribed to the presence of (110) planes on the surface. These planes have double-bonded oxygens pointing out from the surface. The reason for discrepancies in activities observed can be due to different preparation techniques.

## Acknowledgment

The author is grateful to Professor S. T. Lundin for stimulating discussions and his kind interest in this work.

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