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Coordination Geometry and Catalytic Activity of Vanadium on TiO_2 Surfaces

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The Brown–Altermatt model is applied to evaluate the oxidation states of vanadium on the TiO_2(001)–rutile and –anatase surfaces.On the basis of this model, possible correlations between different geometries of vanadium crystallographic sites on these surfaces and the vanadium oxidation states are studied. The study of these geometries helps in interpreting both activity and selectivity in catalyzed reactions. © 1993 Academic Press, Inc.

Titania-supported vanadia are well-known catalysts for industrial heterogeneous catalytic processes, such as NO_x reduction and orthoxylene oxidation (*1, 2*). However, several questions about the catalytic mechanisms, which depend on the nature of the titania/vanadia interface, remain open. In particular the problem concerning the different catalytic activity shown by TiO_2–rutile and TiO_2–anatase supported vanadia is still under discussion. Possible solutions to this problem have been reported, based on different surface versus volume ratios of sintered TiO_2–rutile and TiO_2–anatase (*3*), or different surface electronic structures of rutile versus anatase (*4*), or higher interdiffusion of vanadium ions into the rutile lattice with respect to the anatase lattice (*5*). Therefore one may feel that a deeper knowledge of the titania–vanadia interface is needed. In particular, the effects of the structure of titania–rutile and –anatase surfaces on the oxidation states of supported vanadium ions, and on the related valence-orbital charge densities, are in order.

The aim of this letter is to define proper cluster geometries to describe the TiO_2 (001)–rutile and –anatase supported vanadium interfaces and to calculate the vanadium oxidation states using the ionic model proposed by Brown and Altermatt (B–A) (*6*). The model is based on the valence-sum rule that states that the sum of the bond valences around an atom is equal to its atomic valence. The relationship between bond valence (s_{ij}) between two atoms i and j and bond length (R_{ij}) is monotonic, and over the small range in which most bonds are found it can be approximated by

$$s_{ij} = \exp[(R_0 - R_{ij})/B].$$

Here R_0 and B are fitted constants, R_0 being the length of a bond of unit valence. Values for these constants have been determined by many authors, by requiring that the values of s_{ij} obey the valence-sum rule in many different compounds (7). In the case of vanadium the value of B was found to be 0.37 Å and R_0 is equal to 1.815 Å.

This model has been widely used to calculate the valences of the cations in bulk oxides and mixed oxides and will be applied

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here, for the first time, to oxide surfaces. To simplify this application to oxide surfaces one may consider as the surface the oxygen layer that can be obtained by interrupting the bulk translation symmetry along the [001] crystallographic axis and neglecting the possible relaxation, reconstruction, dangling bonding, or dangling-bonding recombination effects. Moreover, for a correct criticism of the obtained results it should be reminded that the B–A empirical model implicitly assumes that the chemical bond is fully ionic. This assumption is an acceptable approximation in this case, in consideration of the electronegativity difference between metal and oxygen. Within these limits the possible geometrical distortions of the vanadium coordination polyhedra on the TiO_2 (001)–rutile and –anatase surfaces and their effects on the vanadium valence were evaluated.

For the sake of simplicity only the TiO_2(001)–rutile and –anatase surfaces will be considered; however, the model proposed here can be easily extended to other TiO_2–rutile and –anatase surfaces.

Surface dipole arguments and surface structure measurements indicate that both TiO_2(001)–rutile and –anatase surfaces end with an oxygen layer (*8*). However, it is well known that when the TiO_2 single crystals are cleaved under ultrahigh vacuum conditions the topmost TiO_2 surfaces are oxygen deficient (*9*). The ideal TiO_2 stoichiometry is recovered by exposing, at 850 K, the TiO_2 surfaces at a patial pressure of oxygen of 10^{-5} Torr. This procedure is recognized to restore the TiO_2 surface stoichiometry leading, very likely, to a bulk-like oxygen coordination for the titanium topmost layer (*10*) as shown in Figs. 1a and 1b, where the unrelaxed TiO_2 (001)–rutile and –anatase clusters that simulate these surfaces are represented.

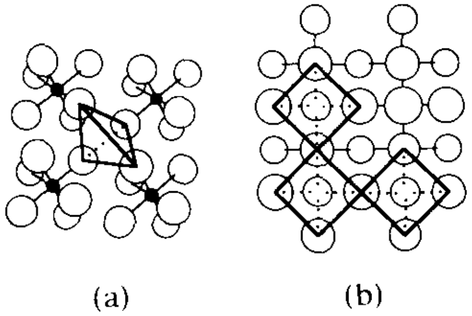

FIG. 1. The idealized (001) surfaces for the rutile (a) and the anatase (b) are shown. The possible coordination polyhedra for V are indicated.

The epitaxial growth of these surfaces implies the titanium ions to be coordinated in a tetrahedral geometry with the surface oxygen for the TiO_2(001)–rutile surface, whereas it has a square–pyramidal geometry on the TiO_2(001)–anatase surface, as shown by the bold lines in Figs. 1a and 1b. In the presence of oxygen the Ti ions assume, as reported in the literature (*11*), the bulk coordination represented by the clusters with the shadowed oxygen atoms reported in Figs. 2a and 2b.

When vanadium is deposited on these surfaces it very likely occupies the Ti ions sites, since titanium and vanadium have quite similar Pauling electronegativities and ionic radii. Moreover, they form Magneli phases (*12*) with the rutile-type structure. These facts suggest that when a monolayer or a submonolayer of vanadium is deposited on the TiO_2 surfaces it tends to grow epitaxially or quasi-epitaxially. In this hypothesis the possible oxygen coordination polyhedra for vanadium ions are similar to those occupied by titanium. However, vanadium tends to have a coordination number (CN) lower than six, as indicated by crystallographic studies of vanadium compounds (*12*). This could imply a distortion of the coordination polyhedra.

In order to calculate the valence of vanadium on TiO_2(001) surfaces the B–A model was applied (see above) (*13*). The vanadium valences calculated for the tetrahedral and the square–pyramidal coordination geometries as a function of the z-coordinate are reported in Figs. 3a and 3b (dashed lines). When the vanadium ion has the z-coordinate of Ti ($z = 0$), its valence is about 2.7 for the

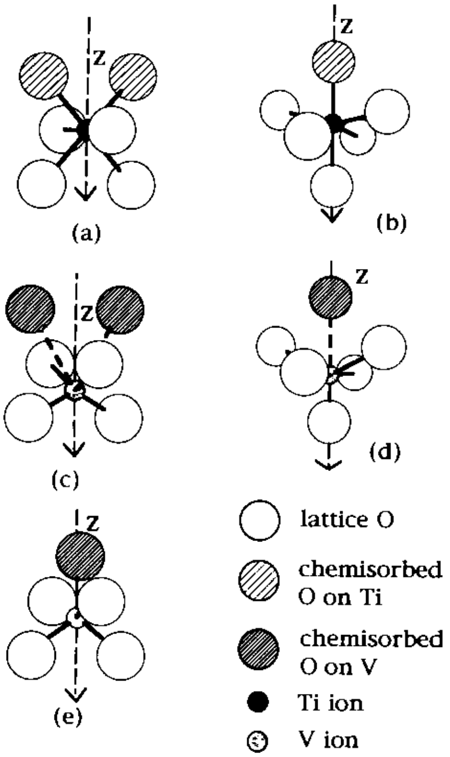

FIG. 2. (a) Octahedron of Ti in the rutile phase; (b) octahedron of Ti in the anatase phase; (c) possible deformation of the V polyhedron on the rutile surface; (d) possible deformation of the V polyhedron on the anatase surface; (e) as in (c) with only one shadowed oxygen ion completing the coordination (CN = 5).

tetrahedral geometry (rutile) and about 3.4 for the square–pyramidal geometry (anatase). These values are significantly lower than those experimentally observed on similar systems (*1*, *14*). In considering the present model higher valences are possible only by increasing the z-coordinate. In particular, in Fig. 3 the valence value of 4 corresponds to z = 0.5 Å for the (001) rutile and to z = 0.3 Å for the (001) anatase surfaces. The corresponding coordination geometries are shown in Figs. 2c and 2d, respectively.

The correlation between the vanadium valences and the bulk-like vanadium oxygen coordination, represented by the clusters with the shadowed oxygen in Figs. 2c and 2d, are given by the solid curves of Figs. 3a and 3b for the rutile and anatase surfaces, respectively. It is interesting that the oxidation state of V is increased by the oxygen chemisorption process for both surfaces, but it is significantly larger on the TiO_2 (001)–rutile surface.

It is important to note that, in the tetrahedral coordination on the rutile surface, chemisorption of the two oxygen ions, necessary for completing the bulk coordination (CN = 6), is difficult due to the shielding by the two oxygen ions of the topmost oxygen layer (see Fig. 2b). However, if only one

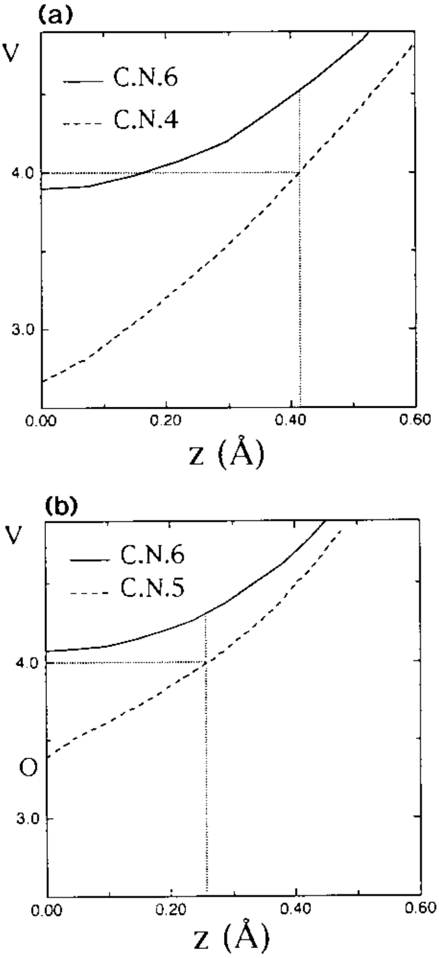

FIG. 3. Valence state of V vs its z-coordinate, i.e., vs its shift (in Å) toward the bulk: (a) for tetrahedral sites; (b) for square-pyramidal sites.

oxygen is chemisorbed, as shown in Fig. 2e, the typical and quite stable trigonal bipyramid, characteristic of V_2O_5, is formed.

The mechanism of bonding of an extra oxygen in the square–pyramidal geometry is elucidated in Fig. 3b. The addition of an "apical" oxygen leads to a small increase of the vanadium valence or to a relatively small decrease of the z-coordinate or to a combination of these effects. It is important to note that the square–pyramidal geometry does not present steric-hindrance effects and the oxygen can easily interact with vanadium. As a consequence a small change of the vanadium valence orbital charge density or z-coordinate can favor the CN_6 or the CN_5, leading to a mechanism of oxygen bonding and oxygen releasing.

These results may suggest that different oxygen polyhedra geometries significantly affect the vanadium electronic structure. In this sense, they can be viewed as a basic premise to fundamental information about these systems, i.e., orbital energies and the nature of the corresponding orbitals, that can be obtained from first principle electronic structure calculations. Furthermore, the cluster models, the coordination polyhedra, the coordination polyhedra distortion, and the oxygen chemisorption mechanisms proposed in the present work may be useful in planning surface structure experiments.

It is possible that, on the anatase surfaces, depending on the environmental redox conditions, small changes of the vanadium valences or vanadium z-coordinates or both will favor oxygen absorption or oxygen releasing mechanisms. They are probably basic to the catalytic behavior of V chemisorbed on anatase surfaces. Indeed, when a V ion is in a square–pyramidal site and, by decreasing its z-coordinate, goes toward the surface, without being shielded by surface oxygen atoms, it can coordinate one atom belonging to molecules of the gas phase (as O_2, NO_x, etc.), changing its CN from 5 to 6. Simultaneously its oxidation state changes to +4, losing some electron charge which is now available for partially filling an antibonding Π^* orbital of the incoming molecule. In the simple case of a dioxygen molecule this proccss leads to its activation and possible reaction with the environment. At this point the vanadium CN goes back to 5 and the V ion is ready for further coordination and activation of dioxygen molecules. Analogous schemes can be used for interpreting the catalytic redox reactions involving NO_x and similar simple molecules. This donation mechanism has already been proposed by others for V surface sites on different oxide supports (*15, 16*).

This simple geometrical model of the V ions on the surface of anatase may help in interpreting not only the activity but also the selectivity in the catalyzed reactions. This may be the case of the very important orthoxylene oxidation, if one considers the fact that the van der Waals distance (about 2.8 Å) between the C atoms of the two $-CH_3$ groups in that molecule is comparable to the minimum V–V distance on the surface of anatase.

In conclusion the model proposed here shows that when vanadium ions occupy the Ti sites on the TiO_2(001)–rutile surface they assume the oxidation state experimentally observed, i.e., V^{4+}, only if they move 0.5 Å under the topmost oxygen layer. If an apical oxygen is chemisorbed on these sites it forms the typical V_2O_5 trigonal bipyramid, which is a stable geometry. Vanadium ions on the TiO_2(001)–anatase surface move about 0.3 Å under the topmost oxygen layer to reach the V^{4+} oxidation state. If an oxygen is chemisorbed on this surface the vanadium ion will be coordinated by six oxygen in a quasi-octahedral configuration (CN_6). However, the valence of vanadium in this configuration (CN_6) is close to that calculated for the square–pyramidal configuration (CN_5).

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