JOURNAL OF CATALYSIS 88, 519–522 (1984)

The Validity of Cluster Models of Localized Charge Transfer in SMSI[1]

1. INTRODUCTION

The localized charge transfer model was one of the first proposed to explain the strong metal–support interactions (SMSI) that occur upon high temperature reduction of metal catalysts dispersed on certain transition–metal-oxide supports (*1*, *2*). In that model, the suppression of CO and H_2 chemisorption and the changes in catalytic activity and selectivity that accompany high temperature reduction result from a transfer of electrons from the cations of the reducible oxide support to the catalyst particles, thus changing their electron configuration (*2*). After 5 years of intensive experimental investigation of SMSI it is still one of the most universally accepted models, although other mechanisms have been proposed (*3*).

The theoretical justification for the localized charge transfer model rests on the 1979 paper by Horsley (*2*) that used Xα-SCF-SW cluster calculations to treat the interaction of Pt with TiO_2. Two clusters were considered, one to represent a stoichiometric TiO_2 surface and the other a reduced surface containing O ion vacancies. Comparison of those clusters with the geometry of TiO_2 surfaces, however, shows that they do not correspond to the actual situation that occurs on TiO_2. Neither of them, in fact, correctly treats the case of a reduced TiO_2 surface.

In this Note the relationship between Horsley's clusters and TiO_2 surfaces will be considered, and the reasons that the clusters fail to represent those surfaces will be discussed. The types of O ion vacancy sites that can occur upon reduction of TiO_2 surfaces will then be considered, along with the types of clusters that must be used to adequately represent a reduced oxide surface.

2. CLUSTERS AND TiO_2 SURFACES

The geometric and electronic structure of the major, low index faces of rutile TiO_2—(100), (110), and (001)—have been described previously (*4*, *5*). Briefly, Ti ions in the bulk of TiO_2 are coordinated with six O^{2-} ions in a slightly distorted octahedron. The electronic configuration of bulk Ti ions is nearly Ti^{4+} ($3d^0$), although there is a small admixture of Ti 3*s*, 3*p*, and 3*d* wave functions near the bottom of the predominately O 2*p* valence band. Surface cations necessarily have a lower O^{2-} ligand coordination than do bulk cations [with the exception of some of the cations on the (110) surface discussed below]. The most stable rutile surface is the (110), a model of which is shown in Fig. 1. (Ignore for now the two shaded circles labeled A and B.) Two O ion vacancy defects are also shown in Fig. 1 and will be discussed in Section 3 below. Half of the surface cations have the full sixfold ligand coordination, while the other half are fivefold coordinated. The next most stable TiO_2 surface is the (100) [see Fig. 3 in Ref. (*4*) and Fig. 3 in Ref. (*5*)], all of whose surface cations are fivefold coordinated. The TiO_2(001) surface has all fourfold coordinated cations and is relatively unstable, facetting upon ion bombardment or annealing.

(The anatase form of TiO_2 has not been considered in detail, but its surface structures are basically similar to those of rutile.

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[1] This work was partially supported by the Department of Energy, Office of Basic Energy Sciences, under Grant DE-AC02-81ER10830.

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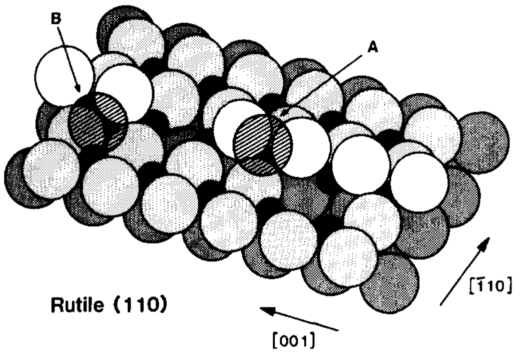

FIG. 1. Model of the rutile $TiO_2(110)$ surface. Large circles are O anions, small circles are Ti cations, and the transparent, shaded circles labeled A and B are adsorbed Pt atoms. Two types of O ion vacancy defects are shown.

The primary difference between the two lattices is the presence of two especially short O–O distances in anatase compared to one in rutile (*6*).)

The electronic structure of the $TiO_2(100)$, (110), and (001) surfaces has been determined experimentally and found to be very similar to that of the bulk for all three faces (*4*). In other words, reducing the ligand coordination of Ti cations at the surface is not sufficient to cause their charge state to deviate appreciably from Ti^{4+}. Recent calculations for TiO_2 surfaces having four-, five-, and sixfold coordinated cations substantiate the experimental results (*7*). In this Note we will consider only the $TiO_2(110)$ surface since it is the most stable one and the only low index face exhibiting sixfold coordination of the surface cations.

The two clusters considered by Horsley (*2*) were $(PtTiO_6)^{8-}$, intended to simulate a perfect TiO_2 surface, and $(PtTiO_5)^{6-}$ to represent a surface O ion vacancy; the geometry of those clusters is shown in Fig. 1 of Ref. (*2*). [A $(PtTiO_5)^{5-}$ cluster was also used to account for the presence of surface Ti^{3+} ions.] In the $(PtTiO_6)$ cluster the Pt atom was positioned in one of the threefold sites that constitute a face of the O^{2-} octahedron; this is its position of closest approach to the central Ti ion. The $(PtTiO_5)$ cluster had one of the six O^{2-} ions removed and replaced by the Pt atom. The removal of the O^{2-} ion was intended to simulate an O ion vacancy formed by the reduction of TiO_2 (*2*).

For the $(PtTiO_6)^{8-}$ cluster, the dominant electronic interaction involving the Pt atom was found to be a repulsive one with the three nearest-neighbor O^{2-} ions. This repulsion was thought to outweigh any attractive interaction between the two cations in the cluster, so the Pt atom would not bond to the cluster in this configuration. For the $(PtTiO_5)^{6-}$ cluster, in which the Ti ion was given a formal charge of 4+, some covalent mixing of the Pt and Ti orbitals was found. However, there was only a small amount of ionic bonding (i.e., localized charge transfer) between the cations, with the Pt atom having an effective negative charge of 0.11 electron. It was argued that, since reduction of the surface creates Ti^{3+} ions, the formal charge on the Ti ion should be 3+ [i.e., the cluster should be $(PtTiO_5)^{5-}$]. In that case a cluster orbital having predominately Pt 6*s* character became occupied, resulting in an effective negative charge of 0.6 electron on the Pt atom (*2*). This was interpreted as the origin of the charge transfer occurring upon high temperature reduction.

The way in which Horsley's clusters translate to TiO_2 surfaces is shown in Fig. 1. The transparent, shaded circles represent the positions that the Pt atoms would occupy for the $(PtTiO_6)$ cluster (site A) and for the $(PtTiO_5)$ cluster (site B). (The atomic radius for Pt^0 has been used in Fig. 1.)

A. $PtTiO_6$

Although the $TiO_2(110)$ surface does contain sixfold coordinated cations and a Pt atom could coordinate to an O octahedron as shown, an isolated $(PtTiO_6)$ cluster is not a good representation of that surface structure. The Pt atom would lie almost as close to two of the fivefold surface Ti ions as it does to the sixfold one, and, more importantly, there are no intervening O ions to screen the Pt atom from those ions (*5*).

Thus the magnitude of the interaction between the Pt atom and the fivefold Ti ions could be comparable to the Pt–Ti interaction within the cluster. The proximity of the two additional Ti ions on the surface would necessitate their inclusion into any cluster used to model the adsorption of a Pt atom at site A.

B. PtTiO$_5$

The $(PtTiO_5)^{6-}$ cluster, in which the Ti ion is assumed to have a formal charge of 4+, is a better approximation to coordination of a Pt atom to a perfect TiO_2 surface. Very little Ti → Pt charge transfer was found for that cluster (*2*), which is consistent with the normal chemisorption and catalytic behavior of Pt supported on stoichiometric TiO_2.

The $(PtTiO_5)$ cluster does *not,* however, correspond to coordination of a Pt atom to an O ion vacancy site on TiO_2; such vacancy sites have a fundamentally different structure and will be discussed in Sec. 3 below (*5*). Since the electronic structure of fivefold surface cations on TiO_2 is essentially the same as that of the bulk cations, it is incorrect to simply change the formal charge on the Ti ion to 3+. The resulting $(PtTiO_5)^{5-}$ cluster would correspond to adsorption on a perfect surface that contained Ti^{3+} ions, a situation that never occurs on TiO_2. [It would more nearly represent Pt adsorption on a perfect $Ti_2O_3(047)$ surface (see Refs. (*5, 8*)), which is in itself a very interesting problem.] Thus Horsley's calculations do not, in fact, account for charge transfer on reduced TiO_2 surfaces.

3. O ION VACANCIES ON TiO_2

The types of O ion vacancy sites that can exist on TiO_2 surfaces have been considered by Henrich (*4, 5, 9*); the chemisorption of small molecules at those sites has been discussed by Henrich (*5*) and by Göpel *et al.* (*10*). Two such sites that can occur on $TiO_2(110)$ are shown in Fig. 1. The simplest point defect consists of the removal of one of the O ions that bridges two sixfold surface cations (i.e., the O ions lying above the cation surface plane). This defect does result in two fivefold coordinated cations having essentially a Ti^{3+} electronic configuration, but the site is fundamentally different than a fivefold cation on the perfect surface. Removal of the bridging O ion greatly reduces the screening between the cations, and the charge that is localized at the defect (required by charge neutrality) is shared between the two adjacent Ti ions (*5*). The Ti^{3+} configuration of the cations at such a defect site is thus associated with *pairing* of the cations.

This O ion vacancy is a potential site for adsorption of a Pt atom on a reduced surface, and the resulting Ti–Pt–Ti electronic interactions could be very strong. A cluster calculation would be a good way to approach this localized bonding situation, but the minimum size cluster that would be useful is $(PtTi_2O_9)$, and an even larger cluster might be required.

The other type of O ion vacancy shown in Fig. 1 consists of removal of one of the in-plane O ions. That results in a more complicated point defect site bordered by two fourfold and one fivefold coordinated Ti ions. Again the removal of the intervening O ion significantly reduces the screening between the cations, and the charge localized at the defect site can be shared by as many as three cations. This is also a possible site for Pt atom adsorption, but to consider such a process at all realistically would require a $(PtTi_3O_{12})$ cluster or larger.

4. CONCLUSIONS

The cluster calculations of Horsley (*2*) for the interaction of Pt with TiO_2 do not correspond to the situation that actually occurs on reduced TiO_2 surfaces. They therefore do not provide an explanation of the role of localized charge transfer in SMSI. In order to correctly treat the interaction of Pt atoms with the Ti^{3+} species that exist at O ion vacancy sites on TiO_2 surfaces, substantially larger and more complex clusters are required.

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Received September 8, 1983