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LETTER TO THE EDITORS

Cluster Models of the Pt–TiO_2 Vacancy Interaction: Reply to V. E. Henrich

Henrich (*1*) has criticized the use of a simplified model for a TiO_2 surface vacancy in my earlier cluster calculations on the Pt–TiO_2 system (*2*). While calculations on larger clusters would certainly be useful, I believe that, contrary to the assertion of Henrich, the simple model I used does account for the essential features of the Pt atom–oxygen vacancy interaction and gives a qualitatively correct picture of the nature of the Pt–Ti bonding.

Tsukada *et al.* (*3*) have carried out calculations on large cluster models of the TiO_2 surface, including calculations with an oxygen vacancy, using the discrete-variational Xα technique. The cluster taken by Tsukada *et al.* to represent the TiO_2 surface was $(Ti_4O_{16})^{16-}$. They also carried out calculations on $(Ti_4O_{15})^{n-}$ clusters, representing a surface oxygen defect, and on clusters representing the bulk and a bulk oxygen defect. Calculations were carried out on the (Ti_4O_{15}) cluster with different numbers of electrons, the relevant calculations for the purposes of this discussion being $(Ti_4O_{15})^{15-}$ and $(Ti_4O_{15})^{16-}$, where the defect level contains one electron (the calculation on $(Ti_4O_{15})^{16-}$ began with two electrons in the defect level but this configuration was found to be unstable). The energy levels for these clusters are given in Fig. 5 of Ref. (*3*). The energy level structure is similar in both cases. There is a single defect level in the "band gap" somewhat below the bottom of the conduction band. This defect level is composed of a mixture of the 3*d* orbitals on the Ti ions around the defect site. We must now consider what happens when a platinum atom is placed in the defect site. My earlier calculations indicated that for a reasonable separation between the Ti ion and the Pt atom there was a certain amount of covalent mixing of the *d* orbitals on the Ti ion and those on the Pt atom. This conclusion depends on the overlap between the *d* orbitals on the Pt atom and the adjacent Ti ion or ions, which will be a function of the internuclear separation chosen in a particular calculation, not on the size of cluster used in that calculation. For reasonable values of that internuclear separation covalent mixing will therefore also be obtained in a calculation based on the Ti_4O_{15} cluster, the principal difference between the smaller and larger clusters being the number of Ti ions coordinated to the Pt atom (which will vary depending on the type of defect site).

However, the covalent bonding was not the most important part of the interaction between the Ti ion and the Pt atom in the earlier cluster calculation. The Pt 6*s* orbital was found to lie below levels that were largely Ti 3*d* in character and so the highest occupied orbital was Pt 6*s*. Without the Pt atom the highest occupied orbital was Ti 3*d* so the addition of the Pt atom resulted in charge transfer from the Ti ion and led to a large ionic contribution to the bond. In a calculation based on the Ti_4O_{15} cluster the corresponding charge transfer will be from the Ti 3*d* surface defect state just below the conduction band into the Pt 6*s* orbital. Whether such charge transfer takes place or not will depend on the relative energies of the surface defect state and the Pt 6*s* orbital. In the smaller cluster calculation the Pt 6*s* orbital was found to be about 1 eV above the O 2*p* nonbonding orbitals. Since the energy of the latter should be independent of the size of cluster this gives some

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indication of the position of the Pt 6*s* orbital relative to the Ti_4O_{15} energy levels. It can be seen from the energy level diagrams given by Tsukada *et al.* (*3*) that placing the Pt 6*s* orbital 1 eV above the O 2*p* orbitals in the Ti_4O_{15} cluster would place it below the Ti 3*d* surface defect state. It can therefore be predicted with some confidence that charge transfer will also be obtained in calculations based on larger clusters than that used in my calculation.

The main conclusions reached in the calculation based on the TiO_5 cluster should therefore also be valid for calculations based on larger clusters. These conclusions were:

(a) Pt atoms are strongly bonded to the TiO_2 surface at oxygen defect sites.

(b) Pt atoms are bonded directly to the Ti^{3+} cations.

(c) The Pt–Ti bond is partly covalent, partly ionic, with a preponderance of ionic character due to charge transfer.

The conclusions were based on considerations of orbital overlap and relative energy level positions that carry over to larger clusters so in this sense the simpler cluster calculation can indeed be said to account for charge transfer in Pt–TiO_2 systems. The Pt atom will, however, be bonded to more than one Ti ion, the number depending on the type of defect site.

REFERENCES

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