A Molecular Orbital Study of Strong Metal–Support Interaction between Platinum and Titanium Dioxide

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Abstract: A molecular orbital study of a strong metal-support interaction (SMSI) catalyst, platinum supported on TiO_2, has been carried out by the $X\alpha$-SW-SCF method using two different cluster models. The calculations favor a model in which platinum atoms are inserted into surface oxygen ion vacancies in the support, with bonding between the titanium cations and the platinum atoms. A possible mechanism for the suppression of H_2 chemisorption on the supported metal in SMSI catalysts is suggested.

Introduction

Recently, a new type of supported metal catalyst exhibiting strong metal–support interaction (SMSI) has been reported.[1] These catalysts consist of a group 8 noble metal (Pt, Ir, Os) supported on a member of a certain class of binary transition metal oxides. The principal characteristic of SMSI catalysts is the almost complete suppression of H_2 and CO chemisorption on the supported noble metal. These catalysts are typically prepared by impregnating the support with a noble metal salt solution, e.g., H_2PtCl_6, drying the impregnated material in an oven, and then heating it to 500 °C under flowing hydrogen gas for 1 h, followed by evacuation to 10^{-5} Torr at 500 °C for 0.5 h. A study of the SMSI activity of a large number of oxide supports has recently been published.[2] It was found that not all binary transition metal oxide supports show SMSI activity. Transition-metal oxides that are extremely refractory to reduction, such as Sc_2O_3 and ZrO_2, do not manifest SMSI behavior. The SMSI effect has been attributed to metal–support bonding but the exact nature of this bonding and its effect on H_2 and CO chemisorption are not known.

Platinum supported on titanium dioxide is a typical SMSI catalyst. Recently, an elegant study of the metal–support interaction in this system has been carried out by high-resolution transmission electron microscopy.[3] This study showed that the platinum particles on the support were in the form of very thin hexagonal rafts and that the platinum had grown epitaxially on the support.

This paper describes $X\alpha$ self-consistent field molecular orbital calculations on molecular cluster models for the Pt–TiO_2 SMSI catalyst. Calculations were carried out on two different molecular cluster models for this catalyst. The first model is shown schematically in Figure 1a. The molecular cluster that is taken to represent the system consists of a single Pt atom interacting with an octahedral $(TiO_6)^{8-}$ cluster. The important feature of this model is that the Pt atom is *outside* the $(TiO_6)^{8-}$ cluster. Its nearest neighbors are the triangle of oxygen atoms a, b, c and any interaction of the Pt atom with the Ti ion must take place across this face. This model bears some resemblance to a model that has been proposed to explain the structure of the hexagonal barium titanates.[4] These are oxides of the general formula $BaM_{1/3}Ti_{2/3}O_{3-x}$. In order to explain the occurrence of face-shared octahedra in the structure of these compounds it was proposed that one out of every two titanium ions is directly bonded to the "donor" cation M, the bonding taking place through the shared face connecting adjacent TiO_6 and MO_6 octahedra. If this suggestion is correct, Pt atoms on a TiO_2 surface could show a similar ability to form direct metal–metal bonds through one face of a TiO_6 octahedron.

In the second model, shown in Figure 1b, one of the oxygen atoms is removed from a TiO_6 cluster and the vacant site is occupied by a Pt atom. Vacant oxygen sites on the TiO_2 surface will be produced in the pretreatment of the SMSI catalyst by heating in H_2. In this model the nearest neighbor of the Pt atom is the Ti ion.

Calculations

The SCF-$X\alpha$ scattered wave method has been described in detail elsewhere.[5] In the "muffin tin" approximation used in the calculations described here the molecular space is divided into three regions: a region of spherical volumes surrounding each nucleus, a region between the atomic spheres and an "outer sphere" surrounding the entire molecule, and a region outside the outer sphere. The molecular potential is spherically averaged inside each atomic sphere and outside the outer sphere and is assumed to be constant in the intersphere region. Solutions of the one-electron Schrodinger equations for the three regions can be obtained, and the wave functions matched at the boundaries of the regions. The exchange part of the total potential is approximated by

$$V_{X\alpha}(\uparrow) = -6\alpha(\tfrac{3}{4}\pi\rho\uparrow)^{1/3}$$

where $\rho\uparrow$ is the local electron density of the spin-up electrons and α is a variable parameter (with a similar expression for the spin-down electrons).

The values of the α parameter for the oxygen and titanium atomic spheres were taken from the compilation of Schwarz[6] and a value of $\alpha = 0.7$ was used for the platinum atomic sphere. The values of α for the intersphere and outer-sphere regions were the average of the atomic sphere values weighted according to their respective numbers of valence electrons. The ratios of the sphere radii of the titanium, oxygen, and platinum atoms were chosen according to the criterion of Norman[7] and the absolute values were obtained by requiring that the oxygen and platinum atomic spheres just touch the titanium atomic sphere. This led to a slight (<10%) overlap between the platinum and oxygen spheres in the case of model I.

The Ti–O distance was taken to be 1.944 Å, the experimental distance in TiO_2,[8] in all the calculations. There is no experimental information on the Pt–Ti distance, so this distance had to be estimated. One possibility would be to take this distance as the sum of the ionic radius of Ti^{4+} and the covalent radius of Pt, on the assumption of a completely ionic model for TiO_2. However, TiO_2 is certainly not completely ionic and it was assumed that the effective charge on the Ti ion was closer to two than to four (an assumption justified a posteriori by the calculation on the $TiO_6{}^{8-}$ cluster). The Pt–Ti distance was accordingly taken as the sum of the Pt covalent radius and the average of the Ti^{4+} ionic radius and the Ti covalent radius. The $X\alpha$ parameters and the interatomic distances are summarized in Table I.

The core orbitals for Pt, Ti, and O were determined from

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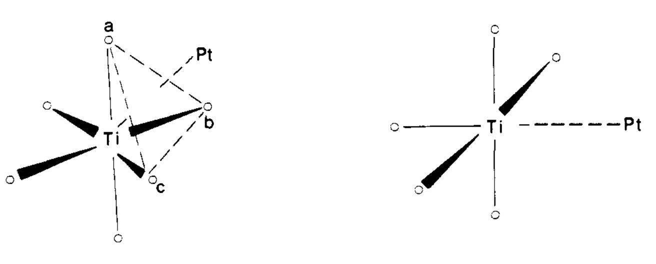


(a) (b)

Figure 1. Cluster models for the Pt-TiO_2, SMSI catalyst: (a) model I, (b) model II.

Table I. Internuclear Distances, Sphere Radii, and Values of α Used in the Calculations

	$(TiO_6)^{8-}$	$(PtTiO_6)^{8-}$	$(PtTiO_5)^{6-}$
Ti-O distance, Å	1.944	1.944	1.944
Pt-Ti distance, Å		2.381	2.381
Ti sphere radius, Å	1.107	1.107	1.043
Pt sphere radius, Å		1.279	1.1337
O sphere radius, Å	0.842	0.842	0.900
outer sphere radius, Å	2.785	3.132	3.281
α_{Ti}	0.7169	0.7169	0.7169
α_{Pt}		0.7	0.7
α_{O}	0.7444	0.7444	0.7444
α_{inter}	0.74	0.73	0.73

atomic calculations and held fixed during the SCF iterations. The core orbitals were considered to be all orbitals up to 5s for Pt, 1s, 2s, 2p for Ti, and 1s for O. A Watson sphere centered at the same point as the outer sphere and having the same radius as the outer sphere was included in the SCF calculations for both models. The charge on the Watson sphere was +9 for model I, $(Pt\ TiO_6)^{8-}$, and +7 for model II, $(Pt\ TiO_5)^{6-}$.

Results

For the purpose of comparison a preliminary calculation was first carried out on an octahedral $(TiO_6)^{8-}$ cluster, with the Ti-O distance given in Table I. In this calculation two Watson spheres were used, both centered on the Ti atom with charges +8 and with radii equal to the radius of the outer sphere and the Ti-O distance, respectively. The energy levels of the valence orbitals and the lowest unoccupied orbitals are shown in Figure 2. The highest occupied orbital is the t_{1g} orbital. In a completely ionic picture the lowest unoccupied orbitals, t_{2g} and e_g, are simply the empty 3d orbitals of the Ti^{4+} ion split by the octahedral field of the O^{2-} ligands. However, the calculation indicates that there is a fairly large covalent contribution to the bonding in $(TiO_6)^{8-}$. The compositions of the valence orbitals and the lowest unoccupied orbitals in $(TiO_6)^{8-}$ are given in Table II. It can be seen that some of the valence orbitals have a fairly high proportion of Ti 3d character. A measure of the covalent character of the bonding in $(TiO_6)^{8-}$ is given by the effective charge on the Ti atom. A method for calculating the effective charge on an atom within the muffin tin approximation of the SCF-Xα-SW method has recently been proposed by Case and Karplus.[9] The total charge on an atom is taken to be the sum of the charge inside the atomic sphere around the atom plus a fraction of the intersphere charge. The intersphere charge is partitioned among the various atoms in proportion to the average charge density at the surface of each atomic sphere, multiplied by the area of that surface bordering the intersphere region. The effective charge on the Ti atom has been calculated in this way, and was found to be only +1.1, showing the large covalent contribution to the bonding in the $(TiO_6)^{8-}$ cluster.

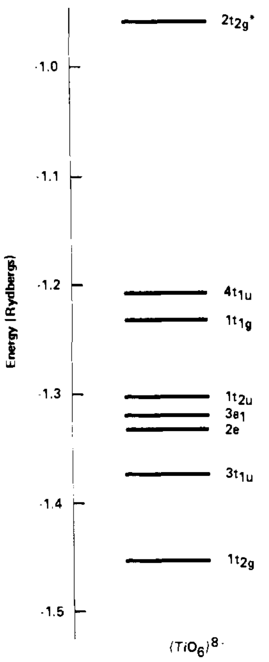


Figure 2. Calculated Xα-SW molecular orbital energy levels for the $(TiO_6)^{8-}$ cluster. Asterisk indicates unoccupied orbital.

Table II. Orbital Energies and Compositions of the Valence Orbitals of $(TiO_6)^{8-}$

orbital[a]	energy, Ry	description[b]
$3a_1$	−1.335	Ti (0.05 s), O (0.95 p)
2e	−1.349	Ti (0.22 d), O (0.78 p)
$1t_{1g}$	−1.251	O (1.0 p)
$1t_{2u}$	−1.319	O (1.0 p)
$1t_{2g}$	−1.464	Ti (0.09 d), O (0.91 p)
$3t_{1u}$	−1.386	Ti (0.01 p), O (0.99 p)
$4t_{1u}$	−1.229	Ti (0.02 p), O (0.98 p)

[a] Orbitals which are predominantly Ti 3s, Ti 3p, and O 2s are omitted. [b] The numbers in parentheses are the fractions of the total charge within the atomic sphere contributed by that atomic species, analyzed according to angular momentum quantum number.

Figure 3 shows the orbital energy levels obtained when a Pt atom was placed outside the $(TiO_6)^{8-}$ cluster (model I). The highest occupied orbital is 12e. The lowest unoccupied orbital, 13e, is predominantly a Ti 3d orbital just as in the $(TiO_6)^{8-}$ cluster. The Pt 5d orbitals are strongly mixed with the 2p orbitals on the adjacent triangle of O atoms, forming bonding-antibonding pairs of orbitals. However, these orbitals are all fully occupied so there is no *net* covalent bonding between the Pt atom and the adjacent O atoms. If there is no net bonding then there must be a strong net coulombic repulsion at these distances because of the interpenetration of the electron clouds around the Pt and O atoms. The compositions of the valence and lowest unoccupied orbitals for this model are given in Table III. The only orbitals that contain a nonnegligible proportion of both Pt 5d and Ti 3d are the $6a_1$ and 7e orbitals. A contour plot of the 7e orbital showed that this orbital is antibonding between the Pt and Ti atoms. However, the $6a_1$ orbital does show some bonding between the Pt and Ti atoms due to overlap between the lobes of the d_{z^2} orbitals, although the charge seems to be strongly polarized toward the Pt atom. A contour plot of this orbital is shown in Figure 4. It seems highly improbable that this interaction could overcome the strong repulsion between the O atoms and the Pt atoms and give a net attractive interaction between the metal and the support. It is unlikely that the Pt atom can get close enough to the Ti ion for bond formation to occur.

There is no evidence that the mechanism proposed by

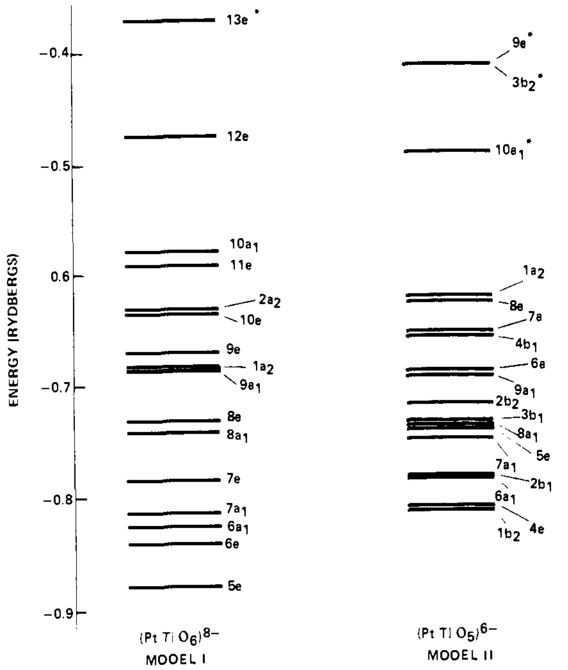


Figure 3. Calculated $X\alpha$–SW molecular orbital energy levels for model I and model II. Asterisk indicates unoccupied orbital.

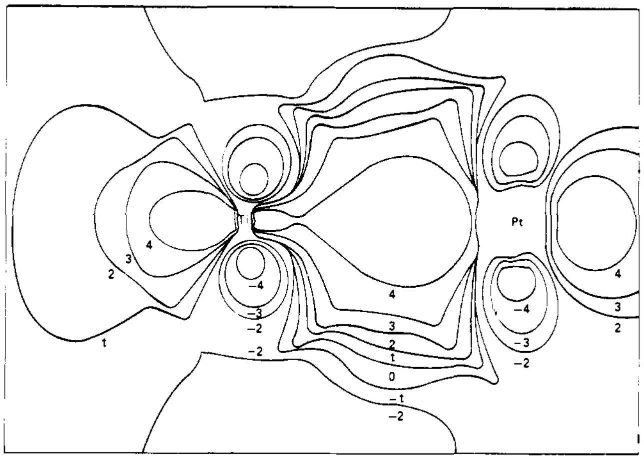


Figure 4. Contour plot of the wave function for the $6a_1$ orbital of $(PtTiO_6)^{8-}$ (model I). Contour values are 1 = 0.01, 2 = 0.025, 3 = 0.05, 4 = 0.1. The sign of the labels gives the sign of the orbital lobes.

Dickenson et al.[4] to account for the structure of the hexagonal barium titanates is operative here. These authors proposed that metal-metal bonding between an "acceptor" cation (Ti^{4+}) and a "donor" cation (e.g., Pt^{4+}) takes place by overlap of the empty d orbitals of the acceptor ion and the filled d orbitals of the donor cation, the electrons necessary for bonding being supplied by the donor cation. The compositions of the occupied orbitals in Table III indicate no such direct interaction. The empty d orbitals of the Ti^{4+} ion correspond to the lowest unoccupied t_{2g} and e_g orbitals of $(TiO_6)^{8-}$ in the molecular orbital picture. The lowest unoccupied orbitals in the $(PtTiO_6)^{8-}$ cluster are again predominantly Ti 3d orbitals, indicating that the empty Ti 3d orbitals in $(TiO_6)^{8-}$ remain empty in the $(Pt\text{-}TiO_6)^{8-}$ cluster.

The orbital energy levels obtained for model II are shown in Figure 3. The highest occupied orbital is $1a_2$. The unoccupied orbitals, $3b_2$ and 9e, are again predominantly Ti 3d orbitals but the lowest unoccupied orbital, $10a_1$, is predominantly Pt 6s. The compositions of these orbitals and the valence orbitals are given in Table IV. There is some covalent mixing of the Ti 3d and O 2p orbitals and, in addition, there is covalent mixing of the Ti 3d and Pt 5d orbitals. Figure 5 shows contour plots of the $6a_1$ and 4e orbitals. The covalent bonding of the Ti and Pt atoms is evident. Further, an analysis of the effective charges on the Ti and Pt atoms by the method of Case and Karplus shows that the Pt atom acquires some negative charge, the effective charge being −0.11. Although any division of the electronic charge is somewhat arbitrary, this suggests that there is some ionic contribution to the Pt–Ti bond. In the model II cluster, $(PtTiO_5)^{6-}$, the Ti ion is formally Ti^{4+} and the O ion formally O^{2-} (although the covalent character of the bonding leads to very different effective charges). However, the reduction of the catalyst in H_2, which creates the surface O ion vacancies, also products Ti^{3+} ions.[3] If the formal charge on the Ti ion is +3 then the lowest occupied orbital in the model II cluster, $10a_1$, becomes singly occupied. It can be seen in Table IV that this orbital is not a Ti 3d orbital but is instead about 50% Pt 6s, the remainder being largely O 2p. An SCF calculation on a cluster in which this orbital is singly occupied did not lead to any significant change in this composition. Thus, in the case where the Pt atom is inserted next to a Ti ion which is formally Ti^{3+} the calculation indicates that the Ti 3d electron is largely transferred to the Pt atom. This will lead to a greater ionic component to the Pt–Ti bond, the effective charge on the Pt atom now being −0.6, and would no doubt lead to a stronger bond. It appears as if the Pt atom is simply acting as one of the

Table III. Orbital Energies and Compositions of the Valence Orbitals of $(PtTiO)_6{}^{8-}$

orbital[a]	energy, Ry	description[b]
$6a_1$	−0.824	Ti (0.02 s, 0.13 d), Pt (0.03 s, 0.28 d), O_1 (0.36 p), O_2 (0.14 p)
$7a_1$	−0.809	Ti (0.04 s, 0.04 d), Pt (0.04 s, 0.23 d), O_1 (0.32 p), O_2 (0.55 p)
$8a_1$	−0.737	Ti (0.02 p), Pt (0.08 s), O_1 (0.32 p), O_2 (0.55 p)
$9a_1$	−0.681	Ti (0.05 s, 0.02 p, 0.03 d), Pt (0.24 d), O_1 (0.06 p), O_2 (0.60 p)
$10a_1$	−0.576	Ti (0.01 p, 0.04 d), Pt (0.26 d), O_1 (0.41 p), O_2 (0.26 p)
$1a_2$	−0.681	O_1 (0.59 p), O_2 (0.41 p)
$2a_2$	−0.625	O_1 (0.57 p), O_2 (0.43 p)
5e	−0.876	Ti (0.08 d), Pt (0.37 d), O_1 (0.47 p), O_2 (0.008 p)
6e	−0.838	Ti (0.01 d), Pt (0.48 d), O_1 (0.47 p), O_2 (0.03 p)
7e	−0.782	Ti (0.25 d), Pt (0.04 d), O_1 (0.43 p), O_2 (0.28 p)
8e	−0.727	Ti (0.11 d), Pt (0.10 d), O_1 (0.07 d), O_2 (0.70 p)
9e	−0.665	Pt (0.19 d), O_1 (0.06 p), O_2 (0.75 p)
10e	−0.631	Ti (0.02 p, 0.02 d), Pt (0.07 d), O_1 (0.32 p), O_2 (0.55 p)
11e	−0.586	Ti (0.01 p, 0.01 d), Pt (0.40 d), O_1 (0.35 p), O_2 (0.22 p)
12e	−0.472	Pt (0.50 d), O_1 (0.44 p), O_2 (0.05 p)
13e[c]	−0.369	Ti (0.91 d), O_1 (0.03 p), O_2 (0.06 p)

[a] Orbitals which are predominantly Pt 5p, Ti 3p, Ti 3s, and O 2s are omitted. [b] For explanation see footnote to Table II. O_1 refers to the triangle of O atoms nearest to the Pt atom; O_2 refers to the remaining O atoms. [c] Lowest unoccupied orbital.

Table IV. Orbital Energies and Compositions of the Valence Orbitals of $(PtTiO_5)^{6-}$

orbital[a]	energy, Ry	description[b]
$6a_1$	−0.781	Ti (0.26 d), Pt (0.25 d), O_1 (0.19 p), O_2 (0.29 p)
$7a_1$	−0.745	Ti (0.02 s, 0.04 d), Pt (0.02 s, 0.02 d), O_1 (0.83 p), O_2 (0.06 p)
$8a_1$	−0.731	Ti (0.03 s), Pt (0.03 s, 0.16 d), O_1 (0.68 p), O_2 (0.08 p)
$9a_1$	−0.689	Ti (0.01 p, 0.01 d), Pt (0.63 d), O_2 (0.34 p)
$10a_1$[c]	−0.493	Ti (0.06 d), Pt (0.50 s), O_1 (0.31 p), O_2 (0.13 p)
$1a_2$	−0.618	O_1 (1.0 p)
$2b_1$	−0.779	Ti (0.32 d), Pt (0.01 d), O_1 (0.67 p)
$3b_1$	−0.728	Pt (0.84 d), O_1 (0.16 p)
$4b_1$	−0.654	Pt (0.23 d), O_1 (0.77 p)
$1b_2$	−0.809	Ti (0.16 d), Pt (0.05 d), O_1 (0.79 p)
$2b_2$	−0.712	Pt (0.96 d), O_1 (0.04 p)
$3b_2$[c]	−0.409	Ti (0.90 d), O_1 (0.1 p)
4e	−0.805	Ti (0.15 d), Pt (0.18 d), O_1 (0.35 p), O_2 (0.30 p)
5e	−0.735	Ti (0.02 p), Pt (0.39 d), O_1 (0.40 p), O_2 (0.18 p)
6e	−0.683	Pt (0.38 d), O_1 (0.52 p), O_2 (0.1 p)
7e	−0.647	Pt (0.18 d), O_1 (0.48 p), O_2 (0.31 p)
8e	−0.626	Ti (0.03 p), Pt (0.04 d), O_1 (0.92 p), O_2 (0.01 p)
9e[c]	−0.411	Ti (0.86 d), Pt (0.03 d), O_1 (0.08 p), O_2 (0.02 p)

[a] Orbitals which are predominantly Pt 5p, Ti 3p, Ti 3s, and O 2s are omitted. [b] For explanation see footnote to Table II. O_1 refers to the four equivalent O atoms; O_2 refers to the unique O atom. [c] Lowest unoccupied orbitals.

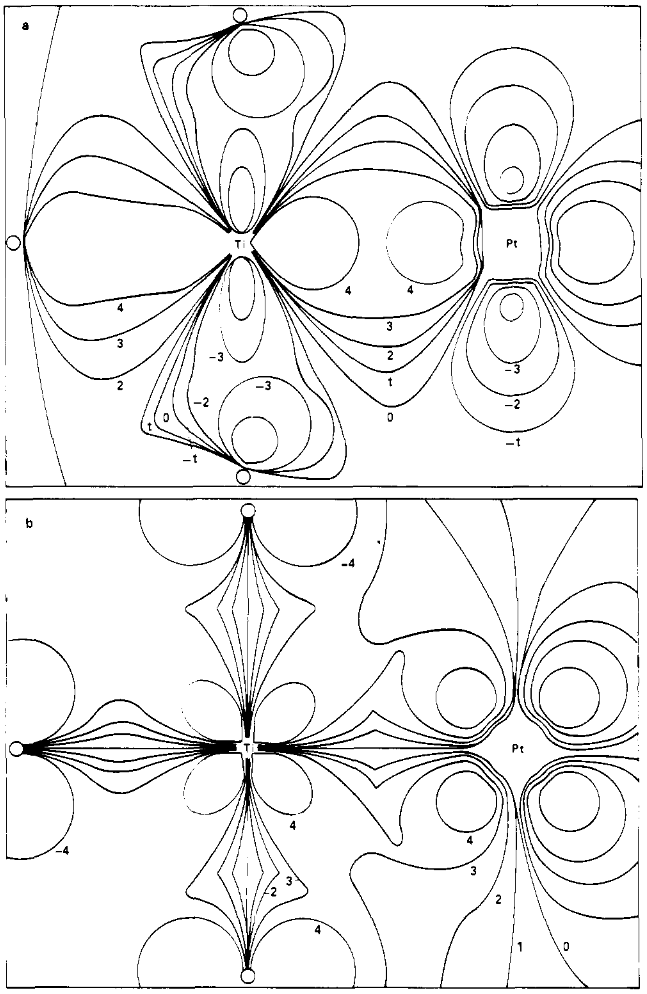


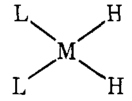
Figure 5. (a) Contour plot of the wave function of the $6a_1$ orbital of $(PtTiO_5)^{6-}$ (model **II**). Contour values as in Figure 4. (b) Contour plot of the wave function of the 4e orbital of $(PtTiO_5)^{6-}$ (model **II**). Contour values as in Figure 4.

ligands of the Ti ion on model II with a bond of mixed covalent-ionic character (although with less ionic character than the bonds to the oxygen ligands).

Discussion

The SCF-Xα calculations indicate significant metal-metal bonding between the platinum atom and the titanium ion in both models. However, for model I there is also a strong net repulsive interaction between the platinum atom and the adjacent oxygen ions and so it is improbable that a platinum atom could approach close enough to the $(TiO_6)^{8-}$ cluster for metal-metal bonding to occur. In model II there is no strong repulsive interaction between the platinum atom and the oxygen ions because the platinum atom occupies a site made available by removing one of the oxygen ions from the $(TiO_6)^{8-}$ cluster. The platinum atom is therefore able to approach close enough to the titanium ion for metal-metal bonding to occur. If the Pt-Ti bonds that are formed are stronger than the Pt-Pt bonds, then the Pt atoms will be preferentially attracted to surface O ion vacancies formed by the reduction of TiO_2 rather than to other Pt atoms. This would explain the thin rafts of Pt atoms growing expitaxially on the support that were observed in the electron microscopy study.[3] It therefore seems probable that the metal-support interaction in the Pt-TiO_2 SMSI catalyst should be represented by model II rather than model I. It is possible that the covalent bonding alone is not sufficient to account for the strength of the metal-support interaction. The ionic component introduced by electron transfer from Ti^{3+} to the Pt atom may be essential in order to obtain a strong bond.

We must now consider the relationship between the formation of Pt-Ti bonds in model II and the ability of the supported platinum to chemisorb hydrogen. Recently, Johnson et al.[10] have carried out a molecular orbital study of interaction between a hydrogen molecule and coordinatively unsaturated complexes of the type L_2M (M = Pt, Rh, etc.). The ligand L is typically triphenylphosphine but could also be another metal atom of the same species as M, in which case the complex can be said to be a model of the corner atoms of a metal surface step. Johnson et al. found that the H_2 molecule is bonded to the L_2M complex in a "partially dissociated" dihydride configuration i. They suggest that the interaction of the metal d orbitals with the ligand orbitals is crucial to the ability of the complex to bond to H_2 in this way. The metal-ligand interaction results in occupied metal (d)-ligand antibonding orbitals which are much closer in energy to the σ_u antibonding orbital of H_2 than are the d orbitals of the isolated metal atom. This facilitates electron flow from the occupied metal-ligand antibonding orbitals into the σ_u H_2 antibonding orbitals, thereby promoting the dissociation of H_2. There is some evidence that chemisorption of H_2 is strongly promoted at corner atom sites



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on metal surfaces[11] and, if this is the case, the above theory would explain why.

Now consider the situation in the two models for the SMSI catalyst. In model I there is a strong interaction between the Pt and O atoms resulting in occupied antibonding orbitals (e.g., 12e) that are split off from the bonding and nonbonding levels and closer in energy to the antibonding H_2 σ_u orbital than the orbitals of the unsupported metal atom. Therefore, following the reasoning of Johnson et al., one would expect that, if the structure of the SMSI catalyst could be represented by model I, then chemisorption of H_2 by the supported Pt would occur readily, contrary to what is observed. Turning now to model II, we see that there are no occupied Pt-O antibonding orbitals split off in energy from the bonding and nonbonding orbitals. If the thin rafts observed in the electron microscopy study consist of monolayers of Pt atoms, then the suppression of H_2 chemisorption could be at least partially explained by the absence of any "active sites" such as the corner atoms of steps. In model II the interaction between the Pt atom and the support does not provide any occupied antibonding orbitals to compensate for the lack of active sites on the metal surface. The $10a_1$ orbital, which is singly occupied in the case where the Ti ion was formally Ti^{3+}, does not have the correct symmetry to interact with the H_2 σ_u orbital, although it does lie in the right energy region.

Finally, the metal-support interaction in SMSI catalysts may be compared with that in catalysts consisting of a transition metal supported on silica. In the case of ruthenium supported on SiO_2 thin (monolayer) raft-like structures have been observed similar to the raft-like structures observed in the Pt-TiO_2 system,[12] and EXAFS studies indicate considerable metal-support interaction.[13] Kolari and Johnson[14] have carried out SCF-Xα-SW calculations on clusters representing Ru atoms on SiO_2, which indicate that in this case there is a strong interaction between the Ru atom and the nonbonding p orbitals of the O atoms, just as in Pt on TiO_2 (model I). However, in this case, unlike Pt on TiO_2, the highest antibonding orbital is not occupied, so that there is a net bonding interaction between the Ru and the surface oxygen atoms. The behavior of this catalyst with respect to H_2 chemisorption is not known, although it has been found that O_2 is chemisorbed molecularly, not dissociatively, as could be predicted by the theory of Johnson et al. The principal difference between the metal-support interaction in the Pt-TiO_2 SMSI catalyst and that in the Ru-SiO_2 catalyst is that in the former case the interaction takes place between the supported metal and the support cations, while in the latter case the interaction is between the metal and the support "anions". In both cases it is proposed that the chemisorption properties are governed by the lack of occupied antibonding orbitals which can match up in energy with the antibonding orbitals of a reactant molecule such as H_2. Future experimental work will undoubtedly reveal further similarities between the properties of the two types of catalyst, and shed more light on the metal-support interaction in SMSI systems. In particular, extended X-ray absorption fine structure (EXAFS) experiments[13] on SMSI catalysts would yield valuable information on the nature of the metal-support interaction that would directly test many of the features of the model proposed in this paper.

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