The Chemical Nature of Atomic Oxygen Adsorbed on Rh(111) and Pt(111): A Density Functional Study

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The bonding of atomic oxygen on Pt(111) and Rh(111) was examined using density functional theory in order to understand their different chemical properties. The oxygen—surface interactions were modeled by bonding atomic oxygen to 10-atom clusters of Pt and Rh designed to model the (111) surface. Density functional theory was applied using the local density and generalized gradient approximations; results were obtained for both double- ζ and triple- ζ basis sets. Optimized geometries and binding energies were computed and favorably compared to available experimental values. Interestingly, the ionic bonding in the two cases is nearly the same, based on the similarities in the charge on oxygen. The Hirshfeld charges on oxygen were -0.225 and -0.207 for Rh₁₀-O and Pt₁₀-O, respectively, using the double- ζ basis set. A more detailed analysis of the covalent bonding using crystal orbital overlap populations indicated that the 2p orbitals of oxygen interact in a greater bonding fashion with both the sp and d orbitals of Rh than with those of Pt. Additional calculations with adsorbed hydroxyl on these metal clusters show differences in covalent bonding similar to that of oxygen. In this case, however, differences in ionic bonding play a role; oxygen in hydroxyl on Rh and Pt compared with oxygen, resulting in differences in chemical reactivity between the two metals, especially with respect to reactions involving hydrogen transfer.

Introduction

The bonding of atomic oxygen to transition metal surfaces is of considerable interest, because understanding the nature of the interaction between atomic oxygen and the metal surfaces is crucial to elucidating the role of oxygen in a variety of catalytic reactions. In particular, partial oxidation reactions have been widely studied because of an interest in the partial oxidation of methane into more useful derivatives such as methanol or formaldehyde. A major challenge in oxidation chemistry is to limit combustion to carbon dioxide and water, which is favored because of the large thermodynamic driving force for combustion and the high temperatures often required for oxidation, especially of methane.

A body of work indicates an interesting difference in the behavior of oxygen on Rh and Pt which is important in determining the product distributions in alkane oxidation on these surfaces. Zum Mallen and Schmidt¹ have studied methanol oxidation over polycrystalline Pt and Rh and found that oxygen on Pt enhances catalytic activity, whereas oxygen passivates the Rh surface. This was attributed to the stability of hydroxyl on Pt vs Rh. The differences in the reactivity of oxygen go beyond hydrocarbon oxidation, indicating a general difference in the ability of oxygen to react with hydrogen on Pt(111) vs Rh(111). For example, oxygen inhibits C–H bond breaking on Rh(111),² whereas it promotes dehydrogenation of cyclohexane on Pt(111).³

Madix⁴ has proposed that oxygen reactions on certain metal surfaces, such as Ag(110), can be interpreted in terms of acid—

base chemistry, where oxygen acts as a Brönsted base, i.e., that the oxygen abstracts a proton from the reactant molecule. This analogy seems reasonable for oxygen on Pt(111) as well, since OH is stable on the surface and oxygen promotes dehydrogenation. Oxygen on Rh(111) cannot be regarded in this framework, however, because OH is not stable on the Rh(111) surface and has never been isolated experimentally; furthermore, oxygen on Rh does not cleave C—H bonds. This present study was undertaken to specifically examine the bonding of oxygen and hydroxyl to Pt and Rh in order to determine if the differences in reactivity can be understood on the basis of differences in the charge on oxygen which would be expected in a Brönsted acid—base formalism. Specifically, the more basic oxygen should have a greater negative charge.

Surprisingly, there are relatively few experimental or theoretical studies of the electronic properties of oxygen on Rh(111) and Pt(111). Puglia et al. used XPS, UPS, and NEXAFS to characterize the bonding of atomic oxygen to Pt(111),⁵ and they concluded that the bonding was through interaction of the $2p_{xy}$ orbitals of oxygen with the 6sp states of the Pt metal and the O $2p_z$ orbital with the 5d Pt orbitals. There are no reports of theoretical studies of oxygen on Pt(111) to compare with these experiments, however. On Rh(111) there are no reported photoemission data, and the only theoretical study was performed using the extended Hückel method.⁶ Although the 3-fold hollow site was preferred for atomic oxygen on Rh(111), in agreement with experiment, there was no detailed orbital analysis of the Rh—O bonding. To date there have been no ab initio calculations of oxygen on Rh or Pt.

In this paper we present the results of cluster calculations using density functional theory to investigate the bonding of oxygen and hydroxyl on the (111) surfaces of Rh and Pt. In addition to determining the lowest energy structures for oxygen

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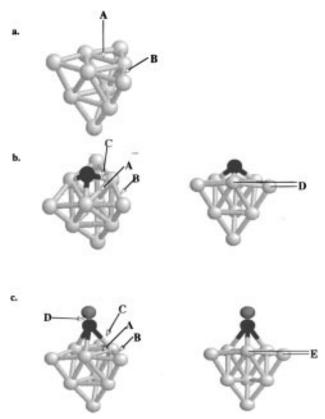


Figure 1. Ten-atom cluster used in calculations: (a) bare cluster; (b) two views of the cluster with oxygen; (c) two views of the cluster with OH. The letter codes signify pertinent optimized parameters that are detailed in Table 1.

on the two surfaces, we perform an orbital analysis to understand the origin of the different chemical behavior in the two cases. Analogous calculations for hydroxyl are also presented. The cluster model compares well with experimental data in that bond lengths are reasonable, oxygen binds in the 3-fold site on both metals, and qualitative trends in adsorption energies are reproduced. Furthermore, the simulated ultraviolet photoelectron spectrum for O on Pt is similar to that experimentally measured.⁷ It was found that the main differences in the bonding of oxygen to Rh and Pt are due to the covalent part of the bonding; the ionic contribution is approximately the same between the two metals. For hydroxyl, however, the oxygen on Pt has a greater charge than on Rh. In this case, hydroxyl on Pt has a greater contribution from ionic bonding than Rh. Although OH is still more strongly bound to Rh by virtue of its covalent bonding, we propose that it is the difference in ionic bonding which is the determining factor in the thermodynamic stability of hydroxyl on these two metals.

Calculation Models

Cluster models were used to represent the (111) surfaces of Pt and Rh metals. The cluster used contained 10 metal atoms, arranged in tetrahedral symmetry with layers containing 6, 3, and 1 atoms. (Figure 1) (The symmetry was reduced to $C_{3\nu}$ upon complex formation with an adsorbate). All clusters were subjected to full geometry optimization with unrestricted spins. In all cases, the structure and energies reported in this paper refer to the most stable (i.e. lowest energy) electronic configuration (Table 2).

Certain requirements must be met for a cluster to reasonably model a metal surface. Specifically, the cluster should be reasonably symmetric, to speed up calculation times and to reproduce the symmetry of the surface site. The M_{10} cluster is

a compromise between computational efficiency and a realistic model of a metal surface. The presence of the second and third layers in the cluster prevents unreasonable adsorbate-induced distortions in the top layer. While there is some debate as to the effectiveness of using a cluster to model a surface, the best test of the cluster approximation is to compare cluster calculations with experimental results. In this case, we are confident that our calculations qualitatively model the metal surfaces, since our bond lengths are in excellent agreement with experiment, and the interaction energies of the adsorbates follow the same trends as those measured.

Calculation Details

All calculations reported here have been performed using the Amsterdam Density Functional Package (ADF). Molecular orbitals are represented as Slater-type functions. Computational efficiency is enhanced by keeping the innermost atomic shells of all atoms except hydrogen frozen, as these core electrons do not contribute significantly to the chemical bonding. The extent of these frozen cores was up to and including the following orbitals: Rh 4p, Pt 5p, O 1s. Two different basis sets were used in the calculations; the first, designated set I, was of double- ζ quality (i.e. two Slater-type functions per filled valence atomic orbital). The second basis set, set II, was triple- ζ quality. In set I, the functions for oxygen were augmented by a single polarization function. In set II, oxygen had two polarization functions added. ADF provides no polarization functions for transition metals.

The Vosko-Wilk-Nusair11 form of the local density approximation (LDA) was employed to solve the Kohn-Sham one-electron equations. Nonlocal (or gradient) corrections to compensate for the overbinding of the LDA were provided by the Becke^{12,13} and Perdew¹⁴ functionals for the exchange and correlation energies, respectively. Relativistic effects within the cores of the heavy atoms were accounted for by using firstorder perturbation theory. 15,16 Both the nonlocal and relativistic corrections were included self-consistently in the calculations, rather than as a postoptimization correction. The maximum possible symmetry was employed in the calculations to reduce computation times. Geometries were optimized until the changes in energy and Cartesian coordinates were less than 0.001 hartrees/Å and 0.001 Å, respectively. Adsorption energies were calculated by subtracting the total energy of the bare substrate and gas-phase adsorbate from the substrate-adsorbate complex energy. Thus, a negative adsorption energy corresponds to a stabilized system. Adsorbates were placed in the 1-, 2-, and 3-fold sites to determine the lowest-energy binding site. However, the size of this cluster did not allow a quantitative comparison of the energetics of the different sites, due to the different coordination of the various metal atoms.

The method of charge analysis used in this study was developed by Hirshfeld.^{17,18} The Hirshfeld analysis is an integral of the self-consistent field (SCF) charge density associated with each fragment, weighted by the fragment's contribution to the initial spherically symmetric fragment density:

$$Q^{\text{frag}(i)} = \int \frac{\rho_{\text{frag}(i)}^{\text{initial}}}{\sum_{j} \rho_{\text{frag}(j)}^{\text{initial}}} (\sum_{k} \rho_{\text{frag}(k)}^{\text{initial}} - \rho_{\text{SCF}})$$

Orbital analysis of oxygen bonding was analyzed using inhouse software which provides the crystal orbital overlap population (COOP).¹⁹ The COOP method, originally developed

TABLE 1: Optimized Distances (Å) from Calculations on the M_{10} Clusters

		Rh		1	?t
		set Ia	set II	set I	set II
M_{10}^{b}	A	2.68	2.72	2.82	2.86
	В	2.52	2.47	2.60	2.60
$M_{10}O$	A	2.89	2.85	2.94	3.02
	В	2.56	2.56	2.62	2.62
	C	1.97	1.96	2.09	2.03
	D	0.20	0.25	0.27	0.39
$M_{10}OH$	A	2.74	2.73	2.86	2.92
	В	2.53	2.51	2.60	2.59
	C	2.27	2.26	2.47	2.50
	D	0.99	0.97	1.00	0.99
	E	0.19	0.22	0.09	0.09

^a See section on calculation details for definition of basis sets. ^b See Figure 1 for labels.

by Hoffman for analysis of extended Hückel slab calculations,²⁰ measures the bonding or antibonding character of the interaction between two orbitals, weighted by their overlap population. Since the finite nature of the clusters in our calculations yields discrete energy levels, the electronic states are artificially broadened by a Gaussian of half-width 0.5 eV to simulate an infinite surface. This broadening is reasonable if one accepts the assumption that there is a smooth transition between the eigenvalue spectrum of a cluster and the density of states of a surface. Furthermore, broadening the states gives a more general picture of the bonding. The orbital analysis also yields the overlap population density of states (OPDOS), which is the COOP summed to the Fermi energy, and is a measure of the net bonding/antibonding character of the projected orbital interactions.

Results

In this section we present the results of our calculations on the adsorption of oxygen and OH on the Rh and Pt(111) surfaces. The geometries of the clusters are considered first, followed by the thermodynamics of adsorption. This allows us to assess the accuracy of the calculated parameters by comparison with experimentally measured values. We then present an analysis of the bonding of oxygen and hydroxyl on the two surfaces.

a. Cluster and Complex Geometries. The optimized bond distances for M_{10} clusters compare favorably with those measured in the bulk metals (Table 1). The most obvious of these are the bulk metal bond distances for rhodium and platinum, which are 2.69 and 2.75 Å, respectively, compared to values of 2.68 and 2.82 Å for distance A in Rh_{10} and Pt_{10} 21 (Figure 1, Table 1). In general, bonds between "inner" atoms of the top layer (atoms 1-3) are slightly overestimated, while bonds to outer or edge atoms are more significantly underestimated. This is as a direct result of the rather small cluster. The bond length in the gaseous Rh_2 molecule has been measured as 2.28 Å, indicating that the contraction is not an artifact of the calculation but rather is a cluster-size effect.²¹

There are two general features of all adsorbate—cluster systems. First, the triangle of metal atoms in the top layer expands laterally by as much as 0.2 Å for O on Rh. In addition, this triangle is displaced toward the oxygen by an average of 0.1—0.2 Å, which is similar to relaxations measured with LEED studies on these systems.²² For both rhodium and platinum clusters, the influence of the basis set size on geometrical values is found to be rather small. Optimized bond lengths only differ by 0.05 Å for sets I and II. The basis set quality has a larger effect on the predicted interaction energies, as discussed below.

TABLE 2: Ground-State Electronic Configurations

	Rh		Pt	
	set I	set II	set I	set II
M_{10}	triplet	triplet	nonet	nonet
$M_{10}H$	doublet	doublet	quartet	quartet
$M_{10}O$	triplet	triplet	singlet	singlet
$M_{10}OH$	quartet	quartet	quartet	quartet

TABLE 3: Interaction Energies a of O, OH, and H on Metal Clusters

		\mathbf{Rh}_{10}	\mathbf{Rh}_{10}		t ₁₀
		set I	set II	set I	set II
M ₁₀ O	calc	-106	-110	-60	-66
	expt	-115 to -144		-48	
$M_{10}OH$	calc	-41	-45	-18	-21
	expt	-34		-48	
$M_{10}H$	calc	-60	-69	-51	-59
	expt	-70		-70	

^a All energies in kilocalories per mole.

A comparison of the optimized parameters in Table 1 to experiment shows that the clusters represent the infinite surface in a reasonable fashion. On the Rh and Pt clusters the lowest energy oxygen binding site was the 3-fold site, consistent with low energy electron diffraction studies which indicate that oxygen binds in the 3-fold hollow site on both Rh(111)^2 and Pt(111).^2 The Pt_{10} model yields a Pt—O bond length equivalent to the experimental value of 2.02 Å. The Rh—O distance is calculated to be 2.02 Å, compared with 2.01 \pm 0.08 Å from experiment.^2 The lifting of the central triangle is rather large in the Rh_10 calculation, 0.25 Å, compared to an experimental value of only 0.07 \pm 0.03 Å. This is purely a cluster size effect.

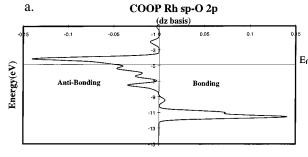
Hydroxyl bonding geometries show similar trends to those of oxygen. Since there are no experimental data with which to compare, one can only state that the bond lengths are reasonable; for example, the O-H bond in Rh and Pt is about 1 Å. For comparison, the OH bond length in trimethylplatinum(IV) hydroxide is 0.93 Å.²⁴ The M-O bond length increases to 2.27 Å for Rh and 2.50 Å for Pt, compared to 2.20 Å in trimethylplatinum(IV) hydroxide. Furthermore, the variation of bond lengths within basis sets is smaller than for oxygen; bond lengths differ at most by 0.03 Å. The basis set had no effect on the ground-state electronic configuration (Table 2).

b. Oxygen-Cluster Bonding. The calculated interaction energies for oxygen on the Rh and Pt clusters are in reasonable agreement with adsorption energies estimated experimentally (Table 3). Molecular oxygen dissociates on clean Rh(111) at 100 K and forms an ordered overlayer upon heating above 200 K.25 The binding of atomic oxygen to Rh(111) is estimated to be in the range of 115-144 kcal/mol based on the desorption temperature of 1200–1300 K.^{26,25} At high oxygen coverages, the desorption temperature decreases to 800-900 K and the adsorption energy is estimated to be 24-29 kcal/mol.²⁷ In contrast, on Pt(111) oxygen adsorbs molecularly at 100 K on the clean surface with a binding energy of 8.8 kcal/mol and dissociates above 150 K;²⁸ the estimated heat of adsorption is 48 kcal/mol.²⁸ The experimental values of the oxygen adsorption energies should be taken as a qualitative guide to the relative bond strengths for Pt vs Rh but do not provide a quantitative measure of the adsorption because the estimates of the energies did not independently measure the preexponential factors. Nevertheless, the trend in M-O bond energies for Rh vs Pt is the same for theory and experiment: in all cases, the Rh-O interaction energy is greater than that of Pt-O.

Intuitively, when an oxygen atom is close to a metal surface, one expects metal electrons to flow to the electronegative

TABLE 4: Hirshfeld Charges of Oxygen

	RI	Rh_{10}		t ₁₀
	set I	set II	set I	set II
О	-0.225	-0.225	-0.207	-0.182
O (in OH)	-0.261	-0.265	-0.319	-0.318



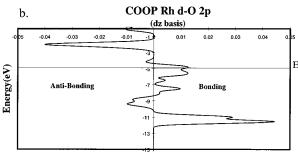


Figure 2. Crystal orbital overlap population plots between the Rh₁₀ bonding metal atoms and the oxygen 2p orbitals, using set I basis: (a) COOP Rh sp—O 2p; (b) COOP Rh d—O 2p.

oxygen, creating a negative charge on the adatom. Therefore, there will be ionic and covalent components to the bonding. By looking at the charges on the oxygen atom in the various metal clusters, one can obtain a rough estimate of the ionic contribution. The charge on an adsorbate such as oxygen is an indication of the amount of charge transfer to or from the metal. The ionic bonding is primarily an electrostatic effect, resulting from the interaction of a partially charged adsorbate with its image charge in the metal. In all cases, oxygen on Rh has a slightly greater charge than oxygen on Pt. However, the difference in charge between the Rh and Pt systems is quite small, so the ionic part of the bonding for oxygen on these metals is relatively constant. As an example of the relative values of the Hirshfeld method, the charge of oxygen changes from -0.298 to -0.353 as one moves from formaldehyde to acetone, 18 indicating that the differences in the values calculated for oxygen on Rh_{10} (-0.225) vs Pt_{10} (-0.21) are insignificant. Notably, the calculated charges for atomic oxygen on the metal clusters do not vary significantly with basis set (Table 4). While we have separated the analysis of bonding into ionic and covalent parts, the fact is that the two are linked. Ionic bonding is due to charge transfer, which will also manifest itself in the results of orbital analysis which clarify the covalent bonding.

To investigate the covalent aspect of the bonding, it is useful to decompose the bonding into interactions between individual metal and oxygen orbitals. In both clusters the covalent interaction is greater for oxygen on Rh than on Pt. However, the magnitude and sign of the orbital interactions varies according to basis set. Both the double- ζ and triple- ζ bases yield qualitatively similar results. The interaction of both the sp and the d orbitals of Rh with oxygen is greater than that of Pt (see Figures 2–5 and Table 5). In the double- ζ basis, the COOP of the metal sp orbitals with the oxygen 2p orbitals is qualitatively similar between the two metals; oxygen interaction

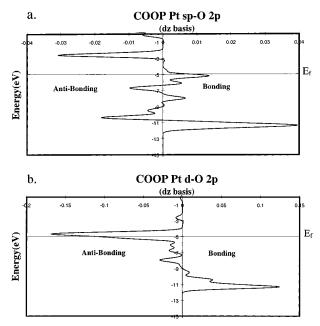


Figure 3. Crystal orbital overlap population plots between the Pt_{10} bonding metal atoms and the oxygen 2p orbitals, using set I basis: (a) COOP Pt sp-O 2p; (b) COOP Pt d-O 2p.

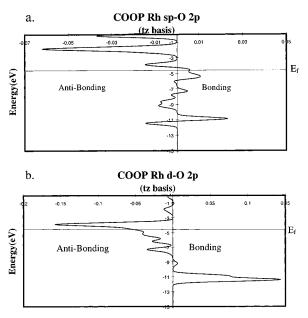


Figure 4. Crystal orbital overlap population plots between the Rh₁₀ bonding metal atoms and the oxygen 2p orbitals, using set II basis: (a) COOP Rh sp-O 2p; (b) COOP Rh d-O 2p.

with the metal sp band creates a set of bonding and antibonding orbitals. For both metals, the antibonding states lie above the Fermi level and are not filled. However, the Rh sp orbitals have a much greater interaction with the oxygen orbitals, leading to a stronger bonding character compared with Pt. The interaction of the metal d states with the oxygen 2p orbital is also more strongly bonding for Rh, as the antibonding states again lie above the Fermi level. In contrast, the greater filling of the d band for Pt means that these antibonding states are partially occupied, making the bonding interaction weaker for Pt. For the triple- ζ basis, the COOP plots once again show that oxygen binds more strongly to Rh than Pt.

Notably, there are some differences in the sign of the OPDOS from the double- ζ calculation. For example, the OPDOS of Pt-O is now negative, indicating net repulsion, whereas it was positive for the double- ζ basis. This change in sign means that

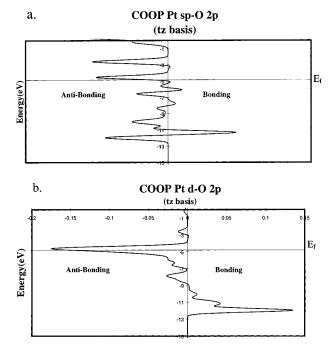


Figure 5. Crystal orbital overlap population plots between the Pt_{10} bonding metal atoms and the oxygen 2p orbitals, using set II basis: (a) COOP Pt sp-O 2p; (b) COOP Pt d-O 2p.

TABLE 5: OPDOS of Metal Orbitals with O 2p Orbitals

		$\mathbf{Rh_{10}O}$		Pt	t ₁₀ O
M orb.	O orb.	set I	set II	set I	set II
sp	p	0.087	0.024	0.049	-0.018
d	p	0.082	0.052	0.063	-0.032

some oxygen-metal orbital interactions are bonding for the double- ζ basis but antibonding for the triple- ζ set. It is interesting to note that these differences between basis sets are not apparent by examining bonding energies or geometries; rather, they are only evident when one makes a detailed analysis of the bonding. The change in the COOP plots between basis sets is most noticeable when the metal sp bands are involved. This is possibly due to the fact that the greatest overlap occurs between the metal sp band and the oxygen orbitals. Because of the large overlap, the resulting electron density does not retain the shape of the individual orbitals; this may not be accurately described by the lower-quality double- ξ basis. This would not be a problem for the metal d bands, which have less overlap with the oxygen and are more localized; these orbitals would not be perturbed as strongly by the oxygen. However, to resolve this issue, a systematic study of the effect of the basis set in calculated overlap populations needs to be performed.

c. OH-**Cluster Bonding.** The bonding of hydroxyl is particularly interesting because of the different chemistry observed for water on the two metals. A stable hydroxyl species is formed above 150 K when water is dosed onto oxygencovered Pt(111).²⁹ In contrast, on Rh(111), when water is dosed on the oxygen-covered surface, a new molecular desorption peak appears at 215 K,30 which is due to recombination of hydroxyl associated with one or more water molecules; isolated OH_a has never been isolated on Rh(111). The only experimental measurement of the energetics of hydroxyl formation and desorption are studies performed on polycrystalline Rh and Pt at high temperatures. In contrast to our cluster calculations, these studies yield adsorption energies that are stronger for Pt than on Rh. However, the experimental values may not be an accurate benchmark with which to compare calculational results. These experimental studies are performed in high pressures

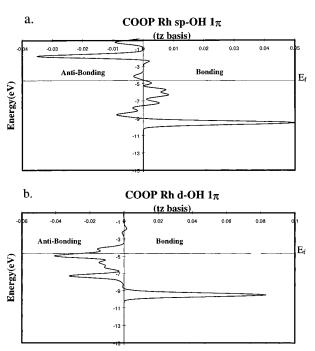
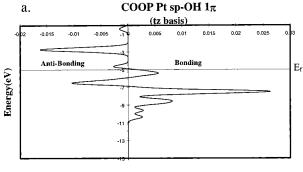


Figure 6. Crystal orbital overlap population plots between the Rh₁₀ bonding metal atoms and the OH 1π orbitals, using set II basis: (a) COOP Rh sp-OH 1π ; (b) COOP Rh d-OH 1π .

(~0.1 Torr) of oxygen and hydrogen gas at temperatures between 1000 and 1800 K, conditions which are markedly different than those simulated in the metal clusters. For the metal clusters, a temperature of 0 K is implicitly assumed and thus would be expected to model low-temperature behavior. Furthermore, because an isolated OH is adsorbed onto the cluster, these calculations would not be suited to predict results in the high-pressure limit. In addition, the experiments cited involve oxygen coverages close to a monolayer on Rh, whereas the surface is essentially free of oxygen on Pt. Given that adsorption energies of charged species, e.g. adsorbed oxygen, decrease with increasing coverage, the difference in coverages might account for the different ordering of the M−OH bond strengths for Pt vs Rh.

The binding energy of hydroxyl was found to be stronger on Rh_{10} than on Pt_{10} in our calculations. The OH adsorbs in the 3-fold site in both cases. Bending the O–H bond off vertical produced a marginal ($\sim 2-3$ kcal/mol) lowering of energy, with the minimum occurring when the OH bond was approximately 20° from the 3-fold axis. The relatively small changes in energy did not justify breaking the high symmetry of the systems, which would have resulted in far longer computation times.

Whereas the differences in the bonding of oxygen on the two metals were related to the covalent bonding, in the case of hydroxyl there are also differences in ionic bonding. In moving from atomic oxygen to hydroxyl, the charge on the oxygen increases in all cases (Table 4). This can be attributed to the increased electron density contributed by the hydrogen. However, for Pt the oxygen charge on OH is greater by 0.06 than on Rh. This indicates that the ionic bonding component of hydroxyl is slightly greater for Pt; charge transfer occurs from the metal orbitals into the 1π OH orbital. The covalent bonding for Rh is stronger, as can be seen from the COOP plots (see Figures 6 and 7 and Table 6). Unlike oxygen, in this case both basis sets yield similar results. The main part of the bonding occurs through the interaction of the metal sp band with the 1π OH orbital. In the case of Rh, all of the sp orbitals contribute approximately equally to the bonding. However, for Pt the main contribution comes from the p_7 orbital of the metal interacting



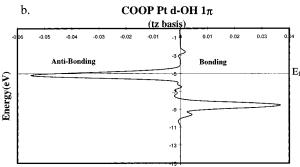


Figure 7. Crystal orbital overlap population plots between the Pt₁₀ bonding metal atoms and the OH 1π orbitals, using set II basis: (a) COOP Pt sp-OH 1π ; (b) COOP Pt d-OH 1π .

TABLE 6: OPDOS of Metal Orbitals with OH 1π Orbital

		Rh_1	$Rh_{10}OH$		ОН
M orb.	O orb.	set I	set II	set I	set II
sp	π	0.064	0.103	0.044	0.050
ď	π	-0.013	-0.006	-0.003	-0.014

SCHEME 1

$$\begin{split} &M_{10}O(ads) + H(g) \xrightarrow{E_{1a}} M_{10}OH(ads) \\ &M_{10}O(ads) + M_{10}H(ads) \xrightarrow{E_{1b}} M_{10} + M_{10}OH(ads) \\ &H_{2}O(g) + M_{10} + M_{10}O(ads) \xrightarrow{E_{2}} M_{10}OH(ads) + M_{10}OH(ads) \\ &H_{2}O(g) + M_{10} + M_{10} \xrightarrow{E_{3}} M_{10}OH(ads) + M_{10}H \end{split}$$

with the 1π OH orbital. The metal d orbitals also interact with the OH 1π . This interaction creates bonding orbitals below the Fermi level and antibonding orbitals which straddle the Fermi level. Because antibonding orbitals are being filled, the COOP between both metal d bands and the OH 1π are net antibonding. The greater amount of ionic bonding for Pt decreases the difference in the interaction energy of hydroxyl bonded to Rh and Pt. This fact has implications for the chemistry of oxygencovered Rh and Pt, addressed in the Discussion.

d. Thermodynamics of OH Formation and H₂O Decomposition. In this section, results that demonstrate the different behavior of oxygen on the surface of Rh an Pt toward water decomposition are described. The "reactions" of interest are shown in Scheme 1. These reactions may be thought of as a test of the basicity of the adsorbed oxygen, by investigating the strength of the complex formed in the presence of hydrogen. Energies are shown in Table 7 for OH formation from the reaction of adsorbed oxygen with gas-phase and adsorbed H atoms. It can be seen that remarkably good agreement is found between values determined on the same cluster using different basis sets.

TABLE 7: Thermodynamics of Test Reactions on Metal Surfaces^a

	\mathbf{Rh}_{10}		Pt_{10}	
	set I	set II	set I	set II
E_{1a}	-46	-50	-69	-66
E_{1b}	14	18	-18	-11
E_2	38	37	38	41
E_3	24	18	56	52

^a All energies in kilocalories per mole.

The decomposition of water is shown in eqs 2 and 3 of Scheme 1. Equation 2 corresponds to decomposition on an oxygen-covered surface; eq 3, to that on a clean surface. The data shown in Table 7 demonstrate a clear difference in the behavior of oxygen on the two metal surfaces. The energetics of the decomposition of water on a partially oxygen-covered surface are predicted to be approximately the same for both rhodium and platinum clusters. On the clean surface, decomposition is thermodynamically more favorable on Rh, relative to the oxygen-covered values, than on Pt. The presence of oxygen on the Rh surface acts as a poison to water decomposition, while oxygen acts as a promoter on Pt.

Discussion

While the ionic component is responsible for the majority of bonding of oxygen to transition metals, the differences in the bonding of oxygen to Rh vs Pt are reflected in the covalent component. One reason that oxygen binds more strongly to Rh than to Pt is the degree of filling of the d band. Newns and Andersen³¹ have shown that when an adsorbate with localized orbitals interacts with a metal which has a band of delocalized states such as the sp band of a metal, the localized orbitals are broadened into resonances. On the other hand, localized d states on the metal interact with the adsorbate to produce bonding and antibonding states. The strongest bonding interaction occurs when the orbitals are half-filled; in this case, all electrons are stabilized by entering the bonding orbital. For Rh and Pt, the d bands of both metals are greater than half-filled. However, the Pt d band is more filled than Rh, which leads to greater antibonding interactions with the O 2p orbital. For the sp band, Rh has a stronger interaction with oxygen as opposed to Pt.

For hydroxyl, bonding arguments similar to those for oxygen can be used to describe the covalent interaction. Because the oxygen is bonded to a hydrogen as well, the oxygen orbitals interact less strongly with the metal orbitals, resulting in a decreased covalent bond. Furthermore, because the hydrogen also contributes electron density to the oxygen, there is a greater ionic component to the bonding. The hydroxyl 1π orbital lies higher in energy than the O 2p orbital, and as a result the hydroxyl orbital lies closer to the middle of the metal bands. As a result, the 1π orbital interacts with more metal orbitals compared to oxygen; this explains the greater charge for the oxygen (in OH) for Pt vs Rh because Pt has more electrons in its d band available for donation. The result of the difference in the bonding of O and OH is seen in the thermodynamics of water decomposition. Interaction energies of hydroxyl on Rh and Pt differ by only ~20 kcal/mol; this is to be compared with the adsorption energies of atomic oxygen, which differ by \sim 40 kcal/mol between Rh and Pt. This subtle change in the energetics leads to profound differences in the chemistry of Pt(111) and Rh(111). Because of the strong Rh-O bond, oxygen passivates the Rh surface, whereas the oxygen promotes activity of the Pt surface. These results also demonstrate that the chemistry of oxygen on Rh cannot be interpreted in terms

of the traditional acid—base framework; rather, there is a delicate interplay between covalent and ionic elements in the bonding.

These density functional calculations on metal clusters illustrate the ability of this theory to reproduce experimental binding sites and geometries. Furthermore, qualitative trends in chemisorption energies can be determined. Experimental studies measuring the chemisorption energy of oxygen to Rh(111), for example, vary by as much as 30 kcal/mol; this variation is dependent on such factors as the choice of preexponential factor, method of calculation, and coverage. ^{26,25} Therefore, while the energies calculated from the clusters seem high compared to experimental values quoted from the literature, a valid comparison to these values is difficult because these clusters model chemisorption at the zero-coverage limit, while experimental studies must extrapolate this value, with uncertain accuracy. At this point, then, it is useful to only examine qualitative trends between metals rather than making quantitative judgments based on calculated energies.

While certain parameters of these systems can be well-modeled using density functional theory, other aspects require further investigation. The effect of several approximations used in the calculations is difficult to evaluate; in particular, the effect of changing basis set is unclear. Furthermore, it is not known whether other exchange-correlation functionals might lead to more accurate calculations. Even though the trends from our calculations are correct, there are differences in bonding between the various basis sets which are qualitatively different. Calculations using slabs would be helpful in this regard, because the effect of cluster size is eliminated; coverage effects could also be studied.

Conclusions

The results from these calculations demonstrate the ability of density functional theory and the cluster approximation to yield qualitatively useful information about the bonding of an atomic adsorbate to various metal surfaces. These cluster calculations reproduce the experimental results that atomic oxygen binds in the 3-fold site on the Rh(111) and Pt(111) surfaces, with the Rh surface binding the oxygen more strongly. This is due to increased bonding interaction between oxygen p orbitals with the Rh sp and d bands. Rh also binds hydroxyl more strongly than Pt; however, ionic as well as covalent bonding plays a role in the differences in hydroxyl bonding on Rh vs Pt. In particular, differences in ionic bonding for hydroxyl which are not present in atomic oxygen bonding determine the different chemistry for oxygen adsorbed on Rh and Pt.

There are several unanswered questions posed by this study. In comparisons of this sort between adsorbates on metals, small differences in energies or bonding overlap often lead to significant differences in chemistry. Therefore, the effect of changing parameters such as basis set needs to be better understood.

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