

Theoretical studies of ethylene adsorption and oxidation on clean and oxygen covered rhodium(111)

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Abstract

The adsorption of ethylene on clean and oxygen-covered rhodium(111) was studied using extended Hückel calculations with the tight-binding approach. Ethylene binds preferentially in a two-fold bridging site with the C=C and Rh–Rh bonds parallel on clean Rh(111). The C=C bond is significantly weakened, both by donation of electrons from the π orbital to the surface and back-donation from the surface to the π^* orbital on the clean surface. The addition of a quarter of a monolayer of oxygen modifies the surface electronically, so that the three-fold site is preferred by ethylene and the on-top site becomes more stable than the two-fold. Steric effects are important for high oxygen coverage ($\theta \approx 0.5$) where close contacts between O and either C or H atoms of the alkene lead to highly repulsive interactions. Steric effects dominate on the Rh(111)–(2×1)–O surface. The C=C bond coordinates across a Rh–O bond to form an oxametallacycle structure which is the lowest energy geometry found for this oxygen rich surface. This species is proposed as a plausible intermediate along the path to ketone production and rationalizes the experimental finding that oxygen-rich conditions favor partial oxidation.

1. Introduction

Friend and coworkers [1] reported the oxidation of various alkenes to ketones on the Rh(111)–(2×1)–O surface under ultrahigh vacuum conditions. We undertook a theoretical investigation of the adsorption of alkenes on the clean and oxygen-covered rhodium(111) surfaces, using extended Hückel calculations with the tight-binding approach [2], in order to understand the molecular interactions leading to this reaction.

Experimental studies have revealed that olefins, such as ethylene, are activated by the clean surface to give an alkylidyne, between 230 and 270 K.

This species forms a p(2×2) lattice with ethylidyne oriented perpendicular to the surface above a hollow hcp site [3]. Unreacted alkenes have not yet been detected on this surface, even working at very low temperatures.

We are interested in comparing ethylene bonding on clean and oxygen-modified surfaces of Rh(111) in order to understand how oxygen modifies the reactivity of ethylene and as a means of better understanding the oxygen addition reaction. We are particularly interested in evaluating the relative contribution of steric and electronic effects in determining reactivity. Selective olefin oxidation is only observed for high oxygen coverages, e.g. on the Rh(111)–(2×1)–O surface, with $\theta = 0.50$. Selective olefin oxidation does not

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occur on the Rh(111)–(2×2)–O surface which has an oxygen coverage of 0.25, for example. Combustion is the only oxidation pathway for oxygen coverages below 0.50. The oxygen on Rh(111) inhibits C–H bond activation so that selective oxidation occurs rather than combustion. One of our goals is to investigate the stability of a proposed oxymetallacycle intermediate for high oxygen coverages and, if possible, to understand the underlying reasons for the inhibitions of C–H bond breaking by oxygen.

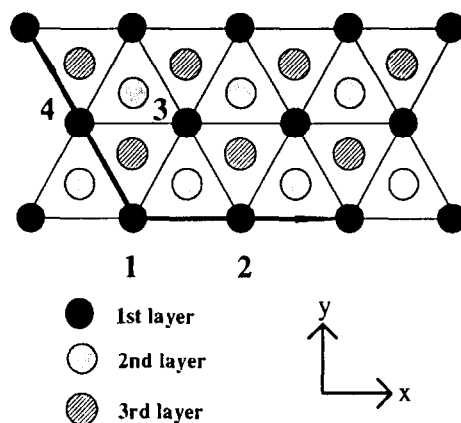
The interaction between ethylene, oxygen, and a metal surface has been extensively studied for silver, both from the experimental and the theoretical sides. Experimental results have shown that silver surfaces containing oxygen exhibit a very different reactivity from rhodium [4]. Ethylene is converted to epoxide, while allylic activation plays a major role in other reactions [5]. Theoretical studies have addressed the problem of determining the oxygen species responsible for the reactivity [6] and also the mechanism of the reaction between oxygen and organic molecules to give products [7].

2. The Rh(111) surface

Metallic rhodium has a face-centered-cubic structure with a lattice constant $a = 3.80 \text{ \AA}$ [8]. The Rh(111) single crystal face is stable toward reconstruction and is the most thermodynamically stable. The metal atoms are disposed triangularly and successive layers are stacked with an ABCABCA... arrangement and a nearest neighbor distance of 2.687 \AA .

Results from previous calculations using the extended Hückel method have shown that a model slab with three metallic layers is an appropriate choice [9]. It provides a reasonable behavior for the surface atoms, as compared to bulk atoms, while maintaining a manageable size for the calculation.

The model used in the following sections is shown in Scheme 1. The 2×2 unit cell was chosen



Scheme 1.

because it will be more convenient in later sections when the adsorbate will be introduced.

The total density of states for this slab is shown in Fig. 1. The d-band is relatively narrow and is situated between -7 and -13 eV , while the s and p bands spread over a large range of energies. As is always the case, the bulk atoms have many more neighbors than the surface ones and thus give rise to a wider band [10]. More levels localized on surface than on bulk atoms will be filled

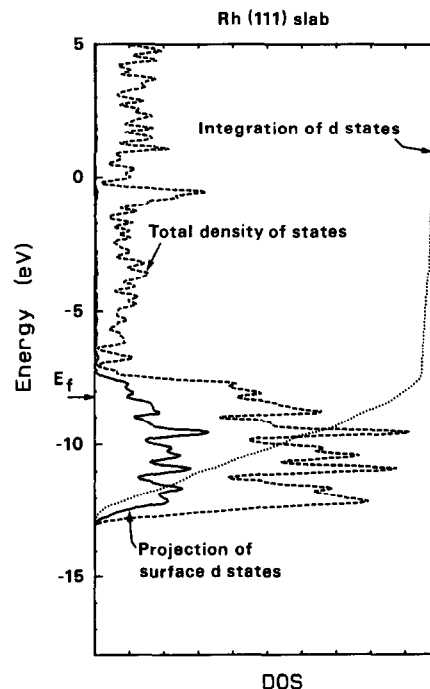


Fig. 1. Total density of states for the Rh(111) slab with projection and integration of the surface states.

for nine valence electrons. The surface atoms become negatively charged by 0.23 electrons while bulk atoms have a positive charge.

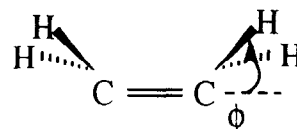
There are two different types of Rh–Rh bonds between nearest neighbors with the same Rh–Rh distance: those within the surface layer and those between the surface and the ‘bulk’. The interlayer Rh–Rh overlap population is 0.138, while it is 0.187 for two adjacent rhodium atoms on the surface. As overlap populations scale as bond strengths, this shows that the metal–metal bonds inside the surface layer are stronger than those between layers. These bonds are going to be affected by the adsorption of any molecule on the surface, as will be discussed in next sections.

2.1. Adsorption of ethylene on clean Rh(111)

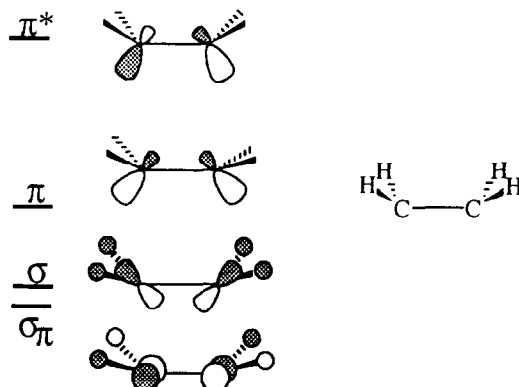
The bonding of ethylene to the closest-packed metal surfaces Ni(111), Pd(111) and Pt(111), has been theoretically studied in detail [11]. Ethylene loses its planarity as a result of adsorption on these metal surfaces, the C–H bonds bending back by an angle defined as ϕ , Scheme 2. A similar distortion of olefins has been reported for many organometallic complexes having ethylene bound to one metal atom [12].

Bending back of the H–C bonds in ethylene lowers the symmetry of the molecule. In particular, there is no longer a mirror plane containing the six atoms so that the π orbitals and the σ orbitals mix. The four frontier orbitals of bent ethylene which are expected to be important in bonding with the surface are shown in Scheme 3. The notation used is taken after [11a]. The orbitals denoted π and π^* descend directly from π and π^* in the planar parent molecule and contribute the most to the bonding with several surfaces studied previously [11a]. The π orbital releases electrons to the surface, while the π^* accepts electrons from the metal.

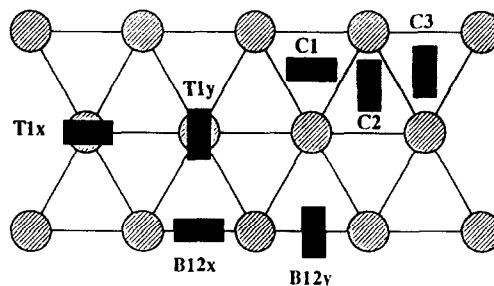
The on-top (T), two-fold (or bridging, B) and three-fold (C for center of the triangle) adsorption sites on the triangular face of Rh(111) were examined. To build the unit cell, the four surface atoms 1, 2, 3, and 4, shown in Scheme 1, are taken.



Scheme 2.



Scheme 3.



Scheme 4.

The adsorbate occupies a fixed position relative to one of these atoms. A two-fold site bridging rhodium atoms 1 and 2 will be called B12, for instance. The orientation of the C=C bond can be parallel to the x axis (label x , as in B12 x) or to the y axis (label y). The difference between the two three-fold sites C2 and C3 is that for C2 there is a rhodium atom belonging to the second layer of the metal slab just below the olefin, while for C3 the rhodium below is in the third layer. Calculations were performed for two different limiting geometries: C–C bond parallel or perpendicular to the x axis. The position of the ethylene molecule relative to the rhodium atoms in the unit cell, 1, 2, 3, 4, is shown in Scheme 4. The local symmetry is different for the two cases. The Rh–C distance was kept constant at 2.3 Å in all cases (see Appendix).

Table 1
Binding energies (BE, eV), optimized bending angles (ϕ) and selected overlap populations

Site	T1y	T1x	B12x	B12y	C1	C2	C3
BE ^a	0.09	0.16	1.25	-1.80	-2.73	0.18	0.14
ϕ ^b	30	30	40	40	40	35	35
Rh-C OP	0.199	0.198	0.342	0.038	0.208	0.333	0.333
						0.112	0.112
C-C OP ^c	0.936	0.933	0.868	0.908	0.948	0.879	0.877
Rh-Rh OP ^d	0.158	0.162	0.147	0.092	0.152	0.147	0.144
			0.116	0.068	0.140	0.140	

^a $(E_{\text{Rh slab}} + E_{\text{ethylene molecule}}) - E_{\text{Rh} + \text{ethylene slab}}$

^b Degrees.

^c C-C overlap population is 1.23 for free, planar ethylene.

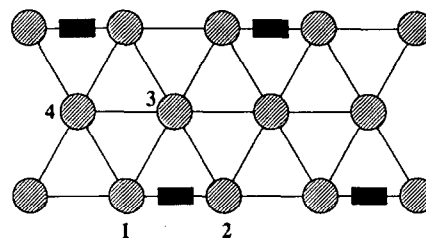
^d The two sets of numbers refer to nonequivalent Rh-Rh bonds in the unit cell.

The bending angle, ϕ (Scheme 2), was optimized, keeping the H-C-H angle constant, for each geometry. Starting from a planar geometry, ϕ was allowed to increase. Minima were always found for the energy, though for different angles depending on the site, larger bending angles being optimum for the higher multiplicity sites. A neutron diffraction study of ethylene coordinated to a binuclear osmium complex, eventually a better model for an ethylene on a two-fold site, reveals that in this particular complex the Rh-Rh-C-C cycle is not planar [13]. This type of geometry optimization was not attempted and the cycle was always kept planar.

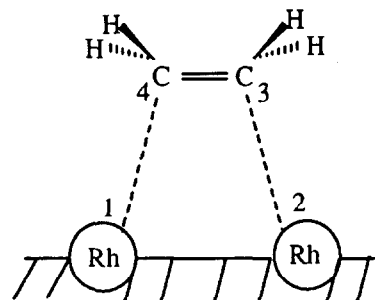
The binding energies, ϕ angles and some relevant overlap populations are given in Table 1. The binding energy, BE, is defined as the difference between the energy of ethylene adsorbed on rhodium(111), the composite slab, and the sum of the energies of the rhodium slab and the ethylene molecule. Positive binding energies indicate an attractive interaction between surface atoms and the adsorbate.

The binding energies refer to one unit cell, containing four Rh atoms per layer and one ethylene molecule, the resulting coverage, θ , being 0.25. This is the same coverage that has been investigated experimentally and for which ethynidyne is known to form [3].

In Scheme 5, we show, as an example, the unit cell for the top layer of the bridging B12x geom-



Scheme 5.



Scheme 6.

etry, containing the four surface rhodium atoms and the ethylene molecule (black rectangle), with the two carbon atoms bonded to Rh1 and Rh2. The eight rhodium atoms belonging to the internal layers are not represented here. It can be clearly seen that the four Rh-Rh bonds in the unit cell are no longer equivalent. In this geometry, Rh1-Rh2 is the surface bond most affected by the adsorption and the overlap population quoted in Table 1 refers to it.

A higher coverage would lead to strong adsorbate-adsorbate repulsions, while a smaller one would require the use of a very large unit cell, leading to very demanding calculations. It should be noted that energy is needed to bend the ethylene molecule and this term is included in the calculation of the binding energy. For $\theta = 0.25$, there are no short H...H contacts between adjacent molecules so that the energy of one layer of ethylene before it is brought into contact with the Rh slab is essentially identical to that of free ethylene.

The bridging site with the C=C bond parallel to a Rh-Rh bond, B12x, Scheme 6, is by far the most favorable adsorption site (Table 1). The top sites have small, though positive, binding energies, while B12y and C1 are both strongly repulsive.

The two adsorption sites C2 and C3 have nearly identical binding energies and overlap populations and are also weakly attractive. The other related geometry (same site as C3 with C=C parallel to x , as in C1) is even more repulsive than C1.

The data in Table 1 illustrate why the bridging geometry, B12 x , is preferred. The two Rh–C bonds formed are stronger than for other geometries. Only one of the Rh–C bonds for the C2 or the C3 geometries has a comparable overlap population.

The Rh–Rh bonds on the surface can be substantially weakened by formation of Rh–C bonds for the geometries investigated, as indicated by the drop in overlap population. The Rh1–Rh2 overlap population for ethylene bound in the B12 x geometry decreases from 0.187 to 0.147. The change is much more relevant when ethylene binds with the other orientation (B12 y) and this may be at the origin of the low stability of such site.

The C=C overlap population is significantly smaller compared to the value calculated for pla-

nar, free ethylene. Greater binding energies of ethylene to Rh are associated with small values for this C=C overlap population (Table 1). This indicates the presence of strong Rh–C bonds, which can be due to both strong donation from the ethylene π orbital to the metal and to strong back-donation from the metal to π^* , though both components of the bonding will reduce the C=C overlap population. The ethylene molecule in the B12 x geometry has the weakest C=C bond and is thus most activated.

A more detailed investigation of the B12 x geometry shows that many electronic levels are pushed down by virtue of the interaction between the ethylene and the surface. Consequently, several ethylene levels, such as the π^* are, as expected, completely split (Fig. 2). The diagram in Fig. 2 shows the total density of states for the Rh(111) slab (left), the density of states for a layer of ethylene which does not interact with the surface (right), the peaks corresponding essentially to the levels of free ethylene, and the total density of states for the composite slab, along with

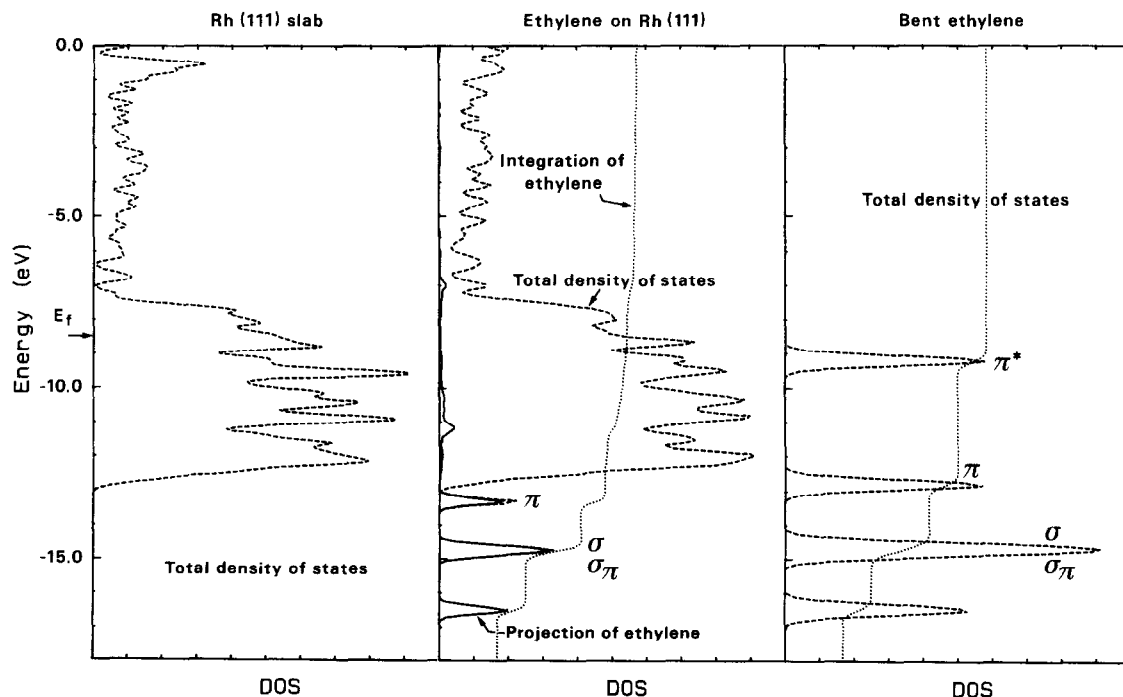


Fig. 2. Total density of states for the Rh(111) slab (left); total density of states for ethylene on Rh(111) in the B12 x site, with projection and integration of the adsorbate states (center); total density of states for bent ethylene.

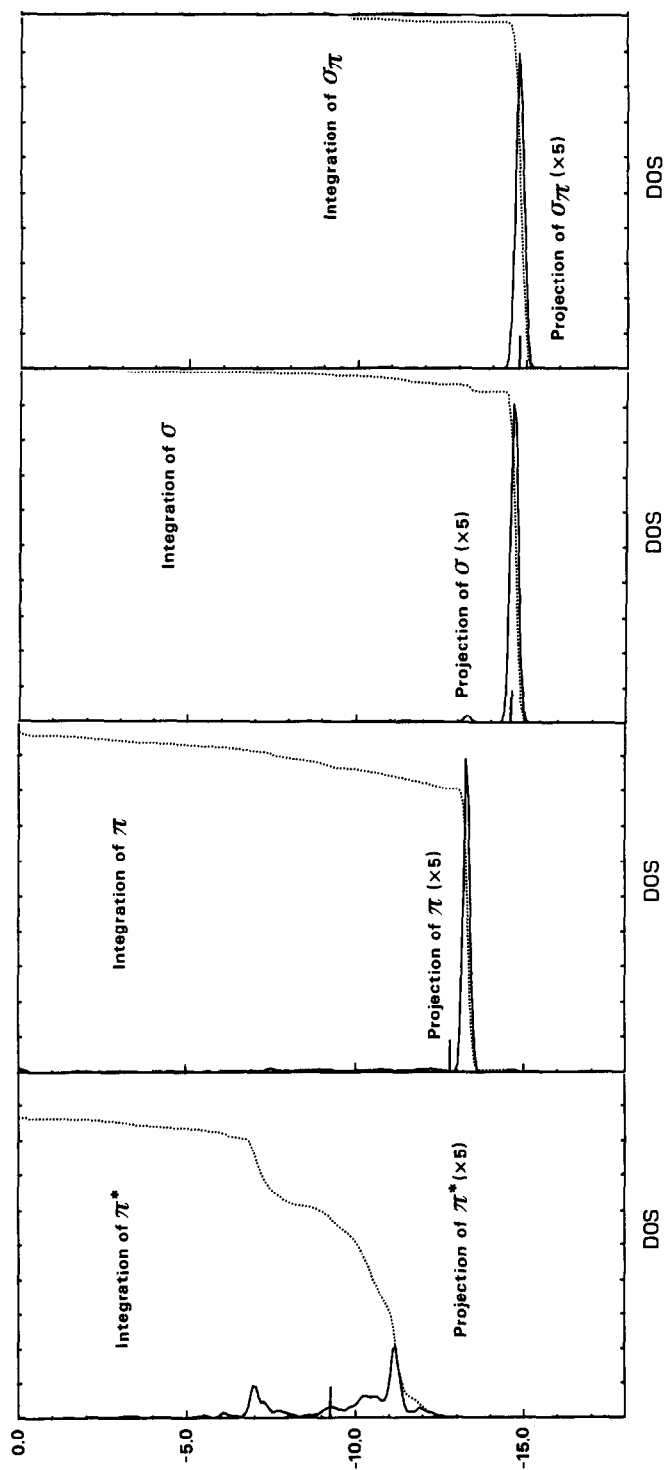


Fig. 3. Projection and integration of the four frontier orbitals of bent ethylene.

Table 2

Contributions of ethylene molecular orbitals to the Rh–C overlap population for one top (T1y) and one bridging (B12x) geometry on clean Rh(111)

Geometry/orbital	B12x	T1y
π^*	0.266	0.091
π	0.101	0.123
σ	-0.004	0.023
σ_π	-0.005	-0.001
Total OP	0.342	0.198

the projection of all the adsorbate states (center panel).

The energy of the orbitals of ethylene which interact with the surface is modified [10]. Those giving rise to bonding levels will be pushed down, while others will have their energy raised through antibonding interactions. In order to evaluate the degree to which different orbitals are altered by the interaction, the four ethylene orbitals shown above in Scheme 3 have been individually projected in Fig. 3. The markings refer to the energy of the same orbital for the free, but bent, ethylene.

The greatest changes are observed, as expected, for π and π^* . The integration line is helpful in showing that instead of having one peak (100% of states) concentrated around a very narrow energy interval, there is a wide spread of levels along a large range of energies. This reflects the fact that ethylene binds to the surface using his π orbital for donation of electrons to rhodium and π^* is involved in back-donation.

There are other ways of interpreting the bonding, rather than projecting the individual orbitals as in Fig. 3. For instance, the total Rh–C overlap population is the sum of terms which are the overlap populations between orbitals, one in ethylene and others in Rh. It is possible to decompose the total overlap population for any chosen bond into such terms. The orbitals in each fragment giving the larger overlap populations are those which contribute more to the bonding. This calculation was done for two sites, B12x and T1y, and the result is shown in Table 2.

For the B12x site, the total overlap population between the Rh and C atoms is 0.342. The greatest

contributions to Rh–C bonding are easily seen to come from π and π^* . The sum of π and π^* contributions is 0.367 and therefore greater than the total overlap population. This is due to interactions between filled orbitals of ethylene, such σ as and σ_π , and filled surface levels. Hence, the σ_π orbital, for example, is slightly antibonding in relation to the total overlap population. Other lower energy molecular orbitals have more substantial antibonding contributions.

The total Rh–C overlap population is considerably lower for the on-top site T1y. In this geometry, however, besides π and π^* , the σ orbital is also participating in the bonding of ethylene to the surface (Table 2).

Having found out which are the orbitals of ethylene which are involved in binding to the surface, it remains to determine which are the surface orbitals with which they interact. In order to do so, we show in Table 3 which are the orbitals of the Rh1 atom (T1y) or Rh1, Rh2 atoms (B12x) which present significant overlap with π , π^* , and σ . The others not listed have negligible values.

The metal orbitals that contribute the most to the bonding are those directed toward the ethylene orbitals and with the appropriate symmetry. For the on-top site, for example, z and z^2 mixed with s , point toward ethylene. The s mixing provides a better overlap. Hence, these orbitals contribute most to the ethylene \rightarrow metal donation. The yz orbital has the appropriate symmetry to interact with π^* and, therefore, it contributes most to the metal \rightarrow ethylene back-donation. Linear combinations of orbitals with the appropriate symmetry on Rh account for the bonding in the bridging

Table 3

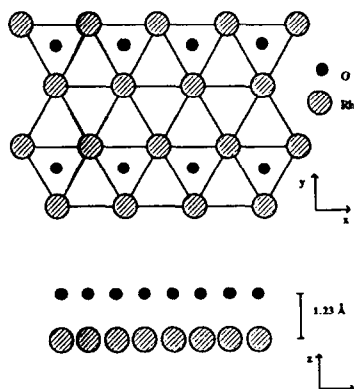
Overlap populations between rhodium atomic orbitals and selected ethylene molecular orbitals

Geometry	B12x	B12x	T1y	T1y	T1y
Ethylene orbital	π^*	π	π^*	π	σ
s	0.072	0.045	-0.001	0.041	0.016
z	0.091	0.035	0.000	0.030	0.008
z^2	0.085	0.017	0.001	0.020	0.000
yz	0.000	0.000	0.101	0.000	0.000
xz	0.014	0.003	0.000	0.000	0.000

B12x site. Again, the s , z and z^2 are involved in donation from the ethylene π to the metal. In this case, xz dominates metal $\rightarrow \pi^*$ interaction due to the different orientation of the ethylene relative to the surface. If the two sites are compared, it can be seen that back-donation is more important for the bridging one, while ethylene to surface donation prevails for on-top site.

3. Oxygen on Rh(111)

The adsorption of oxygen on Rh(111) has been studied experimentally using LEED [14] and later by angle-resolved desorption [15]. This later study was done in conjunction with molecular dynamics calculations which indicated that the oxygen atoms favored the three-fold sites over rhodium atoms of the third layer of the metallic slab, forming a $p(2 \times 1)$ overlayer, Scheme 7, with a coverage of 0.50. The distance between the O overlayer and the first Rh layer on the surface was calculated to be 1.23 Å. LEED indicates, however, that there are three equivalent domains of the (2×1) overlayer present on the surface rotated in the surface plane by 60° with respect to each other. For the purposes of this work, a single domain will be studied even though bonding and reaction at domain boundaries may be important. The investigation of defects at domain boundaries will require cluster calculations since these are, by definition, sites that are separated by large distances and are aperiodic.



Scheme 7.

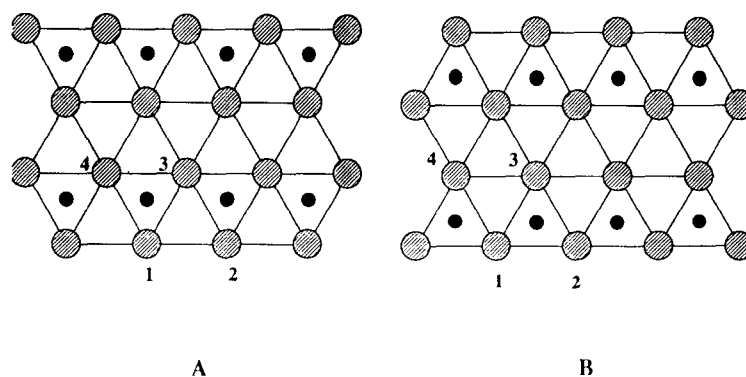
For lower coverages, $\theta=0.25$, there is a $p(2 \times 2)$ oxygen overlayer, with oxygen occupying the same three-fold site. While the study of oxygen on Rh(111) is not in itself an aim of this work, it must first be studied in order to understand the behavior of alkenes on Rh in the presence of adsorbed oxygen. All the available evidence further indicates that the oxygen atoms are not mobile on this surface under the conditions of experiments.

The binding energies and relevant overlap populations for oxygen adsorbed on the two different 3-fold hollow sites, either with oxygen above the rhodium in the third layer of the metallic slab (A) or with one oxygen above the rhodium of the second layer (B), for the $p(2 \times 1)$ lattice, as sketched in Scheme 8, are shown in Table 4.

The binding energies were calculated as in the previous section, but here they are referred to one atom of oxygen (there are two in each unit cell). Our calculations indicate a preference for oxygen to occupy the hollow site in A (over Rh of the third layer); the same site that would be occupied by Rh if another layer were added to the surface. In this geometry, there is an attractive interaction (positive binding energy), strong Rh–O bonds are formed and oxygen acquires a charge which is negative, though small. Oxygen adsorbed on rhodium does not behave as a strong Brønsted base as it does on silver [4], and a small negative charge is thus more in accordance with that.

Considering that typical Rh–O bonds in molecular complexes are shorter [11] than those calculated for the surface, the effect of changing the Rh–O distance was analyzed. The calculations were repeated for a Rh–O bond distance of 1.70 Å, instead of 2.3 Å as before. A higher energy is obtained in these conditions for the two sites. These results suggest that the first calculations qualitatively reproduce the experimentally-determined geometry (long Rh–O distance, type of site) and indicate that the oxygen parameters used model, as well as possible, oxygen on Rh.

The geometry with Rh–O distance 1.98 Å, corresponding to a 1.23 Å separation between the Rh and the O layers, and with oxygen occupying the

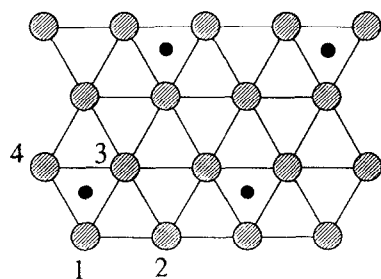


Scheme 8.

Table 4
Relative and binding energies (BE) and selected overlap populations for the $p(2 \times 1)$ oxygen overlayer over Rh(111)

Geometry	O (Rh 3rd layer) A	O (Rh 2nd layer) B
Relative energy (eV)	0.000	5.07
BE (eV)	1.64	-0.89
Rh-O OP	0.300	0.330
Rh-Rh OP	0.193 (1-2) ^a	0.185 (3-4)
Rh-Rh OP	0.122 (3-4)	0.096 (1-2)
Rh-Rh OP	0.068 (1-3)	0.080 (1-3)

^a Numbers in parenthesis indicate the rhodium atoms in the unit cell.



Scheme 9.

3-fold hollow site above Rh in the third layer, was thus used in all subsequent calculations. In spite of the limitations which may be involved in the determination of this distance [9], the extended Hückel method is also not well suited at optimizing distances.

Comparison of Rh(111)- (2×1) -O and clean surfaces reveals that the formation of Rh-O bonds leads to a net transfer of electrons from surface rhodium atoms to oxygen. Atoms 3,4 in the unit cell (Scheme 8A) which have two nearby oxygens acquire a +0.83 charge, higher than the +0.18 charge found for atoms 1,2 which have

only one close oxygen. There are smaller changes for rhodium atoms in other layers. The Rh-Rh bonds between surface rhodiums directly bonded to oxygen are the most affected and they become weaker. For example, the overlap population is now 0.068 between rhodiums 2-3, 1-3, 1-4, and 0.122 between 3-4. On the other hand, the bond between Rh1 and Rh2 is slightly strengthened based on the overlap population of 0.192 compared to 0.187 for the clean surface. Other Rh-Rh bonds between rhodium atoms in adjacent unit cells are not significantly altered.

For comparison, calculations were also performed for the Rh(111)- (2×2) -O surface, focusing on the (2×2) overlayer for which the oxygen atoms maintain the same position as in the (2×1) overlayer: the oxygen layer is 1.23 Å above the Rh layer and the oxygens occupy three-fold sites above Rh of the third layer (Scheme 9). The only difference is the oxygen coverage.

The binding energy (1.71 eV) and the charge on O are comparable on the $p(2 \times 2)$ and the $p(2 \times 1)$ oxygen overlayers. The charges on rhodium are different now, since not all Rh atoms have oxygen neighbors. Rhodium atoms 1,3,4 become positively charged (0.22), while Rh2 keeps its initial negative charge, though slightly increased from -0.22 to -0.32. From an electronic point of view, one might expect Rh2 to behave like the metal atoms of the clean surface, while the others are electronically modified. On the $p(2 \times 1)$ structure, all the rhodium atoms have been modified by the oxygen.

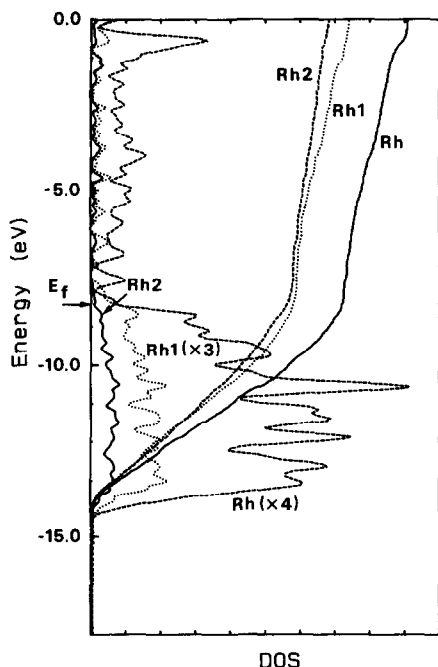


Fig. 4. Projection and integration of the states of Rh1 and Rh2 in the Rh(111)-(2×1)-O slab and projection and integration of Rh in the clean surface.

The different character of the Rh atoms is shown in Fig. 4, where all the states of Rh1 and Rh2 in the Rh(111)-(2×2)-O slab and one Rh of the clean surface are projected.

4. Ethylene on Rh(111)-(2×2)-O

The adsorption of ethylene on rhodium covered with a quarter monolayer of oxygen (one oxygen atom per unit cell) was studied for comparison to the clean surface. The model used for the oxygen overlayer is the same as in the previous section with the site and Rh-O separation maintained constant.

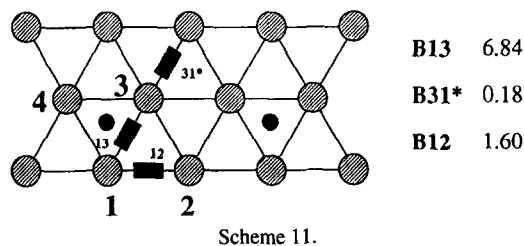
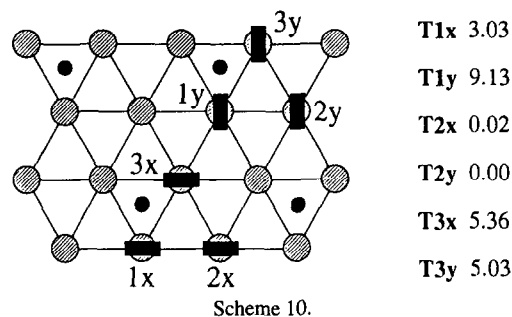
The symmetry of the surface is reduced by the addition of oxygen. Hence, there is a larger number of unique binding sites for ethylene than in the clean surface. Referring to Scheme 9 above, Rh1, Rh3, and Rh4 are equivalent, but distinguishable from Rh2. If ethylene binds on top, however, Rh1 will become different from Rh3 and Rh4. A mirror plane is retained after adsorption on Rh1 (or over

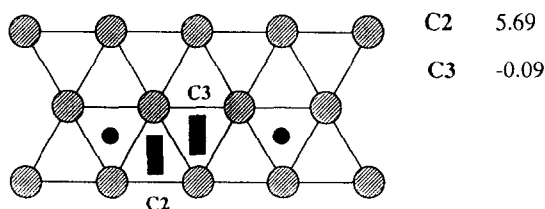
Rh2), while for the two other rhodiums the surface loses all symmetry.

There are three different on top sites, Scheme 10, and we consider the usual two limiting orientations for the C=C bond, either parallel to x or to y . In these calculations the bending of the hydrogens away from the plane of the ethylene molecule, ϕ , was taken as 30° , the optimized value. The relative energies for these geometries are written on the right side of Scheme 10 (in eV). The value of zero corresponds to the most stable configuration which is the site T2y, where ethylene adsorbs on-top Rh2 with the C=C bond parallel to the y axis.

Different bonding configurations are also possible for two-fold bridging coordination of ethylene to the surface. In this case, the optimal bending angle is 45° . Only the C=C orientation parallel to the Rh-Rh bond will be considered, as the other orientation had an extremely high energy for the clean rhodium. Again Rh-Rh bonds which are equivalent will give rise to different adsorption sites, because the distance between oxygen and the alkene depends on the specific site in the unit cell.

There are three nonequivalent Rh-Rh bonds with ethylene bridging them, Scheme 11. The relative energies are given on the right side, in eV, and the reference is again the energy of on-top site





Scheme 12.

T2y. The relative positions of ethylene and oxygen on the rhodium surface are illustrated in Schemes 10 and 11 – a complete unit cell is not shown.

Two three-fold geometries were also considered both with the C=C bond centered over the middle of one Rh–Rh–Rh triangle, as shown in Scheme 12.

Only the geometry with the C=C bond along y was investigated for two different proximities to oxygen. The other one along x (C1 in Scheme 4) had an extremely high energy for the clean surface and will not be considered. The energies (eV), relative to that of T2y, are given on the right hand side of the scheme. The optimal bending angle, ϕ , is 35° .

All these geometries exhibit relatively high energy because there are one or more short contacts between oxygen and an atom in ethylene. Usually, the short distances involve one of the hydrogens but sometimes also carbon. For the on-top sites described in Scheme 10 these O–H distances are respectively 1.807 for T1x, 1.257 for T3x and 1.356 Å for T3y. The shortest O–C distances are 1.284 Å for T1y and 1.393 Å for T3x. There is clearly a correlation between the O–H distance and the repulsive energy: shorter O–H distances give rise to higher energies. The repulsion between the two atoms is apparent from the O–H overlap populations. For instance, the overlap population for T3y, which has a O–H separation of 1.356 Å, is -0.036 . The negative value is characteristic of an antibonding interaction.

Other factors may also contribute to the very high energies of some of the geometries, but a short O–H distance is certainly an important one. Short C–O distances, also found for some of the described geometries give rise to positive overlap populations, suggestive of possible bond forma-

tion. They coexist, however, with short O–H distances and the energies are very high. These sites are thus very unlikely to be occupied by ethylene molecules.

Conversely, adsorption is favored in the sites with less steric crowding. When ethylene bridges Rh3–Rh1*, the B31* site, there are no short contacts and accordingly it has the lowest energy. (The asterisk * indicates that Rh1 is in the next unit cell.) Placing the ethylene in any of the other bridging sites results in short O–H distances. The shortest O–H distances are 1.943 Å for the B12 site, 1.515 Å for the B23 geometry, and 1.751 Å for the B13 case. There is also a C–O distance of 1.43 Å for the B13 geometry.

The difference in energy for ethylene over B12 and B31* probably arises from the repulsive O–H interaction occurring in B12. The energy is greater in B12 by approximately 1.5 eV even though the O–H distance is not exceedingly small, 1.943 Å.

A similar trend is observed in the two 3-fold sites studied. They differ again by the proximity of the hydrogen to oxygen. The C2 site has a short O–H distance (1.336 Å) and is ca. 5.4 eV higher in energy than C3.

A more detailed comparison of the three more stable geometries for each possible type of site (T2y for on-top, B31* for the 2-fold bridging case and C3 for the 3-fold geometry) reveals differences induced by oxygen. Binding energies, charges and relevant overlap populations are listed in Table 5.

The binding energies of ethylene to Rh(111)–(2×2)–O are all negative, though small. This is probably an artifact, due to the fact that the reference Rh(111)–(2×2)–O slab has a much lower energy than the sum of the energies of the rhodium slab and the ethylene layer and absolute energies cannot be accurately determined from extended Hückel calculations. On the other hand, the relative energies are the relevant ones for assigning the most favorable adsorption sites and those are more reliable, as they are all affected by the same errors.

Table 5
Binding energies (eV), charges and relevant overlap populations for three adsorption sites of ethylene on Rh(111)–(2×2)–O.

Geometry	Top (T2y)	2-fold (B31*)	3-fold (C3)
BE	–0.30	–0.49	–0.22
Rh–C OP	0.200	0.323	0.336, 0.056
C–C OP	0.947	0.886	0.883
Charge C	–0.45	–0.52	–0.60, –0.55
Charge O	–0.39	–0.34	–0.38
Charge Rh ^b	0.65 (2)	0.82 (1,3)	0.68
Rh–Rh OP ^a	0.184 0.071 0.083	0.051 0.193 0.094	0.188 0.090 0.050

^a Several sets of nonequivalent bonds.

^b The number in parenthesis defines the Rh atom.

The relative energies (see Schemes 10, 11, 12) indicate that the three-fold, C3, site is the most stable and that the top site became more stable than the 2-fold, as compared to the clean surface. There are no steric constraints for these three sites, so the energies reflect the modifications of the electronic properties of the surface induced by the oxygen adsorption. Although weaker Rh–C bonds are formed on the on-top site, compared to bridging and 3-fold, the C=C bond is stronger than for other geometries and this may help to keep the total energy low. Generally, the higher multiplicity sites appear to lead to stronger Rh–C bonds and weaker C=C bonds. The ethylene molecule is hence more activated towards reaction on multiple coordination sites, similar to findings for clean rhodium(111). It might be expected that this surface behaves essentially like the clean one: alkenes approach it, become activated and break up. Indeed, decomposition is the only reaction path observed experimentally, though desorption also occurs.

All these more stable structures are characterized by the building up of a negative charge on both carbon atoms, reflecting a great contribution of back-donation to the surface–olefin bond, while oxygen stays negatively charged and at least one of the rhodiums on the surface acquires a high positive charge (Rh2 for T2y, Rh1 and Rh3 for

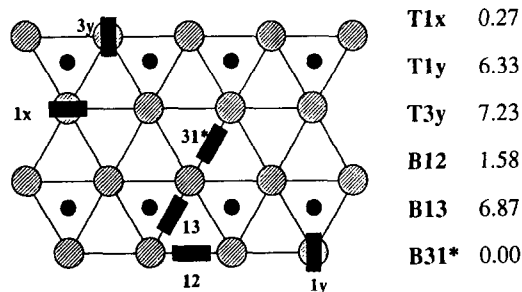
B31*). The binding of the ethylene molecule to the surface is similar to that described above for the clean surface, with π and π^* orbitals contributing most to the bonding (respectively 0.071 and 0.251 for a total overlap population of 0.323). The σ orbital is also important in the on-top position. The overlap populations are comparable to those for clean rhodium. The oxygen atoms affect only slightly the Rh–C bond.

5. Ethylene adsorbed on Rh(111)–(2×1)–O

When ethylene adsorbs on the Rh(111)–(2×1)–O surface which has an oxygen coverage of 0.50 monolayers, there is more symmetry than for the p(2×2) oxygen overlayer. Rh1 and Rh2 are equivalent, for example, and there are fewer unique sites, Scheme 13. Relative energies (eV) are listed on the right and are referenced to the most stable geometry, B31*.

This surface is considerably crowded, since the amount of oxygen has doubled. Hence, short contacts between oxygen atoms and atoms in ethylene are even more prevalent. A first consequence of this is reflected in the relative energies given in Scheme 13. Except for T1x and B31*, all geometries are strongly repulsive, but even those two are much more repulsive than on the (2×2)O surface. The T3x site was not even considered because too short O–H contacts were unavoidable.

The binding energies are all negative and this time in a much greater extent (3 eV) than for the previous study. This is a strong indication that ethylene does not easily bind to the surface in one of these adsorption sites.



Scheme 13.

The C–C bond is not weakened to the degree it was on the clean or Rh(111)–(2×2)–O surfaces, even for the bridging site. Furthermore, the Rh–C bonds are significantly weaker in the Rh(111)–(2×1)–O surface. The high coverage of electronegative oxygen makes the rhodium atoms less electron rich, and thus less effective in back-donating electrons to the ethylene π^* orbital. The contribution of π^* to the Rh–C bond in the B31* site is only 0.218 on Rh(111)–(2×1)–O, compared to 0.251 on Rh(111)–(2×2)–O and the contribution of π to the same Rh–C bond also decreases to 0.071, compared to 0.096 on Rh(111)–(2×2)–O. Even though there are no very short distances between atoms for this bridging geometry, the electronic effect of the oxygen is exhibited in the bonding to the surface.

These results led us to look for other possible adsorption sites which might be more favorable in this oxygen-rich surface, involving, for instance, the oxygen atoms.

6. Oxametallacycle intermediates on Rh(111)–(2×1)–O and Rh(111)–(2×2)–O

An oxametallacycle intermediate was proposed as a plausible intermediate for acetone formation from propene on Rh(111)–(2×1)–O because there are several organometallic analogs [16]. Other intermediates, also detected under different conditions [17], such as cationic species, were ruled out by experiments [1]. Our calculations suggest that the Rh(111)–(2×1)–O surface was much less effective in binding and activating ethylene than Rh(111)–(2×2)–O. Hence, we investigated different bonding modes, in particular those for which an activated oxygen–carbon

bond forms. A possible bonding geometry is represented in Scheme 14a and the metallacycle structure formed is represented in Scheme 14b (including distances in Å and angles).

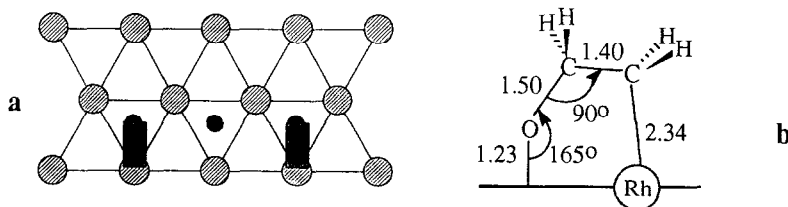
The Rh–C, Rh–O, and C–C bond lengths were fixed at the values used for all the previous ethylene adsorption calculations. The positions of the hydrogens were chosen so that the HCH plane was normal to the OCC or CCRh plane and bisected it. The particular geometry described, which corresponds to the C=C bond bridging a Rh–O bond, with the Rh–C–C–O plane parallel to *yz*, minimized interadsorbate repulsions on the surface.

In the Rh(111)–(2×1)–O surface, the energy of this geometry, shown in Scheme 14b, is 0.91 eV lower than the most favorable ethylene bonding geometry, the B31* site. Hence, the oxametallacycle is energetically favored on the Rh(111)–(2×1)–O surface.

In contrast, on the less oxygen-rich, Rh(111)–(2×2)–O surface, the energy of the oxametallacycle structure is 2.1 eV higher than the energy of the most stable site, T2y and the oxametallacycle is, therefore, not energetically competitive with simple ethylene adsorption, though the Rh–C and C–O overlap populations would be comparable to those obtained for the Rh(111)–(2×1)–O surface. This does not mean that the oxametallacycle is unstable, but that simple adsorption is energetically much more favorable.

The calculations were repeated using a longer C–C bond (1.54 Å) and the metallacycle geometry became more stable by 0.7 eV. Its formation is therefore even more likely for the oxygen rich surface, but not yet competitive with simple adsorption in the case of Rh(111)–(2×2)–O.

Strong bonds are indeed formed between the adsorbate and the surface for the oxametallacycle



Scheme 14.

geometry, Scheme 14b. The Rh–C overlap population is 0.239 and the O–C overlap population is 0.541, for example. The Rh–C bond is thus much stronger than the two which might be formed upon adsorption over the Rh–Rh bond, the B31* geometry (respectively 0.242 and 0.313). The C=C bond of ethylene has become a C–C bond in the oxametallacycle, as expected.

While these calculations do not prove the existence of an oxametallacycle, they show that its formation becomes very competitive, relative to other adsorption geometries, for the oxygen-rich, sterically-crowded, Rh(111)–(2×1)–O surface. Its formation is also generally consistent with results of surface experiments [1]. Vibrational studies are planned to probe for the proposed oxametallacycle.

It can be added that this metallacycle structure is halfway between direct adsorption on the metallic surface and the geometry which has been proposed for the intermediate in the epoxidation reaction on silver. The olefin is considered to approach only the oxygen [7] and two C–O bonds are formed without direct involvement of the silver atoms.

7. Conclusions

The results described above indicate that ethylene adsorbs easily on the clean Rh(111) surface, preferentially in a bridging site, and is activated, mainly via C=C bond activation, toward decomposition. The addition of oxygen (coverage 0.25) to the Rh(111) surface changes it both electronically and by introducing severe steric constraints. Less C=C activation occurs for surfaces containing oxygen, partly because rhodium is less electron rich and hence there is less back-donation to π^* .

Steric effects also play a very important role, making adsorption very difficult on the Rh(111)–(2×1)–O surface, where close O–H contacts are virtually unavoidable, and inhibiting ethylene adsorption. Although not explicitly studied, it is clear that such steric effects will assume even

greater importance for larger olefins, such as propene.

An oxametallacycle intermediate was found to be lower in energy than molecularly bound ethylene on the Rh(111)–(2×1)–O surface, but not on the Rh(111)–(2×2)–O surface. This geometry is more favorable on steric grounds, as on the whole the alkene molecule is farther away from the surface, so that repulsive interactions with oxygen are minimized. Only one carbon reaches a rhodium atom from the surface.

Another problem of interest is C–H activation, but no significant changes in C–H overlap population could be detected for any of the structures studied, suggesting more complicated mechanisms (see Ref. 11c).

8. Appendix

All the calculations were done using the extended Hückel method [2] with the tight-binding approach [2] for the surface calculations. The parameters used for Rh and O are collected in Table 6. Parameters for oxygen were obtained from a charge iteration calculation on the Rh(111)–(2×1)–O surface, keeping the Rh parameters [18] fixed. Standard parameters were used for carbon and hydrogen.

The two-dimensional rhodium surface consisted of three layers. The alkene coverage was kept at 0.25 throughout the calculations. Both 0.25 and 0.50 coverages were used for oxygen to model respectively the (2×2) and the (2×1) oxygen overlayers, fixed 1.23 Å above the rhodium surface. C=C and C–H distances were taken as 1.40

Table 6
Parameters used in the extended Hückel calculations

Atom	Orbital	H _{ii} , eV	ξ ₁	ξ ₂	C ₁	C ₂
Rh	5s	–7.31	2.13			
	5p	–3.39	2.10			
	4d	–10.35	4.29	1.97	0.5807	0.5685
O	2s	–24.82	2.28			
	2p	–9.82	2.28			

and 1.08 Å, respectively, while the value used for the Rh–C bond distance was 2.3 Å and Rh–O 1.98 Å. Other details are given in the text.

Sets of 12 K points in the irreducible wedge of the hexagonal Brillouin zone were used. They were chosen following the geometrical method of Ramirez and Böhm [19].

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