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Decisive role of the energetics of dissociation products in the adsorption of water on O/Ru(0001)

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Using density-functional theory we found that, depending on coverage, coadsorbed oxygen can act both as a promoter and as an inhibitor of the dissociation of water on Ru(0001), the transition between these two behaviors occurring at ~0.2 ML. The key factor that determines this transition is the adsorption energy of the reaction products, OH in particular. The chemistry of this coadsorbed system is dictated by the effective coordination of the Ru atoms that participate in the bonding of the different species. In particular, we observed that a low coverage of oxygen increases the adsorption energy of the OH fraction on the Ru surface. This surprising extra stabilization of the OH with the coadsorption of oxygen can be understood in the context of the metallic bonding and could well correspond to a general trend for the coadsorption of electronegative species on metallic surfaces.

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I. INTRODUCTION

The atomic level understanding of the structure and chemistry of water deposited on metal surfaces has received a lot of attention in recent years.[1–4] H_2O adsorption on close-packed metal surfaces was shown to proceed through adsorption of isolated H_2O monomers that group to form small or extended hydrogen-bonded clusters.[5,6] The most common extended overlayer on closed-packed metal surfaces with hexagonal symmetry was assumed to be a buckled hexagonal bilayer. Feibelman[1] proposed that on Ru(0001) a partially dissociated H_2O-OH bilayer is more stable than a hexagonal icelike bilayer formed by intact water molecules. The greater stability of dissociative versus molecular water adsorption has been confirmed on Ru by several authors.[7–9] More recently the role of coadsorbed species in determining the relative stability of both types of adsorption has been investigated[10–14] on Ru(0001) as well as on other transition-metal surfaces.[10,15,16] In particular, it has been shown that preadsorbed oxygen at a coverage of 0.25 ML on Ru(0001) not only constrains the water layer to follow a p-(2×2) symmetry, instead of the icelike bilayer, but also inhibits its dissociation.[11,12,17] In contrast, experimental evidence suggests that small amounts of oxygen adsorbed on the surface favor the partial dissociation of water molecules.[8,14] Thus, water adsorption on O/Ru(0001) seems to change from dissociative to molecular as a function of the O coverage.

Motivated by these observations, in this work we study the relative stability of intact versus dissociative adsorption of water on the O/Ru(0001) surface as a function of the preadsorbed oxygen coverage (θ_O) between 0 and 0.25 ML. We find that it is the different energies of the dissociation products, particularly OH, as a function of θ_O that trigger the transition between the two types of adsorption; while at low θ_O, the adsorption energy of OH is large thus enhancing the stability of dissociative adsorption, this energy drops abruptly at θ_O around 0.25 ML. Our calculations show that the key factor controlling this transition is the effective coordination of Ru atoms in the substrate.

II. THEORETICAL METHOD

We use density-functional theory (DFT) calculations within a periodic supercell approach to describe the electronic structure of the O/Ru(0001) surface, represented by a symmetric slab of seven Ru layers plus a similar amount of vacuum space; the ensemble periodically repeated. The adsorbates are placed on both sides of the slab. Computational details are similar to previous work.[11] We use a 4×4 supercell that allows for the study of low water coverages down to 0.0625 ML. We have determined the preferred adsorption sites of the H and OH dissociation products for all studied θ_O. For H_2O molecules we have assumed adsorption on top Ru sites at all θ_O, as already established for Ru(0001) (Ref. 7) and $O(2\times2)$/Ru(0001).[11] Preadsorbed oxygen (O_{ads}) atoms occupy hcp sites ~1.16 Å above the topmost layer[18,19] at all studied coverages. Some caution is necessary when comparing our theoretical results with experimental data at similar low oxygen coverages. In our calculations, the O_{ads} atoms are always uniformly distributed on the substrate. In the experiments however, at low θ_O formation of islands of higher local coverage is quite likely. This effect, along with the spatial resolution of the experimental probes, e.g., STM or XPS, has to be taken into account when comparing our calculations with experimental data. Close to our critical coverage of ~0.25 ML, the surface is known to consist of large patches of the $p(2\times2)$ structure,[11,18] reducing considerably the uncertainty linked to the actual O_{ads} distribution.

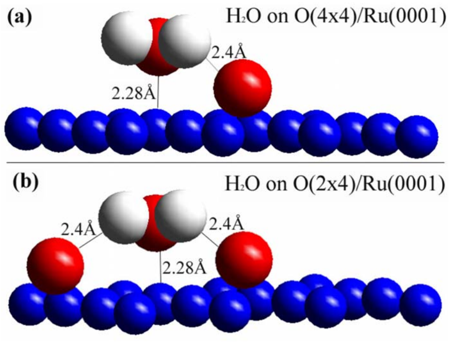

FIG. 1. (Color online) Relaxed geometries of H_2O adsorbed on O/Ru(0001) surfaces for two different θ_O: (a) O(4×4)/Ru(0001) substrate ($\theta_O=0.0625$ ML) and (b) O(2×4)/Ru(0001), corresponding to $\theta_O=0.125$ ML.

III. RESULTS AND DISCUSSION

A. Molecular adsorption

In agreement with previous results, we find that the H_2O molecule lies nearly parallel to the clean Ru(0001) surface $\sim$2.3 Å above a Ru atom.[7,11] The computed adsorption energy ($E_{ads}^{H_2O}$) is 474 meV, which is about 100 meV higher than values presented elsewhere.[7,11] This is due to the larger area of the surface unit cell used in the present work that corresponds to a lower water coverage (0.0625 ML) than in previous works[7,11] (0.25 ML and higher). At all the considered θ_O values, the H_2O molecule continues to sit on a top site position and nearly parallel to the surface. The adsorption height remains almost constant (increasing up to $\sim$2.4 Å at the highest studied θ_O, 0.25 ML). The main difference between the adsorption of water on the clean and oxygen decorated Ru(0001) surfaces is the formation of extended hydrogen bonds between the molecule and the adsorbed O atoms with an O_{ads}-H_2O separation of $\sim$2.4 Å (see Fig. 1). These H bonds increase the adsorption energy to $\sim$612 meV (see Table I and Fig. 1). Notice that in our description, based on the use of a 4×4 surface unit cell, at $\theta_O=0.125$ ML the H_2O has already established the two possible hydrogen bonds between the molecule and the O_{ads} atoms. In fact, $E_{ads}^{H_2O}$ remains unchanged, within our estimated error bar of $\sim$10 meV, at larger values of θ_O (see Table I). Thus, we can conclude that the formation of O_{ads}-H_2O hydrogen bonds is the key factor that determines the energetics of the coadsorption of oxygen and the intact water molecules.

B. Dissociation products

The results on the adsorption of the dissociation products H and OH as a function of θ_O are summarized in Table I. The behavior of the adsorption energies of H and OH is decisive for the balance between dissociative and intact water adsorption as a function of θ_O. The adsorption energy of H (E_{ads}^{H}) is roughly constant at small θ_O. However, on O(2×2)/Ru(0001), due to its preference for adsorption on hollow sites, a H atom must share its three Ru neighbors at the topmost layer with the O_{ads} atoms. The presence of these *overcoordinated Ru atoms destabilizes* the system and decreases the binding energy of H near $\theta_O=0.25$ by $\sim$300 meV, compared to clean Ru(0001). The case of OH is more complex, whereas its coadsorption with oxygen at low θ_O confers extra stabilization to this adsorbate, it suffers a strong destabilization at high θ_O, similar to the case of H. One factor that could be thought to contribute to the initial stabilization is the attractive dipole-dipole interaction between the O_{ads} and OH adsorbates. However, this contribution is too small ($\sim$10 meV) to explain our results. More insights can be gained from the following observations: (i) at $\theta_O<0.25$ ML the most favorable site for OH is the hcp site most distant from the O_{ads} atoms; (ii) at $\theta_O=0.25$ ML all possible hollow sites are such that at least two Ru atoms in the substrate must be simultaneously bonded to the OH molecule and to one of the O_{ads} atoms. This destabilizes the hcp site by more than 500 meV compared to the low θ_O now competing with the less stable top site. From these observations we conclude that the effective OH-O_{ads} *interaction is mediated by the substrate* and, therefore, reflects the preferred coordination of the Ru atoms.

One of the driving forces for the increase in binding energy of OH as a function of oxygen coverage in the low coverage regime comes from the partially ionic character of the Ru-O bond in conjunction with the metallic bonding of the atoms in the surface layer. An excess of electronic charge accumulates around the O_{ads} at the surface. The accompanying charge depletion in the exposed regions of the surface can be interpreted as an effective reduction of the coordination of the metal atoms in those areas. As a consequence, the non-O-bonded metal atoms are less stable and the formation

TABLE I. Adsorption energies (E_{ads}) of H, OH, and H_2O adsorbed on Ru(0001) at different θ_O. Preferred adsorption sites are indicated; two sites into the same parentheses denote equally favorable sites. The energy gained by dissociative adsorption $E_{diss}^{H_2O}$ defined by $E_{diss}^{H_2O}=E_{ads}^{H}+E_{ads}^{OH}-E_{split}^{H_2O}$; where $E_{split}^{H_2O}=5.58$ eV is the required energy for partial dissociation of the water molecule in vacuum. The relative stability of dissociative versus molecular adsorption ΔE is defined by $\Delta E=E_{diss}^{H_2O}-E_{ads}^{H_2O}$. Notice that positive values of ΔE denote favored dissociative over intact adsorption.

Surface	E_{ads}^{H} (eV)	E_{ads}^{OH} (eV)	$E_{ads}^{H_2O}$ (meV)	$E_{diss}^{H_2O}$ (meV)	ΔE (meV)
Ru(0001)	2.90 (fcc)	3.49 (fcc/hcp)	474	821	347
O(4×4)/Ru(0001)	2.89 (fcc)	3.61 (hcp/fcc)	533	925	392
O(2×4)/Ru(0001)	2.86 (fcc)	3.64 (hcp)	612	920	308
O(2×2)/Ru(0001)	2.60 (fcc)	3.10 (top/hcp)	616	127	−489

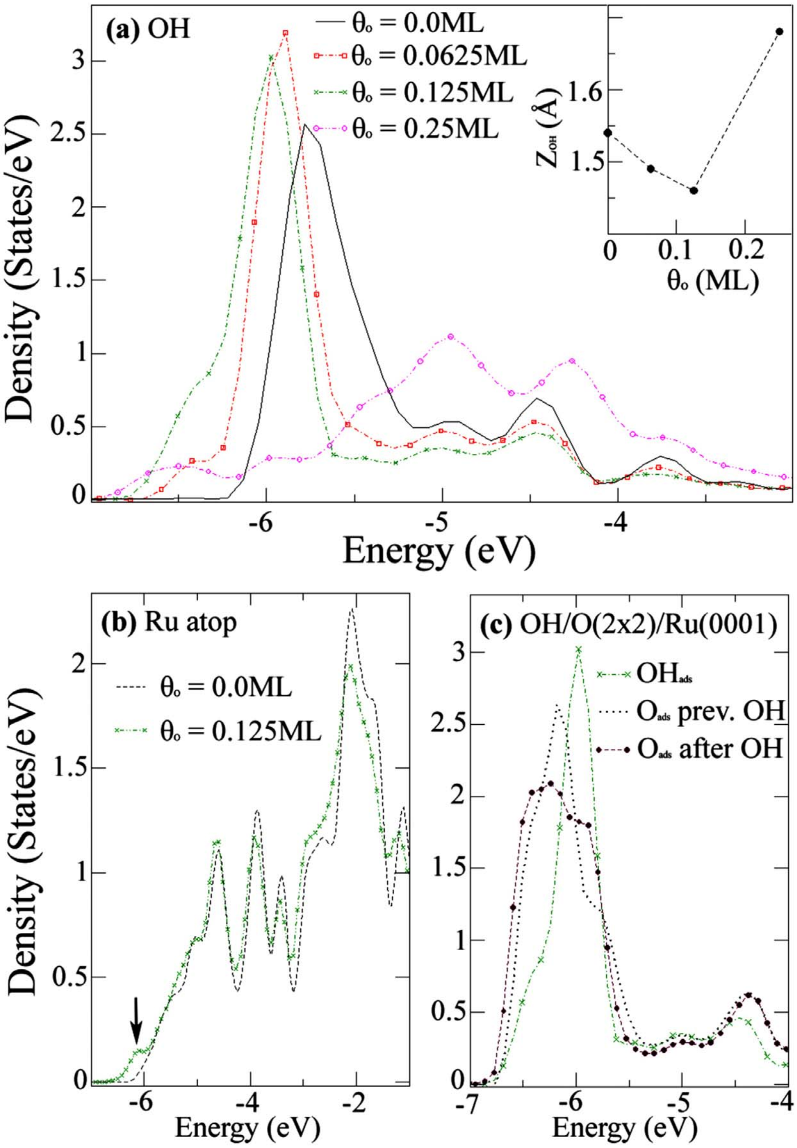

FIG. 2. (Color online) (a) Projected density of states on the p orbitals of the O atom belonging to the OH adsorbed on a hcp site on O/Ru(0001) at different values of θ_{O}. Inset: adsorption height of OH as function of θ_{O}. (b) PDOS on the d orbitals of Ru in the top surface layer and in O(2×4)/Ru(0001) (Ru atom not bound to $\mathrm{O_{ads}}$). (c) PDOS on $\mathrm{O_{ads}}$ and the O atom in OH before and after the adsorption of OH on O(2×4)/Ru(0001).

of an additional bond with an adsorbate will be accompanied by a larger energy release. A similar behavior, although at larger oxygen coverages, was observed for the coadsorption of CO and O on Ru(0001).[20]

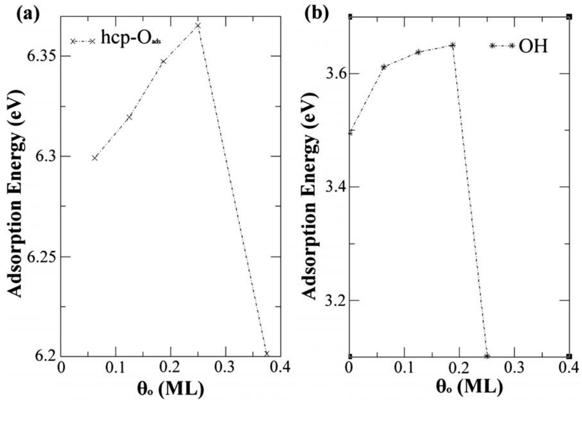

FIG. 3. Adsorption energy of (a) $\mathrm{O_{ads}}$ and (b) OH as a function of θ_{O} on O/Ru(0001) surfaces.

The changes in the stability of OH are reflected in the projected density of states (PDOS). Figure 2(a) shows the PDOS onto the p orbitals of the O atom of an OH molecule adsorbed on a hcp site at different θ_{O}. The downward shift and broadening of the main peak around 6 eV below the Fermi level as θ_{O} increases is in accordance with the decrease of OH-Ru(0001) distance [see the inset in Fig. 2(a)] and is consistent with the increase in adsorption energy. At high $\theta_{\mathrm{O}}=0.25$ ML the PDOS changes completely reflecting the destabilization caused by the $\mathrm{O_{ads}}$ second neighbors of the OH molecule. The PDOS also reveals another mechanism causing the additional strength of the OH binding: the presence of oxygen on the Ru(0001) surface increases the density of states at the lower edge of the Ru d band [shown in Fig. 2(b)] precisely at the energy (~6 eV below the Fermi level) where the PDOS projected onto OH shows the main peak [shown in Fig. 2(c)]. The indirect interaction between OH and $\mathrm{O_{ads}}$ further increases the width of this peak and gives rise to an additional energy gain.

In order to confirm the general character of this unexpected tendency toward a stronger binding as more electronegative adsorbates are added on the surface, we have calculated the adsorption energy of O_{ads} on Ru(0001) as a function of oxygen coverage. As illustrated in Fig. 3(a) the adsorption energy increases by ~70 meV when the coverage grows from 0.0625 to 0.25 ML. These results give a theoretical account for the effective attractive interaction between oxygen atoms on Ru(0001) observed by scanning tunneling microscopy[21] and their tendency to form a well ordered $p(2\times2)$ oxygen adlayer[22,23] by packing to a local coverage of $\theta_O=0.25$ ML. Although ordered adlayers can be found at even higher θ_O ((2×1)-O for 0.5 ML, (2×2)-3O for 0.75 ML, and (1×1)-O for 1 ML) they are less stable as θ_O increases.[24] This is also the case for other transition metals, such as Ag, Pd, Rh, and Au.[25] Therefore, stronger binding occurs as oxygen (and presumably other electronegative adsorbates) covers the surface up to a certain concentration (~0.25 ML for O adsorption). Above this coverage, oxygen atoms start to have *common Ru nearest neighbors* and the lower binding energy mainly *reflects the limited number of bonds* that can be established with the substrate atoms. This is clearly shown by our results: the oxygen binding energy decreases by ~164 meV when an additional O atom is added to the $O(2\times2)$/Ru(0001) surface [corresponding to $\theta_O=0.375$ ML, see Fig. 3(a)]. The same mechanism explains the drop of the adsorption energy of OH on $O(2\times2)$/Ru(0001) ($\theta_O=0.25$ ML) by more than 530 meV, as compared with the case of the $O(4\times4)$/Ru(0001) ($\theta_O=0.0625$ ML) and $O(2\times4)$/Ru(0001) ($\theta_O=0.125$ ML) surfaces [see Table I and Fig. 3(b)]. Indeed, the higher adsorption energy of OH occurs at $\theta_O\sim0.187$ ML, with three O_{ads} atoms in the (4×4) supercell, which corresponds to the maximum θ_O such that a OH molecule can be added without having Ru atoms simultaneously bonded to both types of adsorbates (OH and O_{ads}).

C. Dissociative versus molecular adsorption

Next, we proceed to analyze the balance between dissociative and intact water adsorptions on Ru(0001) as a function of θ_O. On clean Ru(0001) dissociative adsorption of the H_2O monomer is favored by ~347 meV. This is in agreement with the results by Michaelides *et al.*[7] for the adsorption of a water monomer versus the adsorption of the dissociation fractions in separated phases. However, their conclusions were opposite when H and OH were placed in the same 2×2 surface unit cell, since the H product was forced to sit on an unfavorable atop site to allow for coadsorption in such small cell. By contrast, our 4×4 surface unit cell is large enough to place both H and OH at their preferred adsorption sites. Actually, the coadsorption in the 4×4-unit cell of Ru(0001) leads to five possible configurations depending on their relative position. At the optimum one, H and OH fractions seat relatively close to each other, at fcc and hcp sites, respectively, and dissociative adsorption is additionally favored by ~46 meV compared to H and OH calculated separately using a similar 4×4 cell. Therefore, we conclude that water *dissociative adsorption is favored on clean Ru(0001).*

When the O coverage is increased to $\theta_O=0.0625$ ML, the energy released by dissociative adsorption increases by ~100 meV compared with the case of clean Ru(0001). This compensates the slight increase of binding energy of the water molecule and leads to a preference of dissociative over intact adsorption by ~392 meV, i.e., ~45 meV more than on clean Ru(0001). This confirms the recent experimental observation that small amounts of coadsorbed oxygen favor water dissociation on Ru(0001) surfaces.[8,12,14] At $\theta_O=0.125$ ML *dissociative adsorption is still preferred* by ~308 meV (see Table I). These small changes in the energy balance are due to the simultaneous increase of the adsorption energy of H_2O and OH for low and moderate values of θ_O.

Recent x-ray photoelectron spectra, by Gladys and co-workers,[12,14] of O/Ru(0001) at low θ_O (~0.1 ML surfaces) show a drastic reduction of the O_{ads} peak after the adsorption of water in the range 0.5–1.0 ML. They proposed that a significant fraction of the preadsorbed oxygen was converted to OH in the $H_2O_{ads}+\text{hcp-}O_{ads}\rightarrow 2OH_{ads}$ reaction. This idea was assumed by Wang *et al.*[10] to study theoretically the possible dissociation of H_2O on transition-metal surfaces decorated with oxygen. However, our DFT calculations indicate that, at least under the conditions of low water coverage explored in the present work, this reaction is endothermic by ~420 meV. Thus, the coadsorption of two OH molecules in hcp sites on a 4×4 supercell of Ru(0001) is ~800 meV less stable than the coadsorption of one H and one OH molecules in fcc and hcp sites, respectively, on the unit cell of the $O(4\times4)$/Ru(0001) surface, indicating that H is much more stable when adsorbed directly on the metal. Finally, at $\theta_O=0.25$ ML, the case of the $O(2\times2)$/Ru(0001), the dissociative adsorption is exothermic only by ~127 meV. At this coverage, *molecular adsorption is clearly preferred*[11,17] over dissociation by ~489 meV, mainly *as a consequence of the reduction of the adsorption energies of the reaction products* (H and OH).

IV. CONCLUSIONS

We have studied the relative stability of dissociative and molecular adsorptions of a water molecule on O/Ru(0001) as a function of θ_O. The adsorption energy of H_2O increases appreciably at low θ_O due to the formation of hydrogen bonds between the molecule and O_{ads} atoms at the surface. However, the increase of $E_{ads}^{H_2O}$, which saturates when all $O_{ads}-H_2O$ bonds are satisfied, is not sufficient to explain the transition from dissociation to intact adsorption. To understand this transition one must consider the adsorption energy of the dissociation products H and OH. Low oxygen coverages have a minor influence on the binding energy of H and, unexpectedly, increase the adsorption energy of the OH fraction on the Ru surface. This surprising extra stabilization of the OH with the coadsorption of oxygen can be understood in the context of the metallic bonding and could well correspond to a general trend when electronegative species are coadsorbed on metal surfaces. Finally, at high θ_O (~0.25 ML) the adsorption energies of H and OH are strongly reduced, making the dissociation of an adsorbed water molecule endothermic (by ~500 meV). Therefore, assuming a uniform distribution of the O_{ads} atoms over the substrate on average, the transition between dissociative and molecular adsorptions is predicted to take place at a coverage θ_O in the range 0.19–0.25 ML, which is in agreement with recent experiments.[12,14,17]

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