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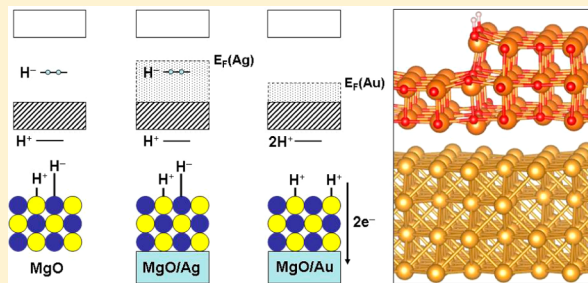
From Heterolytic to Homolytic H₂ Dissociation on Nanostructured MgO(001) Films As a Function of the Metal Support

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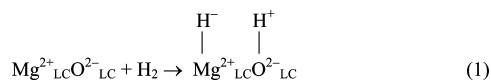
ABSTRACT: It is well-known that the H₂ molecule dissociates heterolytically on stepped MgO surfaces with formation of protons bound to O²⁻ anions (OH groups) and hydride ions bound to Mg cations (MgH groups). Homolytic splitting, with formation of a pair of OH groups per adsorbed H₂ molecule, is only possible in special conditions, like for polar MgO(111) surfaces or under irradiation due to the generation of O⁻ radicals. In this work, we demonstrate, based on first-principles DFT calculations, that homolytic splitting of H₂ is the thermodynamically most favored dissociation mode if MgO(001) films of a few atomic layers are deposited on a metal support. The choice of the support is crucial.

In fact, on MgO/Ag(001) ultrathin films, H₂ dissociation resembles the behavior of the bare MgO surface, while on MgO/Au(001), homolytic dissociation is preferred. The reason lies in the different position of the Fermi level in the two metal/oxide interfaces. The lower Fermi level (higher work function) of MgO/Au(001) favors the transfer of the H₂ electrons to the metal support via electron tunneling through the ultrathin insulating layer (adsorption of protons). This is another manifestation of the unusual behavior of oxides at the nanoscale. It is of general relevance for the splitting and reactivity of covalently bound molecules.

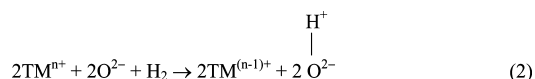


1. INTRODUCTION

Dissociation of the hydrogen molecule on solid surfaces is of key importance for several processes like heterogeneous catalysis, hydrogen storage, fuel cells, sensors, doping of semiconducting oxides, etc.^{1,2} On metals, the H₂ molecule dissociates homolytically via interaction of the metal s, p, and d electrons with the H₂ σ* antibonding orbital, resulting in a pair of adsorbed H atoms.^{3,4} On the contrary, on nonreducible oxides, H₂ dissociates heterolytically, with formation of a proton, H⁺, adsorbed on the oxide O²⁻ anions, and an hydride ion, H⁻, adsorbed on the Mⁿ⁺ cations.^{5,6} This is particularly relevant for very ionic oxides like MgO since the electrostatic potential generated by the low-coordinated (LC) anionic and cationic sites provides the right environment to split the H₂ molecule in two charged fragments, H⁺ and H⁻:



On reducible transition metal (TM) oxides, hydrogen can split homolytically by transferring the H₂ electrons to the TM cations, with reduction of their oxidation state and formation of two OH groups:^{7,8}



This mechanism is not possible on ionic systems like MgO because there are no low energy states where the H₂ electrons can be accommodated; a proton and a hydride ion are thus the only possible reaction products.

Clear evidence for the occurrence of a heterolytic splitting has been reported a long time ago by studying H₂ adsorption on MgO powders^{9–12} and has been confirmed by ab initio calculations using both cluster and slab models.^{13–15} Infrared (IR) spectroscopy clearly reveals the presence of hydroxyl, OH, and hydride, MgH, groups when MgO powders are exposed to a hydrogen atmosphere. In these studies, it was elucidated also the crucial role of LC sites in promoting the dissociation of the hydrogen molecule. The topic has been reviewed by Gribov et al. making use of low-temperature IR spectroscopy.¹⁶ H₂ reaction with the MgO surface leads to the formation of reversible and irreversible OH and MgH species, characterized for reversible adsorption by typical absorption bands at 3454 (OH) and 1325 (MgH) cm⁻¹ and for the irreversible reaction by IR bands at 3712 (OH) and 1125 (MgH) cm⁻¹. This and other studies suggested the important role of reverse corner and reverse step sites in promoting the heterolytic dissociation of H₂.¹⁷ In general, one can say that heterolytic H₂ dissociation on MgO is well understood with a precise assignment of the observed spectroscopic features to well-defined adsorption sites.

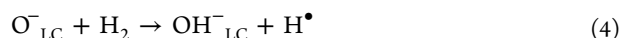
There are, however, examples of homolytic dissociation of H₂ also on MgO surfaces. The first case is related to the effect of light irradiation on the surface chemistry of MgO samples. LC O²⁻ sites under UV light transform into reactive O⁻ radicals^{18–20}

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These centers are bleached by H_2 exposure according to the reaction



The generated H^{\bullet} atom can further react with the surface with formation of an adsorbed proton, H^+ , and a trapped electron, e^{-} , giving rise to $(\text{H}^+)(\text{e}^{-})$ defect centers.^{17,17,21,22} Of course, reaction 4 can also occur with C–H bonds, and indeed, it has been suggested that O^{-} radicals can promote the homolytic scission of hydrocarbon molecules, an important step in reactions like the catalytic coupling of methane to form heavier hydrocarbons.^{23,24} However, the presence of O^{-} radicals remains essential for the process, and it is only under irradiation or by specific doping of the oxide that these centers can be produced in sufficient quantity.

There is another situation where homolytic dissociation of H_2 is expected on MgO. This involves the polar MgO(111) surface.^{25–27} If a MgO crystal is cleaved along the (111) direction, one obtains a stacking of equidistant anionic and cationic layers, producing a macroscopic dipole moment perpendicular to the surface. This results in an intrinsic instability of the two (Mg- and O-terminated) surfaces. There are three main mechanisms to stabilize polar surfaces, i.e., surface reconstruction, change in electronic structure (e.g., metallization), or adsorption of stabilizing species.^{28–30} In the case of MgO(111), the adsorption of H_2 molecules on the O-terminated surface results in the formation of an OH layer (hydroxylated surface). The unrelaxed, O-terminated MgO(111) surface has metallic character, as shown by the fact that the Fermi level crosses the O 2p valence band;²⁶ the addition of H_2 restores the insulating character of the surface by homolytic dissociation of the molecule and formation of OH groups.

To summarize, H_2 molecules dissociate heterolytically on MgO surfaces, and homolytic dissociation is only observed under irradiation, due to the generation of O^{-} radicals, or on polar (111) surfaces where the splitting of the H–H bond into H atoms is due to the metallic character of the unreconstructed surface. No other examples exist in the literature of homolytic splitting of H_2 on MgO(001) surfaces.

In this study, we demonstrate, by means of first-principles density functional theory (DFT) calculations,^{31–33} that H_2 homolytic splitting is also possible on MgO(001) ultrathin films grown on a specific metal substrate provided that the film thickness remains below 1–2 nm. We first report the case of H_2 dissociation on flat and stepped MgO films grown on Ag(001) single crystals, and we show that the dissociation is favorable only at steps where the reaction follows the classical heterolytic mechanism with formation of OH and MgH fragments, as on bulk MgO; on the contrary, the same reaction on MgO(001) films grown on Au(001) results in the homolytic splitting of the molecule with formation of OH groups. The reason for the different reaction mechanisms lies in the different work function of MgO/Ag(001) and MgO/Au(001) interfaces: the larger work function of MgO/Au(001) favors the electron transfer from the adsorbed H atoms to the metallic support via electron tunneling through the ultrathin oxide film,^{34,35} with formation of two OH groups. This result represents another example of the unusual behavior of oxide films at the nanoscale. For the specific case of MgO ultrathin films, this includes the spontaneous charging of metal atoms, clusters, or adsorbed

molecules^{34–37} or the peculiar bonding and dissociation mechanism of water.^{38,39}

2. COMPUTATIONAL METHOD

First-principles calculations based on density functional theory (DFT) were carried out using the Vienna ab initio simulation package (VASP)^{31–33} and the projector augmented wave (PAW) method.^{40–42} The generalized gradient approximation of the exchange–correlation functional proposed by Perdew–Burke–Ernzerhof (PBE)^{43,44} was employed, and the kinetic energy cutoff for the plane-wave expansion was set to 400 eV. Spin polarized calculations have been performed in order to allow the formation of radical species, but in all cases only diamagnetic ground states have been found for the final structures. The Ag(001) and Au(001) substrates were modeled by four metal layers, and a two-monolayer (2 ML) MgO film was deposited on top. It has been shown that, while a MgO monolayer has a specific behavior, properties are already converged for a 2 ML film.³⁴ Thus, a stepped film has been constructed by depositing a 3 ML MgO film and removing part of the top layer, thus leaving a monatomic step, Figure 2. We studied the adsorption and dissociation of an H_2 molecule on the MgO/Ag(001) and MgO/Au(001) thin films as well as on the bare MgO(001) surface represented by a 3 ML MgO slab. Previous work has shown that the MgO adsorption properties are well converged after three layers.⁴⁵ Also in this case a stepped surface has been represented by removing part of the top MgO layer.

The experimental lattice constant of Ag (4.09 Å) and Au (4.08 Å)⁴⁶ is about 3% smaller than that of MgO (4.21 Å).⁴⁷ In the calculations, the optimized Ag, Au, and MgO lattice parameters are 4.17, 4.18, and 4.26 Å, respectively, and the lattice mismatch is reduced to about 2%. Therefore, the MgO layers are slightly contracted when supported on Ag or Au. During the geometry optimization of the MgO/Ag(001) and MgO/Au(001) interfaces, all atoms in the MgO film and in the two outmost Ag and Au layers were relaxed, while the remaining two metal layers were frozen at bulk positions. For the bare MgO(001) surface, the optimization was restricted to the atoms of the two upper layers. For terrace calculations a surface (3×3) supercell was employed, containing 9 MgO units or Ag/Au atoms per layer, and a ($4 \times 4 \times 1$) Monkhorst–Pack grid was used for the k -point sampling. Steps were modeled with bulk (3×3) supercells, with 18 MgO units or Ag/Au atoms per layer, and ($3 \times 3 \times 1$) k -point mesh.

The MgO/Ag(001) and MgO/Au(001) interfaces are characterized by a metal–oxide separation of about 2.7 Å (2.70 Å for Ag and 2.74 Å for Au). The computed work function of the Ag(001) surface is 4.11 eV (exptl 4.22 eV),⁴⁸ while that of Au is 5.01 eV (exptl 5.22).⁴⁹

Our computed adsorption energies do not include zero-point energy (ZPE) corrections.⁵⁰ It has been shown that these contributions are not negligible for reactions involving H containing species.⁵¹ We have checked indeed that the ZPE corrections are of the order of 0.2 eV for reactions involving the formation of two OH groups and up to 0.04 eV for formation of OH and MgH groups. The conclusions of this article do not change once these contributions are considered explicitly.

Dissociation barriers have been determined in selected cases using the dimer method.⁵² This method only requires the first derivatives of the potential energy, and therefore, it can be applied to plane wave DFT calculations with reasonable computational costs. The method involves two replicas of the

Table 1. Properties of H₂ Dissociatively Adsorbed on Terrace and Step Sites of the MgO(001), MgO/Ag(001), and MgO/Au(001) Surfaces

products	surface	site	$d(\text{H}-\text{H})$ (Å)	E_{ad} (eV)	ΔE_{ad} (Au–Ag) (eV)	$d(\text{O}-\text{H})/$ $d(\text{Mg}-\text{H})$ (Å)	Bader charges of H (e)	$\omega_{\text{e}}(\text{O}-\text{H})$ (cm ⁻¹)	$\omega_{\text{e}}(\text{Mg}-\text{H})$ (cm ⁻¹)
OH/MgH heterolytic	MgO(001)	terrace	4.82	1.80		0.98/1.81	0.57/−0.76	3654	1309
	MgO/Ag(001)	terrace	4.72	1.51	0.28	0.98/1.80	0.59/−0.76	3681	1322
	MgO/Au(001)	terrace	4.73	1.79		1.98/1.81	0.58/−0.74	3641	1288
	MgO(001)	step	1.58	−0.43		1.00/1.81	0.60/−0.72	3101	1322, 1021
	MgO/Ag(001)	step	1.72	−0.21	−0.03	0.99/1.85	0.59/−0.76	3308	1249, 976
	MgO/Au(001)	step	1.76	−0.24		0.99/1.86	0.62/−0.76	3352	1236, 961
OH/OH homolytic	MgO/Ag(001)	terrace	4.17	1.07	−1.20	0.98	0.56/0.56	3679, 3678	
	MgO/Au(001)	terrace	4.23	−0.13		0.98	0.56/0.56	3703, 3702	
	MgO/Ag(001)	step	4.28	0.53	−1.15	0.98	0.59/0.59	3714, 3694	
	MgO/Au(001)	step	4.22	−0.62		0.97	0.60/0.60	3727, 3727	

system, a dimer. The dimer is used to transform the force in such a way that optimization leads to convergence to a saddle point rather than a minimum.

Atomic charges are obtained within the scheme of charge density decomposition proposed by Bader,⁵³ while the work function ϕ is estimated as the difference between the vacuum level and the Fermi energy.

3. RESULTS AND DISCUSSION

3.1. MgO(001). We first consider H₂ adsorption on the MgO(001) surface. If the molecule is oriented with the H atoms above two adjacent Mg²⁺_{5C} and O^{2−}_{5C} ions, no bonding occurs and the molecule desorbs. The heterolytic decomposition of H₂ generating an H⁺ bound to O^{2−}_{5C} and H[−] bound to Mg²⁺_{5C} is observed when the distance between O^{2−}_{5C} and Mg²⁺_{5C} is more than 4.7 Å ($d(\text{O}-\text{H}) = 0.98$ and $d(\text{Mg}-\text{H}) = 1.81$ Å, Table 1). However, the reaction is highly endothermic, $E_{\text{ad}} = 1.80$ eV. The behavior is different on a step where H₂ reacts with the two adjacent Mg²⁺_{4C} and O^{2−}_{4C} ions after overcoming a small dissociation barrier, ca. 0.12 eV, followed by formation of OH and MgH groups stabilized by (H⁺)-(H[−]) electrostatic interaction ($d(\text{H}-\text{H}) = 1.58$ Å). The process is exothermic, $E_{\text{ad}} = -0.43$ eV, Table 1. The Bader charges of H(−O) and H(−Mg) are +0.60 |e| and −0.72 |e|, and the vibrational frequencies of OH and MgH are 3101, and 1322 and 1021 cm^{−1}, respectively, Table 1, typical of heterolytic splitting. Notice that the O–H stretching is at relatively low frequency for an OH group due to the residual interaction with the other adsorbed H atom (short H–H separation).

The density of states (DOS) plot for H₂ dissociatively adsorbed on the MgO(001) terrace, Figure 1, shows that the surface O ion with a bound proton, OH group, has the corresponding energy level about 3 eV below the O 2p band; on the other side, the doubly occupied 1s state of the H[−] ion, MgH group, is in the MgO band gap, about 2 eV above the top of the valence band. A similar DOS plot is obtained for H₂ adsorbed on a step (not shown).

3.2. MgO/Ag(001). Turning to H₂ adsorption on 2 ML MgO/Ag(001) films, homolytic splitting (forming two OH groups) was also considered. In fact, on an ultrathin film deposited on a metal support, the H₂ electrons could tunnel through the film and transfer to the Fermi level (E_{F}) of the metal with formation of two adsorbed protons. The existence of an electronic communication through the oxide layer has been predicted theoretically and proven experimentally by adsorbing atoms,^{34,35,54} molecules,^{37,55} or metal clusters,^{56–58} species on

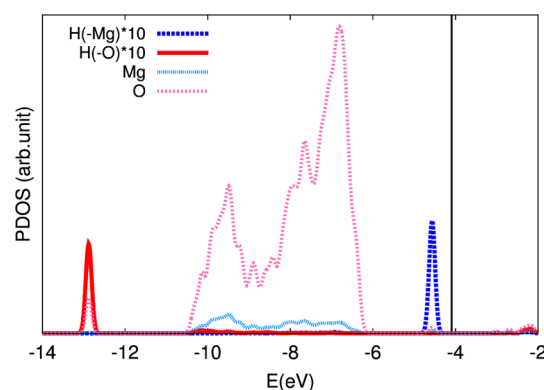


Figure 1. Density of states of an H₂ molecule dissociatively adsorbed on the MgO(001) terrace with formation of an OH/MgH pair, referred to the vacuum level. The states below the vertical line are occupied.

MgO/Ag(001) films.⁵⁹ On bulk MgO, on the contrary, formation of two OH groups is only possible if the associated electrons are transferred to the conduction band or in the presence of defects to the corresponding acceptor states. Both the conduction band and defect states are too high in energy, and the electron transfer is very unfavorable. On a metal supported MgO film, the E_{F} is well below the MgO conduction band,³⁴ which makes the transfer of the H₂ electrons to the metal possible (in principle) with formation of two protons.

Regarding the heterolytic dissociation of H₂ on the terrace of MgO/Ag(001), when two H atoms adsorb on the O_{5C}^{2−} and Mg²⁺_{5C} ions separated by 4.72 Å, their properties are as on MgO(001), Table 1, and the process is endothermic, $E_{\text{ad}} = 1.51$ eV. However, when the H atoms are adsorbed on two O_{5C}^{2−} ions 4.2 Å apart, two hydroxyl groups are formed (O–H bond length 0.98 Å, Bader charge of H +0.56 |e|, vibrational frequencies ca. 3680 cm^{−1} (OH), Table 1), indicating the occurrence of homolytic dissociation and electron transfer to the Ag support. The reaction is still endothermic, $E_{\text{ad}} = 1.07$ eV. This means that on the terrace of a MgO/Ag(001) film, the homolytic dissociation not only is possible but is preferred over the heterolytic one. The ultrathin oxide layer has a crucial role (both structural and electronic) in screening the two adsorbed protons and reducing their repulsion.⁶⁰ However, both reactions are endothermic.

Reactivity is expected to increase at LC sites, such as on a monatomic step. Regarding the heterolytic dissociation of H₂ on a step of MgO/Ag(001), when two H atoms adsorb on two

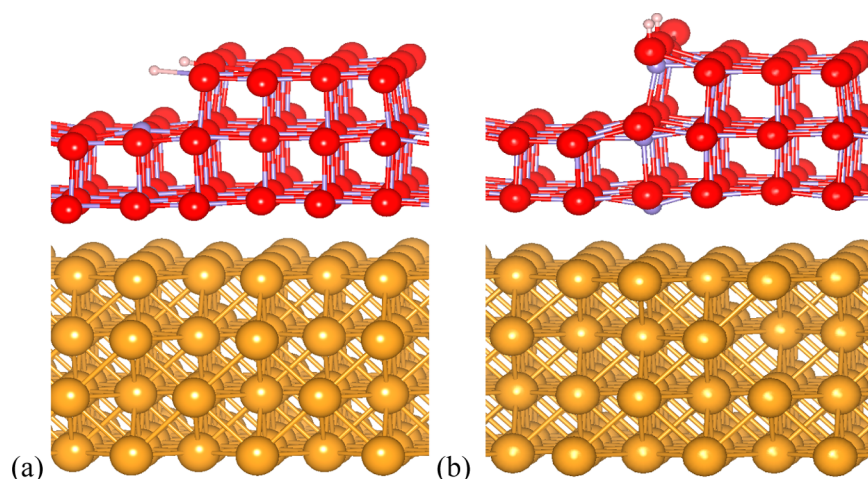


Figure 2. Structure of H_2 adsorption on a stepped $\text{MgO}/\text{Ag}(001)$ or $\text{MgO}/\text{Au}(001)$ film. (a) Heterolytic dissociation into OH and MgH groups (a similar structure is obtained for the bare MgO surface); (b) homolytic dissociation into two OH groups. Small red spheres, O; large orange spheres, Mg; yellow spheres, Ag or Au.

adjacent $\text{O}^{2-}_{4\text{C}}$ and $\text{Mg}^{2+}_{4\text{C}}$ ions along the step, the same site considered for the bare MgO surface, the OH and MgH groups are approximately parallel to the surface, Figure 1a. The vibrational frequencies are 3308 cm^{-1} (OH) and 1249 and 976 cm^{-1} (MgH), typical of heterolytic splitting. The reaction is weakly exothermic, $E_{\text{ad}} = -0.21\text{ eV}$, Table 1. Compared to bulk MgO , the products are similar, but the process is slightly less favorable (on MgO , E_{ad} is -0.43 eV). For the homolytic dissociation of H_2 on a step of $\text{MgO}/\text{Ag}(001)$, the H atoms adsorb on two $\text{O}^{2-}_{4\text{C}}$ ions separated by 4.2 \AA , Figure 1b. This homolytic dissociation is characterized by (i) a typical O–H distance of 0.98 \AA , (ii) a Bader charge of H $+0.59\text{ |e|}$, and (iii) OH vibrational frequencies at ca. 3700 cm^{-1} , Table 1. The two OH groups are oriented perpendicularly to the $\text{MgO}(001)$ plane, Figure 1b. The reaction is endothermic, $E_{\text{ad}} = +0.53\text{ eV}$. Therefore, the homolytic dissociation of H_2 on a step of $\text{MgO}/\text{Ag}(001)$ is energetically easier than on the terrace, but is not competitive with the classical heterolytic dissociation.

In Figure 3, we report the DOS plots for H_2 splitted heterolytically and homolitically on the terrace of $\text{MgO}/\text{Ag}(001)$ films (the DOS plots for the steps are similar and are not shown). The OH group gives rise to an O 2p state at about 3 eV below the O 2p valence band, as for unsupported MgO . The H^- ion (MgH group) has a doubly occupied feature at about 2 eV above the top of the valence band but still below the Fermi level. Thus, also valence band spectroscopies like UPS (ultraviolet photoelectron spectroscopy) or MIES (metastable impact electron spectroscopy) could be used to discriminate between the two dissociation modes.

To summarize, H_2 dissociates on a stepped $\text{MgO}/\text{Ag}(001)$ film with the classical heterolytic mechanism and formation of OH and MgH groups. The ultrathin film behaves as the bulk oxide.

It is important to comment on the position of the metal Fermi level (E_{F}) of $\text{MgO}/\text{Ag}(001)$. In fact, Ag acts as an electron reservoir, and the position of E_{F} is critical for the electron transfer process. E_{F} is measured by the work function of the system, Φ . Φ changes when an oxide film is deposited on a metal surface.^{61,62} For ionic materials such as MgO , Φ decreases due to electrostatic-compressive effects.⁶³ A 2 ML MgO film on $\text{Ag}(001)$ leads to $\Phi = 2.88\text{ eV}$, ca. 1.2 eV lower than that of the $\text{Ag}(001)$ support. This reduction is very close

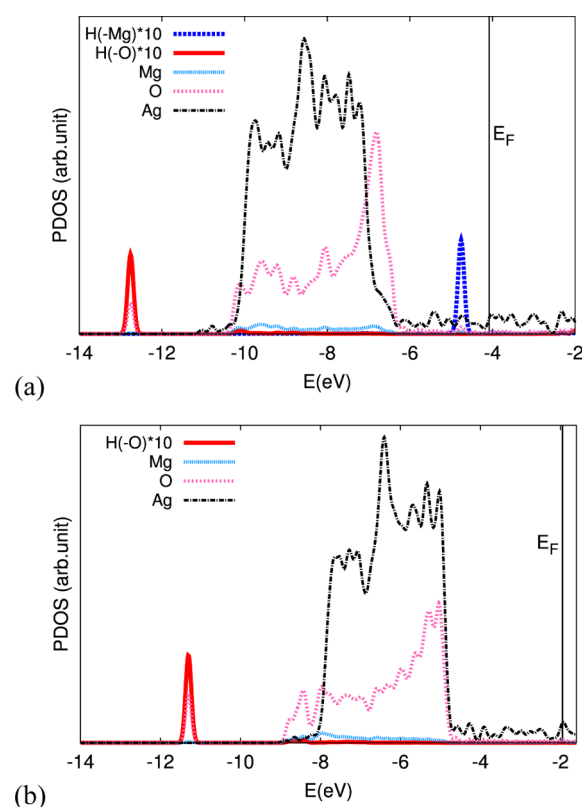


Figure 3. Density of states for an H_2 molecule dissociatively adsorbed on the terrace of $\text{MgO}/\text{Ag}(001)$ 2 ML film: (a) formation of an OH/MgH pair (heterolytic); (b) formation of an OH/OH pair (homolytic). The vertical line indicates the position of the Fermi level.

to that determined experimentally.⁶⁴ This means that an electron added to $\text{MgO}/\text{Ag}(001)$ leads to an energy gain of nearly 3 eV . Apparently, on $\text{MgO}/\text{Ag}(001)$, this is not sufficient to switch the adsorption mode of H_2 from heterolytic to homolytic. In order to obtain this result, one has to find a system with a larger Φ . A potential candidate is a MgO film deposited on Au.

3.3. $\text{MgO}/\text{Au}(001)$. Because of the small lattice mismatch, in principle, it is possible to grow MgO ultrathin films in registry with $\text{Au}(001)$ surfaces as it has been done with

Ag(001) crystals.⁶⁵ However, Au(100) undergoes a temperature-dependent surface reconstruction, from cubic to a distorted and slightly rotated hexagonal phase.^{66,67} It is possible that the deposition of an oxide thin film and the subsequent thermal annealing can stabilize the cubic Au(100) phase. However, MgO(001) films have been prepared by depositing Mg in an oxygen atmosphere on Au(111) surfaces held at elevated temperature.⁶⁸ The symmetry mismatch between the hexagonal Au(111) substrate and the squared MgO overlayer results in the formation of a (6×1) superlattice. Field emission resonance measurements show for MgO/Au(111) a work function of 3.6 eV, with a reduction of 1.6 eV compared to bare Au (5.2 eV).⁶⁸

For our calculations, we used the simpler MgO/Au(001) interface (interlayer distance of 2.74 Å and adhesion energy of 25.29 meV/Å²): in this way, a direct comparison with MgO/Ag(001) is possible. The deposition of 2 ML MgO on Au(001) results in a change in Φ from 5.01 eV in pure gold to 3.45 eV in MgO/Au(001) ($\Delta\Phi = -1.56$ eV). Therefore, both Φ and $\Delta\Phi$ are practically the same in MgO/Au(001) (theory) and MgO/Au(111) (experiment). In this respect, the results of our calculations on the hypothetical MgO/Au(001) films are expected to be valid for the existing MgO/Au(111) films. What counts is that Φ is about 0.6 eV larger on MgO/Au than on MgO/Ag. This is beneficial for a homolytic splitting of H₂ as it should result in an additional energy gain of about 0.6 eV per transferred electron.

In order to verify this hypothesis, we have considered H₂ dissociation on both flat and stepped MgO/Au(001) surfaces. On the terrace of a 2 ML MgO/Au(001) film, adsorption of H atoms on top of Mg²⁺_{5C} and O²⁻_{5C} ions results in the typical heterolytic dissociation found previously ($E_{\text{ad}} = 1.79$ eV, similar to that of bare MgO, 1.80 eV, Table 1). The situation changes completely when we consider the adsorption on two O_{5C} ions: in this case, the dissociation is homolytic (as shown by OH distance and Bader charges) and the process is weakly exothermic, $E_{\text{ad}} = -0.13$ eV, Table 1. Notice that in our analysis this is the first time that H₂ dissociation on the MgO terrace is exothermic. The reason is as anticipated: the additional energy gain associated to the transfer of the H₂ electrons to the Au Fermi level renders the formation of two OH groups preferred over the OH/MgH pair.

Next, we consider the same process on a stepped 3 ML MgO/Au(001) film, Figure 2. The heterolytic splitting on two adjacent Mg²⁺_{4C} and O²⁻_{4C} ions leads to a similar structure as observed on MgO(001) and on MgO/Ag(001); E_{ad} is weakly exothermic, -0.24 eV, as on MgO/Ag(001) ($E_{\text{ad}} = -0.21$ eV). The barrier for dissociation on a MgO/Au(001) step is very low, 0.19 eV, indicating an easy splitting of H₂ into OH and MgH. Thus, the metal support does not affect the heterolytic dissociation since this depends mainly on the electrostatic potential of the ionic oxide film. This is no longer true when we consider the homolytic dissociation involving two O²⁻_{4C} ions separated by 4.2 Å, Figure 1b. The structural, electronic, and spectroscopic properties are very similar to those of MgO/Ag(001), Table 1. The adsorption energy, however, goes from $E_{\text{ad}} = 0.53$ eV in MgO/Ag(001) to $E_{\text{ad}} = -0.62$ eV in MgO/Au(001), with a net gain of 1.15 eV or ca. 0.6 eV per transferred electron, as expected based on the different work function of the two systems. Thus, the formation of a pair of OH groups (homolytic dissociation) becomes the ground state of the system, at variance with bulk MgO and MgO/Ag films.

The next question is how OH groups are formed upon exposure of stepped MgO/Au films to H₂. One possibility is that the dissociation process starts at two adjacent Mg²⁺_{4C} and O²⁻_{4C} ions along the step, with an heterolytic splitting ($E_{\text{ad}} = -0.24$ eV, low barrier, ca. 0.2 eV). Then, the H⁻ moves from a Mg²⁺_{4C} toward the next neighbor O²⁻_{4C} ion, transfers the two electrons to the Au metal, and forms a new OH group at 4.2 Å from the first one. This implies both an atomic displacement and an electron transfer. With a series of constrained optimizations, we estimated the value of the barrier associated to this mechanism, ca. 0.7 eV, that could be overcome at temperatures as low as 200–250 K. Of course other mechanisms are possible, but we have identified at least one reaction path that can lead to formation of OH groups by exposure of the sample to H₂ at room temperature.

4. CONCLUSIONS

The mechanism of H₂ dissociation on bulk MgO and on MgO nanofilms deposited on Ag(001) or Au(001) surfaces is totally different. H₂ dissociates heterolytically on steps of bulk MgO with formation of OH and MgH groups, Figure 4. On oxide

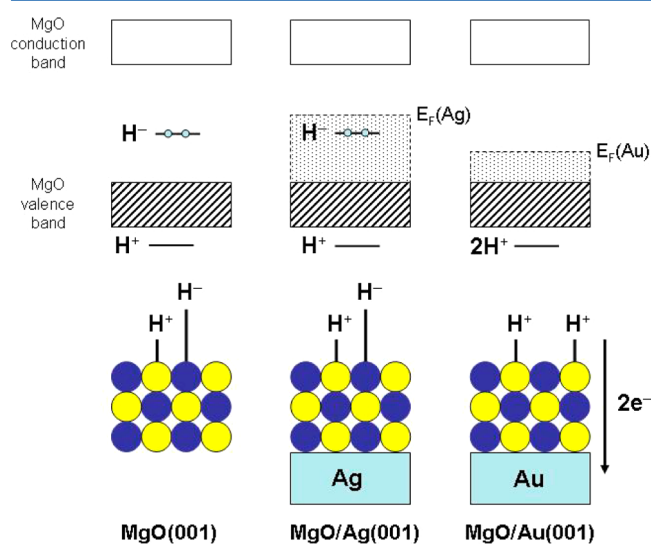


Figure 4. Schematic representation of the energy levels and dissociation products for an H₂ molecule interacting with the MgO surface (step) and MgO/Ag(001) and MgO/Au(001) ultrathin films.

ultrathin films, a direct electronic communication can be established with the underlying metal support.³⁵ Electrons can flow via tunneling mechanisms, leading to a charge transfer from the metal support to species adsorbed on the oxide film or vice versa. The direction of the charge transfer is governed by the relative positions of the metal Fermi level and of the frontier orbitals of the adsorbate.

For H₂ adsorption on MgO on a metal support, the two electrons of the H–H bond can be transferred to the metal/oxide interface with the formation of two OH groups (homolytic splitting). MgO/Ag(001) films behave similarly as the bare MgO surface, Figure 4, while a radically different interaction takes place when Ag is replaced by Au. The higher work function of MgO/Au(001) implies that the transfer of one electron from an adsorbate to the MgO/Au interface leads to an additional energy gain of ca. 0.6 eV, compared to the MgO/Ag interface. This difference is sufficient to greatly modify the adsorption properties of the two systems. On MgO/

Au(001), homolytic H₂ dissociation is largely preferred over the heterolytic one, and on steps, the reaction is significantly exothermic (ca. −0.6 eV). These theoretical expectations could be tested by comparing the adsorption properties of the existing MgO/Ag(001) and MgO/Au(111) films.

The mechanism of H₂ dissociation on MgO/Au is new and unprecedented and is entirely related to the possibility to exploit the nanodimensionality of the oxide film. For thicker films, the classical behavior is recovered. The case discussed here, H₂ dissociation, is only one example, and similar arguments could apply as well to the splitting of other relevant covalent bonds (e.g., C–H or C–C) with considerable impact on surface reactivity and, possibly, on catalysis.

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Notes

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