# Thickness-Dependent Hydroxylation of MgO(001) Thin Films

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Hydroxylation of MgO surfaces has been studied from UHV to mbar pressure for MgO(001) films of different thickness grown on Ag(001) by X-ray photoelectron spectroscopy, infrared reflection absorption spectroscopy, and density functional theory calculations. In agreement with earlier studies on MgO(001) single crystals, a threshold water pressure on the order of  $10^{-4}$  mbar is found for extensive hydroxylation of thick, bulklike MgO films. Decreasing the MgO film thickness shifts the threshold pressure to lower values, being  $10^{-6}$  mbar in the limit of 2 monolayer MgO(001)/Ag(001). This result is explained on the basis of the precursor state of periclase MgO(001) dissolution involving hydrolysis of Mg–O surface bonds. The enhanced structural flexibility (polaronic distortion) of the ultrathin MgO film facilitates surface hydroxylation by lowering the barrier for hydrolysis.

# 1. Introduction

Metals that come in contact with the environment are commonly covered by oxide overlayers. According to the early work of Mott and Cabrera, activation of adsorbed oxygen by electrons represents a precursor for oxidation, which proceeds as long as tunneling of electrons through the growing oxide layer is possible.<sup>1</sup> Recently, oxide overlayers on metals have received renewed interest. On the one hand, submonolayer oxide islands on metal supports may be regarded as inverse catalysts, allowing the investigation of interactions at metal/oxide boundaries. On the other hand, adsorption of suitable atoms or molecules on oxide layers of a few monolayers (ML) thickness was shown both theoretically and experimentally to be substantially modified as compared to the surface of the corresponding bulk oxides.<sup>2–8</sup> The differences have been attributed to (i) lowering of the work function of the metal by the oxide overlayer, (ii) charge transfer, which can take place both into the adsorbate and into the substrate depending on the properties of the adsorbate, and (iii) polaronic distortion in the oxide layer to stabilize the resulting charged adsorbate. Thin layers of MgO supported by Ag(001) are well suited to study these effects due to the perfect epitaxial relationship between MgO(001) and Ag(001). Within this work, we report the MgO thickness dependence of water adsorption on the surface of MgO(001) thin films studied from UHV to mbar pressure.

Water/oxide interaction is of paramount importance in fields as diverse as geochemistry, atmospheric chemistry, biology, catalysis, corrosion, materials science, and interstellar chemistry. These different aspects of water/oxide interaction have been summarized in detail in a number of review articles.<sup>9–12</sup> MgO(001), as the simplest oxide in terms of geometric and electronic structure, is among the oxides that have been most extensively studied with respect to water adsorption and dissociation, both experimentally and theoretically. There is now general consensus that H<sub>2</sub>O adsorbs molecularly at low coverage.<sup>13,14</sup> Spontaneous dissociation of water molecules is energetically not favored on the perfect MgO(001) surface and occurs only at defect sites, such as low-coordinated cation—anion pairs as present, for example, on steps and corners.<sup>13,15–17</sup> In the monolayer regime, however, an ordered overlayer with both molecular and dissociated water molecules in the unit cell is present.<sup>18–20</sup>

Less clear is the mechanism of extensive hydroxylation and dissolution of the MgO(001) surface. Studies on MgO(001) single crystals revealed that a certain threshold pressure of water is necessary to transform the MgO surface from a state of low, defect-mediated hydroxylation, to a fully hydroxyl covered surface.<sup>21</sup> The interpretation of the threshold behavior was based on purely thermodynamic grounds. The fully hydroxylated surface may be regarded as the precursor for dissolution. There is ample theoretical and experimental evidence that the MgO(001) surface is not stable in equilibrium with water and transforms into MgO(111).<sup>22,23</sup> This transformation requires concerted mass transfer and is kinetically controlled.<sup>24,25</sup> AFM investigations provide evidence that the process of dissolution starts at defects such as steps, whereas the regular surface is rather unreactive.<sup>26</sup>

Enhanced dissociation of water has been reported for submonolayer MgO islands deposited on Ag(001).<sup>27,28</sup> Even under typical ultrahigh vacuum conditions with low water background, the boundary ions between the MgO islands and the metallic substrate are easily hydroxylated.<sup>29</sup> This effect fades away with increasing MgO film thickness and has been attributed to the small size of the islands rather than to electronic effects caused by the metallic substrate.<sup>30</sup> Recently, the adsorption and dissociation of water on a 2 ML MgO film supported by Ag(001) has also been studied computationally.<sup>31</sup> It was found that dissociation of H<sub>2</sub>O is not favored on the regular surface of a supported thin film; however, it requires less energy than on bulk MgO(001). Although the thermodynamics of water adsorption is not changed dramatically if MgO is supported, charge transfer between substrate and adsorbate seems to take place and changes the bonding character.<sup>31</sup>

Herein, we present results of experiments performed for water adsorption and dissociation on Ag(001)-supported MgO(001) films

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of various thickness at pressures ranging from UHV to mbar with the aim to investigate the effect of film thickness on the ability for dissociation. Similar to previous reports on MgO single crystals, the surfaces are exposed to water vapor at different pressures and the degree of surface hydroxylation is determined by X-ray photoelectron spectroscopy (XPS). The findings are supported by corresponding infrared reflection absorption spectroscopy (IRAS) experiments and DFT calculations.

#### 2. Experimental and Computational Details

The experiments were performed in a UHV apparatus consisting of a UHV surface analysis chamber combined with a UHV-high pressure reaction cell optimized for grazing incidence IRAS. The UHV section is equipped with low energy electron diffraction (LEED), XPS (nonmonochromatic dual Mg–Al anode and hemispherical electron energy analyzer), and temperature-programmed desorption (TPD).

The Ag(001) single crystal was cleaned by cycles of sputtering and annealing until a  $(1 \times 1)$  LEED pattern with sharp spots was observed. MgO(001) thin films of nominally 2, 5, and 20 monolayer (ML) thickness were grown by Mg evaporation on to Ag(001) at an oxygen background pressure of  $1 \times 10^{-6}$  mbar and a substrate temperature of 573 K. The MgO growth rate was 1 ML·min<sup>-1</sup>. Rate of deposition and thickness was calibrated using a quartz microbalance and by XPS. According to the XPS analysis, the films were on average 2, 4, and 12 ML thick. The differences with respect to the nominally deposited amount (2, 5, and 20 ML) might arise from a systematic error in the calibration of the deposition rate or due to some interdiffusion of Ag at the deposition temperature used here.

For hydroxylation experiments, the sample was transferred into a stainless steel UHV-high pressure cell, which is equipped with a gas inlet for water exposure. Double deionized H<sub>2</sub>O and D<sub>2</sub>O (99.75% Merck) were degassed by repeated freezepump-thaw cycles before background dosing. The samples were exposed to water at 300 K for three minutes at pressures in the range 10<sup>-6</sup> mbar to 1 mbar for hydroxylation studies, and at 90 K to 5 L (1  $L = 1 \times 10^{-6}$  Torr s) for monolayer water studies. Infrared and X-ray photoelectron spectra were obtained at background pressures below 10<sup>-8</sup> mbar after pumping water. XPS data were acquired with a hemispherical multichannel analyzer (Specs, Phoibos150) using an Al Ka X-ray source ( $h\nu = 1486.6 \text{ eV}$ ). The XPS spectra were recorded at electron takeoff angles of  $0^{\circ}$  and  $60^{\circ}$ . The deconvolution of the spectra was performed by using Gaussian-broadened Lorentzian shapes after Shirley background correction and satellites subtraction. The shapes and full width at half-maximum have been fixed and propagated along the serial of spectra. Infrared experiments were performed with a Bruker IFS 66v spectrometer and an external MCT detector connected to the UHV-high pressure cell via CaF<sub>2</sub> windows. The resolution was 4 cm<sup>-1</sup> and 2000 scans were accumulated to obtain a reasonable signal-tonoise ratio. The samples were exposed to D<sub>2</sub>O for IRAS measurements, whereas H<sub>2</sub>O was used for XPS experiments.

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP)<sup>32,33</sup> along with the Perdew–Wang (PW91) exchange-correlation functional.<sup>34</sup> We applied the projector augmented wave (PAW) method,<sup>35,36</sup> and the planewaves basis set with a kinetic energy cutoff of 400 eV. A 4 × 2 × 1 Monkhorst–Pack grid was used for k-point sampling.<sup>37</sup> All structures were confirmed as local minima by vibrational analysis.

We use two types of surface slab models. The first one is used to model unsupported MgO(001) films and constructed as an orthorhombic (3 × 2) MgO(001) surface unit cell with four layers of MgO and lattice constants  $a_0 = 8.988$  Å,  $b_0 = 5.992$ Å. Two bottom layers are fixed to their optimized bulk positions ( $a_0 = 4.237$  Å for bulk MgO). The second model is used for calculations on the 2 ML Mg(001)/Ag(001) film. To model the metallic substrate a (3 × 2) surface unit cell of Ag(001) (8.774 Å × 5.880 Å) was constructed. To investigate the convergence of calculated properties with respect to the metal slab thickness we used 3, 6, and 10 layers of Ag atoms. The upper 2, 4, and 6 upper metal layers were allowed to relax, respectively. On top of the metal slab two layers of MgO(001) were deposited with O atoms positioned directly above the topmost Ag atoms. The resulting 2 ML Mg(001)/Ag(001) slab model was fully relaxed except for the frozen bottom Ag atoms. In all models, the repeated slabs were separated by 14 Å vacuum.

For comparison of molecular and dissociative H<sub>2</sub>O adsorption on supported and unsupported Mg(001) surfaces we use the adsorption energy  $\Delta E$  defined as energy of the following reaction

$$MgO(001) + H_2O \rightarrow H_2O/MgO(001).$$
 (1)

To relate the calculated values to the experimental conditions we also use Gibbs free energies of adsorption

$$\Delta G = G_{\rm H_2O/MgO(001)}^{\rm (s)} - G_{\rm MgO}^{\rm (s)} - \mu_{\rm H_2O}^{\rm (g)}$$
(2)

The Gibbs free energies of the solid and the H<sub>2</sub>O chemical potential are defined as

$$G^{(s)} = E_0 - \operatorname{RTln}(Q_{vib}) \tag{3}$$

$$\mu_{\rm H_2O}^{\rm (g)} = E_0 - \operatorname{RT} \ln \left( Q_{\rm vib} Q_{\rm rot} Q_{\rm trans} \right) + \operatorname{RT}, \qquad (4)$$

where  $E_0$  is the total electronic energy plus the zero point vibrational energy,  $E_{ZPE}$ , and  $Q_{vib}$ ,  $Q_{rot}$ , and  $Q_{trans}$  are the vibrational, rotational, or translational partition functions, respectively. We neglect volume changes of solid components and replace the volume work of the gas phase by RT (ideal gas).

## 3. Results

Figure 1 shows IR absorption spectra of the water (D<sub>2</sub>O) monolayer on Ag(001)-supported MgO(001) films of different thickness. For preparation of the monolayer 5 L D<sub>2</sub>O were adsorbed at 90 K, which initially leads to the formation of an amorphous ice multilayer. Subsequently, the multilayer was desorbed by heating the sample to 160 K, leaving behind an ordered monolayer that is stable up to  $\sim 210$  K.<sup>38</sup> The D<sub>2</sub>O monolayer gives rise to three characteristic and sharp IRAS signals at 2715, 2630, and 2593 cm<sup>-1</sup>.<sup>39-41</sup> These can be assigned to hydroxyl groups in the partially dissociated (3  $\times$ 2)  $-6 D_2O$  monolayer structure (2715 and 2593 cm<sup>-1</sup>) as well as molecularly adsorbed  $D_2O$  molecules (2630  $\mbox{cm}^{-1}).^{41}$  Both positions and relative intensities of the IRAS signals do not significantly change with respect to the MgO layer thickness. Furthermore, no additional spectral contributions that would be indicative for spontaneous dissociation of D<sub>2</sub>O due to special morphological or electronic defects on the surface of the 2 ML MgO(001) film are detected. This suggests that under the



**Figure 1.** IRAS spectra of the water monolayer on Ag(001)-supported MgO(001) thin films of different thickness obtained after  $D_2O$  adsorption at 90 K and subsequent heating to 160 K.



**Figure 2.** O 1s photoemission spectra of 2 ML MgO(001)/Ag(001) after 3 min exposure to  $H_2O$  at the indicated pressures. The lowest trace is the XP spectrum of the clean film. The insert shows the C 1s region in the same order of  $H_2O$  exposure.

conditions employed in this experiment the surface of the 2 ML MgO film behaves similarly with regard to monolayer water adsorption as the surface of a 12 ML, bulklike MgO(001) film.

In addition, the interaction of water with the MgO surface has been studied within a wide pressure interval ranging from UHV conditions to 1 mbar  $H_2O$  for MgO films of different thickness. As an example, in Figure 2 the O 1s photoemission spectra of a clean 2 ML MgO thin film, as well as after 3 min water dosing at the indicated pressures at room temperature are shown.

The clean oxide film is characterized by a single O 1s photoemission peak at 529.9 eV. With increasing water pressure a shoulder appears at high binding energy, which, at higher water pressures, develops into a separate peak (Figure 2). The binding energy shift of 2.4 eV with respect to the oxide peak obtained at the highest water pressure (1 mbar) is consistent with the interpretation of this peak as being due to hydroxyl species on the MgO surface.<sup>21,42</sup> Both the intensity of the hydroxyl peak as well as the intensity ratio OH<sup>-</sup> /O<sup>2-</sup> decrease significantly at a takeoff angle of 0° suggesting that under these conditions hydroxylation affects only the outermost surface layer, which is in agreement with studies on MgO single crystals and

powders.<sup>21,43</sup> In addition to the development of the hydroxyl peak with increasing H<sub>2</sub>O pressure, a shift of the  $O^{2-}$  peak to lower binding energy after exposure of  $10^{-4}$  mbar H<sub>2</sub>O and higher is evident. A concomitant shift of the Mg 2p emission is registered, whereas the position of the Ag 3d peak is not affected by H<sub>2</sub>O exposure. The shift of the O 1s and Mg 2p peaks can consistently be explained by an upward band bending induced by surface hydroxylation.

An unavoidable side effect of water dosing at high pressure is the accumulation of carbon-related impurities on the surface. The insert in Figure 2 shows spectra of the C 1s region at increasing water pressure. Two peaks at 284.7 and 288.9 eV, which are assigned to adventitious carbon (graphitic) and carbonates (and formates) respectively, are clearly detected at high water pressure. The concentration of these impurities was calculated to be  $\sim 0.25$  ML for the highest water pressure. The contribution of oxygen-containing carbon (formates, carbonates), which would also give rise to a signal in the O 1s region, is about 0.1 ML. It has been shown previously that the contribution of the carbon-related species to the O 1s intensity is rather small as compared to the changes induced by hydroxyl formation.<sup>44</sup> For the present case, a maximum contribution of 10% with respect to the OH intensity after 1 mbar H<sub>2</sub>O exposure was estimated and has been taken into account in the quantitative analysis, which is described in the following.

The OH coverage was determined based on models described in the literature.<sup>21,44</sup> Both of these models use the intensity ratio of the O 1s hydroxyl and oxide peaks as well as the inelastic mean free path (IMFP) of the photoelectrons to calculate either the hydroxyl coverage in ML or the thickness of the hydroxyl layer. They can strictly be applied only to bulk materials or thin films with a thickness considerably larger than the IMFP. With the experimental setup used in the present study, the IMFP is 10.5 Å at a O 1s photoelectron kinetic energy of 956 eV and an emission angle of 60°.45 Therefore, the models are only useful for the 12 ML MgO film with a thickness of  $\sim$ 25 Å. With the assumption that only the outermost layer is hydroxylated, the OH coverage obtained for 12 ML MgO can, however, be used to calculate the OH coverage on the thinner films by direct comparison of the absolute OH XPS intensity. In addition, for 2 and 5 ML MgO the OH coverage was calculated from the increase of film thickness upon hydroxylation using the OH and oxide XPS intensities and taking into account the exponential decay of the signal contribution with increasing film thickness. With these procedures, very similar OH coverages were obtained for films of a certain thickness and at a certain degree of hydroxylation. The maximum deviation was  $\pm 0.07$  ML for the highest OH coverage.

Figure 3 summarizes the results of a quantitative analysis of the H<sub>2</sub>O pressure dependent development of the hydroxyl species on MgO films of different thickness. For 12 ML thick MgO(001) films, which can be considered as behaving bulklike, a clear formation of surface hydroxyls is observed only at a pressure of  $\sim 1 \times 10^{-4}$  mbar H<sub>2</sub>O. This result is consistent with earlier studies on MgO(001) single crystals, where a threshold pressure of  $3 \times 10^{-4}$  mbar H<sub>2</sub>O was determined for extensive surface hydroxylation.<sup>21</sup> After water dosing at 1 mbar H<sub>2</sub>O a surface hydroxyl concentration of  $\sim 0.9$  ML was obtained.

The threshold behavior for extensive hydroxylation observed for the thick MgO(001) film is maintained if the film thickness is reduced to 4 and 2 ML, respectively. However, the corresponding threshold pressure shifts to lower values with decreasing film thickness (Figure 3). For surface OH coverages ranging between 0.3 and 0.7 ML the H<sub>2</sub>O pressure required to obtain



**Figure 3.**  $H_2O$  pressure dependent surface hydroxyl coverage on Ag(001)-supported MgO(001) films of different thickness obtained from fits of the O 1s XP spectra.

similar OH concentrations is smaller by 2–3 orders of magnitude for 2 ML as compared to 12 ML MgO films, suggesting an enhanced surface hydroxylation probability of the thin film. This result has been confirmed by respective IRAS experiments. Figure 4 shows the infrared spectra obtained after exposing surfaces of 2, 4, and 12 ML MgO(001) to  $D_2O(10^{-6} \text{ to } 1 \text{ mbar})$  at room temperature.

For water exposure at a pressure of  $1 \times 10^{-6}$  mbar (lowest trace in the series of spectra for each film thickness, Figure 4) an IR signal centered at 2754 cm<sup>-1</sup> is detected on the 2 ML MgO film, whereas only a small signal is observed on 4 ML MgO and no signal on 12 ML MgO (part a of Figure 4). With increasing water pressure the OD IR intensity increases and finally, after 1 mbar D<sub>2</sub>O, a dominating IR signal at 2743 cm<sup>-1</sup> is present for all MgO thicknesses. An interesting detail is the systematic change of the OD region with water exposure for the different films. Whereas for 2 ML MgO an OD band at 2754 cm<sup>-1</sup> appears at low pressure, on the thick, 12 ML MgO film the signal detected after  $10^{-4}$  mbar D<sub>2</sub>O exposure is at 2738 cm<sup>-1</sup>. The spectra of the 4 ML MgO film might be regarded as a mixture of 2 and 12 ML MgO as they contain both the high and low frequency component.

In part b of Figure 4, the spectra are displayed in a wider frequency range including the region below 2680 cm<sup>-1</sup>, where typically a broad signal due to hydrogen-bonded OD is observed on hydroxylated oxides. As expected, the contribution of hydrogen-bonded OD increases with increasing water exposure. This effect is best seen in the spectrum after 1 mbar D<sub>2</sub>O exposure to 12 ML MgO, which shows a broad signal between 2450 and 2680 cm<sup>-1</sup>. The fact that the contribution of hydrogenbonded OD decreases as the films become thinner (part b of Figure 4) might be related either to different orientation of the dipole moment on the thin films, which, according to the IRAS selection rules, would not permit to observe a signal, or to a geometrical effect that prevents the formation of extended hydrogen bonding networks on the thinner film. On the other hand, a small but relatively narrow signal at 2693 cm<sup>-1</sup> is only detected on 2 ML MgO. The frequencies and linewidths of the OD infrared signals of the hydroxylated surfaces are substantially different as compared to the monolayer adsorption (Figure 1) and reflect the different surface states under the respective experimental conditions.

Finally, it has to be noted that the vibrational spectrum after 1 mbar  $D_2O$  on 12 ML MgO agrees well, both in relative intensities as well as in the position of the signals, with the one obtained from MgO nanoparticles hydroxylated under similar conditions (topmost trace of parts a and b of Figure 4). The signals in the region 2720 and 2760 cm<sup>-1</sup> are, however, much narrower on the thin film sample suggesting a more uniform surface morphology.

The experimental results presented above clearly evidence that hydroxylation of the MgO surface depends critically on the experimental conditions and the presence of a supporting metal. DFT calculations have been performed to support these findings. Table 1 summarizes the free energies for molecular and dissociative water adsorption on bulk MgO(001) and 2 ML MgO(001)/Ag(001) in the relevant range of temperatures and for different numbers of Ag layers. Table 2 shows the corresponding structure parameters and relevant vibrational frequencies. The results show that slabs containing between 6 to 10 layers of Ag yield free energies and structures converged with respect to the metal thickness. On both the thin MgO film and



**Figure 4.** IRAS spectra of MgO(001)/Ag(001) films of different thickness after  $D_2O$  exposure to  $10^{-6}$ ,  $10^{-4}$ ,  $10^{-2}$ , and 1 mbar, respectively. a) detail of 2700–2780 cm<sup>-1</sup> region; b) full OD range. For comparison, an IR spectrum of MgO nanoparticles obtained by chemical vapor deposition<sup>46</sup> after hydroxylation at 5 mbar  $D_2O$  and room temperature is shown.

TABLE 1: Adsorption Energies,  $\Delta E$ , Zero Point Vibrational Energy Contributions,  $\Delta ZPE$ , and Free Energies of Interaction at 90 and 160 K,  $\Delta G_{90}$  and  $\Delta G_{160}$ , Respectively for Molecular and Dissociative Adsorption of a Single Water Molecule on Unsupported and Supported MgO(001) Models (kJ/mol)

		molecular				dissociative			
surface model	$\Delta E$	$\Delta ZPE$	$\Delta G_{90}$	$\Delta G_{160}$	$\Delta E$	$\Delta ZPE$	$\Delta G_{90}$	$\Delta G_{160}$	
4 ML MgO(001) unsupp.	-48.8	9.1	-30.4	-21.3	58.9	5.8	73.9	82.6	
2 ML MgO/3 L Ag(001)	-43.3	7.7	-26.6	-18.0	23.2	3.1	35.6	44.4	
2 ML MgO/6 L Ag(001)	-43.0	8.7	-24.8	-15.3	25.8	4.5	40.1	49.7	
2 ML MgO/10 L Ag(001)	-43.5	8.7	-25.3	-15.9	25.2	5.1	40.3	50.3	

TABLE 2: Bond Distances (Å) and Vibrational Frequencies (cm<sup>-1</sup>) for Molecular and Dissociative Adsorption of a Single Water Molecule on Unsupported and Supported MgO Surface Models<sup>*a*</sup>

bond	4 ML MgO unsupp.	2 ML MgO/3 L Ag(001)	2 ML MgO/6 L Ag(001)	2 ML MgO/10 L Ag(001)
molecular (part a of Figure 5)				
Mg <sub>s</sub> -O <sub>water</sub>	2.224	2.233	2.250	2.230
O <sub>1s</sub> -H <sub>1water</sub>	1.716	1.820	1.706	1.746
O <sub>2s</sub> -H <sub>2water</sub>	2.770	3.038	3.218	3.074
dissociative (parts b and c of Figure 5)				
(O-H) <sub>ads</sub>	0.972	0.970	0.970	0.970
Mg <sub>1s</sub> -(OH) <sub>ads</sub>	2.077	2.045	2.045	2.047
$Mg_{2s}-(OH)_{ads}$	2.180	2.105	2.105	2.110
O <sub>s</sub> -H	0.977	0.976	0.976	0.978
Mg <sub>3s</sub> -O <sub>s</sub> H	2.712	3.244	3.244	3.221
$\nu$ (O-H) <sub>ads</sub>	3684 (2714)	3710 (2735)	3714 (2738)	3711 (2736)
$\nu(O_s-H)$	3620 (2671)	3624 (2674)	3615 (2668)	3607 (2662)

<sup>*a*</sup> The numbers in parentheses are the respective OD stretching frequencies.

bulk MgO(001), molecular adsorption of water is exothermic, with adsorption on bulk MgO slightly energetically favored. Similar preference has been found for an ordered ( $3 \times 2$ ) water monolayer.<sup>31</sup> The calculated interaction energy of -48.8 kJ/ mol is in good agreement with -48.2 and -50 kJ/mol inferred from calculations<sup>14</sup> and experimental data,<sup>47</sup> respectively. The structure of an adsorbed water molecule is depicted in part a of Figure 5 and is similar with and without Ag support. The water oxygen atom is almost above a surface magnesium site, whereas hydrogen atoms are asymmetrically oriented with one H pointing to the surface and the second one slightly out of the surface. The somewhat shorter molecule-surface bond distances (c.f. Table 2) indicate stronger binding of water to unsupported MgO(001).

Interaction energies presented in Table 1 show that dissociative adsorption of a single water molecule is energetically disfavored on both surfaces, with +59 kJ/mol on unsupported, and +25 kJ/mol on Ag-supported 2 ML MgO(001).<sup>31,48</sup> In the dissociated structure (parts b and c of Figure 5), the OH fragment of the dissociated H<sub>2</sub>O molecule, (OH)<sub>ads</sub>, is adsorbed in a bridge position between two surface magnesium sites which move upward out of the surface plane (bond distances in Table 2). The hydrogen atom of the dissociated H<sub>2</sub>O molecule binds to the next nearest neighbor surface oxygen site forming an OsH group, which is arranged perpendicular to the surface. Part b of Figure 5 demonstrates strong surface relaxation upon dissociation of the H<sub>2</sub>O molecule. The relaxation is more pronounced for supported MgO (part c of Figure 5). For example, the  $Mg_s$ -O<sub>s</sub>H distance is 0.53 Å larger for the 2 ML MgO(001)/ Ag(001) surface than for unsupported MgO(001) slab. However, despite the differences in the surface relaxation in the supported and unsupported films the O-H bond distance in the O<sub>s</sub>H group remains constant leading to virtually identical vibrational frequencies (Table 2). In contrast, the O-H bond distance in (OH)<sub>ads</sub> is slightly shorter on the 2 ML MgO(001)/Ag(001) film compared to unsupported MgO, which leads to 30 cm<sup>-1</sup> difference in the corresponding vibrational frequency.



**Figure 5.** Structures (side and top view) of a single water molecule a) adsorbed on unsupported MgO(001), and dissociated on b) unsupported MgO(001) and c) 2 ML MgO/Ag(001) surfaces.  $(OH)_{ads}$  and O<sub>s</sub>H denote the hydroxyl groups formed after H<sub>2</sub>O dissociation; labels Mg<sub>1s</sub>-Mg<sub>3s</sub>, O<sub>1s</sub>, and O<sub>2s</sub> are used to distinguish different surface atoms in Table 2.

An important question related to the theoretical treatment is if the additional stresses imposed by the current selection of the slab model are responsible for the lower dissociation energy and the stronger structural relaxation in case of the Ag-supported 2 ML MgO(001) film compared to unsupported MgO(001). To address this question we have repeated the calculations for 2 ML MgO(001)/Ag(001) using slab models with the same lateral dimensions as for unsupported MgO(001) (Tables 1S and 2S of the Supporting Information). Even in this limiting case, the dissociation of water is energetically less demanding on a 2 ML thin MgO(001)/Ag(001) film than on an unsupported MgO(001) surface. This shows that the enhanced structural flexibility of the 2 ML MgO(001)/Ag(001) film is not an artifact of the slab model currently used.

#### 4. Discussion

The experimental results presented in this study indicate that the interaction of water with the surface of Ag(001)-supported MgO films of different thickness is substantially different depending on the experimental conditions. From the IR spectra presented in Figure 1, it is deduced that water monolayer adsorption is qualitatively similar on MgO films with thicknesses ranging between 2 and 12 ML. This result is in line with the theoretical model, which shows only minor modification of the water molecule/surface interaction on supported MgO (ref 31 and Table 1). In contrast, at elevated pressure surface hydroxylation is strongly enhanced in the limit of Ag(001)-supported, ultrathin 2 ML MgO films as compared to thick, bulklike 12 ML films. The latter observation is generally in line with the modified adsorption behavior of strongly electronegative adsorbates on thin MgO films, predicted theoretically and proven experimentally for Au<sup>2,5,6</sup> and NO<sub>2</sub>.<sup>4,8</sup> In these examples, the lowest unoccupied state in the isolated species falls below the Fermi energy of the combined system (adsorbate/MgO film/ metal substrate) leading to charge transfer into the adsorbate. From computational results, it was concluded that charge transfer occurs also for the water dissociation products on supported MgO thin films: into the adsorbate for OH and into the substrate for H.<sup>31</sup> However, the stabilizing effect is not strong enough to change the thermodynamics of the dissociation process, i.e. dissociation of a water molecule is still endothermic on supported MgO films (refs 31 and 48 and Table 1). Previous experiments have shown that enhanced hydroxylation occurs for monolayer MgO islands supported by Ag(001).<sup>27-29</sup> At moderate substrate temperatures during MgO deposition as used here, MgO islands may be embedded into the Ag lattice leading to Ag ad-island formation on the surface.<sup>49,50</sup> It can, therefore, not be excluded that in the present study small patches of Ag are exposed on the 2 ML MgO/Ag(001) sample, giving rise to highly reactive ions at the boundary of Ag and MgO. However, the influence of exposed Ag, if present at all, on the observed hydroxylation behavior of 2 ML MgO films is considered to be small because the reactivity of 2 ML MgO films toward water was shown to be considerably less than for submonolayer MgO islands.<sup>27</sup> An explanation of the reduced hydroxylation threshold observed on the thin MgO film requires, therefore, a different approach.

DFT calculations predict that a fully hydroxylated  $(1 \times 1)$ MgO(001) surface with an OH<sup>-</sup> group on each surface cation and H<sup>+</sup> on each surface anion is not stable with respect to clean MgO(001) and gas-phase water.<sup>22</sup> Rather it is the hydroxylcovered MgO(111) surface that is the most stable surface in humid environment. Recent experiments have nicely shown the gradual transformation of cubic MgO(001) microcrystals in contact with water into octahedral particles exposing (111) facets.<sup>23</sup> Because dissolution rates for periclase (MgO) and brucite (Mg(OH)<sub>2</sub>) were found to be very similar,<sup>51</sup> a two-step process has been proposed for the dissolution of MgO(001): The first step involves a rapid surface hydroxylation by hydrolysis of Mg-O bonds and protonation of surface oxygen with the formation of a brucitelike layer. The second, much slower process, involves Mg2+ transfer from the bulk to the surface and detachment of hydrated Mg<sup>2+, 24,25</sup> It was suggested that this process nucleates on defect sites and brucitelike layers penetrate along (111) planes into the bulk. Such a mechanism has recently been modeled by MD simulations.<sup>52</sup> Under the hydration conditions applied in the present work, complete dissolution of MgO(001) can be excluded because this process requires long contact times. Nonetheless, according to the results presented here the surface hydroxylation can be divided into two regimes.

The first is the initial hydroxylation of the surface observed after  $10^{-6}$  mbar on 2 ML MgO and  $10^{-4}$  mbar on 12 ML MgO, respectively. The XPS data indicate similar OH coverage on both surfaces (~0.35 ML, Figure 3) and IRAS spectra show rather narrow absorption lines due to hydroxyls (Figure 4). Interestingly, the frequency of the observed IR signals differs by about 20 cm<sup>-1</sup> for the different film thicknesses. Signals in this frequency range are typical for single coordinated and hydrogen-bond acceptor OH groups. There is a long-standing discussion about the exact nature of OH groups on MgO and the influence of coordination on the vibrational frequency. 43,46,53-55 However, because the nature and abundance of morphological defects on thin and thick MgO(001) films is considered to be not too different, no immediate connection between the observed signals and the surface morphology is drawn. It seems rather the film thickness that is responsible for the observed frequency shift. The computed frequencies fully support this suggestion. The stretching frequency of the (OH)ads group on 2 ML MgO(001) is shifted by about 30  $cm^{-1}$  to higher wavenumber as the respective vibration on the unsupported MgO due to slightly contracted bond distances. This finding is in good agreement with the experiment, which gives a  $20 \text{ cm}^{-1}$  shift in the OD region. In addition, a slightly red-shifted signal at 2693 cm<sup>-1</sup> is observed on 2 ML MgO(001). According to the calculated result, this vibration can be attributed to the stretching mode of the multiple-coordinated O<sub>s</sub>D resulting from water dissociation. This qualitative agreement provides evidence that isolated OD(OH) groups are present on the MgO(001) surface at this early stage of hydroxylation.

The second regime is that of extensive hydroxylation of the MgO(001) surface. Although the individual IRAS spectra obtained after 1 mbar exposure contain vibrational features reminiscent of the low pressure regime, a dominant signal at 2743 cm<sup>-1</sup> is observed for all MgO thicknesses studied, suggesting similar properties of the oscillators. At this high degree of hydroxylation, an extended hydrogen bonding network is present on the surface, which, on the one hand, gives rise to stretching frequencies different than those of single-coordinated OD(OH), whereas, on the other hand, the lateral interaction through hydrogen bonding might also extenuate the influence of the metallic substrate, leading to vibrational properties that are independent of film thickness.

Although the final hydroxylation state of the surfaces of MgO(001) films of different thickness is observed to be qualitatively similar, the pressure required for extensive surface hydroxylation is considerably lower for thinner films. To explain this result, it is first of all necessary to consider the mechanism of hydroxylation. As pointed out above, the  $(1 \times 1)$  hydroxylated MgO(001) surface is energetically not stable. To reach a high degree of hydroxylation as observed here, the model proposed for dissolution is, therefore, a better starting point.<sup>24,25</sup> This requires that surface bonds are broken, leading to microscopic roughening of the surface and formation of defect sites. In part a of Figure 6, LEED patterns of clean 12 ML MgO(001) and the same sample after exposure to 1 mbar H<sub>2</sub>O are presented. It is clear that the long-range order is maintained,



**Figure 6.** a) LEED pattern of clean 12 ML MgO(001)/Ag(001) and after exposure to 1 mbar H<sub>2</sub>O at room temperature. b) IRA spectra of CO adsorbed at 90 K on clean 12 ML MgO(001)/Ag(001) (upper trace), and after exposure to  $1 \times 10^{-3}$  mbar H<sub>2</sub>O and subsequent evacuation at 500 K (lower trace). c) Model of surface hydroxylation including hydrolysis of a surface Mg–O bond (adapted from ref 25).

however, a more diffuse background in the pattern of the waterdosed sample points to slight disorder. IRAS using CO as a probe has subsequently been used for a spectroscopic detection of low coordinated defects sites (part b of Figure 6). Almost no CO adsorption is observed on a clean MgO surface at 90 K. However, after hydroxylation  $(10^{-3} \text{ mbar})$  and subsequent evacuation at 500 K (a temperature that is sufficient to desorb some of the molecularly adsorbed water but not high enough to restore a flat surface) a signal is detected between 2175 and 2190 cm<sup>-1</sup>, typical of CO adsorbed on low-coordinated Mg<sup>2+</sup> ions.<sup>56</sup> This result provides convincing evidence for the suggested mechanism of hydroxylation involving hydrolysis of Mg-O surface bonds and formation of a defective surface exposing low-coordinated sites. According to this mechanism, the semidetached Mg<sup>2+</sup> ions need to be stabilized by surrounding water molecules, which act as ligands to fill up the coordination sphere of the cation (part c of Figure 6).<sup>25</sup> Because a certain coverage of water is required for this stabilization, the threshold behavior observed in the XPS experiments is explained by this hydroxylation mechanism. Furthermore, the barrier for hydrolysis of a surface Mg-O bond is easier to overcome if the oxide lattice allows for structural flexibility. The calculations show that hydroxylation of 2 ML MgO(001)/Ag(001) results in strong relaxation of the MgO lattice as a consequence of the interaction with the metal-oxide interface. This phenomenon is known as polaronic distortion and affects the lattice much more than in comparable adsorption processes on bulk MgO(001). Therefore, hydrolysis of a Mg-O bond is energetically less demanding on a 2 ML thin MgO(001) film as compared to a thick, bulklike 12 ML film, explaining the reduced water pressure necessary to induce this effect.

## 5. Summary and Conclusions

In this work, the interaction of water with the surface of MgO(001) thin films of different thickness supported by Ag(001) was studied in a wide range of water pressure. The properties of the water monolayer, prepared at low temperature

and under UHV conditions, are qualitatively the same on 2 and 12 ML thin MgO films, indicating similar adsorption behavior, which is in line with results from DFT calculations. At room temperature, initial hydroxylation of the surface results in the formation of isolated OH groups. Surface roughening is observed at increased water pressure providing evidence for a hydroxylation mechanism including hydrolysis of Mg–O surface bonds. Therefore, the simple picture of surface hydroxylation, which results in an unstable state on both bulk and supported MgO according to calculations, is not applicable for extensive hydroxylation of the MgO(001) surface. The observed surface roughening may in part also explain the enhanced stability of small gold clusters on the hydroxylated as opposed to the nonhydroxylated MgO(001) surface.<sup>57</sup>

Hydroxylation is found to be strongly enhanced on a 2 ML thin MgO(001)/Ag(001) film with the threshold water pressure for hydroxylation by 2 - 3 orders of magnitude lower as compared to a bulklike, 12 ML MgO(001)/Ag(001) film. The enhanced reactivity of the 2 ML MgO film is attributed to the possibility of charge exchange with the metallic substrate, inducing a polaronic distortion of the MgO lattice that facilitates the hydrolysis of Mg–O surface bonds.

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**Supporting Information Available:** Interaction energies and structure parameters for H<sub>2</sub>O adsorption and dissociation on 2 ML MgO(001)/Ag(001) using a (3 × 2) unit cell with  $a_0 = 8.988$  Å,  $b_0 = 5.992$  Å. This material is available free of charge via the Internet at http://pubs.acs.org.

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