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Dissociation of Water on a Flat, Ordered Silica Surface

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In this paper, ultraviolet photoelectron spectroscopy (UPS) and metastable impact electron spectroscopy (MIES) results are reported for water adsorption on SiO₂/Mo(112) surfaces. It is shown that UPS spectra are insufficient for the determination of the detailed mechanism for water dissociation. By use of UPS in combination with MIES, however, it is shown that multilayer-induced dissociation is responsible for hydroxyl group formation. It is suggested that hydroxyl groups on oxide surfaces can be stabilized by neighboring water molecules (solvation), even when the interaction between the hydroxyl groups and the surface is weak. These results demonstrate that simultaneous UPS and MIES measurements offer a powerful methodology for the investigation of multilayer-induced reactions which have important implications at the liquid–solid interface.

1. Introduction

The adsorption of water on metal oxide surfaces has attracted much attention due to its technological importance in various fields such as corrosion, degradation of electronic devices, catalysis, and geochemistry. The investigation of water adsorption on solid surfaces is also crucial for providing a basic understanding of the liquid–solid interface, which has important implications in heterogeneous catalysis and electrochemistry.

Even though extensive studies have explored the adsorptive properties of water on solid surfaces, the behavior of water on solid surfaces is still being debated.¹ In particular, water on metal oxide surfaces has received considerable attention. It is generally accepted that water dissociates only on defect sites of oxide surfaces.² However, recent theoretical studies have suggested that a mixed (water + hydroxyl) layer can be energetically more stable than pure water layers on certain metal oxide surfaces.^{3–7} Moreover, recent metastable impact electron spectroscopy/ultraviolet photoelectron spectroscopy (MIES/UPS) studies in combination with theoretical calculations have shown that water can partially dissociate on low-defect MgO(100) surfaces.^{8,9}

Previous MIES studies showed that hydroxyl species can form on MgO(100) surfaces via multilayer-induced dissociation. This conclusion was supported by theoretical studies using the CECILIA (combined embedded cluster at the interface with liquid approach) method which indicated that hydroxyl groups at the water–MgO interface are thermodynamically more favorable than mo-

lecular water.¹⁰ Because the dissociation of water on oxide surfaces can take place through various reaction paths, more experimental studies are needed to develop a more general understanding of water adsorption on oxide surfaces.

In this paper, MIES/UPS results are presented for water adsorption on SiO₂/Mo(112) at 90 K. Even though hydroxyl groups can be detected with increasing water coverage on SiO₂/Mo(112) using UPS, UPS spectra are insufficient for the determination of the detailed mechanism for water dissociation. However, UPS spectra in combination with MIES clearly show that water dissociates to form hydroxyl groups on the surface in the presence of multilayer water. It is likely that the hydroxyl groups on oxide surfaces are stabilized by the surrounding water molecules through hydrogen bonding. This result also demonstrates the unique applicability of a combined UPS–MIES study for the investigation of multilayer-induced reactions on solid surfaces.

2. Experimental Section

The experiments were carried out in an ultrahigh vacuum (UHV) system equipped with an ion gun for sputtering, low-energy electron diffraction (LEED), temperature-programmed desorption (TPD), Auger electron spectroscopy (AES), and MIES/UPS. MIES/UPS spectra were measured simultaneously using a cold-cathode discharge producing both ultraviolet photons and metastable He 2³S (*E** = 19.8 eV) atoms with thermal kinetic energy. Metastable and photon contributions to the signal were separated by a time-of-flight method using a mechanical chopper.^{11,12} MIES and UPS spectra were acquired with photon/metastable beams incident at 45° with respect to the surface normal using a double-pass cylindrical mirror analyzer (CMA). SiO₂ thin films were prepared on a clean Mo(112) surface. A well-ordered SiO₂ thin film could be identified using AES and LEED.^{13,14}

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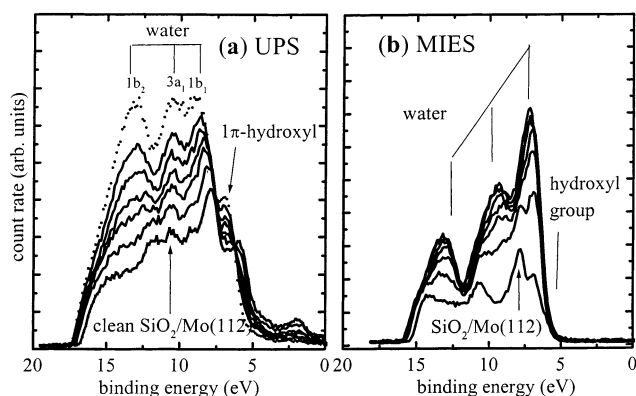


Figure 1. (a) UPS spectra collected from a $\text{SiO}_2/\text{Mo}(112)$ surface as a function of water exposure at 90 K. (b) MIES spectra collected from a $\text{SiO}_2/\text{Mo}(112)$ surface as a function of water exposure at 90 K. The UPS and MIES spectra were acquired simultaneously.

3. Results and Discussion

Figure 1a shows UPS spectra collected as a function of water exposure to a $\text{SiO}_2/\text{Mo}(112)$ surface. For the clean SiO_2 thin film, the $\text{O}(2p)$ peaks of SiO_2 are clearly visible at 5.7 and 7.9 eV. With increasing water exposure, four additional peaks appear concomitantly, whereas the substrate signals attenuate. Three new peaks between 8 and 13 eV can be assigned to the molecular orbitals of water. On the basis of previous MIES/UPS investigations for water adsorption on various solid surfaces² including MgO ,^{8–10} Na/MgO ,¹⁵ and TiO_2 ,¹⁶ the peak at 6.7 eV can be assigned to the $1-\pi$ orbital of hydroxyl groups. In addition, previous theoretical studies of water– MgO systems support this assignment.⁹ The UPS spectra in Figure 1a indicate the partial dissociation of water on the SiO_2 thin film.

On the basis of the UPS data shown in Figure 1a, the following models for water adsorption on $\text{SiO}_2/\text{Mo}(112)$ are suggested: (A) a mixed (hydroxyl + water) monolayer is formed on $\text{SiO}_2/\text{Mo}(112)$ (see Figure 2, model A); and (B) water first molecularly adsorbs, and when the second or higher water layers are formed, the multilayer-induced dissociation of water takes place to form the hydroxyl species (see Figure 2, model B). Previous studies have shown that water can dissociate via these two different mechanisms on $\text{MgO}(100)$. Model A is valid for smooth, low-defect $\text{MgO}(100)$ surfaces,^{8,9} whereas water multilayer induced dissociation (model B) was found for relatively rough, defective $\text{MgO}(100)$ surfaces.¹⁰ On the basis of the UPS spectra in Figure 1a, the mechanism responsible for the dissociation of water on the $\text{SiO}_2/\text{Mo}(112)$ surface cannot be determined because UPS provides information with respect to the electronic structure of the surface and near subsurface simultaneously.

In contrast to UPS, MIES is exclusively sensitive to the topmost surface layer because metastable He atoms with thermal kinetic energies cannot penetrate into the subsurface regime.¹⁷ Many studies have reported a much higher surface sensitivity of MIES in comparison to UPS.¹⁷ The superior surface sensitivity of MIES has even been used to determine molecular orientation at sample surfaces by showing preferential sampling of orbitals with a spatial distribution away from the repulsive van der

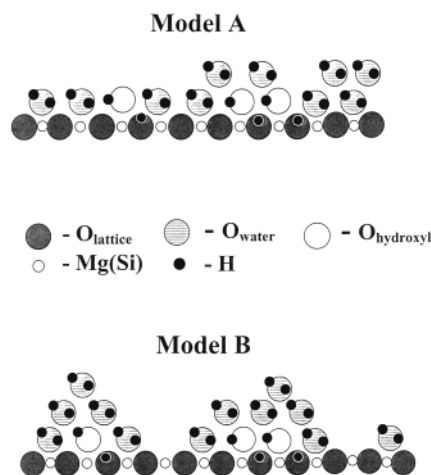


Figure 2. Two different possibilities for the partial dissociation of water on the surface: (A) formation of a (hydroxyl + water) mixed monolayer and (B) multilayer-induced dissociation. It is important to emphasize that metastable He atoms selectively interact with the outermost surface layers. Therefore, in MIES, features for water and hydroxyl groups should appear concomitantly for model A, whereas only water can be detected for model B. Since UPS is sensitive to the surface as well as the subsurface regime, hydroxyl groups can be detected for both models using UPS.

Waals surface.^{18,19} In contrast, UPS spectra show only minor changes for different molecular orientations.¹⁹ In addition, Xe monolayers on the surface completely quench the substrate signals in MIES, confirming that MIES is exclusively sensitive to the topmost surface layer.²⁰

When the hydroxyl species are trapped between water multilayers and the SiO_2 surface (Figure 2B), they cannot be detected using MIES due to its high surface sensitivity. Hydroxyl group features should appear in MIES for the mixed (hydroxyl + water) monolayer (Figure 2A). A mixed (hydroxyl + water) monolayer of this type has been detected using MIES/UPS for water adsorbed on a low-defect $\text{MgO}(100)$ surface.^{8,9}

MIES spectra collected as a function of water exposure are shown in Figure 1b. In contrast to the UPS results of Figure 1a, no hydroxyl species can be detected, and only three features from molecular water are apparent. The fact that molecular and dissociated water are detected in UPS but only molecular water is detected using MIES indicates that multilayer-induced dissociation of water takes place on $\text{SiO}_2/\text{Mo}(112)$ at 90 K.

The TPD spectra of Figure 3 show a single peak at 160 K that exhibits zeroth-order kinetics. This indicates that water adsorbs on $\text{SiO}_2/\text{Mo}(112)$ not in a layer-by-layer manner but rather three-dimensionally, consistent with a very weak water (and hydroxyl group)– SiO_2 interaction. There is no evidence for the presence of two different species (molecular and dissociated water); however, recent density functional theory calculations have predicted partial dissociation of D_2O on $\text{Ru}(1000)$,¹ even though evidence of two species was not found using TPD.²¹ Also, molecular water and the recombination of hydroxyl groups cannot be clearly resolved in TPD when a mixed (hydroxyl + water) monolayer forms on $\text{MgO}(100)$.⁸ Most probably, hydroxyl groups are stabilized by hydrogen bonding to

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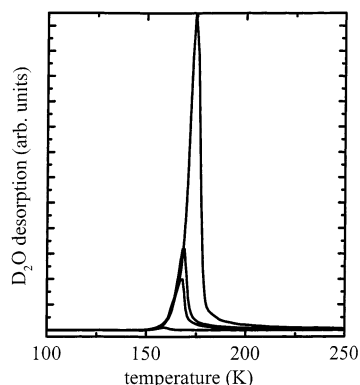


Figure 3. TPD spectra from a $\text{SiO}_2/\text{Mo}(112)$ surface as a function of water exposure. The water was dosed at 90 K.

the surrounding water molecules, and as soon as these surrounding water molecules desorb, the hydroxyl groups recombine to form water molecules that desorb from the surface. Lone hydroxyl groups are not stable on low-defect oxide surfaces under UHV conditions. However, hydroxyl groups on flat $\text{MgO}(100)$ and SiO_2 surfaces can be stabilized via hydrogen bonding to surrounding water molecules.

4. Conclusions

Hydroxyl species formed by multilayer-induced dissociation have been detected using UPS in combination with MIES. Most probably, the hydroxyl species at the interface can be stabilized by hydrogen bonding to the surrounding solvent. It is likely that the stabilization of hydroxyl groups by neighboring water molecules via hydrogen bonding is an important step for the hydroxylation of flat and well-ordered oxide surfaces under realistic conditions. On the sole basis of UPS data, no conclusions can be reached regarding the water dissociation mechanism on SiO_2 . However, when UPS and MIES are combined, an understanding of the water dissociation mechanism is possible. These results show that simultaneous UPS and MIES measurements offer a powerful methodology for the investigation of liquid–solid reactions.

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