Water Dissociation Associated with NO$_2$ Coadsorption on Mo(110)-(1 × 6)-O: Effect of Coverage and Electronic Properties of Oxygen

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Water dissociation on an oxygen-covered Mo(110) surface was investigated using temperature-programmed reaction spectroscopy (TPRS) and infrared reflectance absorbance spectroscopy (IRAS). Adsorbed hydroxyl formation is enhanced by increasing the coverage of chemisorbed oxygen prior to exposure to water up to saturation (0.66 ML). Additional oxidation of the surface using NO$_2$ suppresses the formation of hydroxyl species (OH). There is no detectable change in the reaction of NO$_2$ on Mo(110)-(1 × 6)-O when either the water or hydroxyl is adsorbed on the Mo(110)-(1 × 6)-O surface prior to NO$_2$ adsorption. In contrast, NO$_2$ induces the displacement of water into the gas phase and the conversion of hydroxyl species to molecular water. Infrared spectra show that the dissociation of NO$_2$ populates three types of terminal oxygen sites on Mo(110)-(1 × 6)-O, and the population of the terminal oxygen at step sites increases with respect to the amount of NO$_2$ deposited. Overall, these results suggest that the oxidic property of oxygen results in a lack of activity for the water dissociation.

Introduction

The interaction of water with solid surfaces has received considerable attention because it may have an effect on the rates and selectivities of reactions in many technologically important areas, such as catalysis, electrochemistry, geochemistry, and corrosion. To date, numerous studies have been carried out on various metal surfaces, and the current understanding of the water−metal interaction was well-established in two review articles.[1,2] Among the range of issues related to water−metal interactions, water dissociation is especially important since many chemical processes are affected by the presence or absence of water dissociation.[1,2] In addition, water dissociation on oxide surfaces has long been a controversial issue due to its relation to the presence of defects.[1,2]

Water dissociation on many metal surfaces, e.g. Ni, Cu, Pd, Ag, and Pt, is known to be activated by oxygen on the surface;[3−5] however, water dissociation shows a maximum at a specific oxygen coverage and then diminishes at higher oxygen coverage due to either site blocking or the electronic properties of oxygen (e.g. chemisorbed or oxidic).[5,8,9] In contrast to the extensive studies of coadsorption of water and oxygen on transition metals, water dissociation has not been studied on oxygen-covered molybdenum.

Understanding HO$_x$ and NO$_x$ chemistry is vital for modeling atmospheric concentrations of a range of species that may be significant in the environment including ozone, nitrous acid, and hydroxyl radical.[10,11] Though gas-phase HO$_x$ and NO$_x$ reactions account for a large portion of atmospheric chemistry, heterogeneous (gas−solid) reactions must also be taken into account to provide accurate models. For example, models relying solely on gas-phase reactions and rate constants overestimate

the ratio of [HNO$_3$] to [NO$_x$] by as much as 1 order of magnitude.[10] Heterogeneous formation of HNO$_2$ is proposed to be a significant contributor to the high HNO$_2$ concentrations observed in polluted air masses where combustion sources release large amounts of soot and NO$_x$.[12] Recognizing the need to explore the role of interfaces in atmospheric reactions, several groups have performed studies of water, NO$_x$, and nitrous acid on glass, silica, soot, alumina, and NaCl surfaces.[13−18] Still, questions remain regarding the possibility of yet undocumented reactions or products, the effects of surface concentrations and contaminants, and the ways in which HO$_x$ and NO$_x$ reactions change surfaces. One important issue is discerning the effect of hydroxylation of metal and metal oxide surfaces thus making it important to study the effect of adsorbed OH on NO$_x$ reactions. Though the conditions of ultrahigh vacuum studies differ significantly from the atmosphere, the controlled environment has the potential to provide insight into key reactive events that involve surface hydroxyl species.

In this work, we used Mo(110)-(1 × 6)-O as a substrate for water adsorption and for studies of the reactions of NO$_2$ in the presence of adsorbed water and hydroxyl species. On this surface, all oxygen atoms are populated on a mixture of 2-fold and quasi-3-fold sites. Importantly, there are few vacancies in high coordination sites. Using the combination of temperature-programmed reaction spectroscopy (TPRS) and infrared reflectance absorbance spectroscopy (IRAS), we investigated the effect of coverage and electronic properties of oxygen on water dissociation.

Experimental Section

All experiments were performed in an ultrahigh vacuum chamber described in detail elsewhere.[19] The chamber has a base pressure of <3 × 10^{-10} Torr and is equipped with a quadrupole mass spectrometer (UTI model 100C), an Auger electron spectrometer, and low-energy electron diffraction optics

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(LEED). It is interfaced with a Fourier transform infrared spectrometer (Thermo Nicolet 670).

The Mo(110)-(1 × 6)-O surface was prepared by dosing O_2 at 100 K and subsequent annealing to 500 K and was characterized by low-energy electron diffraction (LEED). This procedure saturates high coordination sites on the surface without inducing dissolution of oxygen into the bulk.[20]

NO_2 (Matheson, anhydrous) was used as received without further purification. Purity of the NO_2 dosed through the baked manifold was confirmed by mass spectrometry of condensed multilayers. Distilled water (H_2O) was stored in a glass equilibration flask and subjected to freeze−pump−thaw cycles to remove air. Purity was confirmed with mass spectrometry. The hydroxylated (OH-covered) surface was prepared by dosing ∼2 ML of H_2O on Mo(110)-(1 × 6)-O at 100 K and then heating to 300 K, above the temperature of molecular water desorption. The presence of hydroxyl was confirmed by Fourier transform infrared spectroscopy.

Temperature-programmed reaction experiments were performed with the crystal biased at −100 V to avoid any electron-induced effects from the mass spectrometer filament. Infrared reflectance absorbance spectroscopy experiments were performed with the crystal temperature at ∼100 K with 4 cm^{-1} resolution. A set of 400 scans was collected for each sample and background spectrum. The background spectrum was created by heating the crystal to 1400 K, past the point at which terminal oxygen and N-containing products desorb. Data were recorded with a liquid-nitrogen-cooled MCT-A semiconductor photodiode detector. For consistency we made sure the peak-to-peak intensity of the reflected infrared radiation was the same when aligning the crystal. We also monitored the peak-to-peak intensity while acquiring spectra.

All gases were deposited on the substrate by direct dosing, where stainless steel dosers were positioned ∼2 cm away from the sample. The coverage of water and NO_2 is referenced to θ = 1 ML for the saturation monolayer coverage of a given adsorbate on the oxygen covered Mo(110) surface which was determined by temperature-programmed reaction. In contrast, the coverage of oxygen was determined by Auger electron spectroscopy (AES) using a calibration curve. This curve expressed the relationship between the intensity ratio of oxygen (KLL) to molybdenum (MNN) and the oxygen exposure. It shows a linear increase of the AES intensity ratio followed by saturation with the appearance of a (1 × 6) diffraction pattern. The saturation coverage of oxygen corresponds to 0.66 ML.

Results and Discussion

Water Adsorption on the Mo(110)-(1 × 6)-O Surface. As observed on many other surfaces, the water−metal interaction is strongly affected by the presence of oxygen atoms on the surface.[3−5] For example, depending on the specific metal surface, water dissociation is promoted, deactivated, or unaffected by oxygen.[21,22] Several mechanisms of water dissociation have been addressed in the literature including disproportionation, reversible decomposition, and irreversible decomposition.[1,2] Water on the clean Mo(110) surface is almost completely dissociated by irreversible decomposition leading to mainly H_2 evolution and deposition of oxygen atoms on the surface during temperature-programmed reaction.[23] On the other hand, our temperature-programmed reaction data indicate that water on the oxygen-covered Mo(110) (0.66 ML) surface partially dissociates resulting in H_2O evolution from hydroxyl species at ∼400 K (see below).

There are three major water desorption peaks observed in temperature-programmed reaction following exposure of H_2O
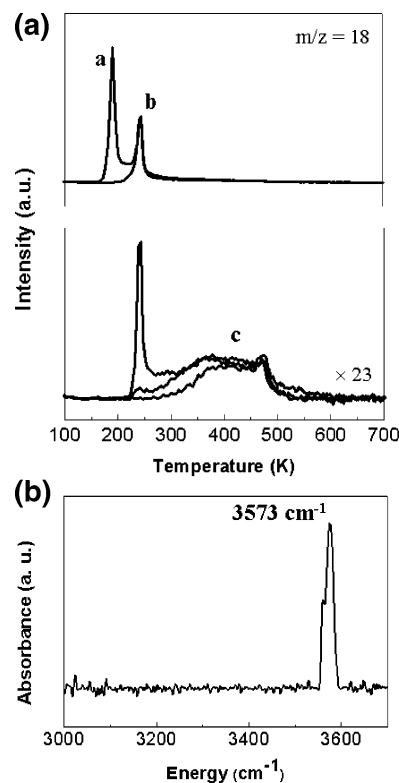

Figure 1. (a) Temperature-programmed reaction data ($m/z = 18$) as a function of water coverage (0.10, 0.20, 0.25, 1.0, and 2.5 ML from bottom to top, respectively) on the Mo(110)-(1 × 6)-O surface. Peaks a−c are assigned to H_2O sublimation from condensed multilayers, water in the first layer, and disproportionation of hydroxyl species, respectively. (b) Infrared reflectance absorbance spectroscopy (IRAS) data of the region including the OH stretch taken after deposition of a small amount of water (0.2 ML) at 100 K, showing the presence of hydroxyl species.

to Mo(110)-(1 × 6)-O at 190, 250, and ∼400 K, labeled a−c, respectively (Figure 1). In analogy to other work,[1−3] these water peaks are assigned to sublimation of H_2O multilayers (a), H_2O adsorbed in the first layer (b), and H_2O formed via disproportionation and/or recombination of OH groups (c). Temperature-programmed reaction data also show successive population of water desorption states from c to a with respect to water coverage, which is consistent with these assignments. It is important to note that peak c is very broad, implying that there may be more than one process contributing to this feature. To confirm that water dissociates and produces hydroxyl species even at 100 K on the oxygen-covered Mo surface, IRAS data was acquired for a low coverage (0.2 ML) of water. The infrared spectrum (Figure 1b) shows a sharp peak for the OH stretch at 3573 cm^{-1}, which arises from hydroxyl species instead of molecular water.

At higher water exposures, the typical, broad feature associated with the OH stretch for hydrogen-bonded water in the range 3000−3500 cm^{-1} dominates the spectrum (Figure 2). At temperatures below 170 K the broad infrared spectrum for water is evident with the peak centered at 3310 cm^{-1}. Surprisingly, the sharp peak at 3573 cm^{-1} observed for hydroxyl species at low water exposures is not visible. We attribute the suppression of the ν(OH) of adsorbed hydroxyl to hydrogen bonding to water condensed on the surface in analogy to work performed on silica glass and to previous studies of CH_3SH on oxidized Mo-(110).[24,25] Heating to 225 K, a temperature above that for sublimation of the multilayer, induced a change in the peak shape, showing two clear shoulders at 3100 and 3240 cm^{-1}
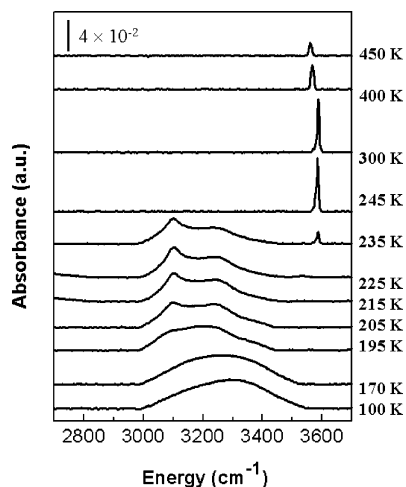
Figure 2. Infrared reflectance absorbance spectroscopy (IRAS) data of the O−H stretch region obtained after exposing the Mo(110)-(1 × 6)-O surface to a sufficient amount of water to form multilayers and heating to various temperatures. After being heated to each temperature, the sample was then cooled to 100 K before recording infrared spectra.

(Figure 2). This transformation has been attributed to a phase transition from amorphous to crystalline structure by others.[26] A sharp OH stretch at 3584 cm^{-1}, characteristic of isolated, adsorbed hydroxyl appears in the infrared spectrum after heating to 235 K, a temperature at which all multilayer water desorbs. After heating to above 250 K, only the OH stretch from hydroxyl species was observed with its peak intensity being maintained up to room temperature. Intensity loss followed by a decrease in the vibrational frequency occurred with water desorption from hydroxyl species above room temperature. These infrared data are corroborating evidence for the partial dissociation of water on oxygen-covered Mo(110).

NO$_2$ Coadsorption on the Water-Precovered Mo(110)-(1 × 6)-O Surface. To investigate thermal behavior of water associated with NO$_2$ coadsorption, a multilayer coverage of NO$_2$ was deposited on Mo(110)-(1 × 6)-O covered with condensed multilayers of water at 100 K. NO$_2$, NO, N$_2$, H$_2$O, and H$_2$ are all detected in temperature-programmed reaction spectra. There are no features that would be characteristic of HNO$_3$ and HONO, which are plausible reaction products between water and NO$_2$.[27,28] The only change observed was in the yield of H$_2$O desorption after NO$_2$ coadsorption (Figure 3). First of all, multilayer H$_2$O sublimation is no longer observed, and the broad peak above 300 K arising from recombination of hydroxyl species is significantly diminished. Furthermore, the integrated intensity of the H$_2$O desorption peak is decreased by ~30%. This was a reproducible result and not due to variation in the conditions of the experiment. Since there are no reaction products such as HNO$_3$ and HONO, we conclude that there is some displacement of condensed water during NO$_2$ deposition. However, this explanation alone is not sufficient to explain the significant decrease of the desorption feature due to hydroxyl species. We performed studies of the effect of NO$_2$ on the reactions of adsorbed OH to address this issue, as described in following section.

Infrared spectra of the region containing the OH stretch following condensation of multilayers of water were also altered by the presence of NO$_2$ (Figures 2 and 4). Specifically, there is no change in the peak shape associated with the phase transition between amorphous and crystalline water structure (Figure 4). Also, the ν(OH) of H-bonded water disappeared, while a small ν(OH) peak due to hydroxyl species is observed at 215 K, a lower temperature than for pure water. Furthermore, the intensity
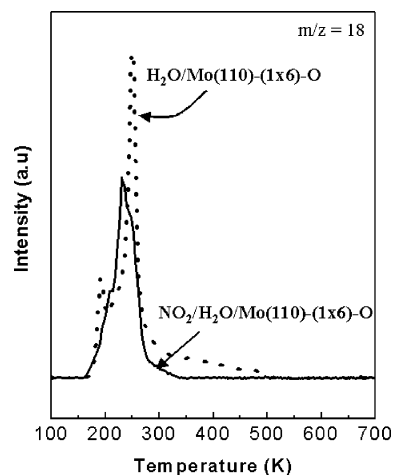

Figure 3. Temperature-programmed reaction data comparing water evolution ($m/z = 18$) after adsorption of: pure water (1.5 ML) on the Mo(110)-(1 × 6)-O surface (dashed line) and after adsorption of NO$_2$ multilayers on Mo(110)-(1 × 6)-O covered with water multilayers (1.5 ML) (solid line). There is a reproducible loss (~30%) in the total amount of water after NO$_2$ coadsorption.
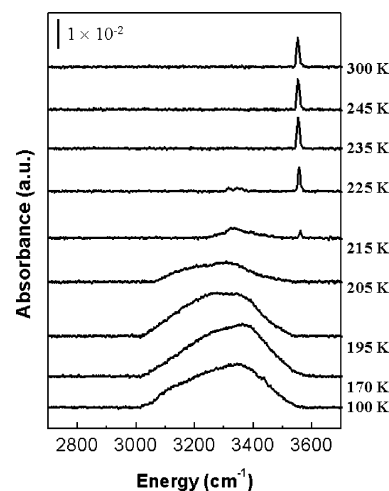

Figure 4. Infrared reflectance absorbance spectroscopy (IRAS) data of the ν(O−H) region obtained following exposure of NO$_2$ to Mo-(110)-(1 × 6)-O containing ~2 ML of condensed water and subsequently heating to various temperatures. The multilayer of NO$_2$ and water were formed at 100 K. After being heated to each temperature, the sample was then cooled to 100 K before recording infrared spectra.

of the ν(OH) peak of hydroxyl species is only 13% of that of water, indicating loss of hydroxyl species due to NO$_2$ coadsorption, which is consistent with temperature-programmed reaction data.

NO$_2$ Coadsorption on the Hydroxylated Mo(110)-(1 × 6)-O Surface. To probe the interaction between hydroxyl species and coadsorbed NO$_2$, multilayers of NO$_2$ were deposited on hydroxylated Mo(110)-(1 × 6)-O, which was prepared by condensing water and heating to room temperature. On the basis of our infrared and temperature-programmed reaction results (Figures 1 and 2), heating water condensed on Mo(110)-(1 × 6)-O to 300 K yields a surface covered with hydroxyl species. The kinetics for H$_2$O and H$_2$ evolution, which will be discussed in more detail later, are substantially altered when NO$_2$ is adsorbed on the OH-covered surface in comparison to the analogous data for a surface containing only OH (Figure 5). In particular, H$_2$O is evolved in two sharp peaks at 180 and 250 K when *both* OH and NO$_2$ are present, whereas H$_2$O is mainly evolved in a broad feature between 300 and 500 K when OH alone is on the surface. Furthermore, considering only the H$_2$O
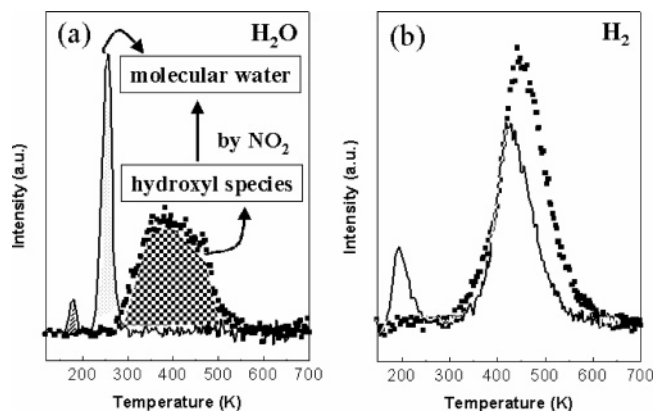
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Figure 5. Temperature-programmed reaction data of (a) H_2O ($m/z =$ 18) and (b) H_2 ($m/z = 2$). Scattered and solid lines indicate desorption spectra from the hydroxylated Mo(110)-(1 × 6)-O surface and the NO_2 (multilayer) adsorbed hydroxylated Mo(110)-(1 × 6)-O surface, respectively. The broad desorption feature between 300 and 500 K due to hydroxyl species is replaced by molecular water desorption at 250 K when NO_2 is coadsorbed. Hydroxyl species were prepared by water deposition (multilayer) at 100 K followed by heating 300 K, above the temperature for molecular water desorption.

desorption peak at 250 K (not the peak at 180 K, which is an artifact as described below), the integrated intensity is decreased by ~55%, after NO_2 is adsorbed. Notably, the temperature for H_2O evolution of 250 K is close to that of molecularly adsorbed water (Figure 1). Similar changes were also observed for H_2 (Figure 5b). The intensity of the H_2 desorption peak decreased by ~50%, and a new peak at 200 K is observed when NO_2 and OH are coadsorbed. The H_2 peaks are not due to fragmentation of water since the peak shapes and temperatures are different for water vs H_2.

The small H_2O desorption peak at 180 K is tentatively assigned to water desorption from the chamber walls induced by NO_2 desorption from the sample during the acquisition of temperature-programmed reaction data. This conclusion is based on several experimental observations: (i) This desorption took place at a temperature (~180 K) similar to that for NO_2. (ii) The intensity of this peak increased with respect to the amount of NO_2 deposited. (iii) The desorption of H_2O was observed at the same temperature when only NO_2 was deposited on the Mo-(110)-(1 × 6)-O surface. The peak at 200 K in the desorption of hydrogen is also explained by the same mechanism.

We concluded that there is a dual role for NO_2 coadsorbed with OH: NO_2 could promote recombination of hydroxyl species and/or the NO_2 could displace hydroxyl from the surface during NO_2 adsorption. We determined that some OH is displaced by NO_2 because the amount of H_2O evolved diminishes with an increase in the amount of NO_2 deposited.

Infrared spectroscopy provides supporting evidence that NO_2 induces recombination of hydroxyl species (Figure 6). A $\nu(OH)$ peak due to hydroxyl species was not observed in the temperature range of 100−300 K. Interestingly, no $\nu(OH)$ peaks were detected at 100 K despite the presence of water, which may be due to the fact that the water molecules form H-bonding with NO_2 with an orientation parallel to the surface. In such a scenario, the dynamic dipole moment of the OH stretch perpendicular to the surface would be small, rendering the vibration undetectable by IRAS. A small, broad peak due to water was observed at 3300−3500 cm^{-1} after desorbing NO_2 by heating to 225 K. This peak is not present at 300 K since all water desorbs below this temperature. However, we saw a very small peak (10-fold of that in Figure 2) at 3546 cm^{-1} associated with hydroxyl species when submonolayer NO_2 was deposited
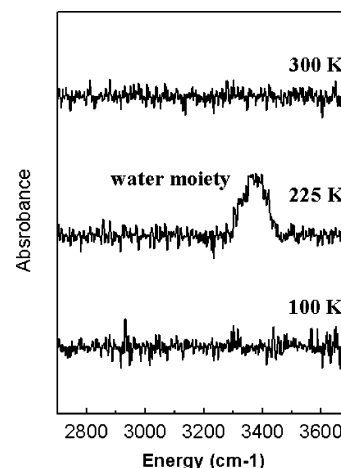

Figure 6. Infrared reflectance absorbance spectroscopy (IRAS) data of the $\nu(O-H)$ region obtained following exposure of NO_2 (multilayer) to hydroxylated Mo(110)-(1 × 6)-O at 100 K and after successively heating to 225 and 300 K. The data show a small water feature at 3300−3500 cm^{-1} after heating to 225 K. This peak is not present at 300 K, which is above the desorption temperature for molecular water.

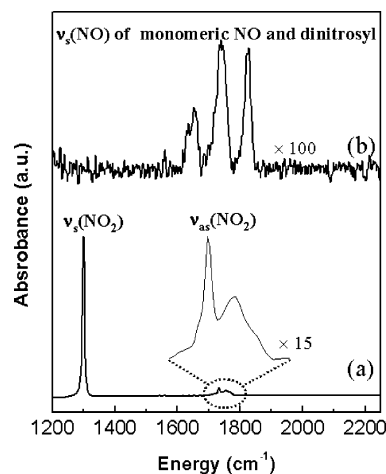**Figure 7.** Infrared spectra in the range 1200−2200 cm^{-1} obtained following condensation of multilayers of NO_2 on hydroxylated Mo-(110)-(1 × 6)-O at (a) 100 K and (b) after heating to 300 K. Hydroxyl species were prepared by depositing water (multilayer) at 100 K followed by heating to 300 K, above the temperature for molecular water desorption. Infrared spectra were acquired at 100 K. No new features due to reaction between NO_2 and OH were detected.

(data not shown), indicating that NO_2 induced water formation and displacement is dependent on the coverage of NO_2 deposited.

The N-containing products of the NO_2 reaction on hydroxylated Mo(110)-(1 × 6)-O are essentially the same as those evolved from the reaction of NO_2 on the Mo(110)-(1 × 6)-O surface.[29] Product distributions for the N-containing products are also similar for NO_2 alone, indicating that there is no apparent reaction between water and NO_2 on the Mo(110)-(1 × 6)-O surface.

Infrared spectra arising from N-containing products are also very similar to those observed for NO_2 alone (Figure 7). The peaks associated with condensed N_2O_4, NO_2, NO monomer, and dinitrosyl species have been assigned previously primarily on the basis of the analogy to infrared spectra of NO_2 in the gas phase, in an inert-gas matrix, and organometallic analogues.[29] Peaks characteristic of condensed N_2O_4 are the $\delta_s(NO_2)$ mode at 784 cm^{-1}, the $\nu_s(NO_2)$ mode at 1296 cm^{-1}, and the split $\nu_{as}(NO_2)$ mode at 1731 and 1754 cm^{-1}. Upon heating of the

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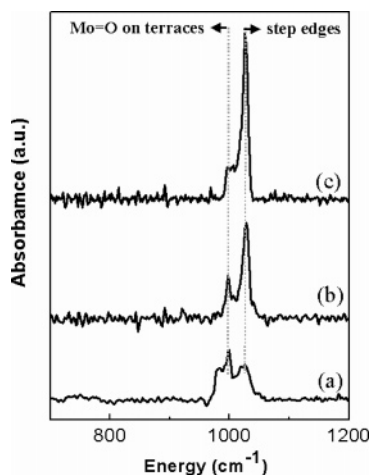*J. Phys. Chem. B, Vol. 109, No. 43, 2005* **20467**

Figure 8. Infrared spectra in the range 700−1200 cm⁻¹ obtained after heating to 750 K for several NO₂ coverages (submonolayer to multilayer for bottom to top) on Mo(110), showing the population of terminal oxygen (Mo=O) at terraces, 997 cm⁻¹, and step edges, 1026 cm⁻¹.[28]

surface to 300 K, NO₂ and N₂O₄ features disappear and new peaks appear at 1654, 1739, and 1827 cm⁻¹ (Figure 7b). These peaks are associated respectively with monomeric NO and dinitrosyl and were also observed in the reaction of NO₂ on the oxygen-covered Mo(110) surface.

The adsorption of NO₂ on the OH-covered Mo(110)-(1 × 6)-O surface drives additional oxidation of the surface, on the basis of Auger electron and infrared data. Specifically, the ratio of the AES intensity (I_O/I_{Mo}) was increased by 15% after temperature-programmed reaction of NO₂ coadsorbed with adsorbed OH. These data are consistent with our studies of NO₂ on Mo(110)-(1 × 6)-O in which we observe deposition of Mo=O species at low temperature from NO₂ reaction.[29] There is likewise deposition of terminal oxygen after heating the coadsorbed NO₂ and OH to 750 K, as is evident from the appearance of peaks characteristic of terminal oxygen ν(Mo=O) at 984, 997, and 1026 cm⁻¹ (Figure 8). The peaks at 997 and 1026 cm⁻¹ were previously assigned as terminal oxygen at terraces and step edges of a thin film oxide on Mo(110), respectively.[30] As the oxygen coverage increases, the intensity of the ν(Mo=O) peak at 1026 cm⁻¹ gradually grows, indicating an increase in the population of oxygen at step sites. Our group's previous STM and IRAS study showed that this vibrational peak is associated with the formation of multiple steps bunched together on the surface.[30]

Oxygen Coverage Dependence of Water Dissociation. On many surfaces, the amount of water dissociation increases as a function of oxygen coverage up to a certain point (e.g. 0.15 ML of oxygen for Ni(110)[31]) and then declines above that coverage. The dependence of water dissociation on oxygen coverage is also important in understanding the effect of NO₂ since oxygen is deposited from NO₂ dissociation at low temperature.[29] To investigate the effect of oxygen coverage on water dissociation on the Mo(110) surface, we obtained temperature-programmed reaction data for H₂O and H₂ after depositing varying amounts of oxygen first and subsequently condensing multilayers of water and preheating to 300 K to remove all molecular water. Oxygen coverages above 0.66 ML, which is the saturation coverage using O₂, were attained by cycles of NO₂ deposition and desorption.

The amounts of both H₂ and H₂O evolved depend on the amount of oxygen present (Figure 9). The peak intensities are normalized to those measured for the saturated oxygen coverage obtained with O₂, 0.66 ML. On clean Mo(110), H₂ is primarily
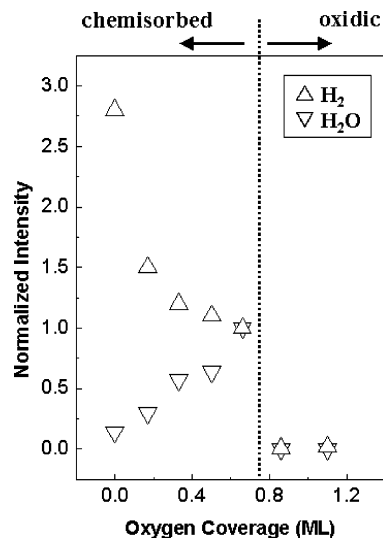

Figure 9. Dependence of water dissociation with respect to oxygen coverage. The amount of water dissociation was determined using the integrated intensities of H₂ and H₂O desorption peaks. The integrated intensities are expressed relative to those measured for the Mo(110)-(1 × 6)-O (0.66 ML) case. Oxygen was deposited using deposition and desorption cycles of O₂ up to 0.66 ML and similar cycles of NO₂ for larger coverages. There are no residual N-containing species on the surface after exposure to NO₂ and heating to 700 K to form the oxygen layer. Upward and downward pointing triangles correspond to the integrated intensities of hydrogen and water, respectively. The amount of water evolved from the surface increases with oxygen coverage up to 0.66 ML and then abruptly drops off.

formed with a little water evolved (∼10% compared to that from oxygen-covered (0.66 ML) Mo(110)). As the oxygen coverage increases the amount of H₂O evolved increases essentially linearly with oxygen coverage up to saturation coverage (0.66 ML) of oxygen in high coordination sites. The amount of H₂ evolved is significantly diminished by increasing oxygen coverage. The intensity of the ν(OH) peak of hydroxyl species in infrared data (not shown) increases over this same coverage range, up to 0.66 ML.

The dissociation pathway arising from the reaction of the water and oxygen by hydrogen abstraction from water (H₂O$_a$ + O$_a$ → 2OH$_a$ (1)) can partly explain the dependence of water dissociation on oxygen coverage. However, this mechanism alone does not explain why H₂ evolution accompanies H₂O desorption on the oxygen-covered Mo(110) surface. Unimolecular dissociation of water (H₂O$_a$ → OH$_a$ + H$_a$ (2)) and complete dissociation (H₂O$_a$ → 2H$_a$ + O$_a$ (3)) will be alternative plausible pathways for hydroxyl formation and atomic hydrogen formation. In the reverse processes, water could be evolved by disproportionation (2OH$_a$ → H₂O$_g$ + O$_a$ (4)) of adsorbed OH which was formed by either dissociation pathway (1) or (2). Hydrogen could also desorb by recombination of hydrogen atoms followed by dissociation pathways of (2) and/or (3).

Oxygen coverage dependent water dissociation on molybdenum surface seems to be similar to many other transition metals such as Ag, Pd, Pt, Cu, and Rh in terms of the fact that the formation of hydroxyl species increases with respect to oxygen precoverage. However, in contrast to oxygen coverage dependence of those metals via reaction pathway 1, that of molybdenum is due to suppression of irreversible dissociation of water (reaction pathway 3) by oxygen atoms, leading to the predominance of reaction pathway 2. This behavior is more close to the case of Re.[22]

Infrared data illustrate that further oxidation of Mo(110)-(1 × 6)-O by NO₂ results in terminal oxygen (Mo=O) at terraces

as well as step edges which was previously observed in an oxide Mo thin film which was synthesized by oxidation at 1200 K.[29,30] The population of Mo═O sites on the Mo(110) surface with higher oxygen coverage suppresses water dissociation such that there is no detectable evolution of either H_2 or H_2O during temperature-programmed reaction after water adsorption and heating to 300 K (Figure 9). Similar suppression of water dissociation was also observed in the Mo oxide thin film. These results are consistent with a lack of activity of oxidic oxygen for water dissociation.[5,8] Overall, these results indicate that water dissociation to yield OH is not favored on fully oxidized surfaces.

In summary, the reactions of NO_2 with OH or H_2O to form HONO and/or HNO_3 have been observed on many surfaces. For example, the reaction of NO_2 on fresh soot in the presence of ambient water leads to some reduction of NO_2 to NO and N_2 and also some HNO_3 formation.[12] On silica, adsorbed water and NO_2 react to form HONO and HNO_3.[32] Even under ultrahigh vacuum conditions, HONO and HNO_3 are produced from NO_2 reaction on Au(111) covered with water.[27,28,33] However, we clearly did *not* observe reactions of the NO_2 with OH or H_2O on the oxygen-covered Mo(110) surface. Instead, we observed NO_2-induced displacement of water or hydroxyl species and NO_2-promoted recombination of hydroxyl species to form molecular water. The underlying reason for the difference on Mo(110)-(1 × 6)-O compared to the other surfaces studied may be the strong interaction of NO_2 with the Mo(110) surface and the associated great facility for oxidizing the Mo-(110) surface.[34] The driving force for metal oxidation by NO_2 is so great that the OH reaction to form water and water displacement is driven, perhaps due to the formation of "hot" water, i.e., water not equilibrated with the surface. This suggests the more general principle that oxophilic metal substrates are not likely to be significant contributors to the heterogeneous formation of environmentally important species such as HONO.

Conclusion

Hydroxyl formation via water dissociation on the Mo(110) surface is activated by oxygen bound in high coordination sites up to an oxygen coverage of 0.66 ML. Further oxidation of the surface by NO_2 inhibits water dissociation, and indeed, the dissociation of NO_2 which yields Mo═O species drives the formation of water from adsorbed OH and desorption of condensed water from the surface. This oxidic property of oxygen may prevent water dissociation on the Mo(110) surface. NO_2 coadsorption on the water- or hydroxyl-precovered Mo-(110)-(1 × 6)-O surface did not show any change in N-containing reaction products compared to NO_2 adsorption alone.

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