Enhancing Dissociative Adsorption of Water on Cu(111) via Chemisorbed Oxygen

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ABSTRACT: We have used X-ray photoelectron spectroscopy to study the dehydrogenation of H2O molecules on the clean and oxygenated Cu(111) surfaces. The clean surface does not show reactivity toward H2O dehydrogenation. By contrast, H2O molecules on the oxygenated Cu(111) dissociate into OH species by reacting with chemisorbed oxygen until the complete consumption of the chemisorbed oxygen at which the surface loses its reactivity toward H2O dehydrogenation. Increasing the temperature to 200 °C and above decreases molecularly adsorbed H2O for dehydrogenation, thereby resulting in less loss of chemisorbed O. In conjunction with density-functional theory calculations, a three-step reaction pathway is proposed to account for the chemisorbed O assisted dehydrogenation of H2O molecules and the net loss of surface oxygen. These results provide insight into understanding the elemental steps of the dehydrogenation of H2O molecules and the controllable conditions for tuning H2O dissociation on metal surfaces.

1. INTRODUCTION

The catalytic properties of metal catalysts can be altered by the introduction of a small amount of impurities that can speed up or slow down certain reaction steps. Surface oxygen has been shown to play such a role in influencing the dehydrogenation reactions catalyzed by transitional metals. However, discrepancies remain regarding the effect of surface oxygen either as a promoter or poison. For example, it is generally believed that the formation of strong chemisorbed atomic oxygen poisons the active surface sites and thus inhibits dehydrogenation reactions. However, it has been also shown that surface oxygen can strongly activate the oxygen-, carbon-, sulfur-, and nitrogen–hydrogen bonds and thus promote the dehydrogenation reactions.

Many studies have been conducted to identify the role that preadsorbed oxygen atoms play on H2O adsorption and dissociation on various transitional metal surfaces. DFT calculations showed that preadsorbed oxygen atoms strengthen the adsorption of H2O and lower the energy barrier of H2O dissociation compared to the clean surfaces of Al(111), Au(100), Fe(100), and Cu surfaces. These modeling results indicate that the adsorption energy of preadsorbed oxygen atoms as well as the distance between the preadsorbed oxygen atom and H2O molecule plays significant roles in the promotion effect. The preadsorbed oxygen may form a hydrogen bond with an H atom of the H2O molecule. When the distance between the preadsorbed oxygen atom and H2O molecule is shorter, the stronger the promotion effect is. The more strongly the oxygen atom binds to the metal surface, the less promotion effect it has on H2O dissociation.

The dehydrogenation reactions at metal surfaces are relevant to a wide variety of catalytic processes. Good examples include the water–gas-shift reaction (WGS) (H2O + CO = H2 + CO2) and steam reforming (SR) (CH4 + H2O = CO + 3H2) for massive H2 production based on Cu catalysts, both of which are cornerstones of today’s large-scale chemical industry and form the basis for ammonia and methanol synthesis. In low-temperature WGS catalyzed by Cu, for example, the dissociative adsorption of H2O has been identified as a rate-limiting step. This has therefore motivated much interest for understanding the fundamental interactions involved in the H2O–Cu system. Recent developments in this area involve X-ray photoelectron spectroscopy (XPS) investigations under near-ambient conditions of water vapor pressure, which showed that H2O dissociates on Cu(110) via an autocatalytic process enabled by the formation of stable H2O–OH complexes, by contrast, H2O does not dissociate on the Cu(111) surface under the identical condition (e.g., 1 Torr of H2O vapor pressure). The difference in H2O dissociation for the two Cu surfaces is attributed to the different activation barriers for OH...
formation, i.e., a lower H₂O dissociation barrier on Cu(110) than Cu(111). The dissociation barriers have been determined experimentally by near ambient pressure kinetic measurements in a micro reactor to be 0.87 eV\(^{-1}\) and 1.17 eV\(^{-1}\) for Cu(110) and Cu(111), respectively.

Similar ambient-pressure XPS experiments have shown the presence of absorbed oxygen can make the Cu(111) surface hydrophilic.\(^2\) This happens because the absorbed oxygen induces H₂O dissociation into OH groups that stabilize water molecules on the surface via forming strongly bound H₂O–OH complexes. These results have demonstrated that the presence of OH species can facilitate the dehydrogenation reaction by anchoring H₂O molecules on the surface but also raise some questions: How do H₂O molecules interact with the chemisorbed oxygen to form OH species? How stable are adsorbed OH species? What is the chemical state of the metal atoms at the surface? With the aim of developing basic insights into these questions and understanding the fundamental interactions involved in the H₂O–Cu system, we conduct a comparative study of the interaction of H₂O with clean and oxygenated Cu(111) at temperatures varying from 100 to 450 °C. Using XPS, the temporal evolution of adsorbed surface species of O and OH during H₂O exposure at the different temperatures is determined. Detailed analysis of the spectral features and binding energies reveal that the H₂O dehydrogenation reaction requires consumption of adsorbed oxygen, which results in the gradual loss of the surface activity toward H₂O dissociation.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

The experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure of \(\sim 1 \times 10^{-8}\) Torr. The system is equipped with an XPS SPECS Phoibos 100, MCD-5 electron analyzer and an Ar-ion sputtering gun. A non-monochromatized Mg Kα X-ray source (\(h\nu = 1253.6\) eV) with the electron energy analyzer operated at 10 kV anode voltage and 30 mA emission current was used for the XPS studies. The Cu(111) single crystal (Princeton Scientific Corp., purity: 99.9999%) is a top-hat shaped disc (1 mm in thickness and 8 mm in diameter), cut to within 0.1° of the (111) crystallographic orientation and polished to a mirror finish. The sample was heated via a ceramic button heater, and its temperature was monitored with a type-K thermocouple. The Cu(111) surface was cleaned by repeated cycles of Ar\(^+\) bombardment (2 \(\times 10^{-5}\) Torr of Ar gas, 2.8 μA cm\(^{-2}\), 1.5 keV) at room temperature followed by annealing at 600 °C for 10 min until no O and C spectra could be detected by XPS. The XPS detection angle \(\theta\) between the axis of the photoelectron analyzer and the normal to the sample surface was set at 0° in our geometry.

Oxygen gas (purity = 99.9999%) was directly introduced to the system through a variable-pressure leak valve to form a chemisorbed oxygen layer on the Cu(111) surface before water vapor dosing. To perform water vapor exposure, water (18.2 MΩ) was put into a flask and purified with several freeze–pump–thaw cycles before dosing through a variable-pressure leak valve separate from the one for O₂ dosing. An ion gauge was used to measure the gas pressure in the chamber. The effect of the ion gauge sensitivity correction was not accounted during the pressure measurements due to the minor difference in the gas correction factors for O₂ and H₂O (O₂ = 1.01 and H₂O = 1.12 relative to N₂ = 1.00). XPS measurements showed that the freshly cleaned Cu(111) and the surface after O₂ and H₂O exposure remain free of carbon contamination (see the Supporting Information).

First, the freshly cleaned Cu(111) surface was exposed to \(p(H₂O) = 1 \times 10^{-5}\) Torr at \(T = 100, 300,\) and 450 °C, respectively. Cu 2p and O 1s XPS spectra were obtained to monitor the surface species and chemical states right after the H₂O exposure. Then the freshly cleaned Cu(111) surface was first exposed to \(p(O₂) = 1 \times 10^{-5}\) Torr at 400 °C for 60 min to form a chemisorbed layer of oxygen. Oxygen dosing under this condition results in ordered “29” (\(\sqrt[3]{13R46.1°} \times 7R21.8°\)), and “44” (\(\sqrt[3]{73R5.8°} \times \sqrt[3]{21R10.9°}\)) reconstructions, as shown previously\(^2\) and also confirmed by our own scanning tunneling microscopy (STM) imaging. These structures comprise hexagonal arrays of chemisorbed O atoms arranged in parallel lines in the first layer, with the unit cell areas 29 and 44 times larger than that of the substrate Cu(111). After being confirmed by XPS, the oxygenated Cu(111) surface was exposed to water vapor at \(T = 100, 200, 300,\) and 450 °C, respectively. To obtain a clear trend of the reaction behavior, three water vapor pressures were examined for each temperature: \(p(H₂O) = 1 \times 10^{-7}, 1 \times 10^{-8},\) and \(1 \times 10^{-9}\) Torr. Cu 2p and O 1s XPS spectra and Cu LMM X-ray excited Auger electron spectra (XAES) were obtained to monitor the surface.

Figure 1. Photoemission spectra of the Cu 2p (a) and O 1s (b) region for a freshly cleaned Cu(111) surface and its exposure to \(p(H₂O) = 1 \times 10^{-5}\) Torr for 60 min at \(T = 100, 300,\) and 450 °C, respectively.
species and chemical state right after each O$_2$ and H$_2$O exposure. To minimize the chance of the measurement errors (including temperature effect on the intensity attenuation) and obtain sufficiently reliable XPS data for quantification, all of the XPS and XAES were acquired at room temperature and under UHV condition. Meanwhile, all of the XPS data acquisition parameters were kept constant including the geometry of the X-ray gun, sample, and analyzer. Also, the surface coverage was obtained by measuring the relative O 1s and Cu 2p regions and calibrating against the saturated oxygen coverage ($\sim$0.50 monolayer, ML) of the “29” or “44” structure. The DFT calculations were performed using the Vienna ab initio simulation package (VASP) with the PW91 generalized gradient approximation (GGA) and projector augmented wave (PAW) potentials. We have performed both spin and nonspin polarized calculation tests to ensure that the spin did not have an effect in describing the transition state and found that there was no significant difference in the results. The Brillouin-zone integration was performed using (4 x 4 x 1) K-point meshes based on Monkhorst–Pack grids and with broadening of the Fermi surface according to Methfessel–Paxton smearing technique with a smearing parameter of 0.2 eV. We calculated the lattice constant of Cu to be 3.64 Å, consistent with previous work. The Cu(111) surface was simulated by a four-layer 4 x 4 slab model. The bottom two layers of the Cu surface were fixed at the lattice position, and all other atoms were allowed to fully relax during optimization until all force components acting on the atoms are below 0.02 eV/Å. Successive slabs are separated by a vacuum region of 12 Å. We applied the climbing image nudged elastic bands (CI-NEB) method to calculate the reaction barriers, where we used five intermediate images between the initial and final states. The atomic structures are visualized using the VESTA package.

3. RESULTS

The dissociation of water molecules on clean and oxygenated Cu(111) surfaces was comparatively studied by XPS. Figure 1a shows typical XPS spectra of the Cu 2p peaks obtained from the freshly cleaned Cu(111) surface and subsequent exposure to p(H$_2$O) = 1 x 10$^{-5}$ Torr for 60 min at T = 100 °C, 300 °C, and 450 °C, respectively. The shape and position of the Cu 2p core level peaks (binding energies (BE) = 952.3 and 932.6 eV) remain all the same for the clean and H$_2$O exposed Cu(111) surfaces, indicating that Cu is not oxidized and remains its metallic state after the H$_2$O exposure at the different temperatures. In addition, the intensity of the Cu 2p peaks for the H$_2$O exposed surfaces remains nearly the same as the clean Cu(111) surface, suggesting that the H$_2$O exposure does not result in any adsorbed species on the Cu(111) surface. The lack of the surface activity toward H$_2$O dissociation is also confirmed by XPS O 1s spectra obtained from the H$_2$O exposed surfaces, as shown in Figure 1b. Same as the clean surface, there is no detectable intensity of the O 1s spectra after the H$_2$O exposure. These XPS measurements confirm that H$_2$O does not dissociate on the clean Cu(111) surface under the conditions of the vapor pressure and temperatures examined here.

We then examined the activity of the oxygenated Cu(111) surface toward H$_2$O dissociation. Figure 2a shows the XPS spectra of the Cu 2p peaks obtained from the Cu(111) surface that is first exposed to p(O$_2$) = 1 x 10$^{-5}$ Torr at T = 400 °C for 60 min to form a saturated chemisorbed oxygen layer, followed by exposure to p(H$_2$O) = 1 x 10$^{-5}$ Torr at T = 100, 200, 300, and 450 °C, respectively, until the surface reaches a steady state at each temperature (note that a freshly formed oxygenated Cu(111) surface is used for each H$_2$O exposure at the different temperatures). The Cu 2p peaks located at BE = 952.3 and 932.6 eV correspond to the metallic Cu and they remain the same after the oxygen exposure at p(O$_2$) = 1 x 10$^{-5}$ Torr and T = 400 °C. The subsequent H$_2$O exposure of the oxygenated Cu(111) surface to p(H$_2$O) = 1 x 10$^{-5}$ Torr at the different temperatures results in no changes in the shape and position of the Cu 2p peaks. Similarly, no noticeable changes are observed in the Cu 2p peaks from the exposure of the oxygenated Cu(111) surface to p(H$_2$O) = 1 x 10$^{-6}$ and 1 x 10$^{-7}$ Torr, respectively.

Cu 2p XPS spectra can differentiate between metallic Cu (Cu$^0$) and Cu$^{2+}$ but cannot distinguish between Cu$^+$ and Cu$^{2+}$ because their binding energies are very close. Peak positions and line shapes of XAES have proved to be sensitive enough for Cu oxidation state analysis for providing more unambiguous
There are differences between Cu$^0$ and Cu$^+$ than Cu 2p XPS core level shifts. Therefore, XAES of the Cu LMM peaks are also acquired to further confirm the valence states of Cu, as shown in Figure 2b. The clean Cu(111) surface shows the Cu LMM line peak at a kinetic energy of 918.6 eV, which is associated with metallic Cu$^0$. The O$_2$ exposure at $p$(O$_2$) = 1 x 10$^{-5}$ Torr and $T$ = 400 °C and the subsequent H$_2$O exposures at the different vapor pressures and temperatures result in no changes in the line position and shape of the Cu LMM spectra. These combined XPS and XAES measurements demonstrate that the Cu(111) surface still maintains its metallic state (Cu$^0$) although the surface is covered with chemisorbed O and OH species as shown below. It should be noted that at higher temperatures there is a small intensity loss of Cu 2p XPS peak and Cu LMM Auger peak in Figure 2 for unknown reasons.

O 1s spectra are also obtained from the Cu(111) surface exposed to O$_2$ and subsequently to H$_2$O. Figure 3 illustrates the evolution of the O 1s core level region, where the freshly cleaned Cu(111) surface is first exposed to $p$(O$_2$) = 1 x 10$^{-5}$ Torr and $T$ = 400 °C to form a chemisorbed oxygen layer prior to the H$_2$O exposure. It can be seen that the O$_2$ exposure results in appreciable intensity in the O 1s core level centered at BE = 530.0 eV. This is completely different from the H$_2$O exposure to the clean Cu(111) surface, where no detectable O 1s spectra are observed. Therefore, Cu in the metallic state as shown in Figure 1, the O 1s intensity is related to the chemisorbed oxygen on the Cu(111) surface.

Figure 3a corresponds to the evolution of the O 1s spectra from the exposure of the oxygenated Cu(111) to $p$(H$_2$O) = 1 x 10$^{-7}$ Torr at 100 °C. The O 1s peak gradually shifts to higher BE and becomes broader and asymmetrical with a shoulder on the high BE side. Using the same fitting parameters for the chemisorbed O does not provide an overall good fitting to the O 1s peak after the H$_2$O exposure, and a second peak at the higher BE arises. The spectra are deconvoluted into two peaks with BE = 530.0 and 530.9 eV, respectively. The peak at 530.0 eV is associated with the chemisorbed O, and the other peak at BE = 530.9 eV is attributed to the O in adsorbed OH species, which is in good agreement with the literature value. H$_2$O exposure under the near ambient pressure of 1 Torr has been shown to result in molecular H$_2$O adsorption that produces a peak in the 532.4–533.0 eV range. In contrast, no stable molecular H$_2$O adsorption occurs on the oxygenated Cu(111) surface exposed to the low H$_2$O pressure shown here. As seen in Figure 3a, the OH peak increases while the chemisorbed O peak decreases in intensity as the H$_2$O exposure continues. The

Figure 3. Photoemission spectra of the O 1s region for the exposure of the oxygenated Cu(111) to $p$(H$_2$O) = 1 x 10$^{-7}$ Torr at (a) 100, (b) 200, (c) 300, and (d) 450 °C, respectively, until reaching the steady state.

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Table 1. Binding Energies (eV) of O (1s) and OH Spectra at the Steady State from the H2O Exposure of the Oxygenated Cu(111)

<table>
<thead>
<tr>
<th>Water vapor pressure (Torr)</th>
<th>100 °C</th>
<th>200 °C</th>
<th>300 °C</th>
<th>450 °C</th>
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<tbody>
<tr>
<td></td>
<td>O 1s</td>
<td>OH</td>
<td>O 1s</td>
<td>OH</td>
</tr>
<tr>
<td>1 × 10⁻⁷</td>
<td>530.9</td>
<td>530.9</td>
<td>530.0</td>
<td>530.9</td>
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<td>530.9</td>
<td>530.9</td>
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<tr>
<td>1 × 10⁻⁵</td>
<td>530.9</td>
<td>530.9</td>
<td>530.0</td>
<td>530.9</td>
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</table>

Figure 4. Evolution of the surface coverage of chemisorbed O (a), OH species (b), and total oxygen-containing components (both chemisorbed O and OH) (c) upon the exposure of the oxygenated Cu(111) surface to p(H2O) = 1 × 10⁻⁷ Torr at the different temperatures.

The temperature effect on the dissociation of water molecules on the oxygenated Cu(111) surface is also examined for H2O exposure at p(H2O) = 1 × 10⁻⁶ and 1 × 10⁻⁵ Torr. Table 1 summarizes the positions of the chemisorbed O and OH peaks at the steady state of the surface for all three water vapor pressures examined at T = 100, 200, 300, and 450 °C. The positions of the chemisorbed O and OH peaks are constant. The chemisorbed O peak disappears completely for H2O exposure at 100 and 200 °C for all three vapor pressures. H2O exposure at 300 °C results in a weak OH peak in addition to the dominant chemisorbed O peak for all three vapor pressures. The H2O exposure at 450 °C results in only the chemisorbed O peak for p(H2O) = 1 × 10⁻⁷ Torr and p(H2O) = 1 × 10⁻⁶ Torr while both the chemisorbed O and OH peaks are observed for p(H2O) = 1 × 10⁻⁵ Torr.

Figure 4 shows the evolution of the intensity ratio for chemisorbed O, OH, and their total (O + OH) to the Cu 2p peak at p(H2O) = 1 × 10⁻⁷ Torr and the different temperatures. The first point (i.e., t = 0 min) in each plot corresponds to the freshly prepared “29” or “44” oxygenated Cu(111) before H2O exposure. As shown in Figure 4a, chemisorbed O gradually decreases with time for H2O exposure at T ≤ 300 °C and chemisorbed O remains unchanged for H2O exposure at T = 450 °C. Figure 4b shows that OH gradually increases with time for H2O exposure at T ≤ 300 °C, and no OH formation at 450 °C. It can be also noted that OH at the steady state decreases as the H2O exposure temperature increases. The total amount of the oxygen containing components (O and OH) gradually decreases over time (Figure 4c), indicating that the loss of chemisorbed O is more than the formation of OH species (there is only chemisorbed O at 450 °C because of the lack of OH formation at this temperature). This suggests that the formation of adsorbed OH species is accompanied by the concomitant removal of chemisorbed O from the surface. It is noticeable that chemisorbed O drops to zero after 300 min of H2O exposure at 200 °C and after 240 min of H2O exposure at 200 °C, beyond which no further OH formation occurs. This indicates
that the prechemisorbed O is required for dissociative adsorption of H$_2$O molecules. For H$_2$O exposure at $T$ = 300 $^\circ$C, chemisorbed O does not drop to zero at the steady state. For H$_2$O exposure at $T$ = 450 $^\circ$C, there is neither OH formation nor O loss, indicating that H$_2$O does not dissociate under this condition.

The temperature effect on H$_2$O dissociation is also examined at $p$(H$_2$O) = 1 $\times$ 10$^{-7}$ and 1 $\times$ 10$^{-6}$ Torr. Chemisorbed O is completely consumed after reaching the steady state for H$_2$O exposure at $T$ = 100 or 200 $^\circ$C. For H$_2$O exposure at 300 $^\circ$C, only a small amount of chemisorbed O is consumed. However, for H$_2$O exposure at 450 $^\circ$C, the steady-state surface species depend on the vapor pressure; there is no OH formation and the amount of chemisorbed O remains unchanged for the H$_2$O exposure at $p$(H$_2$O) = 1 $\times$ 10$^{-7}$ Torr and $p$(H$_2$O) = 1 $\times$ 10$^{-6}$ Torr; the amount of chemisorbed O decreases slightly with the concomitant formation of a small amount of OH species for H$_2$O exposure at $p$(H$_2$O) = 1 $\times$ 10$^{-7}$ Torr. This indicates that H$_2$O dissociation at $T$ = 450 $^\circ$C does not occur for the two lower pressures, and increasing the pressure to $p$(H$_2$O) = 1 $\times$ 10$^{-5}$ Torr results in dissociative H$_2$O adsorption by consuming chemisorbed O, suggesting there is a pressure gap in driving H$_2$O dissociation.

**Figure 5.** Evolution of the surface coverage of chemisorbed O (a), OH species (b), and the total (both O and OH) (c) after reaching the steady state from the exposure of the oxygenated Cu(111) surface to water vapor at 100 $^\circ$C and three different vapor pressures.

**Table 2.** Surface Coverage (ML) of Chemisorbed O ($\theta_O$) and OH ($\theta_{OH}$) at the Steady State from the H$_2$O Exposure of the Oxygenated Cu(111)

<table>
<thead>
<tr>
<th>Water vapor pressure (Torr)</th>
<th>100 $^\circ$C</th>
<th>200 $^\circ$C</th>
<th>300 $^\circ$C</th>
<th>450 $^\circ$C</th>
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<tr>
<td>$\theta_O$</td>
<td>$\theta_{OH}$</td>
<td>$\theta_O$</td>
<td>$\theta_{OH}$</td>
<td>$\theta_O$</td>
</tr>
<tr>
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<td>0.140</td>
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<td>0.308</td>
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</table>

**Figure 6.** Temperature and pressure dependence of the surface coverage of chemisorbed O (a), OH (b), and total (both O and OH) (c) after reaching the steady state from the H$_2$O exposure of the oxygenated Cu(111).

**Figure 5** shows the effect of vapor pressure on the temporal evolution of the intensity ratio of O and OH to the Cu 2p peak for H$_2$O exposure at $T$ = 100 $^\circ$C. The first point (i.e., $t$ = 0 min) corresponds to the freshly prepared “29” or “44” oxygenated Cu(111) before H$_2$O exposure. Chemisorbed O gradually drops to zero at all three pressures and with a faster rate at the higher pressure (Figure 5(a)). OH gradually increases at all three pressures and with a faster rate at the higher pressure, and the amount of OH species at the steady-state decreases as the vapor pressure increases (Figure 5b). Figure 5c shows that the total amount of the oxygen-containing species (O + OH) gradually decreases at all three pressures, and the oxygen-containing species drops faster and more as the vapor pressure increases. The pressure effect on H$_2$O dissociation is also examined at $T$ = 200, 300, and 450 $^\circ$C, respectively. The intensity ratio of chemisorbed O and OH to the Cu 2p peak at the steady state is summarized in Table 2 and is plotted in Figure 6 as a function of temperature and vapor pressure. The XPS measurements show that OH species decrease with the temperature increase for the same vapor pressure, and OH also decreases with vapor pressure increase for the same temperature. Meanwhile, chemisorbed O is only partly consumed at $T$ = 300 and 450 $^\circ$C, indicating that the molecularly adsorbed H$_2$O becomes less as the temperature increases, which
are necessary to remove OH species, i.e., \(2\text{OH(ab)}\) after the dehydrogenation reaction. Therefore, additional steps amount of oxygen-containing species (O and OH) decreases hindered: the driving force \(\Delta H = 0\) (thermoneutral) on clean Cu(111).41–43

4. DISCUSSION

The results described above show that the clean Cu(111) is nonreactive toward \(\text{H}_2\text{O}\) dissociation; that is, the clean surface is hydrophobic. By contrast, the oxygenated Cu(111) is reactive toward \(\text{H}_2\text{O}\) dissociation which results in the loss of chemisorbed O. From a kinetic point of view, the activation barriers \(E_{\text{diss}}\) for \(\text{H}_2\text{O}\) dissociation on the clean and oxygenated Cu(111) surfaces are different, i.e., \(E_{\text{diss}}(\text{clean}) > E_{\text{diss}}(\text{oxygenated})\). The \(\text{H}_2\text{O}\) dissociation barrier for clean Cu(111) was measured to be 1.17 eV from the WGS reaction.21 This barrier was also proved by other studies in the intermediate pressure region of \(p(\text{H}_2\text{O}) = 1\) Torr and temperature varying from −5 to +60 °C.20 Also, the linear Bronsted–Evans–Polanyi (BEP) relationship between enthalpy changes and activation energies for water dissociation can be explored to explain why water dissociation is kinetically hindered: the driving force \(\Delta H = 0\) (thermoneutral) on clean Cu(111).41–43

In contrast, the oxygenated Cu(111) shows reactivity toward \(\text{H}_2\text{O}\) dehydrogenation into OH species by reacting with chemisorbed O. Compared to the freshly prepared oxygenated Cu(111), the overall intensity of the O 1s spectra (including the chemisorbed O and OH components) decreases after reaching the steady state of the \(\text{H}_2\text{O}\) exposure, indicating that more chemisorbed O is consumed than the amount of OH species formed. Mirdula et al. reported the reaction sequence of \(\text{Cu}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{CuOH}, 2\text{CuOH} \rightarrow 2\text{Cu} + \text{H}_2 + \text{O}_2\) for \(\text{H}_2\text{O}\) dissociation on Cu2O.44 The first step of the reaction should result in increased amount of oxygen-containing species (i.e., O and OH) because of the incorporation of additional O from \(\text{H}_2\text{O}\), i.e.

\[
\text{O(ab)} + \text{H}_2\text{O(g)} \rightarrow 2\text{OH(ab)}
\]

The water molecules can dissociate as the reaction described above is because the reaction barrier for \(\text{H}_2\text{O}\) dissociation is lowered by the chemisorbed O to 0.76 eV.46 However, as shown from our XPS measurements (Figures 4–6), the total amount of oxygen-containing species (O and OH) decreases after the dehydrogenation reaction. Therefore, additional steps are necessary to remove OH species, i.e., \(2\text{OH(ab)} \rightarrow \text{H}_2\text{(g)} + \text{O}_2\text{(g)}\). The calculation results reported by Chen et al. showed that the direct dissociation of OH species is difficult at both low and high water coverages, but they also reported that OH species can react with another adjacent OH to form O + \(\text{H}_2\text{O}\).47 If two OH species combine to form O + \(\text{H}_2\text{O}\), our entire reaction will be \(\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH} \rightarrow \text{O} + \text{H}_2\text{O}\). Therefore, \(\theta_{\text{OH}}\) will either keep constant (if all OH species combine to form O + \(\text{H}_2\text{O}\)) or increase (if partial OH species or no OH species combine to form O + \(\text{H}_2\text{O}\)). Then we introduce the intermediate–peroxo-type (OOH), which is induced through the reaction

\[
\text{H}_2\text{O(g)} + 2\text{O(ab)} + \text{OH(ab)} \rightarrow \text{OOH(ab)} + 2\text{OH(ab)}
\]
covered by chemisorbed O. To further investigate the feasibility of OOH species on the surface during the reaction, we employed DFT calculations to study the OOH species. We can ignore the OH term in reaction step 2 as it does not react with any other adsorbates and reform and determine if the interaction between H$_2$O and two chemisorbed O atoms can result in forming OOH. We determined the most stable configurations by varying orientation and adsorption sites for both H$_2$O molecule and two chemisorbed O atoms, as well as for the OH with OOH on the Cu(111) surface. The two most stable configurations are our initial and final images in our NEB calculation for determining the reaction barriers. Our DFT calculations show that the first H$_2$O molecule adsorbs on top of a Cu atom on Cu(111) with an adsorption energy of 0.21 eV, which is in good agreement with a previous study of 0.24 eV. Shown in Figure 7a, is the first H$_2$O, which then interacts with two nearby chemisorbed O atoms to form OH and OOH species, shown in Figure 7b. One H atom from the H$_2$O molecule dissociates and adsorbs with a chemisorbed O atom to form OH. The remaining OH from the H$_2$O molecule then diffuses to the other chemisorbed O atom to form OOH. The energy barrier for this reaction is just 0.17 eV, and the total energy increase by 1.79 eV. The formation of OOH requires a low energy barrier, but the OOH species is not thermodynamically favorable. This suggests that the OOH species is a metastable state that can be formed on an oxygen-covered Cu(111) surface.

5. CONCLUSIONS

The interactions of H$_2$O molecules on the clean and oxygenated Cu(111) surfaces are comparatively studied with the temperature ranging from 100 to 450 °C and vapor pressure from $1 \times 10^{-7}$ to $1 \times 10^{-3}$ Torr. The clean surface does not show reactivity toward H$_2$O dehydrogenation. By contrast, H$_2$O dissociates into OH species on the oxygenated Cu(111) by reacting with chemisorbed O. When the temperature is higher than 200 °C, the amount of molecularly adsorbed H$_2$O available for dehydrogenation decreases, which results in a smaller amount of OH species and less loss of chemisorbed O. The dehydrogenation of molecularly adsorbed H$_2$O is suggested to proceed via a three-step reaction pathway that results in the net loss of chemisorbed oxygen from the surface, (1) H$_2$O(g) + O(ab) → 2OH(ab), (2) H$_2$O(g) + OH(ab) + 2O(ab) → OOH(ab) + 2OH(ab), followed by (3) OOH(ab) + OH(ab) → H$_2$O(g) + O$_2$(g), in which the formation of OOH species is not directly demonstrated in the experiments but is supported by DFT calculations. These results provide insight into understanding the elemental steps of the dehydrogenation of H$_2$O molecules and may find broader applicability for tuning the surface reactivity toward H$_2$O dehydrogenation for catalytic gas-surface reactions in which H$_2$O dissociation is involved.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b12897.

C 1s XPS spectra showing that there is no carbon contamination for the freshly cleaned surface and after the O$_2$ and H$_2$O exposures. (PDF)

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The authors declare no competing financial interest.

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REFERENCES

O. The oxidation of the more negatively charged O and OH to the less negatively charged OOH would normally only occur under electrochemical and photochemical conditions.