Structure Revealing H/D Exchange with Co-Adsorbed Hydrogen and Water on Gold

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Supporting Information

ABSTRACT: A fundamental understanding of the interactions between coadsorbed water and hydrogen on metallic surfaces is critical to many chemical processes including catalysis and electrochemistry. Here, we report on the strong and intricate interactions between coadsorbed H/D and water on the close-packed (111) surface of gold. Deuterium isotopic labeling shows H/D exchange in H–D2O and D–H2O systems, indicating water dissociation and suggesting a nonrandom scrambling process by revealing the origin of hydrogen evolution (from surface H atoms or from water molecules) during annealing. In this reaction, the protonation of the H-bonding ice network (i.e., the formation of (H2O)nH+) is energetically favorable and is responsible for water dissociation. Density functional theory (DFT) modeling suggests that the thermodynamics and structure of the protonated clusters are predominant factors for yielding the traceable H2 desorption features from the surface interaction with H atoms, providing insights into reaction mechanisms.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

Nanoscale gold-based catalysts have been found to be highly active for a variety of chemical transformations, at low temperatures, including selective hydrogenation reactions. However, relevant fundamental, model studies of catalytic hydrogenation chemistry over gold are severely lacking. Model investigations could provide valuable insights into the reaction mechanisms and catalytic properties of gold, and help advance the state of the art. Although there is a large energetic barrier to H2 dissociation on pristine gold surfaces, it is clear that the metal oxide–gold interface can readily dissociate hydrogen, and hydrogen spillover onto the gold surface results in a very weakly bound H atom that is quite reactive, leading to the high hydrogenation activity observed at low temperatures in classical catalysis experiments.

Here, we further demonstrate the remarkable surface chemistry of gold via a study involving adsorbed H/D atoms that activate the dissociation of water on a Au(111) sample. Pt surfaces have also shown hydrogenic isotopic exchange via an interaction between adsorbed hydrogen and water; however, here, the Au(111) surface reveals new details regarding the structure of the hydrogen–water overlayer on the surface. Because water and hydrogen are prevalent in the chemistry and physics of many processes, we believe that our studies will be of utility regarding (1) gold-catalyzed chemical reactions involving H and H2O, such as the water–gas shift reaction, and steam re-forming of hydrocarbons and alcohols; (2) applications of gold electrodes in aqueous solutions; and (3) the formation of hydronium (H3O+) and protonated water clusters [(H2O)nH+] that are associated with proton transfer and transport in water and which have been studied widely in many fields of chemistry and biology. It is well-known that water adsorbs intact on Au(111) and has a small binding energy with the surface. However, in the present work, we observe that coadsorbing H atoms and water molecules on Au(111) reveals newly formed desorption features for both species in temperature-programmed desorption measurements that indicate stronger interactions. Employing an isotopically labeled reaction system, such as D2O + H or H2O + D, we have discovered the production of scrambled H2, HD, and D2. Our results suggest a reaction of water with H adatoms on Au(111) and further identify the origins of H (from surface H atoms or H2O molecules) for each H2 desorption feature in the H + H2O system. Density functional theory (DFT) calculations are employed to understand the mechanisms; clusters of water play a key role in the reaction with H atoms on the surface. Formation of protonated water (H2O)nH+ as an intermediate is energetically favorable, and its thermodynamics and structure account for the nonrandom H/D exchange in H–D2O and D–H2O systems.

Our experiments were performed on a Au(111) single-crystalline surface under ultrahigh vacuum (UHV) conditions (base pressure of 1 × 10–10 Torr). We employed a custom-built H-atom generator to populate the surface with a 0.74 relative coverage of adsorbed H-atoms (θH,rel = 0.74). Subsequent to hydrogen adsorption, a neat molecular beam of...
water vapor was used to deliver 2.68 monolayers (ML) of adsorbed H$_2$O to the H-precovered surface. Using a quadrupole mass spectrometer (QMS), temperature-programmed desorption (TPD) measurements were then conducted to measure the gas-phase species evolving from the surface and to further identify the surface reaction steps with varying temperatures. RAIRS (reflection–absorption infrared spectroscopy) was also used to study surface reaction intermediates. Prior to every experiment, the sample was cleaned by exposure to NO$_2$ at 800 K, and the cleanliness was verified by TPD and Auger electron spectroscopy (AES). A detailed description of the experimental apparatus and procedure is included in the Supporting Information.

Figure 1 displays our first indications of the intricate interactions between adsorbed hydrogen and water on gold. At the outset, it is perhaps instructive to examine the TPD spectra for adsorbed H and H$_2$O independently, as shown in Figure 1a and b in order to better appreciate the interactions revealed for the coadsorbed system. Figure 1a displays TPD spectra for H$_2$O from the clean Au(111) surface at a heating rate of 1 K/s. Water desorption has only a single feature on clean Au(111) at 157 K, as shown in Figure 1a. Recombinative hydrogen desorption from Au(111) also shows a single feature, peaking at 110 K, as displayed in Figure 1b.

Now turning our attention to TPD spectra regarding the H and H$_2$O coadsorbed surface as shown in panel c of Figure 1, the measurements exhibit three H$_2$ desorption features that are denoted as $\alpha$, $\beta$, and $\gamma$ and are centered at 136, 158, and 175 K, respectively. The $\alpha$ peak is assigned to H atoms recombining but with a higher temperature compared to that of characteristic H$_2$ desorption (~110 K) from the clean surface, as illustrated in Figure 1b. The other two desorption peaks ($\beta$, $\gamma$) are newly formed and clearly involve the coadsorbed water. On the basis of the integrated TPD area under each peak, we estimate the proportion of the three features to be 83.5, 2.8, and 14.3%, respectively, for the $\alpha$, $\beta$, and $\gamma$ peaks.

Similarly, water desorption is also strongly affected by adsorbed hydrogen, as shown in Figure 1c with a new feature appearing at a higher temperature, ~175 K, aligned with the $\gamma$ peak in H$_2$ desorption. It should also be noted that the $\beta$ peak from H$_2$ desorption reproducibly appears at a slightly higher temperature (158 K) than the primary water desorption peak at ~157 K, as illustrated in Figure 1a and c.

In order to better understand the interaction between water and hydrogen on Au(111), we employed isotopes in the form of deuterium atoms and/or deuterated water to further probe reaction pathways. Figure 2 shows TPD spectra for two different experiments, (a) H ($\theta_{H,rel} = 0.74$) precovered Au(111) with coadsorption of 2.68 ML of D$_2$O and H ($\theta_{D,rel} = 0.74$) and (b) 2.68 ML of H$_2$O and D ($\theta_{D,rel} = 0.63$). All species were adsorbed on the surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a–c) have the same y-axis scale.

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further indicates that the \( \gamma \) feature in the \( \text{H}_2 \) thermal desorption spectrum in Figure 1a stems exclusively from a hydrogen-exchange reaction between \( \text{H} \) and \( \text{H}_2\text{O} \) rather than the recombination of originally adsorbed \( \text{H} \) atoms. We notice that the desorption of \( \text{HD} \) and \( \text{D}_2 \) in Figure 2a yields similar integrated areas, further indicating that \( \sim 75\% \) of the hydrogen in the \( \gamma \) peak in Figure 1c is from water. This finding suggests that the yield of exchanged \( \text{H} \) atoms on the surface is \( \sim 10.7\% \) (the \( \gamma \) peak is estimated to contribute 14.3\% of \( \text{H}_2 \) desorption in Figure 1c). However, HD and \( \text{D}_2 \) have slightly different ionization sensitivities in QMS measurements (leading to some uncertainty here).

In contrast, \( \text{D}_2\text{O} \) desorption shows two features at 160 and 180 K, similar to the observations for \( \text{H} \) and \( \text{H}_2\text{O} \) coadsorbed on \( \text{Au}(111) \). The new feature for \( \text{D}_2\text{O} \) at 180 K is at a slightly higher temperature than the similar one from \( \text{H}_2\text{O} \) desorption (175 K), and this feature is likely due to an isotope effect in which the \( \text{H} + \text{D}_2\text{O} \) system generates HD and \( \text{D}_2 \) via breaking of the original O–D bond in \( \text{D}_2\text{O} \), as discussed in detail later in the paper. The mass 19 signal during TPD represents HDO, which can also be observed in nominally pure \( \text{D}_2\text{O} \) desorption on \( \text{Au}(111) \) and is identified as an impurity. Stronger mass 19 signals have been observed at 160 K during TPD from the H/D\( \text{D}_2\text{O} \)-covered surface; this result is indicative of the production of HDO. This newly formed HDO desorbs at the same temperature as water desorption on clean \( \text{Au}(111) \), and we believe this isotopic mixing is due to proton transfer in the solid water film.

We also studied the \( \text{Au}(111) \) surface with coadsorbed deuterium and \( \text{H}_2\text{O} \). Figure 2b shows TPD spectra acquired from 2.68 ML of \( \text{H}_2\text{O} \) adsorbed on \( \text{D} \) (\( \theta_{\text{D}_{\text{rel}}} = 0.63 \)) precovered \( \text{Au}(111) \). There are significant similarities with the \( \text{H}+\text{D}_2\text{O} \) system shown in Figure 2a; (i) \( \text{H}_2\text{O} \) shows a higher-temperature desorption feature at 175 K; (ii) \( \text{D}_2 \) yields a sharp desorption peak at 160 K; (iii) the production of HD and \( \text{H}_2 \) has been observed, and the \( \text{H}_2 \) desorption peak appears at the highest temperature; and (iv) compared to the surface with adsorbed \( \text{H}_2\text{O} \) only, there is an increase in mass 19 (HDO) at 160 K, which is indicative of deuterium transfer in \( \text{H}_2\text{O} \) on \( \text{Au}(111) \).

We conducted DFT calculations to uncover the detailed mechanism of the interaction of adsorbed \( \text{H} \) atoms with water (procedural details are contained in the Supporting Information). The TPD spectra presented in Figures 1 and 2 indicate a specific reaction mechanism, isotopic mixing dictated via overlay structure. The high-temperature \( \text{H}_2 \) peak, \( \gamma \) in Figure 1, originates exclusively from the water; however, the two lower-temperature \( \text{H}_2 \) peaks are derived exclusively from the surface-bound atoms. The fact that the sources of these peaks are related for both surface \( \text{D}/\text{H}_2\text{O} \) as well as surface \( \text{H}/\text{D}_2\text{O} \) indicates that this effect cannot be ascribed entirely to random isotopic scrambling.

We first used DFT to model the behavior of surface-bound \( \text{H} \) at low temperatures. The three-fold fcc hollow sites are the most favorable adsorption sites for \( \text{H} \) atoms, as Mavrikakis has reported previously. As shown in Figure 3, there is a small barrier for a hydrogen atom to move from a fcc hollow to a hcp hollow. In this manner, the surface-bound atoms may diffuse randomly across the surface at low temperatures. \( \text{H}_2 \) formation as well as interaction with water, however, requires \( \text{H} \) atoms to sit atop a surface \( \text{Au} \) atom. From this position, the reaction for two adjacent top-bound \( \text{H} \) atoms to form \( \text{H}_2 \) is barrierless and exothermic by over 0.75 eV (Figure S1, Supporting Information). Thus, the formation of \( \text{H}_2 \) is not apparent until the temperature is such that the surface-bound protons may diffuse to top sites. This barrier, approximately 0.25 eV from a hcp hollow, represents the energy cost of extracting a surface-bound \( \text{H} \) atom from the \( \text{Au}(111) \) surface, and all related processes, such as \( \text{H}_2 \) formation or the interaction with water, have similar barriers.

In contrast, water is weakly chemisorbed on \( \text{Au}(111) \) and has little barrier to diffusion. Thus, multiple water molecules move around on the surface until clustering and stabilizing. This phenomenon has been demonstrated by the low surface wettability of \( \text{Au}(111),^{18} \) which is a hydrophobic surface and induces the formation of water clusters with a double-bilayer structure. Specifically, water molecules have much stronger \( \text{H}_2\text{O}–\text{H}_2\text{O} \) interactions than \( \text{H}_2\text{O}–\text{H}_2\text{O} \)–surface interactions on \( \text{Au}(111),^{18} \) causing a single desorption feature. On other metal surfaces (such as \( \text{Ir},^{36} \text{Pt}^{37} \text{Ni}^{38} \) etc.), there is a discernible transition from the monolayer to the multilayer desorption indicating a stronger interaction between the first layer of water and the surface atoms.

Our DFT calculations for the \( \text{H}_2\text{O} + \text{fcc-site H} \) reaction show a 0.29 eV energetic barrier with a 0.22 eV endothermicity. The final \( \text{H}_2\text{O}^{+} \) state has three fully equivalent protons and a low barrier for the reverse reaction; therefore, if this reaction were to occur at low temperatures, random isotopic scrambling would occur. The lack of low-temperature scrambling of surface-bound \( \text{H} \) with water indicates that water molecules form ice before the energetic barrier for surface-bound \( \text{H} \) to escape the surface can be met. Note that the formation of hydronium has been reported on the \( \text{H}–\text{and water-covered Pt(111)} \) surface by Wagner and co-workers, who detected a \( \text{H}_2\text{O}^{+} \) intermediate based on the appearance of a 1150 cm\(^{-1}\) loss in high-resolution electron energy loss spectroscopy (HREELS).

We next studied the interaction of \( \text{H} \) atoms with water dimers and clusters employing DFT. Protonated water clusters of the form \( \text{(H}_2\text{O)}_n \text{H}^+ \) are likely to form due to the strong exothermicity of the product state and a large barrier to the reverse reaction. DFT calculations investigated the protonation of a water dimer and a water tetramer as a representative of a
water cluster. Protonation of the dimer is exothermic by 0.27 eV compared to that of the fcc hollow. Importantly, the H-bonded proton of the dimer becomes shared between the two molecules with an equal bond length, as shown in Figure 4. It is this stretching mechanism that allows the original water molecule to dissociate; when the dimer breaks apart at higher temperatures, it is the H atom that is originally part of the water molecule that creates the H2 desorption observed at 175 K in Figure 1c.

When a water tetramer is considered, protonation of the central water molecule is exothermic by 0.95 eV as compared to the fcc hollow, as shown in Figure 5. Thus, when surface-bound H atoms become free to move about the surface, they can either recombine to form H2 or encounter an undercoordinated water molecule at the edge of an ice cluster and bind irreversibly. Infrared spectroscopy provides evidence for this process. Figure S2 (Supporting Information) shows that the infrared spectrum of the tetramer is strongly exothermic, and the in-network bond lengthens.

In TPD measurements of coadsorbed H and H2O, recombinative H2 desorption shows two new features (β, γ), and water desorption reveals an additional peak at higher temperature. DFT results show that the (H2O)nH+ clusters require a higher-energy input to break up than (H2O)n, and lead to the new high-temperature desorption feature of water at 175 K. Each water cluster breaks apart into progressively smaller units, and the ultimate effect of the breakup involves cleavage of an O–H (or O–D) bond that was originally part of a water molecule. The H (or D) atom in this bond is ultimately left on the surface as an adatom that can recombine with other H or D on the surface. In experiments involving isotopes, as illustrated in Figure 2, this process can produce scrambled HD and D2/H2 (in the H–D2O/D–H2O systems).

Thus, our DFT calculations demonstrate the origins of the α, β, and γ peaks. The α peak arises from the surface-bound H atoms that are free to diffuse on the surface and recombine. The hydrophobic Au(111) surface may induce water clustering upon heating, opening up more water-free surface area and increasing the ability of two H adatoms to recombine. However, ultimately, the water clusters lengthen the H atom diffusion distance, leading to the shift in the α peak to higher temperatures with increasing water coverage, as shown in Figure S3 in the Supporting Information. The β peak is the result of surface-bound H whose dihydrogen recombination is obstructed by large ice clusters and that is not free to recombine until the water clusters begin to break apart at higher temperatures. More specifically, we speculate that the β peak is likely due to a physicochemical process: (i) water adsorbs on the H-
precovered surface and forms clusters covering the H atoms; (ii) the water cluster bottom, which is fully coordinated to other H2O molecules, has a weaker interaction with H atoms than the edge water molecules; (iii) this interaction inhibits the mobility of H atoms; and (iv) H atoms combine with one another and immediately leave the Au(111) surface once water desorbs at ∼160 K, leading to a slightly high desorption temperature due to the reaction kinetics. The final peak, γ, consists of protons exclusively from the water and originates from surface-bound H atoms bonding with water molecules at the edges of ice layers to form (H2O)H+ clusters that do not break apart until 175 K. This mechanism is consistent with the isotopic results presented in Figure 2, in which isotopic scrambling occurs based on the origin of the species (from the surface or from water). In addition, Figure S3 (Supporting Information) shows that increasing water coverages cause greater desorption features of H2O and H2 at 175 K, suggesting that more water clusters form at high coverages and generate a larger number of edge sites to promote the interaction between H and water. These results are in agreement with our DFT calculations that show that water clustering plays a key role in this process.

Kinetic isotope effects (KIEs) have been studied by comparing coadsorption of H and H2O to a fully deuterated surface at 77 K. The heating rate during TPD was 1 K/s. Note that (a) has the same scale on the y-axis.

Figure 6. (a) TPD spectra from Au(111) with coadsorption of 2.68 ML of D2O and D (θD,rel = 0.63) on Au(111) yields TPD spectra, shown in Figure 6a, that show several characteristic properties of the interaction between hydrogen and water. The D2 desorption contains three features corresponding to the peaks α, β, and γ in Figure 1c,

and D2O similarly shows a new high-temperature desorption feature. We also observed desorption of HD (mass 3) and H2 (mass 2) in a temperature range of 175–180 K. These features likely result from the surface-mediated interaction between H−D2O or D−H2O because D2O and D2 have a considerable amount of HDO (19%) and HD (7%) impurities, respectively, as indicated by multiple control experiments via TPD and FTIR measurements (Figures S4–S6, Supporting Information).

In order to identify the effect of deuterium on the reaction between hydrogen and water, we integrated the desorption features of D2, HD, and H2 that peak at 175–180 K and show the results in Figure 6b with a comparison to the reaction of H with H2O. Note that we normalized the difference between H and D coverages by assuming a proportional relationship between coverages and areas under the γ feature in H2/D2 desorption. The integrated areas indicate that the interaction between H and H2O generates a significantly larger amount of H2 than the desorption of D2 from the D−D2O reaction by a factor of ∼4. This result suggests a primary KIE for this surface reaction. In addition, we note that the sum of D2, HD, and H2 from D−D2O is still smaller than H2 desorption in the case of H + H2O, as shown in Figure 6b. This observation is a further demonstration of the KIE influence, which is likely due to the elementary steps of water protonation and subsequent decomposition of (H2O)H+.

In summary, hydrogen and water have a strong interaction that results in nonrandom isotopic scrambling on the Au(111) surface at low temperature (<175 K) under UHV conditions. Coadsorbed H and H2O lead to a new feature appearing at ∼175 K in the water desorption spectra, which is in contrast to the characteristic desorption peak on clean Au(111) at 160 K. Furthermore, two new features have been observed in H2 desorption (at 160 and 175 K), as well as a shift in the characteristic H2 recombination desorption feature to higher temperatures. We used two reactant combinations, H2O + D and D2O + H2, to study these phenomena and show production of HD, HDO, and H2(D2) via a mixing reaction based on the overlayer structure of isotopically labeled water and hydrogen. This study provides evidence that the hydrogen evolving at 175 K from the H−H2O-coadsorbed surface is exclusively from bond breaking in water rather than surface-bound H2 recombinative desorption. RAIRS spectroscopy and DFT calculations predict that protonated water clusters (H2O)nH+ are intermediates, which dissociate at higher temperature to cause the appearance of new desorption features for water and H2. Purely deuterated reactants D and D2O have been employed in this reaction and show a lower reactivity, indicative of a primary KIE.

### ASSOCIATED CONTENT

**Supporting Information**

Detailed experimental and computational procedures, reflection absorption infrared spectroscopy measurements from Au(111) with coadsorption of D2O and H2 and TPD spectra of H2 and H2O from H-precovered Au(111) with coadsorption of a variety of H2O coverages, TPD and FTIR results for D and D2O on clean Au(111). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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