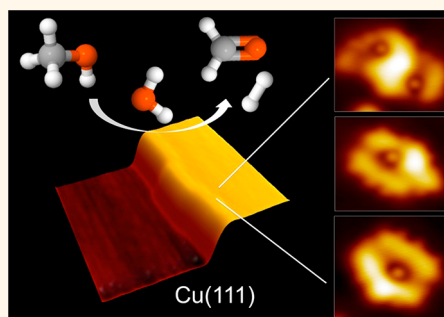


# Molecular-Scale Perspective of Water-Catalyzed Methanol Dehydrogenation to Formaldehyde

Matthew B. Boucher,<sup>†</sup> Matthew D. Marcinkowski,<sup>‡</sup> Melissa L. Liriano,<sup>‡</sup> Colin J. Murphy,<sup>‡</sup> Emily A. Lewis,<sup>‡</sup> April D. Jewell,<sup>‡</sup> Michael F. G. Mattera,<sup>‡</sup> Georgios Kyriakou,<sup>‡,§</sup> Maria Flytzani-Stephanopoulos,<sup>†,\*</sup> and E. Charles H. Sykes<sup>‡,\*</sup>

<sup>†</sup>Department of Chemical and Biological Engineering and <sup>‡</sup>Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States. <sup>§</sup>Present address: Department of Chemistry, University of Hull, Cottingham Road, Hull, HU6 7RX, United Kingdom.

**ABSTRACT** Methanol steam reforming is a promising reaction for on-demand hydrogen production. Copper catalysts have excellent activity and selectivity for methanol conversion to hydrogen and carbon dioxide. This product balance is dictated by the formation and weak binding of formaldehyde, the key reaction intermediate. It is widely accepted that oxygen adatoms or oxidized copper are required to activate methanol. However, we show herein by studying a well-defined metallic copper surface that water alone is capable of catalyzing the conversion of methanol to formaldehyde. Our results indicate that six or more water molecules act in concert to deprotonate methanol to methoxy. Isolated palladium atoms in the copper surface further promote this reaction. This work reveals an unexpected role of water, which is typically considered a bystander in this key chemical transformation.



**KEYWORDS:** methanol · water · copper · palladium · alloy · steam reforming

Methanol is one of the largest volume chemicals produced worldwide.<sup>1</sup> While methanol is primarily used for the production of other chemicals, its transportability, low boiling point, and high hydrogen/carbon ratio make it suitable for on-demand hydrogen production.<sup>1</sup> On selective catalysts, steam reforming of methanol (SRM) produces carbon monoxide-free hydrogen, which is a requirement for proton exchange membrane (PEM)–fuel cell operation. It is widely accepted that the SRM reaction on group IB metals proceeds through a complex mechanism involving formaldehyde, methyl formate, and formic acid intermediates.<sup>2,3</sup> The elementary step of the dehydrogenation of methoxy to formaldehyde is especially important, as the manner in which formaldehyde interacts with the support dictates the final reaction pathway.<sup>4</sup> Cu-based catalysts are distinguished by their high selectivity to CO<sub>2</sub> and H<sub>2</sub> via the above reaction pathway. They do not catalyze the decomposition of methanol<sup>2,3,5</sup> and are thus not limited by the water-gas shift reaction equilibrium.

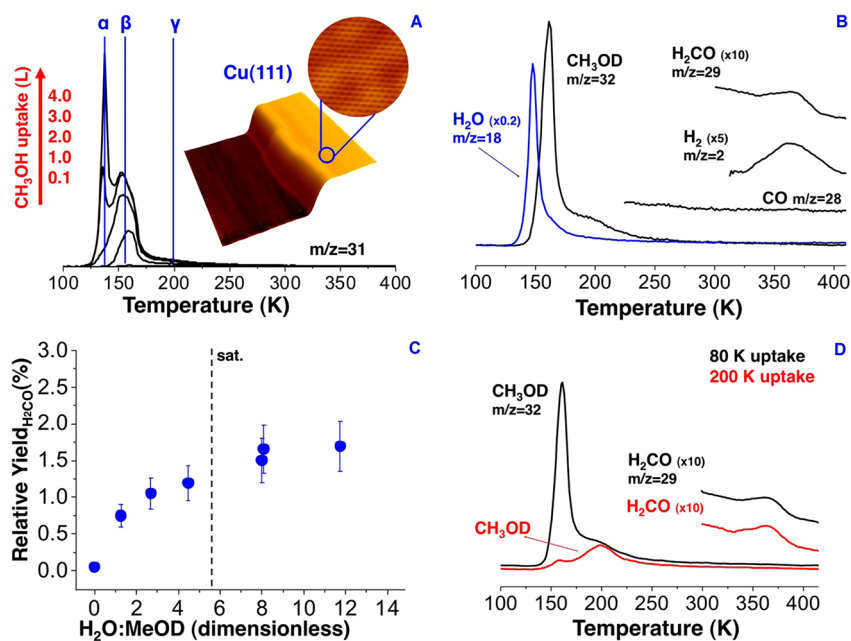
Due to the importance of methanol reactions on Cu catalysts, surface science techniques have been used extensively to investigate the interaction of methanol with well-defined Cu surfaces under ultrahigh vacuum (UHV) conditions.<sup>6–12</sup> In pioneering work, Madix and co-workers<sup>6,7,12</sup> have examined the nature of methanol activation on Cu(110) surfaces. These and subsequent studies have demonstrated that either oxygen adatoms or oxidized Cu are required to stabilize methoxy on Cu.<sup>1,6–9,12</sup> The deprotonation of methanol by oxygen on Cu(110) results in the formation of water, which desorbs at low temperatures and leaves methoxy on the surface that subsequently dehydrogenates to formaldehyde.<sup>7</sup> Bowker and co-workers<sup>8,9,13,14</sup> have used scanning tunneling microscopy (STM) to image the active sites involved in the oxidation of methanol on Cu(110). While it is generally accepted that oxygen facilitates this chemical transformation, it is feasible that other adsorbates are capable of promoting the same chemistry. For instance, it has been shown that sulfur

\* Address correspondence to maria.flytzani-stephanopoulos@tufts.edu, charles.sykes@tufts.edu.

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**Figure 1.** TPD spectra and corresponding data points illustrating the formation of formaldehyde from methanol in the presence of water on Cu(111). (A) TPD spectra of methanol ( $m/z = 31$ ) from Cu(111) after methanol uptake at 85 K. (B) TPR spectra of 0.15 ML of partially deuterated methanol ( $\text{CH}_3\text{OD}$ ) coadsorbed with 0.45 ML of water on clean Cu(111). (C) Relative yield of formaldehyde (370 K) as a function of water coverage adsorbed with 0.15 ML of partially deuterated methanol ( $\text{CH}_3\text{OD}$ ) on Cu(111). The vertical line indicates saturation of the monolayer. (D) TPR spectra of methanol adsorbed at 85 and 200 K on Cu(111); in each case, water was coadsorbed on the surface at 85 K.

overlayers are capable of dehydrogenating methanol to methoxy on Ni(100).<sup>15</sup>

## RESULTS AND DISCUSSION

Given water's ability to accept protons, its effect on the SRM reaction in the absence of atomic oxygen is of general interest. In a series of low-temperature STM and temperature-programmed desorption/reaction (TPD/R) experiments, we have investigated the reactivity of methanol and methanol–water mixtures on oxygen-free Cu(111) and Pd/Cu(111) surfaces. We demonstrate for the first time that water, which is generally thought to be a spectator species,<sup>1</sup> is capable of deprotonating methanol to produce methoxy at low temperature. Methoxy is stabilized on the surface to higher temperature, where it dehydrogenates to formaldehyde on both the Cu(111) and Pd/Cu(111) surfaces.

**Thermal Desorption Spectroscopy of Methanol–Water Mixtures on Cu(111).** As expected, our TPD experiments show that the Cu(111) surface was completely inert toward methanol dehydration, and molecular desorption of methanol was characterized by three distinct features, as shown in Figure 1A; these results are in agreement with those previously reported for methanol desorption from Cu(111).<sup>11,16</sup> The desorption features labeled  $\alpha$ ,  $\beta$ , and  $\gamma$  in Figure 1A correspond to methanol desorbing from multilayers (143 K), terraces (163 K), and step edge sites (200 K) on Cu(111), respectively.<sup>16</sup>

Interestingly, when 0.15 ML of methanol was coadsorbed with 0.45 ML of water on clean Cu(111), desorption of formaldehyde (370 K) and hydrogen (370 K)

was observed. Wachs *et al.* reported the desorption of reactively formed formaldehyde at 365 K on oxygen-precovered Cu(110) surfaces, corresponding to an activation energy of 22.4 kcal/mol.<sup>7</sup> In our control experiments described in the Supporting Information, we demonstrate that formaldehyde is formed in the absence of atomic oxygen on Cu(111). Furthermore, no CO formation was detected at high temperatures; the only products were formaldehyde and hydrogen. Partially deuterated methanol ( $\text{CH}_3\text{OD}$ ) was used in order to identify desorption peaks corresponding to the activation of the O–D and C–H bonds (Figure 1B). Surprisingly, neither  $\text{D}_2$  nor HD was detected in the TPR profile shown in Figure 1B; rather, a single desorption peak for  $\text{H}_2$  was observed at 370 K, and a contribution from HDO ( $m/z = 19$ ) was observed at 153 K. The HDO and  $\text{D}_2\text{O}$  contributions to the TPR profile in Figure 1B are shown in Figure S3B in the Supporting Information. In the absence of adsorbed oxygen, a likely explanation for the formation of HDO is *via* isotopic exchange between  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OD}$  or D atoms resulting from O–D bond scission.<sup>17,18</sup> The absence of large quantities of  $\text{D}_2\text{O}$ , in contrast to what was observed by Wachs *et al.*,<sup>7</sup> confirms that our Cu(111) surface was oxygen-free. Furthermore, Mullins and co-workers have reported the low-temperature exchange of D atoms with either water<sup>17</sup> or methanol,<sup>18</sup> individually, on a Au(111) surface. Our results indicate that an excess of water ( $\geq 6$  water molecules per methanol) is required to convert methanol to formaldehyde and hydrogen in the absence of oxygen on Cu. It has been shown that D

atoms on Au(111) readily exchange with adsorbed water.<sup>17</sup> Therefore, the D atoms released from MeOD are scrambled with the H atoms of the adsorbed H<sub>2</sub>O, which is present in excess. Furthermore, both H<sub>2</sub>O and HDO were completely desorbed from the surface below 200 K, implying that O–D bond activation by water takes place at low temperature (Figure 1B and Figure S3B).

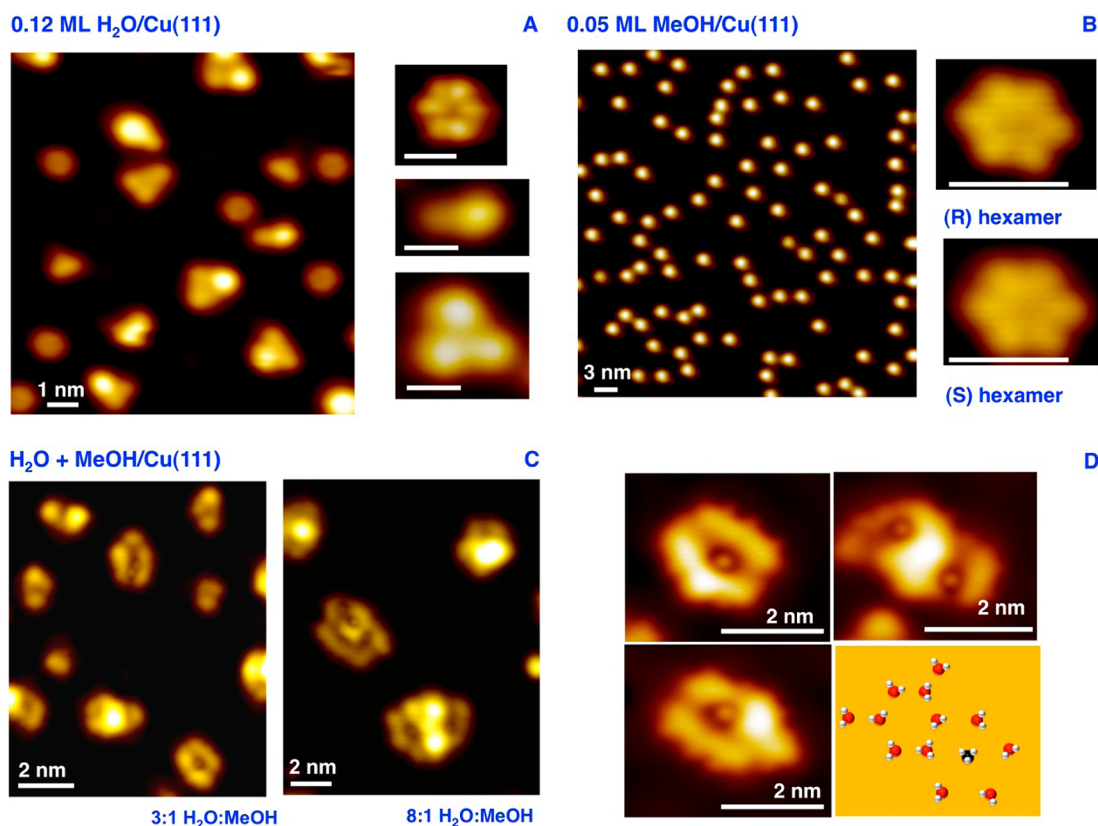
Molecular desorption of formaldehyde from low-index Cu surfaces is known to occur below 250 K.<sup>7,19,20</sup> In the present study, the formaldehyde peak was detected at 370 K (Figure 1B), well above its measured desorption energy, and therefore its desorption must be reaction-rate-limited. Thus, methoxy is stabilized on the surface up to 370 K where it dehydrogenates to formaldehyde and immediately desorbs. Since water has desorbed from the surface below 200 K, our data indicate that C–H bond scission at 370 K is activated by the Cu surface. Figure 1C demonstrates that the concentration of coadsorbed water has a large effect on the relative yield of formaldehyde. When the total coverage of methanol and water exceeded one monolayer, the relative yield began to saturate. The correlation between water coverage and relative yield reveals that, in the absence of surface oxygen, multiple water molecules activate the dehydrogenation of methanol to methoxy. In order for methoxy to further react to formaldehyde, it must be stabilized on the surface up to 370 K, as formaldehyde desorption took place at this temperature (Figure 1B). The total amount of formaldehyde product never exceeded 0.5% ML over the range of water/methanol ratios (3–10:1) investigated, as presented in Figure 1B. Based on the yield of formaldehyde at surface saturation, it is possible that the reaction is limited by the availability of a particular type of active site on the surface. The active site was further examined by adsorbing methanol at 200 K so that it only populated the Cu step edges. Figure 1D compares the methanol and formaldehyde desorption spectra from methanol uptake (0.15 ML) at 200 and 85 K; in each case, 0.45 ML of water was coadsorbed at 85 K. It is clear from 1D that even when a small amount of methanol is available, populating the Cu step edges, the amount of formaldehyde formed remains unchanged, resulting in a much higher yield (~10–20%, depending on water coverage). This result demonstrates that undercoordinated Cu atoms at the step edges are required to stabilize the methoxy<sup>21</sup> up to 370 K, at which temperature it reacts to produce formaldehyde, as water leaves the surface below 200 K.

**Molecular-Scale Imaging of Methanol–Water Interactions on Cu(111).** In order to elucidate the molecular-scale interaction of methanol and water that appears to be critical for the reaction, low-temperature STM was performed on pure water and methanol, as well as various mixtures of both species coadsorbed on Cu(111). The STM images in Figure 2 reveal that a new structure was formed

when methanol/water mixtures were adsorbed on the Cu(111) surface; these structures were not present when either methanol or water was adsorbed alone. STM images of water adsorbed on the Cu(111) surface are shown in Figure 2A; the repeating structures are assigned as ordered, hydrogen-bonded water clusters.<sup>22–25</sup> STM images of methanol adsorbed on the Cu(111) surface are shown in Figure 2B; the majority of methanol on the surface was in the form of hexamers in both the R and S chiral configurations arising from counterclockwise and clockwise hydrogen-bonded networks, respectively, as previously reported by Lawton *et al.*<sup>26</sup>

Figure 2C,D contains STM images from methanol and water coadsorbed on the Cu(111) surface. In each case, water was in excess of methanol with water/methanol ratios ranging from 3:1 to 8:1; other ratios are shown in the Supporting Information (Figure S4). The new structures consist of a large ring or multiple rings of molecules surrounding a central entity. On the basis of previous reports of hydrogen-bonded networks of water<sup>22,23</sup> and methanol<sup>26</sup> on surfaces imaged with STM, we hypothesize that these structures consist of a ring of hydrogen-bonded water molecules surrounding a deprotonated methanol molecule. In this configuration, the water molecules act in concert to deprotonate the methanol molecule to methoxy, which does not hydrogen bond to the same degree and appears as a localized protrusion in the cluster. These methanol/water complexes are typically  $\geq 2$  nm in width and contain tens of water molecules; therefore, the larger protrusions in the ring are not individual molecules, but rather raised parts of the complex that contain many molecules and hence are larger in appearance than the isolated methoxy species. There is also undoubtedly some methanol in the complexes, but the high degree of hydrogen bonding between the species makes it impossible to resolve individual molecules. The interpretation that water molecules act in concert to deprotonate a methanol molecule to methoxy is supported by experiments and density functional theory (DFT) calculations performed by Mullins, Henkleman, and co-workers for water on Au(111) surfaces.<sup>17</sup> Their results indicate that it is more energetically favorable for a H atom to be stabilized by small clusters of water than to be isolated on the Au(111) surface. In this report, they calculated that protonation of four waters is exothermic by  $\sim 1$  eV. In related work, Mullins and co-workers<sup>18</sup> discovered that adsorbed methanol was significantly stabilized (by 50–100 K) on the Au(111) surface by the presence of H atoms. They achieved these results by generating a H-precovered Au(111) surface using a hydrogen cracker; H atoms were not formed as a result of bond activation on the surface.

It has been shown experimentally and by DFT that water on the Cu(110) surface above a critical coverage undergoes autocatalytic dissociation.<sup>27–30</sup> The activation barrier for water dissociation is significantly lower

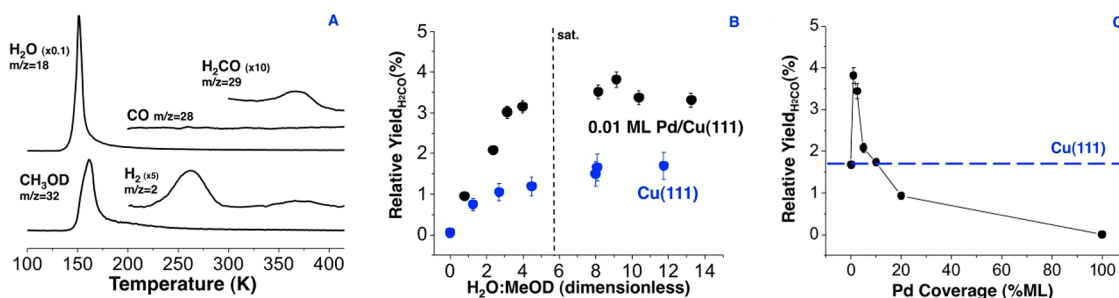


**Figure 2.** STM images of methanol and/or water adsorbed on Cu(111). (A) STM image of water (0.12 ML) on the Cu(111) surface, deposited and imaged at 5 K; inset scale bar = 1 nm. (B) STM image of methanol (0.05 ML) on the Cu(111) surface, dosed and imaged at 5 K; inset scale bars = 1 nm. (C) Co-adsorption of methanol and water at 5 K and annealing to 60 K led to the formation of new structures. In each case, water was in excess to methanol in ratios of 3:1 and 8:1. (D) High-resolution STM images and proposed structure of the most common type of complexes observed when co-adsorbing methanol and water on Cu(111) at conditions described in (C).

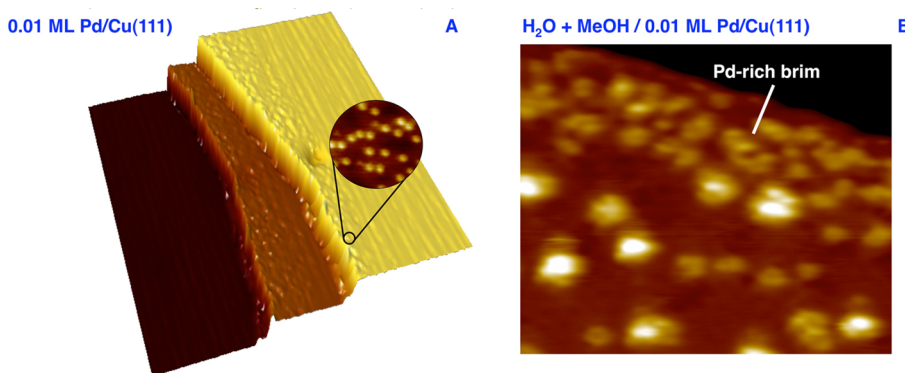
in a 2D hydrogen-bonded structure than for a water monomer (by 0.3–0.4 eV), while the desorption energy is much higher (by 0.18 eV).<sup>27,28</sup> We therefore postulate that a similar effect is at play in methanol–water mixtures, whereby the protonation of small water clusters provides the driving force for methoxy formation. As water desorbs from the surface at low temperature (<200 K), this implies that O–H bond activation by water also takes place at low temperature. In support of our hypothesis that a hydrogen-bonded cluster is needed to stabilize a H atom removed from methanol, Chen *et al.*<sup>31</sup> reported the formation of formaldehyde when only methanol was adsorbed on Cu(210); however, they observed a critical coverage of methanol (>0.5 ML) below which formaldehyde was not formed. While no explanation of this phenomenon was provided, a likely reason for the dependence on methanol coverage is the autocatalytic dehydrogenation of methanol, which may require larger clusters of methanol molecules to stabilize a proton. This is supported by the increased stability of methanol in the presence of H atoms on Au(111) as reported by Brush *et al.*<sup>18</sup> On a related note, water-assisted diffusion of protons, or “proton hopping”, was recently observed on FeO films by Besenbacher and co-workers with the aid of DFT

calculations by Mavrikakis and co-workers; proton diffusion was shown to proceed through a  $\text{H}_3\text{O}^+$  transition state.<sup>32</sup> In the present study, the deprotonation of methanol by an active complex consisting of several water and/or methanol molecules enables the formation of methoxy on the surface, while the removed H atoms are stabilized in the complex itself until the water desorbs, leaving H atoms to recombine and leave the Cu(111) surface at a higher temperature. The protrusions in the complexes shown in Figure 2 are indicative of a discontinuity in the hydrogen-bonded network, which most likely arises from the methyl group of methoxy. A schematic of the proposed intermediate structure is shown in Figure 2D.

**Thermal Desorption Spectroscopy and Molecular-Scale Imaging of Methanol–Water Mixtures on Pd/Cu(111) SAAs.** The addition of Pd adatoms to the Cu(111) surface allowed us to further probe the mechanism of methanol dehydrogenation to formaldehyde in the presence of water. Our previous work has demonstrated that Pd/Cu alloys are formed at the Cu step edges by place exchange into the Cu surface.<sup>33,34</sup> Furthermore, at low Pd concentrations (0.01 ML), Pd was present exclusively in the form of individual, isolated atoms, which allowed hydrogen to dissociatively adsorb and desorb at low



**Figure 3.** TPD spectra and corresponding data points illustrating the formation of formaldehyde from methanol in the presence of water on Pd/Cu(111). (A) TPR spectra of 0.15 ML of partially deuterated methanol (CH<sub>3</sub>OD) coadsorbed with 1.5 ML of water at 85 K on 0.01 ML Pd/Cu(111). (B) Relative yield of formaldehyde (370 K) at varying water/methanol ratios dosed at 85 K on 0.01 ML Pd/Cu(111) and clean Cu(111). The vertical line indicates saturation of the monolayer. (C) Relative yield of formaldehyde (370 K) as a function of Pd coverage.



**Figure 4.** STM images of methanol and water on 0.01 ML Pd/Cu(111). (A) STM Image of 0.01 ML of Pd alloyed in Cu(111). Image size  $50 \times 48 \text{ nm}^2$ . (B) STM image of methanol and water adsorbed at a Pd-rich brim on Cu(111) after annealing to 100 K, revealing stabilization of the methanol–water complexes on the Pd-rich areas at step edges. Image size  $30 \times 24 \text{ nm}^2$ .

temperatures.<sup>33,35,36</sup> In the present work, in the absence of water, the 0.01 ML Pd/Cu(111) surface was unreactive toward methanol, as no decomposition products were observed by TPR. When 0.15 ML of methanol was coadsorbed with varying coverages of water on a 0.01 ML Pd/Cu(111) surface, the desorption of formaldehyde (370 K) and hydrogen (260 and 370 K) was observed. Figure 3A contains TPR profiles obtained after dosing 0.15 ML of methanol with 1.5 ML of H<sub>2</sub>O on 0.01 ML Pd/Cu(111). A higher dose of water than in Figure 1B is shown here to highlight both of the hydrogen desorption features. The reactively formed hydrogen desorbed at both 260 and 370 K from the 0.01 ML Pd/Cu(111) surface, whereas it desorbed from the Cu(111) surface at 370 K. The low-temperature desorption of hydrogen, enabled by the addition of isolated atoms of Pd into Cu, provides conclusive evidence that O–H (or O–D) bond activation takes place at low temperature. On a clean Pd/Cu(111) surface, molecular hydrogen desorbs around 200 K. The 260 K desorption peak observed in these experiments corresponds to desorption from Pd if it is blocked or “corked” by adsorbates on the surface.<sup>37</sup> Hydrogen desorbs from a 1% Pd/Cu(111) surface at 210 K, but when adsorbates bind strongly to the Pd recombination site, the hydrogen is released at a higher temperature

only once these adsorbates have enough energy to either desorb or diffuse away from the Pd as we have shown for CO and styrene.<sup>37</sup> It should be noted that the hydrogen desorption peak measured at 260 K contained contributions from both reactively formed and background-adsorbed hydrogen; further clarification of this point is provided in the Supporting Information. In support of our earlier conclusion, the desorption of formaldehyde is reaction-rate-limited by the scission of the C–H bond in methoxy, while water is able to activate an O–H (or O–D) bond below 200 K.

A marked improvement in the relative yield of methanol to formaldehyde by isolated Pd atoms is illustrated in Figure 3B,C. A similar overall water/methanol trend to that of Cu(111) is observed for 0.01 ML Pd/Cu(111); however, the relative yield is saturated at a higher overall yield of formaldehyde (0.01 ML). Similar to the Cu(111) surface, the relative yield saturated when the total coverage of methanol and water on the surface exceeded 1 ML. Our work indicates that O–H bond activation requires a complex interplay between the molecular interaction of adsorbed methanol and water and the strong interaction of methoxy with the Cu surface. We have already demonstrated that step edges are necessary for methanol conversion to formaldehyde in the presence of water

(Figure 1D). Moreover, our STM data indicate that the addition of small amounts of Pd atoms (0.01 ML) concentrated near the Cu step edges (Figure 4A) stabilizes the methanol/water complexes on the surface, as shown in Figure 4A. Therefore, we suggest that the addition of Pd to Cu(111) allows more methanol to remain on the surface at higher temperatures where a greater degree of O–H bond activation can take place.

Increasing the Pd content in the Cu(111) surface led to a decrease in the relative yield of formaldehyde, as shown in Figure 3C. At high concentrations of Pd ( $>0.10$  ML), where Pd dimers, trimers, and islands are present (Figure S2C), the decrease in the relative yield of formaldehyde can be explained by a loss in selectivity. While methanol is still converted on these surfaces, it is completely decomposed to CO and H<sub>2</sub><sup>38</sup> on larger Pd ensembles. At lower Pd concentrations ( $<0.10$  ML), where primarily Pd monomers are present, the decrease in relative yield can be explained by compressive strain of the surface at the Pd-rich brims that weakens methanol binding.<sup>39</sup>

## CONCLUSIONS

Our results demonstrate that molecularly adsorbed water, in the absence of atomic oxygen, catalyzes the deprotonation of methanol to methoxy below 200 K on both the Cu(111) and 0.01 ML Pd/Cu(111) surfaces. Hydrogen-bonded networks of water comprise an active complex on which it is energetically favorable to bind a proton. On an atomically flat Cu(111) surface,

where methoxy can only be formed as a transient species, the addition of hydrogen-bonded water complexes that stabilize H atoms drives O–H bond scission, leaving methoxy stabilized on Cu step edge atoms. Our STM data suggest that the addition of isolated Pd atoms to the Cu(111) surface promotes this reaction by allowing more methanol to remain on the surface at higher temperatures, which facilitates a greater degree of O–H bond activation. Methoxy stabilized at Cu step edges and/or Pd atoms remains on the surface until it dehydrogenates selectively to formaldehyde at higher temperatures. These results are fundamentally important when considering the mechanism involved in methanol reforming to products including CO, CO<sub>2</sub>, and H<sub>2</sub>. The water-assisted dehydrogenation of methanol to formaldehyde comprises a new elementary step in the methanol steam reforming pathway. While it is believed that atomic oxygen on the catalyst surface is necessary for this reaction step, we show here that molecular water, alone, is capable of the same deprotonation. Furthermore, the weak binding of formaldehyde on the surface is critical to the formation of key intermediates in the selective reforming of methanol to CO<sub>2</sub> and H<sub>2</sub>; strong binding can lead to the complete decomposition of methanol to CO and H<sub>2</sub>. By studying well-defined surfaces, we have shown that both under-coordinated Cu step edge atoms and isolated Pd atoms at Cu(111) step edges can act as selective methanol dehydrogenation sites, as no decomposition of methanol to CO was observed.

## MATERIALS AND METHODS

**STM Experiments.** All STM experiments were performed in ultrahigh vacuum with an Omicron NanoTechnology low-temperature STM. The base pressure in the STM chamber was  $1 \times 10^{-11}$  mbar. The Cu(111) single-crystal sample was cleaned by cycles of Ar<sup>+</sup> sputtering (14  $\mu$ A, 1 kV) and annealing (1000 K). The sample was then transferred into the precooled STM stage with a base temperature of 5 K. Deionized H<sub>2</sub>O obtained from a Nanopure water system and Ultrapure HPLC grade methanol (99.8+%, Alfa Aesar) were further purified through freeze–pump–thaw cycles. Varying ratios of H<sub>2</sub>O and methanol were deposited onto the Cu(111) surface through high precision leak valves at 5 K followed by a thermal anneal to 60 K. The sample was then cooled back down to 5 K. Images were taken with bias voltages between 30 and 70 mV and currents between 15 and 50 pA.

**TPD/R Experiments.** Methanol, water, and methanol–water TPD/R experiments were performed in a UHV chamber with a base pressure of  $1 \times 10^{-10}$  mbar. The chamber incorporates a quadrupole mass spectrometer as well as a system for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Deionized H<sub>2</sub>O obtained from a Nanopure water system, Ultrapure HPLC grade methanol (99.8+%, Alfa Aesar), partially deuterated methanol (99.5+%, Alfa Aesar), and methanol-<sup>13</sup>C (99%, Sigma Aldrich) were further purified through freeze–pump–thaw cycles. Varying ratios of water and methanol were deposited onto the Cu(111) surface through a high-precision leak valve at 85 K. To obtain the TPD profile in Figure 1D, CH<sub>3</sub>OD was deposited onto Cu(111) through a high-precision leak valve at 200 K. Subsequently, the sample was cooled to 85 K, and water was dosed through a separate

high-precision leak valve. The 1 ML coverage of methanol was determined by a calibration consisting of a series of CH<sub>3</sub>OH-TPD measurements and deconvolution of the monolayer/multilayer peaks. The TPD spectra used for the calibration are shown in Figure 1A. Desorption of reactants and products was monitored using a heating rate of 1 K/s. In order to deposit very small amounts of Pd in a reproducible manner, Focus EFM 3 electron beam evaporators with internal flux monitors were used. Pd coverages were calibrated using both AES and carbon monoxide 99.99% (Airgas) titration. Pd was deposited at 380 K, at which temperature Pd alloys into the surface layer of Cu(111) in the form of individual, isolated atoms at low coverage. The error bars in Figure 1C and Figure 3B,C represent one standard deviation of the average of three repeated experimental measurements.

*Conflict of Interest:* The authors declare no competing financial interest.

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*Supporting Information Available:* Additional STM images and thermal desorption spectra, a description of control experiments for the demonstration of an oxygen-free surface, characterization of the product distribution, and additional experimental conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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