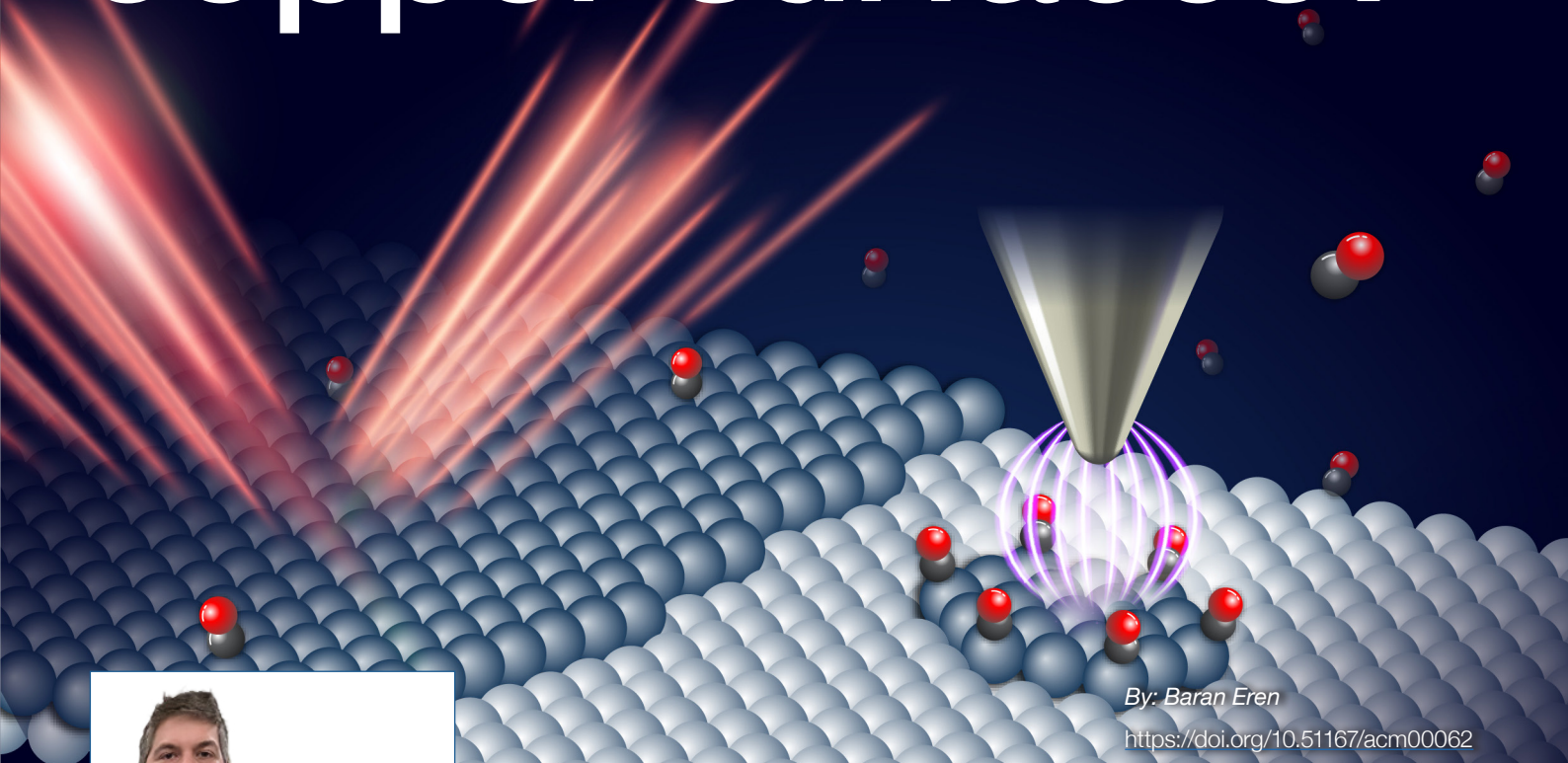


# How do small gas molecules interact with copper surfaces?



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Every material has boundaries, the last frontier of atoms that are separating the material from the matter or vacuum around it. These surface atoms are arranged differently than the rest of the atoms comprising the material. Therefore, the chemical and electronic properties of surface atoms and bulk atoms are disparate. The field of 'surface science' was conceptualized when over a century ago, this phenomenon intrigued the chemists and physicists of the time. Since then, a variety of experimental spectroscopy, microscopy, and scattering techniques have been developed to probe surfaces in their pristine, clean states, in highly rarefied vacuum conditions. Theoretical models and simulations have also been developed to provide a rationale for experimental observations. Thanks to these invaluable efforts, we have a deep understanding of the surfaces of solid materials at the atomic level.

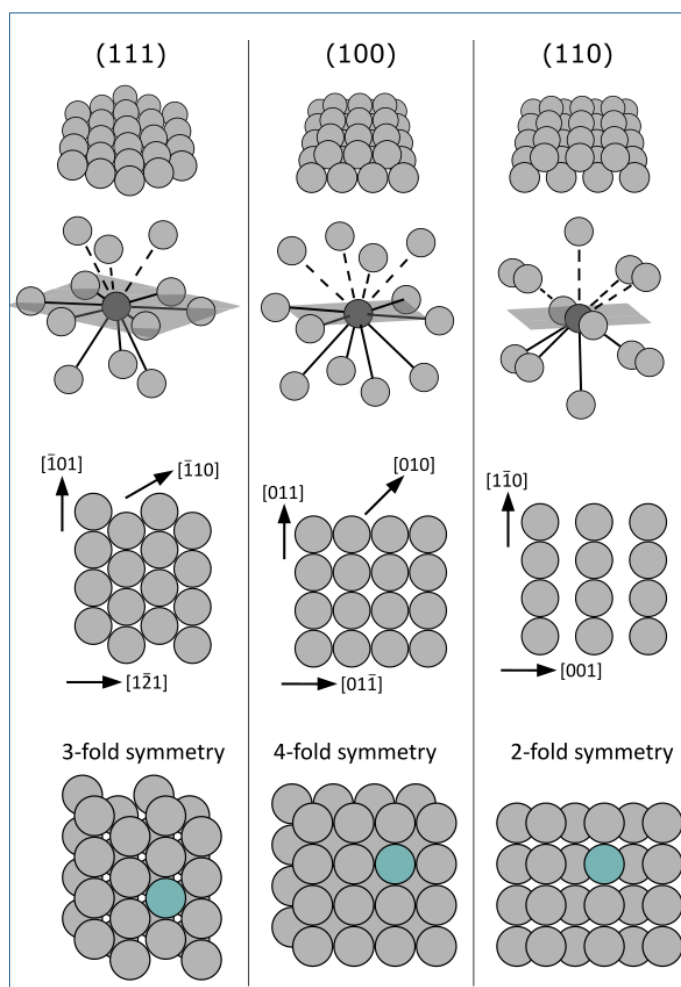
As opposed to materials measured under vacuum conditions, the surface atoms of materials exposed to ambient conditions are constantly interacting with the surrounding gas-phase or liquid-phase molecules. The surface atoms adapt to their surroundings and rearrange themselves accordingly, changing their chemical and electronic properties. This is one of the main motivations behind performing surface-sensitive experiments in ambient conditions of pressure and temperature. The importance of reaching relevant ambient conditions can be understood by considering the gas-phase chemical potential,  $\Delta\mu = kT \cdot \ln(p/p_0)$ , where  $T$  is temperature and  $p$  is pressure. This is equal to the adsorbate chemical potential in equilibrium. The change in free energy upon adsorption of gas-phase molecules to a surface is then  $\Delta G = \theta \cdot [E_b + T\Delta S_{ad} - \Delta\mu] + 2\Delta\gamma$ , where  $\theta$  is the adsorbate coverage in monolayers,  $E_b$  is the adsorbate binding energy (i.e., adsorption energy) which is always negative,  $\Delta S_{ad}$  is the entropy change for adsorption (note that  $\Delta S_{ad}$  is positive but the total  $\Delta S$  of the system that also includes gas-phase species is negative), and  $\Delta\gamma$  is the surface energy. For instance, the difference in chemical potential between the conditions used for studying model catalysts in ultra-high vacuum (UHV) and catalytic reactions under mild conditions (1 bar, 25 °C) can be as high as 0.7 eV. This energy difference is large enough to alter which chemical phases and surface structures are thermodynamically stable, as well as to lift certain kinetic limitations, thereby changing the reaction pathways.

We performed a series of studies on the interaction of small molecules such as carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and methanol (CH<sub>3</sub>OH) vapor with various copper (Cu) surfaces. Cu is a special transition metal in the sense that it has no d-states at the Fermi level, which significantly changes its interaction with adsorbed molecules (i.e., electron transfer from and to certain molecular orbitals are different). However, most molecules chemically interact with Cu surfaces (as opposed to a weaker physical interaction). This makes Cu a unique material and therefore, most of the surface phenomena observed on other metals cannot be extrapolated to Cu. From a technological standpoint, Cu-based catalysts are used in the conversion of syngas (synthesis gas, mixture of CO<sub>2</sub>, CO, and hydrogen) into methanol which is a value-added product. Cu-based catalysts are also used in methanol-to-hydrogen conversion reactions such as methanol partial oxidation or methanol stream reforming. Therefore, understanding the interaction between gases such as CO, CO<sub>2</sub> and CH<sub>3</sub>OH and various Cu surfaces is not only of academic interest, but is also highly relevant for chemical technologies.

CO usually adsorbs strongly on transition metals through the backdonation of electrons from the metal's d-states to the CO's 2π\* anti-bonding orbitals. The stronger the adsorption, the weaker the bond between carbon and oxygen becomes. The adsorption strength of CO on Cu is naturally weaker, but still involves electron transfer, making the bond chemical in nature. CO can only stay on Cu surfaces at low pressures (in the order of a micro-Torr and below) at cryogenic temperatures. At room temperature however, a high coverage can be obtained in equilibrium with a sufficiently high pressure (e.g., 0.1 Torr and above). We studied the interaction of CO with all three low Miller-index surfaces of Cu, which are the Cu(111), Cu(100), and Cu(110) surfaces. These are the most close-packed surfaces of Cu. A Cu atom on the surface is coordinated to 9, 8, and 7 different Cu atoms respectively (in comparison, a Cu atom in the bulk is coordinated to 12 other Cu atoms). These low-index surfaces are also the most commonly occurring facets of nanoparticles, nanocrystalline thin films, and polycrystalline foils, representing the configurations with the lowest surface energies (energy penalty for terminating the crystalline material is lowest). Additionally, these surfaces are highly symmetric. The Cu(111) surface has a 3-fold rotational symmetry (quasi-hexagonal), whereas the Cu(100) surface has a 4-fold rotational symmetry (square), and the Cu(110) surface has a 2-fold

rotational symmetry (rectangular). Figure 1 illustrates the differences between these three low-index surfaces. The adsorption energies of CO on Cu(111), Cu(100) and Cu(110) are 0.49 eV, 0.53 eV and 0.56 eV respectively, measured with thermal desorption spectroscopy.<sup>1</sup>

There are three techniques that are suitable to probe the changes occurring on Cu surfaces in the presence of gases. The first one is scanning tunneling microscopy (STM), which is a technique that can atomically resolve electrically conducting metal surfaces if they are atomically flat. This is the case for single crystals. The second technique is infrared (IR) spectroscopy in the reflection mode with grazing incidence. This is the ideal technique for identifying adsorbed molecules and their adsorption sites. It is also a non-invasive technique. The final technique is ambient pressure X-ray photoelectron spectroscopy (APXPS), which can be used to both detect changes in the chemical state of the surface and identify adsorbed species on the surface. In some cases, APXPS can be invasive, that is, the



**Figure 1.** Top panel: When a Cu crystal is cut along the (111), (100), and (110) planes 3, 4, and 5 neighboring Cu atoms respectively are removed from the topmost layer. This leads to coordination numbers of 9, 8, and 7 for the Cu(111), Cu(100), and Cu(110) surfaces, respectively. Middle panel: Different surface orientations along the (111), (100), and (110) planes. Bottom panel: Any atom on the surface exhibits 3-fold, 4-fold, and 2-fold rotational symmetries for the Cu(111), Cu(100), and Cu(110) surfaces, respectively. Note that the second layer has to be included in order to illustrate this symmetry for the Cu(111) surface (it would appear to have 6-fold symmetry without the second layer). These crystallographic properties are true not only for Cu, but for any other face-centered cubic (fcc) material that is not reconstructed.

photoionized gas molecules or the secondary electrons created inside the material can affect the surface chemistry. These are not severe issues for studies with single crystals since the X-ray beam can be defocused. Furthermore, the X-ray spot on the sample can be changed in between data acquisition to mitigate these issues.

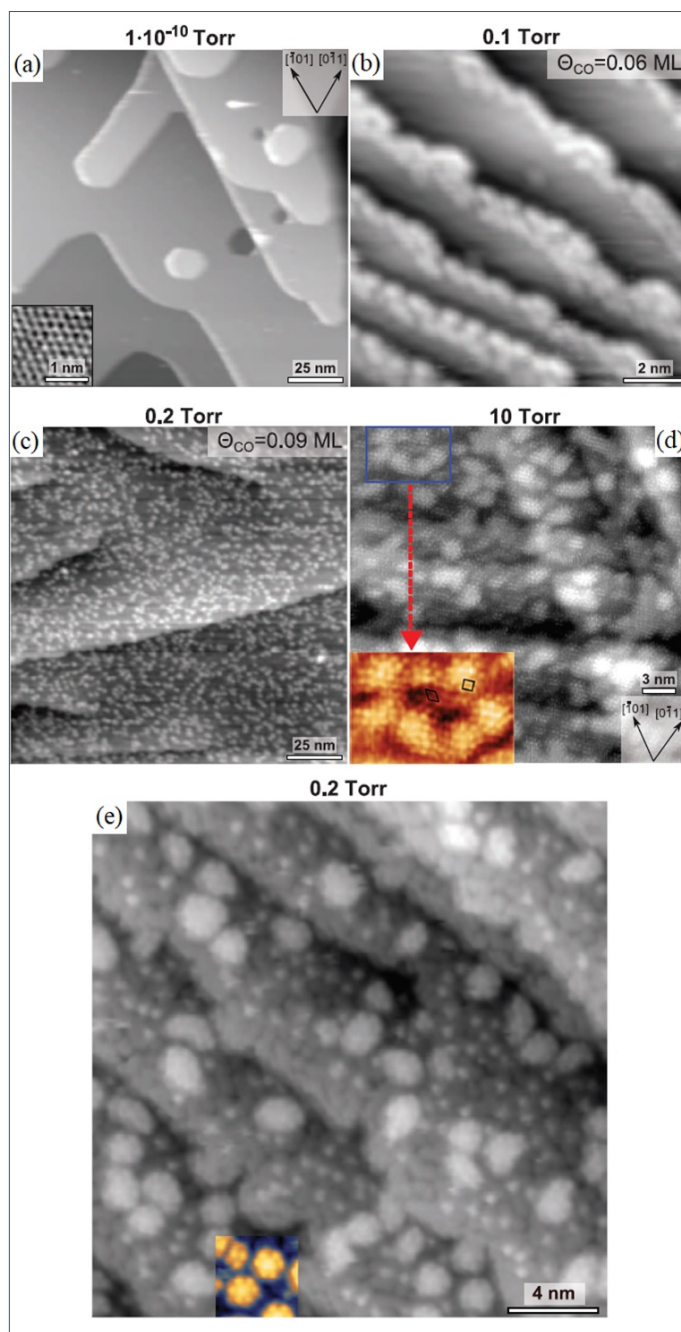
The most common structure of an adlayer of CO molecules forming on Cu(111) at low temperatures is the  $(\sqrt{3}\times\sqrt{3})R30^\circ$  structure.<sup>2</sup> (This is Wood's notation; it indicates a unit cell of CO molecules that is  $\sqrt{3}\times\sqrt{3}$  larger than the unit cell of Cu atoms and rotated by  $30^\circ$ ). However, there is a plethora of different condensed and dilute CO adlayer structures on the Cu(111) surface which depend on the dose and sample temperature.<sup>2-3</sup> In our STM study at ambient CO pressures at room temperature, we found that the Cu(111) surface behaves very differently when it is exposed to CO gas at ambient pressures than in UHV, as Figure 2 illustrates.<sup>4</sup> An image of a clean Cu(111) surface in UHV is presented in Figure 2a, together with an atomically resolved image of the terrace in the inset. Such a surface consists of flat terraces that are separated by step edges, typically atomically thick. Following the introduction of 0.1 Torr CO into the chamber, a new structure is observed along the step edges, while the rest of the terrace remains atomically flat (Figure 2b).<sup>4</sup> At 0.2 Torr, a very striking phenomenon takes place: the terraces are covered with clusters of Cu atoms (Figure 2c), which increase in number with increasing CO pressure. For instance, above 10 Torr the clusters nearly completely fill the surface as shown in Figure 2d. These clusters are densely covered by CO molecules, imaged as bright spots with the STM. The CO molecules are separated by distances of  $\sqrt{3}$  and 2 times the atomic periodicity of Cu, and are aligned in directions forming 60 and 90 degrees between them. These bright spots can be interpreted as arising from atop CO molecules in local  $(2\times 2)$ -3CO and  $c(4\times 2)$  (in Wood's notation) geometries and coverages of 0.75 and 0.5 monolayers, respectively. Figure 2e shows a magnified image of the surface in the presence of 0.2 Torr CO at room temperature. The surface consists of small metal clusters formed by Cu atoms. A roughly bimodal size distribution is apparent, larger hexagonal-like shaped clusters with  $\sim 1.5$  nm diameter and smaller poorly resolved triangular shaped clusters with  $\sim 0.5$  nm diameter. The larger clusters are assigned to 19-Cu-atom clusters that form hexagonal structures. The formation of 19-atoms is not random; in fact, 19-Cu-atom clusters are often observed in homoepitaxy of Cu atoms on Cu(111).

The phenomenon described above was novel for its time, as this was the first time that a complete break-up of a compact (111) surface was shown. Prior to this, there were reports of similar phenomena taking place on nanoparticles or vicinal surfaces, but never on a (111) surface. Instead, a dense layer of adsorbed molecules was observed on (111) surfaces. It turns out, that Cu is special in the sense that it has a low cohesive energy, i.e., the bond between neighboring Cu atoms is weaker than that in most other metals. This makes Cu atoms at the step edges and other low-coordinated sites already mobile at room temperature, and thus more readily available to reconstruct into clusters. In other words, the kinetic barrier for breaking the surface into clusters is low for Cu. Kinetics is only half of the story; the formation of clusters should also be energetically preferred for it to take place. (Technically, if the energetics of clustered and flat surfaces are similar, cluster formation will still be thermodynamically preferred, due to entropy). Density functional theory (DFT) indeed predicts that adsorption of CO molecules to each Cu atom at the periphery of the clusters results in net energy. The driving force here is the gain in energy by adsorbing CO to the newly formed under-coordinated sites, which overcomes the energy penalty to detach the Cu atoms from the steps and form the clusters. We also found that the clusters are not static with time, but they undergo changes by means of coalescing with other clusters or by adding atoms as well as splitting in two in time scales of minutes, as evidenced with time-lapse STM

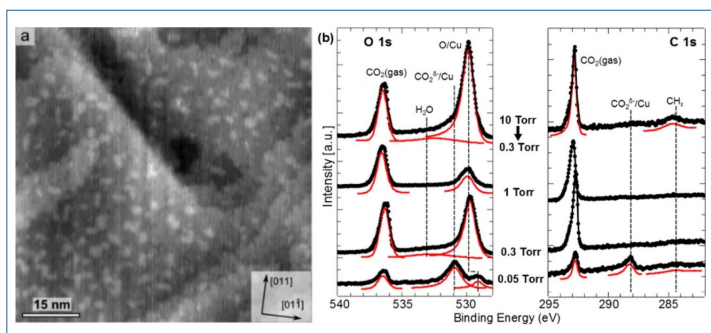
images that could be captured due to the slow kinetics of the process at room temperature.<sup>4</sup>

We performed similar studies on the Cu(100) and Cu(110) surfaces as well, which behave similar to

the Cu(111) surface in the presence of CO gas at room temperature. According to studies in UHV and at cryogenic temperatures, CO forms a dense  $(\sqrt{2}\times\sqrt{2})$  adlayer on Cu(100).<sup>5</sup> However, at Torr pressures of CO and at room temperature, CO breaks up the Cu(100)



**Figure 2.** (a) STM image of the bare Cu(111) surface. STM image of the Cu(111) surface in the presence of (b) 0.1 Torr CO, (c,e) 0.2 Torr CO, and (d) 10 Torr CO. All images were acquired at room temperature. The STM images show the breaking up of the Cu(111) surface into clusters as a function of CO pressure. The hexagonal 19-atom clusters can be seen in (e), and they are visually clearer in the two-color contrast used in the inset. Reproduced with permission from Ref.<sup>4</sup>. Copyright 2016 American Association for the Advancement of Science.



**Figure 3.** (a) STM image of the Cu(100) surface in the presence of 20 Torr CO<sub>2</sub> at room temperature. The surface breaks up into clusters, roughly half of them with edges oriented along the <011> directions. In comparison, the step edges of the clusters were oriented along the <001> directions in the presence of CO. (b) O 1s and C 1s regions of the APXPS spectra in the presence of CO<sub>2</sub> at room temperature on the Cu(100) surface at various pressures. The peaks above 536 and 292 eV are from gas-phase CO<sub>2</sub>. CO<sub>2</sub> adsorbs as CO<sub>2</sub><sup>δ-</sup> and produces the peaks at 531.4 and 288.4 eV. The atomic oxygen peak appears at ~529.8 eV. CH<sub>x</sub> and water contamination produce the peaks at 284.2–284.7 and 532.5–533.0 eV, respectively. The former typically appears in the absence of atomic oxygen, and the latter typically appears in the presence of atomic oxygen on the surface. Reproduced with permission from Ref.<sup>10</sup>. Copyright (2016) American Chemical Society.

surface into rectangular clusters, with the smallest cluster consisting of 5 atoms.<sup>6</sup> Similar to Cu(111), the clusters increase in size and number when the CO pressure is increased. In fact, the small clusters coalesce into nanoclusters a few nanometers long and 3-atoms wide that are fully covered with adsorbed CO molecules.<sup>6</sup> Most of the one-dimensional nanoclusters are separated from each other by roughly 1 nm, due to steric repulsion. The Cu(110) surface also breaks up into clusters, but less rigorously compared to the Cu(111) and Cu(100) surfaces.<sup>7</sup> This is because the coordination number of the Cu(110) surface is lower than that of the other two surfaces. Hence, on the Cu(110) surface CO adsorption to the surface atoms is stronger and there is less energy gain in the creation of more low coordinated Cu atoms. Cu(110) surfaces restructure into short (1–3 nm) linear clusters separated by two lattice distances when exposed to 1 Torr pressure range at room temperature.<sup>7</sup>

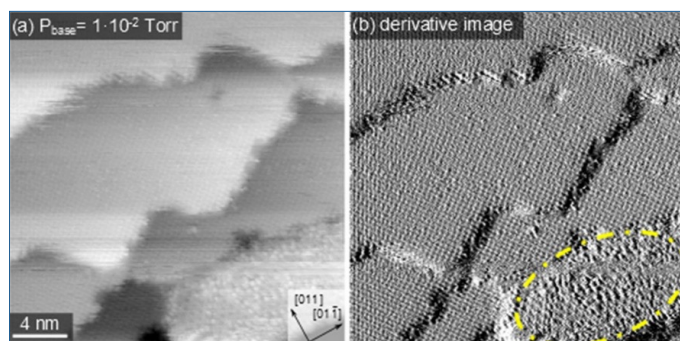
Thus far we have shown that all three low-index surfaces of Cu break up into clusters in the presence of CO at room temperature. This has led to phenomenological and theoretical studies predicting which other metals should break up into clusters in the presence of CO<sup>8-9</sup>. For instance, although palladium also has a relatively low cohesive energy, there is not much of an energy difference between the CO adsorption energies on flat terraces and step edges. In other words, clustering is not thermodynamically favored since not enough energy is gained through CO adsorption to palladium to compensate for the breaking of metal-metal bonds during cluster formation. On platinum, the CO adsorption energy on newly formed platinum clusters may compensate for the energy penalty for breaking metal-metal bonds. However, platinum has a high cohesive energy, so even if clustering is thermodynamically favored, the kinetic barrier for clustering is high. This means that higher temperatures and pressures (i.e., higher chemical potential) are needed for clustering to occur on platinum.

CO is an excellent choice of adsorbate for studying the clustering of metals because it adsorbs associatively with a reasonable adsorption strength on most transition metals. Moreover, there is

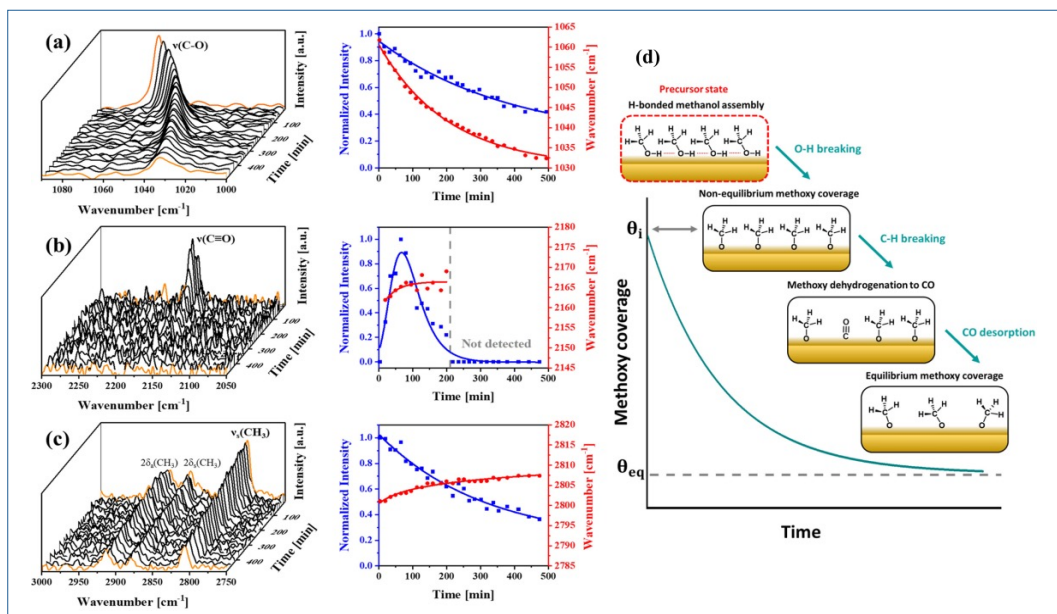
vast surface science literature available on CO adsorption which can be used as reference material. It would be interesting to learn if other gases can break up Cu surfaces and induce clustering. Many small molecules adsorb dissociatively on metal surfaces at ambient conditions, as they either have enough energy to overcome the activation barrier for dissociation or dissociation is a non-activated process. For instance, CO<sub>2</sub> and CH<sub>3</sub>OH vapor both adsorb dissociatively on Cu surfaces, as we observed in the studies described below.

CO<sub>2</sub> is a linear molecule. Upon its adsorption on metal surfaces, charge transfer from the metal forms anionic bent CO<sub>2</sub><sup>δ-</sup>. In the presence of 1 Torr CO<sub>2</sub>, the Cu(100) surface becomes covered with a fraction of a monolayer of atomic oxygen. The atomic oxygen originates from the dissociation of CO<sub>2</sub> on the surface, as evidenced by the APXPS spectra and from the appearance of dark spots formed by O atoms in the STM images.<sup>10</sup> Once the CO<sub>2</sub> pressure is increased to 20 Torr, the terraces become covered with clusters, with roughly half of their edges oriented along the <011> orientations and the other half showing no preferential orientation (Figure 3a).<sup>10</sup> We think that the formation of clusters in the presence of CO<sub>2</sub> is likely driven by the energy gained from the binding of oxygen atoms generated by the dissociation of CO<sub>2</sub>, and from the CO adsorbed on the step edges, which favors the detachment of Cu atoms. However, CO does not remain attached to the clusters at room temperature due to its low binding energy and only the atomic oxygen remains on the surface. The surface in Figure 3a is in fact covered with atomic oxygen that originates from CO<sub>2</sub> dissociation, as evidenced from the APXPS results (Figure 3b). The O 1s and C 1s regions of the XPS spectra obtained on Cu(100) in the presence of CO<sub>2</sub> at room temperature are shown in Figure 3b. While some CO<sub>2</sub><sup>δ-</sup> was observed at 0.05 Torr, indicating molecular adsorption, remarkably no CO<sub>2</sub><sup>δ-</sup> was detected on the Cu(100) surface at 0.3 Torr and above. In contrast, the atomic oxygen coverage increases with CO<sub>2</sub> pressure. These results show that no CO<sub>2</sub> can adsorb on a Cu surface after it is covered with atomic oxygen, generated through CO<sub>2</sub> dissociation. This is self-poisoning, and it might explain the need for CO in the industrial feed for CO<sub>2</sub> hydrogenation, since it removes oxygen from the surface. In fact, in a later study, we establish this proposed role of CO as a scavenger during CO<sub>2</sub> hydrogenation on Cu.<sup>11</sup> We explain this study in more detail below.

Unlike the case of CO and CO<sub>2</sub>, no clustering of the Cu(100) surface was observed in the presence of methanol vapor.<sup>12</sup> STM images taken in the presence of 0.01–0.2 Torr CH<sub>3</sub>OH at room temperature show a ( $\sqrt{2} \times \sqrt{2}$ )R45° adlayer structure (Figure 4). This is due to a methoxy



**Figure 4.** (a) STM image of the Cu(100) surface in the presence of 0.01 Torr methanol vapor at room temperature. (b) Derivative image of (a) to enhance the contrast on the terraces. Most of the surface exhibits a ( $\sqrt{2} \times \sqrt{2}$ )R45° structure due to adsorbed methoxy, except for the area inside yellow ellipse. Reproduced with permission from Ref.<sup>12</sup>. Copyright (2018) American Chemical Society.



**Figure 5.** Temporal evolution of IR spectra on Cu(111) at 50 °C following 0.7 Torr methanol vapor exposure: (a) 1000–1090  $\text{cm}^{-1}$ , (b) 2050–2300  $\text{cm}^{-1}$ , and (c) 2750–3000  $\text{cm}^{-1}$ . The peak positions (red circles) and relative intensities (blue squares) of  $\nu(\text{C}-\text{O})$ ,  $\nu(\text{C}=\text{O})$ , and  $\nu_s(\text{CH}_3)$  (top to bottom) versus time are plotted on the right-hand side. (b) Schematic presentation of the proposed model for the evolution of methoxy coverage ( $\theta$ ) and surface intermediates with time. Note that the precursor state is not directly observed as it is a short-lived state. Other states are modelled with respect to our observation and interpretation of the IR spectra. Reproduced from Ref.<sup>15</sup>, which is licensed under Creative Commons.

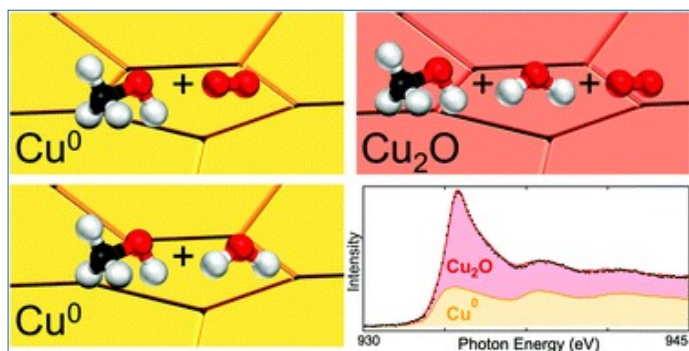
saturated surface, as shown by APXPS.<sup>12</sup> Sum frequency generation studies in Ref.<sup>13</sup> also suggest that polycrystalline Cu foils are covered with methoxy in the presence of methanol vapor. The absence of cluster formation could be explained by the small difference in the adsorption energy of methoxy on cluster edges compared to on terraces, which is not sufficient to compensate for the energy cost required for the detachment of Cu atoms necessary to form clusters. Methoxy adsorption energies calculated by DFT in the literature vary widely, but a study comparing the adsorption energies on terraces and step edges predicts very similar energies,<sup>14</sup> which supports the lack of cluster formation in the presence of methanol.

Using IR spectroscopy, we conducted a comprehensive study of the interaction of methanol with the three low-index Cu surfaces, Cu(111), Cu(100) and Cu(110).<sup>15</sup> Figures 5a-c show the temporal evolution of the IR data of a Cu(111) surface at 50 °C and under 0.7 Torr  $\text{CH}_3\text{OH}$  pressure. Similar data was acquired at 25 °C, 75 °C, and 100 °C on Cu(111), as well as on Cu(100) and Cu(110). Plots of the frequency and the normalized intensity of the various bond-stretching vibrations,  $\nu(\text{C}-\text{O})$ ,  $\nu(\text{C}=\text{O})$ , and  $\nu_s(\text{CH}_3)$  are illustrated on the right-hand side of each set of spectra.  $\nu(\text{C}-\text{O})$  and  $\nu_s(\text{CH}_3)$  are due to adsorbed methoxy ( $\text{CH}_3\text{O}-\text{Cu}$ ), a product of dissociative  $\text{CH}_3\text{OH}$  adsorption.  $\nu(\text{O}-\text{H})$  is absent, as methoxy formation requires cleaving the O-H bond.  $\nu(\text{C}=\text{O})$  is the stretching mode of adsorbed CO molecule. The  $\nu(\text{C}-\text{O})$  frequency exponentially decreases in  $\sim 500$  min, while the intensity drops by  $\sim 60\%$ , indicating that the surface coverage of methoxy decreases with time. The intensity and frequency trends of the C-H vibrational modes also supports this interpretation (Figure 5c). We suggest that the initially formed methoxy coverage is higher than the equilibrium coverage under these temperature and pressure conditions. The mechanism behind the decreasing methoxy coverage can be understood by analyzing the  $\nu(\text{C}-\text{O})$  peak position and the temporal evolution of an additional band at  $\sim 2165$   $\text{cm}^{-1}$  (Figure 5b), which we assign to CO coadsorbed on methoxy. The peak for chemisorbed CO usually appears at 2070–2080  $\text{cm}^{-1}$ . This means that the peak position of the CO produced through methanol

dehydrogenation is roughly 90  $\text{cm}^{-1}$  higher compared to that of chemisorbed CO on bare Cu(111). When CO is adsorbed on the cationic sites of oxides through  $\sigma$ -bonding, its stretching frequency is observed at higher values than the stretching frequency of the free CO molecule, which is a purely electrostatic effect. Although Cu is metallic, we think that methoxy can draw significant amounts of electrons from the surface atoms. We believe that this is the main reason behind such a significant blueshift in  $\nu(\text{C}=\text{O})$ . Since CO is relatively weakly adsorbed on Cu surfaces, its lifetime on the surface at ambient methanol pressures and ambient temperatures is limited, and it eventually desorbs to the gas phase. Hence, the peak-like profile of  $\nu(\text{C}=\text{O})$  intensity (Figure 5b, right), which can be derived from the balance between CO production from methoxy dehydrogenation and CO desorption. Following the  $\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CHO} \rightarrow$

CO reaction pathway, the three C-H bonds break in a stepwise manner via formaldehyde ( $\text{CH}_2\text{O}$ ) and formyl ( $\text{CHO}$ ) intermediates. These results indicate that a high temperature-independent coverage layer of methoxy rapidly forms after the exposure of methanol to Cu surfaces. This transient coverage of methoxy is higher than the equilibrium coverage at this temperature, and thus partial desorption of methoxy occurs with time via dehydrogenation into CO. Eventually, a temperature-dependent equilibrium coverage is reached. This behavior cannot be described by standard models of adsorption, which predict that the coverage evolution with time will rapidly increase. Therefore, we propose a mechanistic model that explains the initial formation of a metastable methoxy layer by considering the preliminary adsorption of a methanol precursor in the form of compact H-bonded assemblies. Figure 5d illustrates our model. Finally, the kinetics of methoxy dehydrogenation on the three Cu surfaces reveals a remarkable structure-sensitivity, with Cu(110) being much more active than Cu(111) and Cu(100).

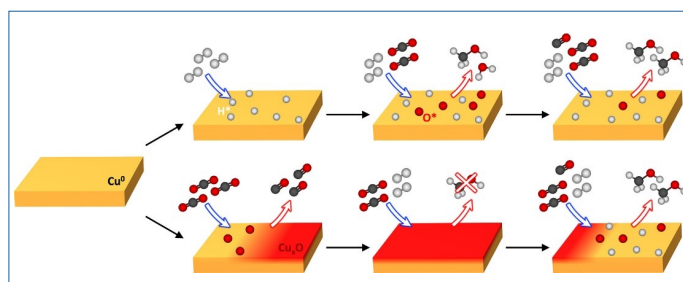
So far, we have discussed how small molecules such as CO,  $\text{CO}_2$ , and  $\text{CH}_3\text{OH}$  adsorb on Cu surfaces. Here, we would like to briefly mention two of the reaction studies we performed involving these molecules.<sup>11,16</sup> In the first study, we investigated methanol conversion on relatively more active polycrystalline Cu surfaces.<sup>16</sup> Four chemical processes can be used to produce hydrogen from methanol: methanol decomposition ( $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$ ), methanol partial oxidation ( $\text{CH}_3\text{OH} + 0.5\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2$ ), methanol steam reforming ( $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$ ), and autothermal methanol reforming (oxidative steam reforming). Using a sample temperature of 200 °C and reactant pressures of a few tenths of a Torr, we reveal that the surface remains highly metallic in the presence of methanol vapor and oxygen, even at equal partial pressure ratio conditions. However, once water vapor is added to the gas admixture, the surface begins to oxidize towards  $\text{Cu}_2\text{O}$ . We attribute this to a shift in the  $\text{CH}_3\text{OH}-\text{Cu} + \text{O}-\text{Cu} \rightleftharpoons \text{CH}_3\text{O}-\text{Cu} + \text{OH}-\text{Cu}$  equilibrium on the surface towards the left-hand side, as adsorbed OH is readily available on the surface due to the presence of water vapor (Figure 6). As a result, when all three gases



**Figure 6.** Schematic showing how Cu remains metallic in the presence of mixtures of methanol and O<sub>2</sub> and methanol and water, but oxidizes when all three gases are present. Reproduced with permission from Ref.<sup>16</sup>. Copyright (2020) Royal Society of Chemistry.

are present, the ongoing removal of atomic oxygen from the surface through reaction with methanol is suppressed and the oxidation of the Cu surface is promoted. In addition, under these reaction conditions we detect reaction intermediates such as methoxy, formate, hydroxyl, atomic oxygen, and lattice oxygen with AP-XPS. In the second study, we investigated unsupported Cu catalysts using a combination of APXPS and atmospheric-pressure X-ray absorption spectroscopy (Atm-XAS) bridging pressures from 0.07 Torr to 1 bar.<sup>11</sup> We tracked how the atomic oxygen coverage and catalyst oxidation state evolved with the composition of the reaction feed at temperatures (200 °C) and pressures (up to 1 bar) more representative of industrial methanol synthesis than any prior interface-sensitive studies. For metallic Cu surfaces exposed to H<sub>2</sub>, the addition of a similar CO<sub>2</sub> partial pressure leads to the formation of atomic oxygen, confirming that CO<sub>2</sub> activation is taking place. Ongoing H<sub>2</sub> activation regulates the atomic oxygen coverage and suppresses Cu oxidation. However, at high relative CO<sub>2</sub> partial pressures, excess atomic oxygen leads to Cu oxidation, poisoning the surface against CO<sub>2</sub> and H<sub>2</sub> activation. On removing CO<sub>2</sub>, a metallic Cu surface is not recovered, indicating a high kinetic barrier for H<sub>2</sub> activation on Cu<sub>2</sub>O. Mass spectrometry measured at 1 bar corroborated Cu deactivation following CO<sub>2</sub> exposure without H<sub>2</sub> present: A lower H<sub>2</sub>O signal is observed when H<sub>2</sub> is reintroduced, indicating that the CO<sub>2</sub> hydrogenation and reverse-WGS (RWGS) reactions are suppressed. When CO is added to the feed, recovery of metallic sites is possible. These sites are most active for CO<sub>2</sub> and H<sub>2</sub> activation, allowing methanol generation to proceed. Figure 7 summarizes our findings in this study. These findings highlight the important function of CO in industrial methanol synthesis from CO<sub>2</sub>-rich feeds, where it serves as a scavenger for adsorbed oxygen preventing saturation of the catalytically active Cu sites and making the process more robust to variations in reaction conditions.

CO<sub>2</sub> is a greenhouse gas as it absorbs and emits IR light at its IR-active vibrational frequencies, which warms the surface of the Earth and the lower atmosphere. In addition to optimizing the existing industrial processes and transitioning to renewable sources of energy, the search for feasible and effective methods for the utilization of CO<sub>2</sub> warrants particular attention. Methanol synthesis by hydrogenation of CO<sub>2</sub> offers a means of utilizing captured CO<sub>2</sub> that, when combined with on-board methanol-to-hydrogen conversion in vehicles, yields net zero carbon emissions, considering the required energy input comes from renewable sources. This is the so-called 'methanol economy' envisaged by the late great chemist George Olah.<sup>17</sup> Our reaction studies provide a basic understanding of the surface processes occurring on Cu surfaces during both CO<sub>2</sub> hydrogenation and methanol-to-hydrogen conversion reactions.



**Figure 7.** Schematic illustration of the proposed reaction pathways on a Cu substrate exposed to H<sub>2</sub>, CO<sub>2</sub>, and CO. The top row represents the pathway that occurs when H<sub>2</sub> is dosed first, while the bottom row represents the pathway that occurs when CO<sub>2</sub> is dosed first. Reproduced from Ref.<sup>11</sup>, which is licensed under Creative Commons.

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