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Tuning the Properties of Copper-Based Catalysts Based on Molecular in Situ Studies of Model Systems

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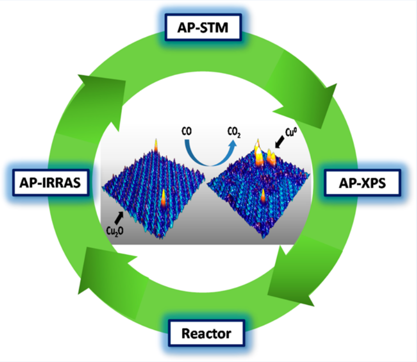

CONSPECTUS: Studying catalytic processes at the molecular level is extremely challenging, due to the structural and chemical complexity of the materials used as catalysts and the presence of reactants and products in the reactor's environment. The most common materials used on catalysts are transition metals and their oxides. The importance of multifunctional active sites at metal/oxide interfaces has been long recognized, but a molecular picture of them based on experimental observations is only recently emerging. The initial approach to interrogate the surface chemistry of catalysts at the molecular level consisted of studying metal single crystals as models for reactive metal centers, moving later to single crystal or well-defined thin film oxides. The natural next iteration consisted in the deposition of metal nanoparticles on well-defined oxide substrates. Metal nanoparticles contain undercoordinated sites, which are more reactive. It is also possible to create architectures where oxide nanoparticles are deposited on top of metal single crystals, denominated inverse catalysts, leading in this case to a high concentration of reactive cationic sites in direct contact with the underlying fully coordinated metal atoms. Using a second oxide as a support (host), a multifunctional configuration can be built in which both metal and oxide nanoparticles are located in close proximity. Our recent studies on copper-based catalysts are presented here as an example of the application of these complementary model systems, starting from the creation of undercoordinated sites on Cu(111) and $Cu_2O(111)$ surfaces, continuing with the formation of mixed-metal copper oxides, the synthesis of ceria nanoparticles on Cu(111) and the codeposition of Cu and ceria nanoparticles on $TiO_2(110)$. Catalysts have traditionally been characterized before or after reactions and analyzed based on static representations of surface structures. It is shown here how dynamic changes on a catalyst's chemical state and morphology can be followed during a reaction by a combination of in situ microscopy and spectroscopy. In addition to determining the active phase of a catalyst by in situ methods, the presence of weakly adsorbed surface species or intermediates generated only in the presence of reactants can be detected, allowing in turn the comparison of experimental results with first principle modeling of specific reaction mechanisms. Three reactions are used to exemplify the approach: CO oxidation ($CO + 1/2O_2 \rightarrow CO_2$), water gas shift reaction (WGSR) ($CO + H_2O \rightarrow CO_2 + H_2$), and methanol synthesis ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$). During CO oxidation, the full conversion of Cu^0 to Cu^{2+} deactivates an initially outstanding catalyst. This can be remedied by the formation of a $TiCuO_x$ mixed-oxide that protects the presence of active partially oxidized Cu^+ cations. It is also shown that for the WGSR a switch occurs in the reaction mechanism, going from a redox process on Cu(111) to a more efficient associative pathway at the interface of ceria nanoparticles deposited on Cu(111). Similarly, the activation of CO_2 at the ceria/Cu(111) interface allows its facile hydrogenation to methanol. Our combined studies emphasize the need of searching for optimal metal/oxide interfaces, where multifunctional sites can lead to new efficient catalytic reaction pathways.

1. INTRODUCTION

To understand heterogeneous catalytic processes at the molecular level, the field of surface science introduced the use of atomically "smooth" single crystals under pristine ultrahigh vacuum (UHV) conditions.[1,2] Transition metals are regarded as the most critical component on most catalysts. Oxides are generally considered to serve as high surface area substrates on which to disperse the metal nanoparticles. It is clear that this is not the only function of oxides. The study of model oxides was initiated at a later stage due to inherent complications related to the materials. They can adopt a much richer number of structures, and in many cases cannot be studied with electron based techniques due to their insulating nature. The growth of atomically resolved thin film oxides on conducting substrates has solved in many cases this shortcoming.[3,4] Synergistic effects between metal and oxide sites were discussed earlier on, in particular the formation of special multifunctional sites at metal/oxide interfaces.[5−7] But interrogating these special interfacial sites experimentally is

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challenging. There has also been considerable progress in the development and use of surface science techniques to follow catalytic reactions in situ. Photon-in/photon-out techniques, such as IR and sum frequency spectroscopy,[8] were used early on, but photoelectron spectroscopic techniques, where electrons interact strongly with the reactants in the gas phase, took much longer to become widely available.[9] Electron based structural techniques, such as scanning tunneling microscopy (STM), are still only available in a limited number of laboratories.[10−12] To show an example of how the use of complementary in situ techniques including ambient pressure (AP) X-ray photoelectron spectroscopy (AP-XPS), infrared reflection absorption spectroscopy (AP-IRRAS), and AP-STM can be applied to study complex model catalysts, we present here a review based on our recent published work at Brookhaven National Laboratory (BNL) on copper-based catalysts. Due to their natural abundance and catalytic properties, copper-based catalysts are widely used in major industrial processes, and are actively being investigated for new applications, such as for the replacement of noble metals on three-way catalytic convertors. In addition to copper single crystals, model catalytic systems include supported Cu metal nanoparticles,[13−15] inverse catalysts [MO_x/Cu(111)],[16,17] and mixed oxides MO_x/Cu_2O.[18] In sections 2 and 3, it will be described how the complementary set of in situ techniques can be used to track changes on catalysts under reducing environments. In section two it is shown how the interaction of hydrogen with copper can reconstruct the surface and influence the coordination number (CN) of exposed sites and their reactivity. In section three it is shown how the interaction of Cu_2O(111) films with CO leads to the formation of highly active transient structures with both metal nanoparticles and reduced cuprous oxide in direct contact. In sections 4 and 5, three reactions involved in the oxidation and reduction of carbon oxides are presented: (I) the CO oxidation by oxygen on plain copper and a mixed-oxide $CuTiO_x$ film, (II) the CO oxidation by water in the water gas shift reaction (WGSR) on inverse ceria/Cu(111) catalysts, and (III) the reduction of CO_2 to methanol by hydrogen on ceria/Cu(111) and Cu/CeO_x/TiO_2(110) catalysts. In the final section, the conclusions of the overview are included.

2. CHEMICAL ANNEALING OF UNDERCOORDINATED COPPER SITES

The active metal nanoparticles present on catalysts contain a variety of adsorption sites, with a significantly higher number of undercoordinated atoms than those on a model flat Cu(111) surface. Therefore, investigating the adsorption of molecules on a controlled number of defect sites on Cu(111) and monitoring the dynamic morphological changes during adsorption/desorption processes can help us to understand processes under catalytic reaction conditions. The interaction between molecules and sites with a lower number of metal neighbors increases. CO is widely used as a probe molecule to characterize catalyst's surfaces due to its very intense IR signal and its sensitivity to changes in local environments and adsorption sites. Table 1 shows a compilation of the observed frequency shifts in IRRAS spectra taken during the adsorption of CO on copper samples presenting sites with CNs: 6−9.[15,19,20] It is observed that the lower the CN of a copper site, the higher the IR frequency of the adsorbed CO molecule.

Table 1. CO Stretch IR Frequency on Copper Sites (See References in Text)

sample	CN	wavenumber (cm^{-1})
Cu(111)	9	2071
Cu(100)	8	2085
Cu(110)	7	2091
Cu(211)	6	2100
Cu/SiO_2/Mo(110)	particle	2106

In order to study the effect from the adsorption and absorption of hydrogen on the morphology of Cu surfaces, we prepared nanopitted Cu(111) surfaces, with pits from one to several atomic layers.[21] Figure 1A shows the nanopits created on a Cu(111) sample by gentle sputtering of the surface. Figure 2a shows the formation of sites with a low CN = 6 on the nanopitted Cu(111), tested by using CO as a probe molecule. No changes on the pits were observed when this surface was exposed to molecular H_2 up to pressures of 1 atm at 300 K. When the pitted surface is exposed to atomic hydrogen at 300 K, full reconstruction of the surface is observed even under small exposures (Figure 1B−D). The presence of hydrogen on the surface can be detected spectroscopically by IRRAS.[22] Upon adsorption of hydrogen at low temperatures (160 K) on the pitted Cu(111) surface, a feature is observed at 1144 cm^{-1} (Figure 2b), which is associated with adsorbed Cu−H as previously reported on smooth Cu(111). Using CO as a probe molecule, it can be determined that CO can coexist with H on the surface (Figure 2c), but that the CO coverage is lower than that on the clean surface and that the sites with under-coordinated surface copper atoms have disappeared. Annealing of the surface with CO and H to 200 K results in the complete desorption of CO and the disappearance of surface H (Cu−H) (Figure 2d). At 200 K, atomic H migrates to subsurface sites, leading to the formation of a thin copper hydride (CuH) layer.[22] CO can be used once more as a probe molecule to test

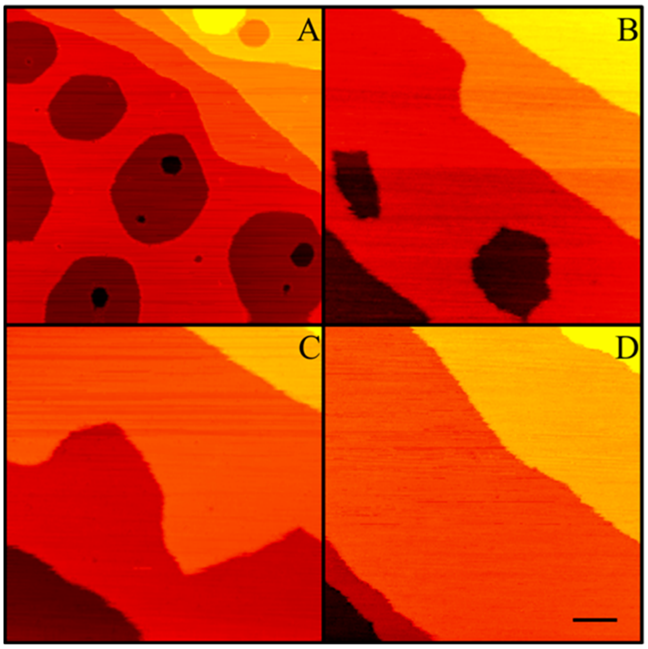

Figure 1. STM images of the pitted-Cu(111) surface before and after atomic hydrogen treatment at 300 K. (A) Pitted-Cu(111) surface as prepared; (B−D) exposure to increasing amounts of atomic hydrogen. Scale bar = 15 nm; 0.51 nA, 1.00 V. Reproduced with permission from ref 21. Copyright 2015 the PCCP Owner Societies.

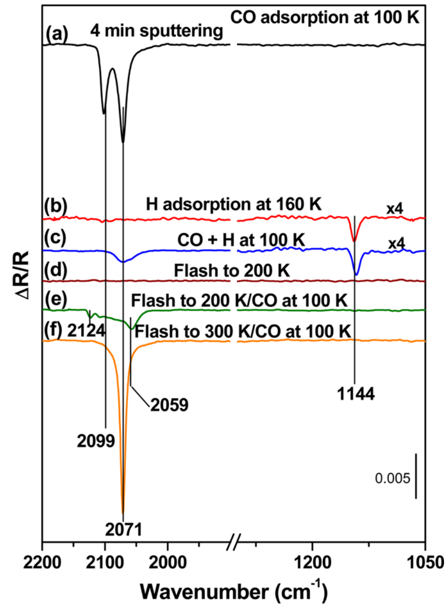

Figure 2. IRRA spectra collected: (a) after saturation of CO on pitted-Cu(111); (b) adsorption of H at 160 K; (c) coadsorption of CO on the system in (b); (d) after annealing of the system in (c) to 200 K; (e) after readsorption of CO on the system in (d); (f) after the annealing of the system in (e) to 300 K followed. Reproduced with permission from ref 21. Copyright 2015 the PCCP Owner Societies.

the formation of the thin copper hydride layer as shown in the spectrum of Figure 2e. The IR feature observed at 2059 cm^{-1} and accompanied by several small peaks at higher frequencies is indicative of the appearance of a CuH layer. All the hydrogen present on the Cu(111) surface can be desorb by annealing to 300 K, as proven by TPD experiments (not shown). After annealing to 300 K the Cu(111) surface and readsorbing CO at low temperature, it is shown in Figure 2f that the interaction of atomic hydrogen with the pitted-Cu(111) has completed healed the surface.

To understand the mechanism for the healing process induced by atomic hydrogen, we can first refer to the interaction of hydrogen with bulk copper. Bulk copper hydride (CuH) forms a hexagonal structure. We can then infer that the reconstruction of our heterogeneous nanopitted Cu(111) surface in the presence of atomic hydrogen proceeds by the formation of a thin surface hydride with a hexagonal structure, which upon desorption of the hydrogen fully relaxes to the hexagonal structure of the bulk crystal Cu(111). These adsorbate-driven morphological changes occur ~150 K below the temperature required to remove the roughness of the pitted-Cu(111) by simply annealing in vacuum. These results highlight the importance of investigating the properties of the adsorption sites in the presence of adsorbates or under reaction conditions to identify dynamically formed active phases.

3. CHEMICAL RESTRUCTURING OF Cu_2O

Cu(111) can be easily oxidized at 300 K, producing an amorphous Cu_2O layer.[23] A well-ordered $Cu_2O(111)$ film with a strained hexagonal network structure can be formed by annealing to elevated temperatures.[24] The $Cu_2O(111)$ film can be reduced during long exposures to moderate pressures of CO.[25] During the process of growing the $Cu_2O(111)$ film or during its reduction, different ordered phases can be resolved. A particularly well-ordered relaxed hexagonal network can be converted into a network with 5, 6, and 7 (hex/5−7) member rings, thanks to a Stone Wales transformation of two hexagons into a pentagon−heptagon topological defect.[26] Certain surface species and catalyst phases are only stable in the presence of reactants, indicating a need for AP in situ characterization to be able to obtain an accurate picture of active catalysts. We have studied the reduction of $Cu_2O(111)$ in situ using milliTorr pressures of CO at 300 K. Low energy electron microscopy imaging shows the propagation of metallic fronts, preferentially from steps, as the reduction progresses.[25] AP-XPS and AP-IRRAS show that the reduction of Cu_2O proceeds in the presence of only adsorbed CO molecules, without the formation of carbonates or other intermediate species. Using AP-STM, the reaction could be monitored at the nanoscale, observing the structural transformation from the $Cu_2O(111)$ film to glasslike hex/5−7 ring structures and ultimately to metallic Cu. The hex/5−7 intermediate phase propagated across the surface as a front and was a precursor to the formation of a metallic phase. In situ measurements show that the reduction begins at defects in the $Cu_2O(111)$ film terraces and step edges. At terrace defects, the oxide buckles during reduction, appearing as bright protrusions before converting into the ring structures. Copper atoms appear on top of the oxide layer, and quickly sinter into small metallic copper clusters, as shown in Figure 3. Most of the Cu atoms released by reduction of Cu_2O in the presence of CO undergo mass transfer to step edges, causing a massive reconstruction and phase separation between the oxide and metal. The rate of the reduction process increases significantly during the phase where small copper clusters coexist with the oxide layer, indicating that this dynamically formed structure involving an oxide/metal interface may be optimal for oxidation/reduction processes on copper-based catalysts. The AP in situ experiments presented here show the dynamic nature of catalytic surfaces, including oxidation state changes and morphological restructuring. This visualization can help to promote the generation of new models for the understanding of catalysis at the molecular level.

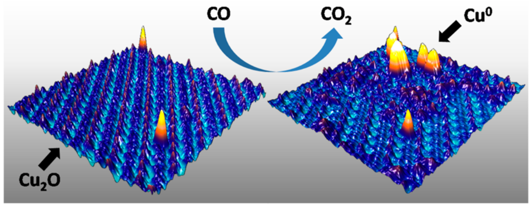

Figure 3. AP-STM images of the CO reduction (45 mTorr) of Cu_2O/Cu(111) at 300 K. Scanning: 0.9 V, 0.78 nA, scale bar = 2 nm.[25]

4. CO OXIDATION ON COPPER AND $CuTiO_x$ MODEL CATALYSTS

The oxidation of CO is commonly used in surface science as a test reaction. The natural abundance of copper and its oxidation catalytic properties make it very attractive for practical uses.[27] The Achilles heel of Cu_2O catalysts is its deactivation by complete oxidation to CuO.[28] Extensive catalytic and kinetic studies have been conducted on the oxidation of CO over Cu-based catalysts.[27,28] It was reported that, for Cu thin films, the activity decreases as the degree of oxidation increases.[28] Based on research over powder catalysts, it has been suggested that Cu_2O is more active than metallic copper,[27] which contradicts the Cu film results. A more

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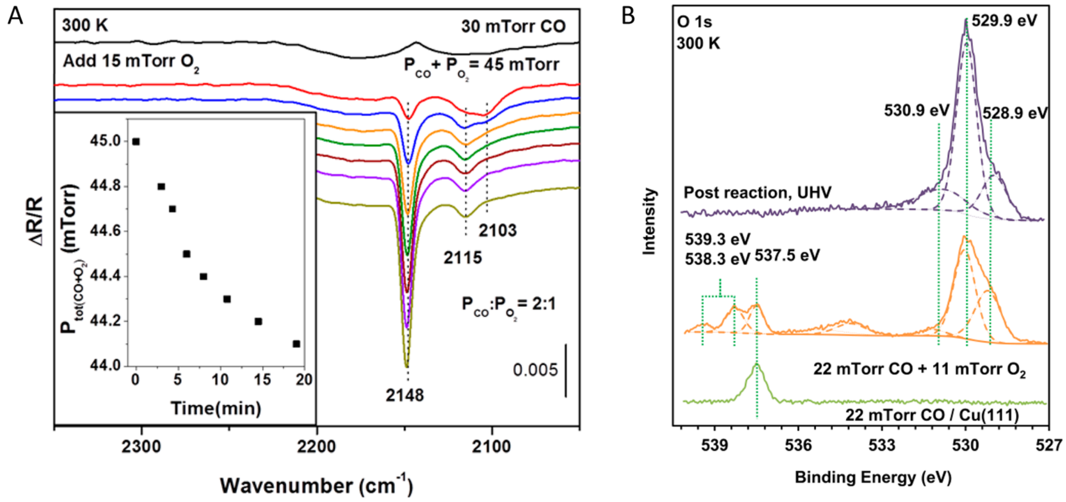

Figure 4. In situ spectroscopic data for CO oxidation over Cu(111). (A) AP-IRRAS results: Top spectrum for pure CO, and the following correspond to CO + O_2 at increasing reaction times. Inset: total pressure as a function of time. (B) AP-XPS O 1s spectra: Spectra from bottom to top obtained after exposure of Cu(111) to CO, CO + O_2, and after evacuation of the AP cell. Reproduced with permission from ref 32. Copyright 2014 American Chemical Society.

extensive body of research exists on the study of CO oxidation over Pt-group catalysts[29] (and references therein), where the oxidation state of the most active phase for these metal catalysts has similarly been widely debated. The facile oxidation of copper limits the possibility of maintaining a single phase over the course of the CO oxidation reaction. Either ex situ measurements have been reported postmortem after high pressure experiments,[28] or in situ measurements under low pressure conditions.[30] However, the topography and activity of catalysts change from UHV to high pressure.[25,31] Morphological studies of the substrate and adsorbates conducted on Cu(110) using STM during CO oxidation at moderate pressure showed that defects on the oxygen overlayer served as active sites, and once defects were created the reduction took place rapidly along oxygen rows.[30]

The oxidation of CO on Cu(111) was tested in situ by IRRAS.[32] When the Cu(111) surface is initially pressurized to 30 mTorr of CO at 300 K, only a gas-phase CO peak is observed in the IRRAS data (top spectrum in Figure 4A). A pressure closer to 100 mTorr is required to detect adsorbed CO at ∼2070 cm^{-1} on a smooth Cu(111) surface. When O_2 is added to the IRRAS cell containing CO, two peaks related to adsorbed CO are observed. Based on results from control experiments, the peak at 2115 cm^{-1} is assigned to adsorption of CO on disordered Cu_2O, and as discussed above the peak at 2103 cm^{-1} can be assigned to adsorbed CO on under-coordinated Cu^0 sites, which disappear under longer exposure to O_2. With longer exposures to oxygen, the Cu is further oxidized, resulting in an increase in the intensity of the peak at 2115 cm^{-1}, and the appearance of a new dominant peak at 2148 cm^{-1}. There were no assignments for this peak in the literature, and we have assigned it to CO adsorbed on fully oxidized CuO regions. The formation of CuO films has not been reported under UHV conditions, but it can be stabilized under elevated pressure and temperature conditions. The growth of the peak associated with the presence of CuO slows down after 8.0 min of the reaction, corresponding to a decrease in the reaction rate, which is shown as an inset in Figure 4A. Early experiments over oxidized Cu also showed a decrease in activity of CuO as compared to Cu_2O for the CO oxidation reaction.[28]

In order to confirm the appearance of CuO on the surface of Cu(111) during the oxidation of CO and validate our IR assignments, we proceeded to carry AP-XPS experiments. In the data shown in Figure 4B, the O 1s peak at 537.5 eV is assigned to gas-phase CO. Upon the addition of O_2, features at 538.3 and 539.3 eV, corresponding to gas-phase O_2, are observed. Under CO oxidation conditions on Cu(111), the surface is oxidized, and peaks were observed for CuO (at 528.9 eV), Cu_2O (at 529.9 eV), and surface oxygen (at 530.9 eV), which is in agreement with the formation of CuO and Cu_2O deduced from the IRRAS data. The broad feature at ∼4 eV above the Cu_2O signal matches data collected upon adsorption of CO on $Cu_2O(111)$ at low temperature.

Copper oxide domains form even under heavily reducing conditions at 300 K, and the surface reconstructs constantly through a redox cycle between CuO, Cu_2O, and Cu. The Cu atoms released during the redox cycle diffuse to the step edges leading to a flat surface with highly mobile step edges that are faceted along the ⟨110⟩ direction. Metallic copper is the most active phase, but it cannot be stabilized under reaction conditions. Cu^+ is also very active, and the formation of Cu^{2+} deactivates the catalysts. Strategies to stabilize structures with Cu^+ cations, such as the formation of mixed-oxides,[18] could lead to stable Cu oxidation catalysts.

We decided to add Ti to the Cu_2O thin films, in order to synthesize titanium−copper mixed oxide films, and explore the possibility of chemically stabilizing Cu^+ sites.[18] STM images (Figure 5) of the Ti modified film show the formation of well-ordered surfaces. Adsorption of CO on the $TiCuO_x$ thin film indicates that the surface exposes exclusively Cu^+ cations, while near edge X-ray absorption fine structure data establishes that the Ti in the mixed-oxide film remains isolated in the subsurface region. A model to simulate the mixed-oxide film was constructed starting from the structural motif of a well-defined monoclinic Li_2TiO_3 slab, and replacing the Li ions by Cu. The two structures predicted by the density functional theory (DFT) calculations are shown in Figure 5A and C, and the corresponding simulated STM images are superimposed to

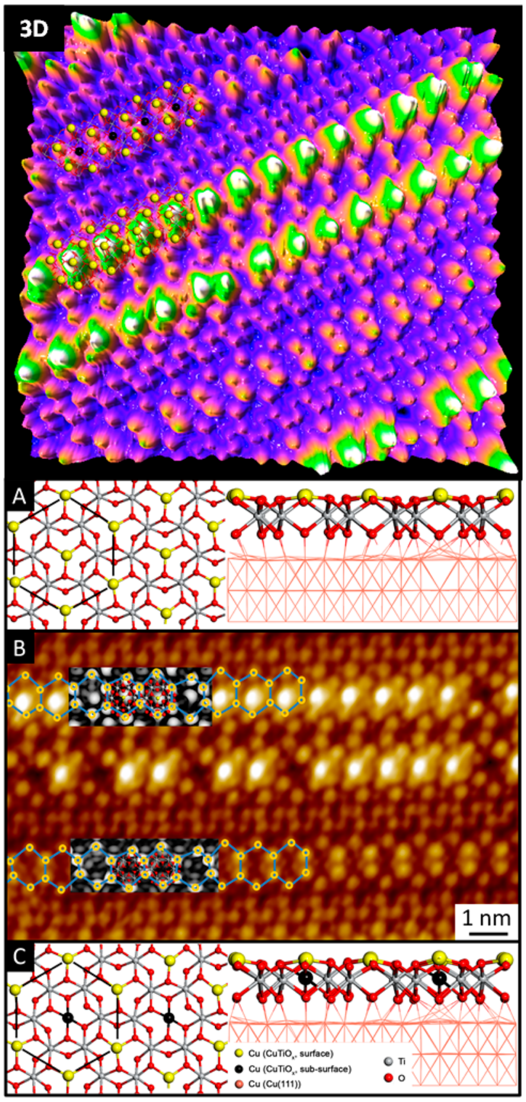

Figure 5. Comparison of DFT predicted structures with an STM image from $TiCuO_x$ terraces. (A) All Cu atoms at the surface layer; (B) DFT structures and simulated images superimposed to an STM image (−0.50 V, 0.27 nA); (C) central Cu atoms (black) in the subsurface of the film. Reproduced with permission from ref 18. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

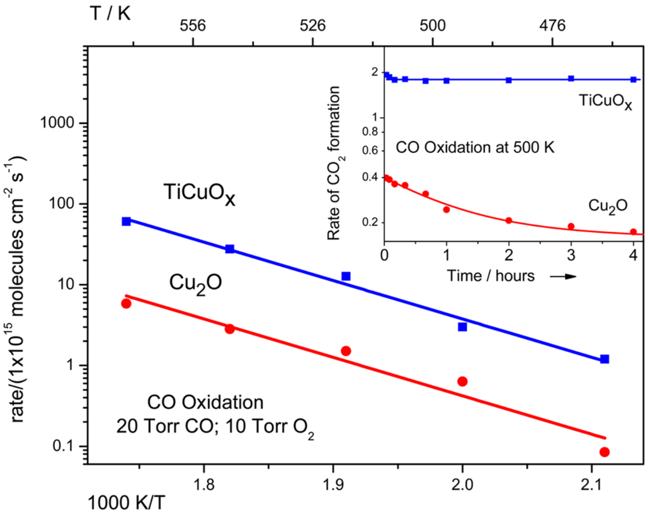

Figure 6. Arrhenius plot of the CO oxidation rate on Cu_2O and $TiCuO_x$ (~0.6 ML Ti) films. Inset: Catalysts stability under reaction at 500 K. Reproduced with permission from ref 18. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

the experimental data in Figure 5B. In both structures, all the surface atoms are Cu^+ cations, with a local CN of three, instead of the observed CNs of 2 and 4 for Cu_2O or CuO samples, and a longer distance that surface atoms on Cu_2O, which prevents the facile dissociation of O_2 molecules and the corresponding further oxidation of the film.

The $TiCuO_x$ film was tested for the oxidation of CO. Figure 6 presents Arrhenius plots for the CO oxidation rate on both Cu_2O and $TiCuO_x$ films, where the CO_2 production rate is significantly improved by the addition of Ti to the Cu_2O film. More importantly, the formation of the mixed oxide film helps to stabilize the active sites on the surface of the catalyst (Figure 6, inset). The corresponding AP-XPS spectra shows that the $TiCuO_x$ film with a submonolayer load of Ti presents only a small CuO peak (529.1 eV), compared to the much larger peak observed on the Cu_2O film. The presence of Ti preserves the highly active Cu^+ sites on the surface, and thus prevents deactivation of the catalysts. At the higher reaction temperatures used on catalytic converters and presented in Figure 6, the oxidation of Cu_2O is more pronounced and the protection of the $TiCuO_x$ becomes critical.

We have synthesized stable $TiCuO_x$ films, which are very active for CO oxidation, and by combining microscopic and spectroscopic experimental studies with theoretical simulations we have been able to describe their complex structure at the atomic level. The presence of Ti stabilizes Cu^+ ions on the surface locally coordinated to three oxygen atoms, which act as better adsorption sites for CO than sites on pure TiO_2 or Cu_2O. This discovery and the description of its origin could help to develop stable Cu-based oxidation catalysts.

5. WGSR AND METHANOL SYNTHESIS ON $Cu/CeO_x/TiO_2$ MODEL CATALYSTS

As mentioned in the Introduction, the importance of metal/oxide interfaces has been long recognized,[5,7] but a molecular determination of their properties and role is only now emerging.[33,34] It is shown in this section how sites associated with a copper/ceria interface can dramatically change the reaction mechanism for the WGSR and methanol synthesis from CO_2.

The WGSR is critical in the production of hydrogen. Multiple reaction mechanisms have been proposed.[35−37] In the redox mechanism, CO reacts with O derived from the dissociation of H_2O. In the associative process, the formation of a critical carbonaceous CO_xH_y intermediate must precede the production of H_2 and CO_2. In situ studies are essential to detect surface species and active phases only present under reaction conditions.[9] Inverse (oxide/metal) model catalysts can be used to highlight the importance of defects from oxide nanoparticles at the interface with fully coordinated sites from the metal substrate.[38,39] As an example, Au(111) is completely inactive for the WGSR but can be activated in the presence of CeO_x nanoparticles.[38] A large enhancement in activity is also found for CeO_x/Cu(111) over Cu(111), a typical benchmark for WGSR studies. The rate of H_2 production for these catalysts is compared in Figure 7.[16]

In both redox and associative mechanisms, a critical step is the dissociation of H_2O. Metal surfaces have a weak interaction

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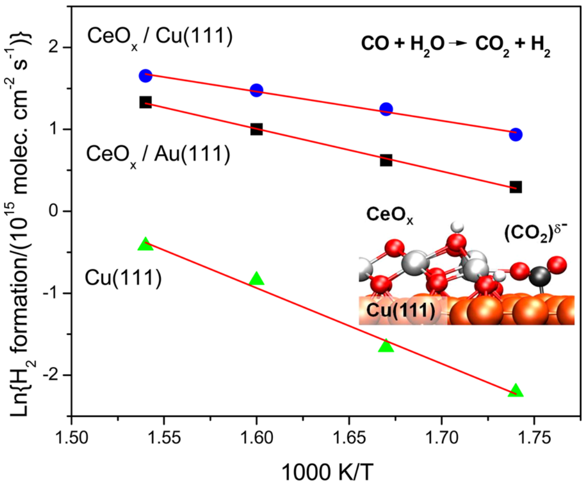

Figure 7. Arrhenius plots for the WGSR rate (20 Torr CO and 10 Torr H_2O) on clean Cu(111), CeO_x/Cu(111), and CeO_x/Au(111). Reproduced with permission from ref 16. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

with H_2O and a strong one with CO. Oxide surfaces behave in the opposite manner. The Cu(111) and Cu_2O/Cu(111) surfaces are not active for the dissociation of water under UHV conditions or even under WGSR conditions, where no intermediates other than CO were observed (AP-XPS data at the bottom of Figure 8). Since intermediate species other than CO and OH were not observed on Cu(111) under reaction conditions, we concluded that most likely the redox mechanism is the dominant WGSR pathway on Cu(111).

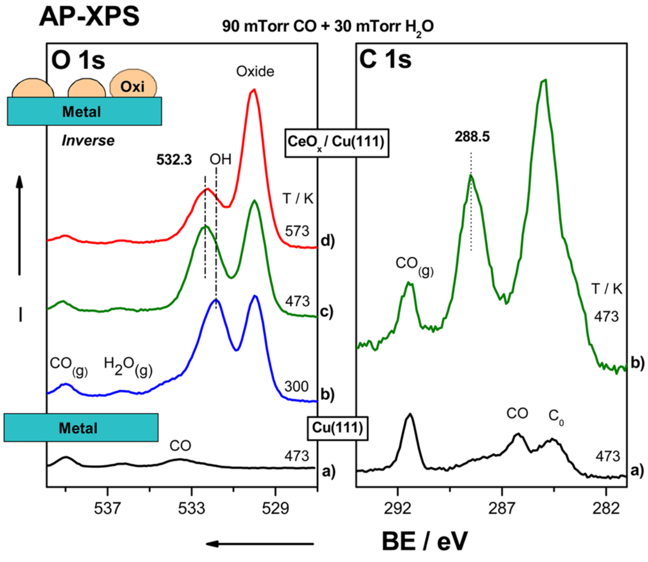

Figure 8. AP-XPS from Cu(111) and CeO_x/Cu(111) under WGSR. Reproduced with permission from ref 16. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In contrast, when the more reactive ceria/Cu(111) interface is formed, trapped OH and $CO_2^{\delta-}$ species are identified even under mild WGSR conditions by AP-XPS (top spectra in Figure 8), and reduction of Ce^{4+} to Ce^{3+} is observed. A combination of results from AP-XPS, IRRAS, and DFT calculations show that $CO_2^{\delta-}$ species are derived from a carboxyl intermediate and stabilized at the interfaces of CeO_x/Cu(111).[16] Even though the WGSR over CeO_x/Cu catalysts can occur via both redox and associative mechanisms, our studies indicate that the presence of the oxide/metal interface activates a more efficient associative mechanism pathway and leads to more than 1 order of magnitude increase in the activity of the CeO_x/Cu(111) system compared with Cu(111). Our studies illustrate the power of in situ mechanistic studies on well-defined catalysts and the important role that metal/oxide interfaces can play in catalysis. The simultaneous participation of atoms present in the metal and oxide make possible the formation and stabilization of HOCO and $CO_2^{\delta-}$, favoring a reaction mechanism for hydrogen production that is not observed on bare copper or ceria surfaces. Thus, when optimizing this type of catalyst, one must pay special attention to the properties of the metal/oxide interface.

Copper-based catalysts are also used in the industry for methanol synthesis (MS) from syngas.[13,40] The transformation of CO_2 into alcohols or other hydrocarbon compounds is challenging because of the difficulties associated with the chemical activation of CO_2 by heterogeneous catalysts.[41] Pure metals and bimetallic systems used for this task have usually low catalytic activity. The combination of metal and oxide sites in the copper/ceria interface affords complementary chemical properties that lead to a superior reaction pathway for the $CO_2 \rightarrow CH_3OH$ conversion. A comparison of activity for MS from the hydrogenation of CO_2 between Cu(111) and a model of the industrial Cu/ZnO(000$\bar{1}$) catalyst points to an enhancement in the catalytic activity when Cu is present as nanoparticles.[40] We investigated the hydrogenation of CO_2 on catalysts generated by codepositing nanoparticles of copper and ceria on TiO_2(110). Ceria forms dimers on TiO_2(110) and has Ce^{3+} and Ce^{4+} states of almost equal stability.[14,42] Kinetics data for MS on a catalyst with ∼0.1 ML of Cu on a TiO_2(110) surface precovered by 0.15 ML of ceria nanoparticles show that this surface is significantly better than the industrial reference Cu/ZnO(000$\bar{1}$) catalyst. The rate of methanol production on Cu/CeO_x/TiO_2(110) is ∼1000 times faster than on Cu(111) and ∼100 times faster than on Cu/ZnO(000$\bar{1}$). The synthesis of methanol on 0.1 ML of Cu supported on TiO_2(110) or CeO_2(111) surfaces has catalytic activities somewhat greater than that of Cu/ZnO(000$\bar{1}$) but much less than that of Cu/CeO_x/TiO_2(110) or even CeO_x/Cu(111). Plain CeO_x/TiO_2(110) had no activity for MS. Therefore, the extremely high activity of Cu/CeO_x/TiO_2(110) is a consequence of generating a metal/oxide interface involving copper and ceria nanoparticles.

STM images show a close contact between copper and ceria on a TiO_2(110) substrate.[42] Thus, CeO_x/Cu(111) can be used to understand the process occurring in Cu/CeO_x/TiO_2(110). An in situ AP-STM image of one of these ceria islands on Cu(111) is shown in Figure 9, left. The ceria islands are predominantly one layer thick, exhibiting rough surfaces with CeO_2(111) termination. After exposing the as prepared CeO_2/Cu_2O/Cu(111) to 1.5 Torr H_2, the complete reduction of Cu_2O to Cu and the formation of clusters of O vacancies in the ceria are observed (Figure 9 right). Reduction in H_2 increased the surface roughness of the ceria particles, expanding the ceria/Cu interface. To provide a molecular description of the MS mechanism on our system, we performed DFT calculations, looking for possible intermediates and screening them to build a plausible thermodynamic reaction pathway (Figure 10). Following previous studies for CO_2 hydrogenation on clean Cu(111),[13] we considered reaction pathways that involved formate ($HCOO^-$) species, but abandoned them because of the

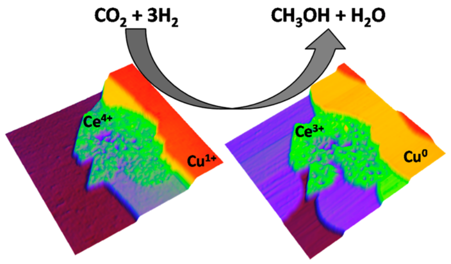

Figure 9. STM image of a $CeO_x/Cu(111)$ surface as prepared and during exposure to 1.5 Torr H_2 at 300 K. Scanning parameters: 0.3 nA, 1.0 V.[40]

high stability of this species. The experimental measurements point to the simultaneous production of methanol and CO during CO_2 hydrogenation. The reaction path in Figure 10 shows the best calculated route for the reverse-WGSR and MS. The critical step in the reaction is the adsorption and activation of CO_2 at the metal/oxide interface. The interaction of CO_2 with clean Cu(111) is to weak and prevents a facile adsorption on the surface, while the adsorption on top of ceria leads to the formation of strongly bound carbonates or formate species in the presence of hydrogen. This study illustrates the substantial benefits that can be obtained by tuning the properties of a metal-oxide interface in catalysts. In a metal/oxide interface, one can have adsorption/reaction sites with complementary chemical properties, truly bifunctional sites which would be very difficult to generate on the surface of pure metal or alloy systems.[13]

6. CONCLUSIONS

The use of well-defined model catalysts allows the characterization of systems at the molecular and atomic level. Studies of these model catalysts by complementary in situ ambient pressure spectroscopy and microscopy gives direct evidence of dynamically generated active phases and adsorbed surface species which are produced or stabilized only under reaction conditions. The experimental in situ information can then be used to test potential catalytic reaction mechanisms with first principle modeling. In the case of copper-based catalysts, the integrated approach described above shows that for oxidation reactions the surface of the catalyst is quickly deactivated by full oxidation of copper sites, while for reactions with carbon oxide molecules their weak interaction with copper metal precludes the reactant's adsorption. Adding Ti to copper oxide generates a mixed-oxide surface with chemically stabilized Cu^+ cations very active for oxidation reactions. The formation of ceria/copper interfaces leads to the generation of multifunctional sites, with partially oxidized Cu atoms and Ce cations partially reduced near the interface, that stabilize the formation of carboxylate species critical for highly efficient WGSR and CO_2 hydrogenation reaction pathways.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

Biography

Darío J. Stacchiola is a Chemist at BNL and Adjunct Professor at Michigan Technological University. He obtained his B.S. degree (1997) at UNSL (Argentina) and his Ph.D. (2002) at the University of Wisconsin—Milwaukee and was a Humboldt Research Fellow at the Fritz-Haber-Institute in Berlin (2005−2007). His research interests are in surface chemistry studied by in situ tools, and in particular in structure−reactivity relationships in catalysis.

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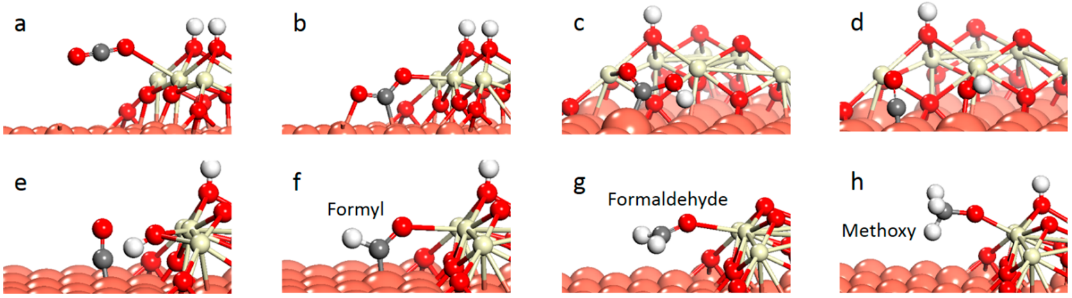

Figure 10. Reaction path for methanol synthesis from CO_2 hydrogenation on the $CeO_x/Cu(111)$ system. Optimized structures for the main intermediates and transition states. Reproduced with permission from ref 40. Copyright 2014 AAAS.

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