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Nanopattering in CeO$_x$/Cu(111): A New Type of Surface Reconstruction and Enhancement of Catalytic Activity

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ABSTRACT: Our results indicate that small amounts of an oxide deposited on a stable metal surface can trigger a massive surface reconstruction under reaction conditions. In low-energy electron microscopy (LEEM) experiments, no reconstruction of Cu(111) is observed after chemisorbing oxygen or after reducing O/Cu(111) in a CO atmosphere. On the other hand, LEEM images taken in situ during the reduction of CeO$_2$/CuO$_{1-x}$/Cu(111) show a complex nonuniform transformation of the surface morphology. Ceria particles act as nucleation sites for the growth of copper microterraces once CuO$_{1-x}$ is reduced. Can this reconstructed surface be used to enhance the catalytic activity of inverse oxide/metal catalysts? Indeed, CeO$_x$ on reconstructed Cu(111) is an extremely active catalyst for the water–gas shift process (CO + H$_2$O → H$_2$ + CO$_2$), with the Cu microterraces providing very efficient sites for the dissociation of water and subsequent reaction with CO.

SECTION: Surfaces, Interfaces, Catalysis

CO + H$_2$O

H$_2$ + CO$_2$

1 μm
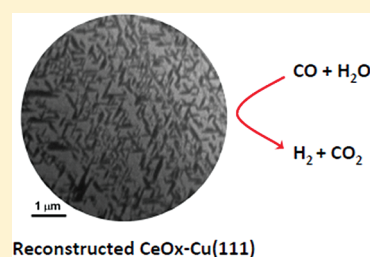
Reconstructed CeOx-Cu(111)

Metal surfaces are used extensively as catalysts in most areas of the chemical industry and in energy conversion processes. In principle, a metal surface can adopt a large range of configurations exposing different types of sites over which molecules can react and undergo chemical transformations.[1] The understanding of the structure dependence of surface reactions has advanced tremendously in the last three decades.[1,2] In broad terms, there are two ways in which the surface geometrical structure can affect the stability of reaction intermediates and the activation energy of chemical reactions.[1,2] A purely geometrical effect comes from different surface geometries, providing different configurations to the reactant molecules for bonding. An electronic effect appears due to differences in the surface electronic properties caused by variations in surface geometry, which eventually affect the way in which the electrons of a surface site respond to the presence of adsorbates.[2] In catalysis, a main goal is to induce changes in surface morphology to enhance catalytic activity.[1−3] The phenomenon of "faceting" is perhaps the most extensive reconstruction that a metal surface can undergo.[4−6] It can be induced by the deposition of metals or the adsorption of oxygen on surfaces that have a low morphological stability.[4,5] Thus, the adsorption of oxygen can induce faceting of Cu(115) and Cu(119) surfaces.[7] By contrast, no faceting has been observed for the O/Cu(111) system.[8,9] In this study, we report a new type of massive surface reconstruction on a highly stable Cu(111) substrate. It is triggered by the presence of cerium oxide nanoparticles on the metal surface and leads to a very large enhancement in the catalytic activity of the system.

The in situ grown of ceria nanoparticles is depicted in Figure 1 (left) as observed under a low-energy electron microscope
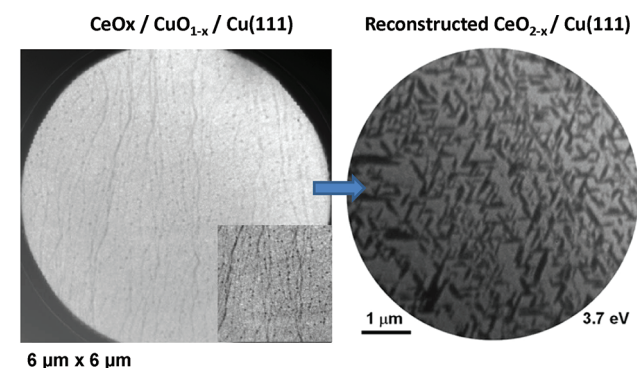
CeOx / CuO$_{1-x}$ / Cu(111)   Reconstructed CeO$_{2-x}$ / Cu(111)

1 μm   3.7 eV

6 μm x 6 μm

Figure 1. Bright-field LEEM images obtained in situ after the growth of cerium oxide on Cu(111) at 590 K under an O$_2$ atmosphere (5 × 10^{-7} Torr). The oxidized Cu(111) surface is decorated with small islands of ceria (inset). (Right) Bright-field LEEM image (3.7 eV) of a reconstructed CeOx-Cu(111) surface with a low coverage of ceria, depicted post reduction in CO at 590 K under a CO atmosphere of 4 × 10^{-7} Torr.

(LEEM) (bright-field, E = 3.7 eV).[10] The ceria (CeO$_2$) nanoparticles are grown by depositing Ce (at approximately

0.5 ML/min) on to a Cu(111) surface at 590 K under a background pressure of O_2 (4×10^{-7} Torr). The surface is initially composed of a rapidly formed oxide of Cu_2O (as evidenced from the low-energy electron diffraction (LEED) pattern, which showed a "44" structure that appears prior to the exposure of ceria.) The ceria (~0.3 ML) grows homogenously as small islands (10−20 nm) (inset) and appear with no distinct site preference for nucleation. Due to the limited size resolution of the LEEM, the image in Figure 1 does not show ceria nanoparticles that have sizes below 10 nm and have been observed with scanning tunneling microscopy (STM).[11] X-ray photoelectron spectroscopy (XPS) indicates that the system consists of islands of CeO_2 on a thick layer of CuO_{1-x}.[11] In the LEEM data, or in STM images,[11] we see *no evidence* for a surface reconstruction of ceria−Cu(111), or pure Cu(111), after oxidation. Overlayers of different phases of CuO_{1-x} grow epitaxially on the Cu(111) substrate.[8,9,11] These results contrast the faceting observed for the morphologically unstable Cu(115) and Cu(119) surfaces upon oxygen adsorption.[7]

In many catalytic processes, a catalyst is activated by pretreatment under carbon monoxide.[1] After exposing CuO_{1-x}/Cu(111) to carbon monoxide at 500−700 K, the surface oxide undergoes reduction, $CO(gas) + O(surf) \rightarrow CO_2(gas)$, but there is no significant reconstruction of the Cu(111) surface as seen in STM experiments[12] or in our LEEM studies. In contrast, the result of the reaction on the CeO_2/CuO_{1-x}/Cu(111) system with carbon monoxide, as depicted in Figure 1 (right) and observed in situ with LEEM (bright-field, 3.7 eV), shows significant morphological change resulting from the reduction process. The $Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^0$ transformation occurs at different rates on different regions of the surface depending on the initial concentration of defects and surface imperfections. After removing all the CuO_x from the CeO_2/CuO_{1-x}/Cu(111) system, we are left with a stable surface with elongated areas attached to the steps, with *a strikingly different* superstructure from that of Cu(111) or reduced CuO_x/Cu(111) (see above). A copper surface with a step density of 25−35% is generated. The ceria islands are not clearly visible during or after the CO reduction process due to the resolution limits of the LEEM. From XPS data,[11] it is known that part of the Ce^{4+} cations has been reduced into Ce^{3+} and the system contains dispersed islands of CeO_{2-x} on a metallic copper substrate.

Using STM,[12] we found the presence of ceria nanoparticles embedded at the corner edges of the microterraces formed after the reduction of CeO_2/CuO_{1-x}/Cu(111). These ceria nanoparticles play a key role in the surface reconstruction process. When they are not present, the reduction in CO of CuO_{1-x}/Cu(111) does not lead to a massive reconstruction of the copper substrate. The ceria nanoparticles may act as nucleation sites for the growth of the copper microterraces in specific directions once CuO_{1-x} is reduced. The formation of the copper microterraces is probably due to thermodynamic reasons rather than kinetic ones, since the microterraces survived upon annealing at 600−700 K or after reaction with oxygen. We are in the process of studying the exact mechanism for the reconstruction of a stable surface such as Cu(111). As we will see below, the behavior seen for the reduced CeO_2/CuO_{1-x}/Cu(111) system suggests a new approach for inducing the surface reconstruction of morphologically stable metal surfaces and enhancing catalytic activity.

Indeed, we have found that reduced CeO_2/CuO_{1-x}/Cu(111) surfaces have a much higher catalytic activity for the water−gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) and CO oxidation

($CO + 0.5 O_2 \rightarrow CO_2$) than regular Cu(111). The water−gas shift (WGS) reaction is a very important chemical process that is used in the industry for carbon-based fuel processing and to clean the hydrogen used in fuel cells.[13] There is a constant search for better WGS catalysts.[14−16] Figure 2 compares the
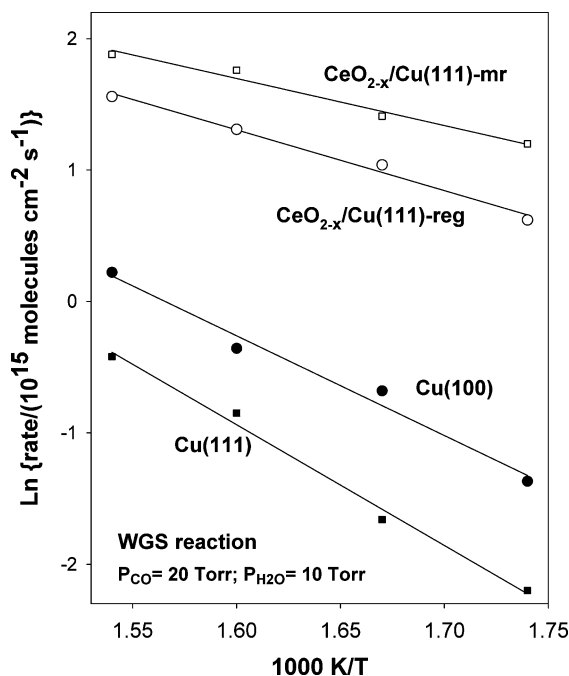

Figure 2. Arrhenius plot for the WGS reaction rate on clean Cu(111), Cu(100), and on copper surfaces covered ~20% by ceria (measured by ion-scattering spectroscopy (ISS) after treatment in CO[19]). The CeO_x/Cu(111)-reg and CeO_x/Cu(111)-mr catalysts were prepared as described in the text. The CeO_x/Cu(111)-mr system involves a massive surface reconstruction.

WGS activity[17] of Cu(111), Cu(100), and ceria−copper surfaces in which there is either no surface reconstruction, CeO_{2-x}/Cu(111)-reg, or a massive reconstruction, CeO_{2-x}/Cu(111)-mr. In the two ceria−copper systems, ~20% of the copper substrate was covered by ceria (as determined by ion scattering measurements[18]). The CeO_{2-x}/Cu(111)-reg system was prepared by dosing Ce to Cu(111) at 650 K under a limited background pressure of O_2 ($p \sim 5 \times 10^{-7}$ Torr).[19] On the other hand, the CeO_{2-x}/Cu(111)-mr system was prepared in conditions similar to the experiments in Figures 1, providing extra oxygen to favor the oxidation of copper and the formation of microterraces on the Cu(111) substrate after reduction in CO. XPS spectra taken after performing the WGS reaction showed that the dominant oxidation state for cerium in the CeO_{2-x}/Cu(111)-reg and CeO_{2-x}/Cu(111)-mr catalysts was "+3". The copper was all in a metallic state. In Figure 2, Cu(100) displays a substantially higher WGS activity than Cu(111). From previous studies,[19] it is known that the WGS is a structure-sensitive reaction. The generation of copper microterraces in CeO_{2-x}/Cu(111)-mr produces the catalyst with the *highest WGS* activity from the set in Figure 2. When going from regular Cu(111) to CeO_{2-x}/Cu(111)-mr, the apparent activation energy for the WGS reaction decreases from 18 kcal/mol to 7 kcal/mol.

What is causing the high catalytic activity of the CeO_{2-x}/Cu(111)-mr system? How can the massive surface reconstruction

840

dx.doi.org/10.1021/jz300159p | J. Phys. Chem. Lett. 2012, 3, 839−843

in $CeO_{2-x}/Cu(111)$-mr help in the catalytic process? The low WGS activity of $Cu(111)$ is due to the fact that this close-packed surface binds CO poorly[20] and does not dissociate water well.[21,21,22] From experimental measurements, a value of 17 kcal/mol has been estimated for the activation energy for water dissociation on $Cu(111)$.[23] Density-functional calculations give an activation energy of 21−27 kcal/mol.[22] The theoretical calculations also show that the introduction of steps on the copper surface can reduce the activation energy for the dissociation of water up to 30%, substantially enhancing the rate of dissociation of the molecule.[23] In the reaction cell used to carry out the experiments shown in Figure 2,[18] we exposed clean $Cu(111)$ to 1 Torr of water at 300 K and found no indication of adsorbed OH groups on the copper surface.

Figure 3 shows the corresponding results for the $CeO_x/Cu(111)$-mr catalyst. Initially (spectrum a), one sees only the
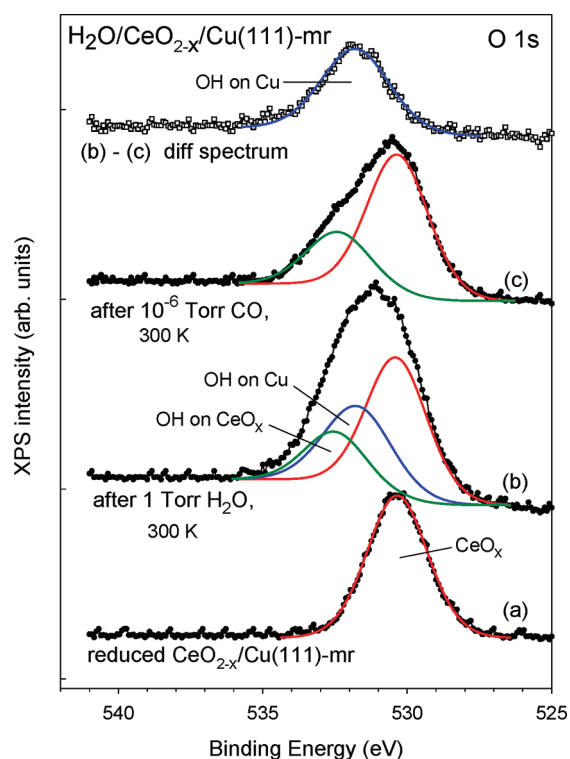
Figure 3. O 1s XPS spectra taken before (a) and after (b) adsorbing H_2O on a $CeO_x/Cu(111)$-mr catalyst at 300 K. In the final step, the sample was exposed to CO at 300 K (c). At the top of the figure, we show the amount of OH removed from the sample by reaction with CO. The $CeO_x/Cu(111)$-mr sample was prepared as described in the text. ~20% of the copper surface was covered by ceria.

features of the ceria in the O 1s XPS region. Exposure to water leads to a broad O 1s peak (spectrum b), which contains contributions from three types of O-containing species (CeO_x−OH (532.4 eV), Cu−OH (531.5ev), and CeO_x−O (530.2 eV)). The peak at ~531.5 eV (Cu−OH) can be removed by heating to 400 K (Figure 4) or after dosing CO to the sample (spectrum c). It is important to mention that the intensity of the 531.5 eV peak was negligible when water was dosed to a $CeO_x/Cu(111)$-reg surface, producing a smaller amount of surface OH groups than in the case of water adsorption on $CeO_x/Cu(111)$-mr (see Figure 4).

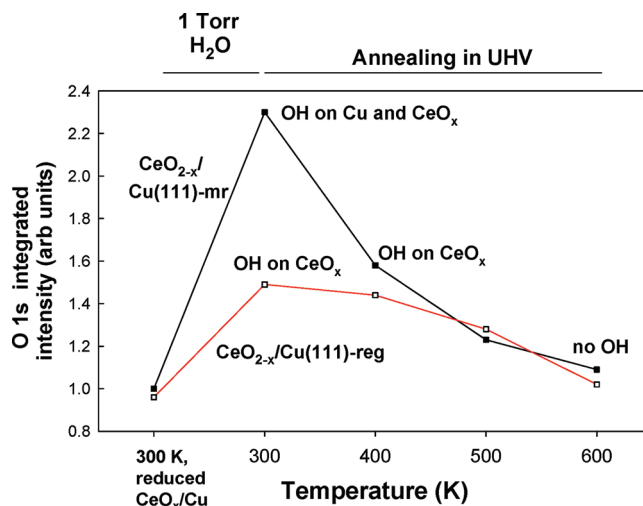In Figure 5, we use synchrotron-based high-resolution photoemission to determine and compare the O 1s XPS binding

Figure 4. O 1s XPS intensity measured after exposing $CeO_x/Cu(111)$-mr (black trace) and $CeO_x/Cu(111)$-reg (red trace) to 1 Torr of water at 300 K. In both experiments, ~20% of the copper surface was covered by ceria. After exposing the surfaces to water in the microreactor, the water was pumped out, and the sample was transferred to the UHV chamber for surface characterization with XPS. The samples were then heated from 300 to 400, 500, and 600 K. Evolution of O_2, H_2O, and H_2 was detected with a mass spectrometer after heating the $OH/CeO_x/Cu(111)$ surfaces in UHV. The $CeO_x/Cu(111)$-mr surface was prepared following the same methodology used to generate the surface that yielded spectrum b in Figure 3.

energies of OH bound to copper (A), generated after adsorbing water on $O/Cu(111)$, and OH bound to ceria (B), generated after adsorbing water on $CeO_x/Cu(111)$.[19] A difference of ~1 eV is found between the O 1s binding energies of the OH bound to copper and the OH bound to ceria. These results can be used to confirm the assignment of the O 1s peaks seen in Figure 3. In this figure, the binding energy and thermal stability of the O 1s features at ~531.5 eV match those found for OH bonded to copper in Figure 5. On the other hand, the O 1s peak at ~532.4 eV in Figure 3 exhibits a binding energy and thermal stability that match those seen for OH bound to CeO_x in Figure 5. The two types of OH groups seen in spectrum b probably contribute to the high WGS activity of the $CeO_x/Cu(111)$-mr catalyst. The OH bound to Cu sites provides a fast reaction channel. It can be removed by reaction with CO at room temperature (Figure 3, spectrum c), producing a rise in the signal for CO_2 and H_2 when the sample is put in front of a mass spectrometer. The OH bound to CeO_x does not react with CO under ultrahigh vacuum (UHV) conditions, but when exposed to 1 Torr of CO at 300 K, formate and carbonate-like species were detected in the C 1s XPS region. These species decomposed into CO_2 and H_2 upon heating to 500 K. Thus, the Cu microterraces present in $CeO_x/Cu(111)$-mr *do facilitate* the interaction of water (OH) and CO and make this system a better WGS catalyst than $Cu(111)$ or $CeO_x/Cu(111)$-reg where the reaction only takes place at a fast rate on the interface between copper and ceria.

In summary, we have found that small amounts of an oxide deposited on a stable metal surface can trigger a massive surface reconstruction under reaction conditions. LEEM images taken in situ during the reduction of $CeO_2/CuO_{1−x}/Cu(111)$ show a complex nonuniform transformation of the surface morphology. The $Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^0$ transformation occurs at different rates on different regions of the surface. Ceria particles act as
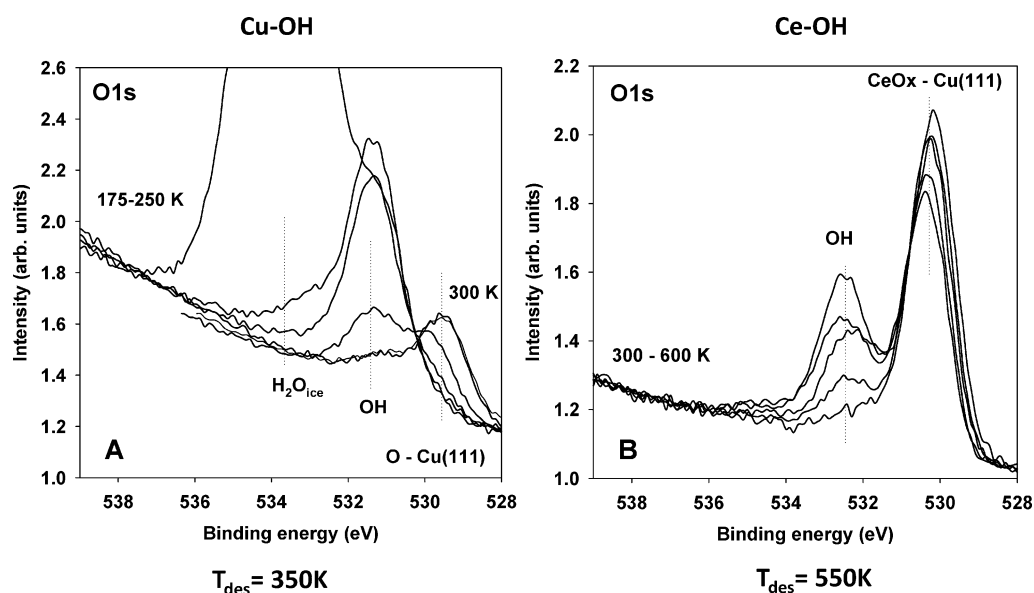
Figure 5. O1s XPS spectra taken after adsorbing H_2O on O/Cu(111) (left (A)) and CeO$_x$-Cu(111) (right (B)). The dosing of water was done at 90 K followed by sequential annealing to the indicated temperatures.

nucleation sites for the growth of copper microterraces once CuO_{1-x} is reduced. The Cu microterraces provide active sites which are very efficient for the dissociation of water and subsequent reaction with CO. In a reconstructed CeO_x/Cu(111) system, the WGS reaction can take place at a fast rate on the Cu microterraces and on the copper−ceria interface.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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842

dx.doi.org/10.1021/jz300159p | *J. Phys. Chem. Lett.* 2012, 3, 839−843

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