Bimetallic alloy catalysts show strong structural and compositional dependence on their activity, selectivity, and stability. Often referred to as the “synergetic effect” of two metal elements in the alloys, their detailed dynamic information, structurally and chemically, of catalyst surface under reaction conditions remains largely elusive. Here, using aberration-corrected environmental transmission electron microscopy, we visualize the atomic-scale synergetic surface activation of CuAu under a water–gas shift reaction condition. The unique “periodic” structural activation largely determines the dominating reaction pathway, which is related to a possible “carboxyl” reaction route corroborated by density functional theory–based calculation and ab initio molecular dynamics simulation. These results demonstrate how the alloy surface is activated and catalyzes the chemical reaction, which provides insights into catalyst design with atom precision.

Significance

Atomic-level in situ environmental transmission electron microscopy observation of the dynamic activation process on a low-indexed CuAu surface under water–gas shift reaction (WGSR) condition has been revealed. The atomic-scale structural activation of a CuAu surface features a gas-dependent periodic surface restructuring and elemental ordering, explaining the “synergy effect” from the structural point of view. These real-time changes under relevant reactant gases and temperature are correlated with the reaction route of WGSR corroborated by density functional theory–based calculation and ab initio molecular dynamics simulation and can provide insights for atom-precision catalyst design.
solid solution phase to a Cu₃Au phase in the near surface. The CuAu surface was first heated to the reaction temperature (300°C) and exposed to pure H₂ to remove native oxide for 30 min and then exposed to the desired gas reactants for 10 min before the HRTEM imaging. The detailed sample preparation process and sample geometry are described in Methods and SI Appendix.

Upon exposure to CO and H₂O gases, the CuAu(110) surface shows pressure-dependent surface atomic restructuring. Fig. 1A shows the HRTEM image of pristine CuAu(110) surface under high-vacuum conditions (<1 x 10⁻⁸ mbar), which has perfect lattice points with uniform contrast, indicating no structural change of the alloy surface under this condition. After we increase the pressure to ~1 x 10⁻⁶ mbar, within 10 min CuAu(110) surface restructures to a rough "sawtooth" structure with periodic protruded surface atoms as shown in Fig. 1B. The surface change can be related to the transition of a solid solution phase to a Cu₅Au phase in the near surface region induced by both elevated temperature and CO gas adsorption, which has been reported previously (28–30). A periodicity of 5 Å along the [110] direction can be seen with the top surface enriched by Au atoms. Further increasing CO pressure to ~1 x 10⁻⁶ mbar leads to more vigorous surface reconstruction after 10 min as shown in Fig. 1C. The lattice points in the surface layer (yellow arrow) are elongated laterally, resulting from the deviation of surface atoms from its original position induced by strong interaction between metal atoms and CO molecules. Meanwhile, the subsurface layer starts to show different contrast between adjacent lattice points (black and white arrows), which indicates the segregation of one element in the alloy.

From the above observations, we can see a CO gas pressure dependence of surface reconstruction, i.e., at a lower pressure, the thermal-driven Au segregation is responsible for forming the "sawtooth" surface structure, while the adsorption of CO gas molecules dominates the surface reconstruction at a higher pressure as summarized in the schematic of Fig. 1D. On the other side, the H₂O molecules could also dissociate on and activate the CuAu(110) surface through structural and chemical modifications depending on its gas pressure, as shown in Fig. 1E-G. As shown in Fig. 1E, at a lower H₂O vapor pressure of 1 x 10⁻⁶ mbar, we can see small periodic bright dots (white arrows in the right column) between two adjacent bright dots on the clean CuAu surface. These additional contrasts in the HRTEM image result from the dissociated products of H₂O molecules (OH or O groups) on the CuAu surface. As the H₂O vapor pressure increases to 1 x 10⁻⁴ mbar, the intact CuAu surface is largely disturbed, as evidenced by a stepped interface (white dashed line) between CuAu substrate and reconstructed surface phase as shown in Fig. 1F. The enlarged lattice distance in the reconstructed surface phase indicates the possible penetration of O or OH into the CuAu substrate. When the H₂O pressure further goes up to 1 x 10⁻² mbar, surface oxides are formed on the CuAu surface through selective oxidation of Cu, as evident by clear lattice points in the enlarged right column of Fig. 1G. This pressure-dependent H₂O adsorption and reaction on the CuAu surface are illustrated in the schematic atomic models in Fig. 1H, which is in accordance with our previous observations on pure Cu surface (27). This CO and H₂O adsorption-induced surface restructuring also takes place on the CuAu(100) surface, as shown in SI Appendix, Fig. S1, where Au atomic ordering in CO and selective oxidation of Cu are both found.

To understand these chemisorption-induced surface reconstructions we performed DFT calculations to rationalize the possible CO and H₂O adsorption sites. Based on our ETEM observations, we constructed three different types of CuAu(110) surfaces, i.e., Cu₉Au₁, Cu₃Au₁, and Cu₃Au₁_rgh, as shown in Fig. 2A. The first two surfaces are perfect flat surfaces and the third one corresponds to the reconstructed "rough" surface as observed in Fig. 1B and C. The general trend of Au segregation to CuAu surface was considered to build these surface models as shown in SI Appendix, Computational Details and Fig. S2. The detailed structural models and calculation results are summarized in SI Appendix, Fig. S3 and Table S1. We found that both Cu and Au have a strong affinity with CO molecules, but generally Cu sites have larger adsorption energies than that of Au sites for all three model surfaces, as shown in Fig. 2B. With the increase of Au concentration near the surface (from Cu₉Au₁ to Cu₃Au₁ to Cu₃Au₁_rgh), the adsorption energies of CO on Cu sites becomes more comparable to that on Au sites until they are identical for Cu₃Au₁_rgh surface. Besides, for the Cu₃Au₁_rgh surface, the most favorable sites for CO adsorption are top-Au and bridge-Cu sites with an adsorption energy of ~0.64 eV, which helps us to understand the reconstructed surface structure under CO gas. As shown in Fig. 1C, CO molecules preferably adsorb on the top Au site and exhibit elongated lattice points (yellow arrow), which is in accordance with the simulated HRTEM image (Fig. 1C, Inset) based on the DFT-calculated structure model.

On the other hand, the adsorption energies of H₂O molecules on the CuAu surface are generally smaller than that of CO, as shown in Fig. 2C. H₂O molecules prefer to be adsorbed on Cu sites because of their large adsorption energies, and with the increasing Au concentration in the surface layer the adsorption energy difference between Cu and Au sites also decreases. This is in accordance with the experimental observations in Fig. 1E-G, i.e., the bridge-Cu sites are the preferred adsorption site for H₂O molecules, which is relatively stable under a low gas pressure (1 x 10⁻⁶ mbar), as shown in Movie S1 and SI Appendix, Fig. S4. With increasing H₂O pressure, the dissociated O selectively reacts with surface Cu atoms and causes vigorous surface changes (SI Appendix, Fig. S5), leading to the formation of CuOₓ phase on the surface, as shown in Fig. 1F and G. The preferred CO and H₂O adsorption sites and corresponding electron density difference (EDD) analysis are shown in Fig. 2D and E. The EDD results confirm that the electrons transfer from the CuAu surface to CO and H₂O reactants through Cu(Au)–C and Cu(Au)–O bonds and the CO could get more electrons than H₂O from the corresponding CuAu surface. Combined with our experimental observations, we can see the activated CuAu surface under reaction condition deviates from the ideal flat surface structure and also shows different adsorption status, and Cu₃Au₁_rgh may be more accurate to describe the metal catalyst surfaces in real conditions.

Given the above information of structural response of CuAu surface to individual gas reactant, we anticipate a competitive adsorption and reaction process of CO and H₂O on the CuAu surface. After we introduce the gas mixture of CO+H₂O (1:1, atomic ratio) into the ETEM column, we see a "periodic" structural activation of CuAu surface featured by a unique surface atomic registry reinforced with the increasing gas pressure.
as shown in Fig. 3 A–D and Movie S2. The gas pressure was gradually increased from vacuum condition \(1 \times 10^{-8} \text{ mbar}\) to \(1 \times 10^{-6} \text{ mbar}\), and then \(1 \times 10^{-4} \text{ mbar}\), and finally to \(1 \times 10^{-2} \text{ mbar}\) with a 30-min staging time for each pressure. Compared to the pristine CuAu(110) surface in the vacuum (Fig. 3A), a slightly wavy surface atomic layer (white dashed line) at a pressure of \(1 \times 10^{-6} \text{ mbar}\) is seen in the HRTEM image of Fig. 3B. The disturbance of perfect atomic positions on the CuAu surface indicates the initiation of the competitive CO and H2O adsorption. It is noted that the contrast of the surface layer starts to show a periodic nature, as shown in SI Appendix, Fig. S6, which is related to different adsorption species. When the gas pressure reaches \(1 \times 10^{-4} \text{ mbar}\), we can clearly see lattice points with elongated contrast (white arrows) and additional lattice points on the CuAu surface (yellow arrows) in Fig. 3C. Then, a stabilized surface structure is achieved when we increase the pressure to \(1 \times 10^{-2} \text{ mbar}\); the repeated registry of surface atoms (yellow boxes in Fig. 3D) with adsorbate indicates an equilibrium state is established for the metallic surface and reactant molecules under this condition.

To understand the chemical processes related to this unique structural activation, we perform detailed AIMD simulation on a CuAu(110) surface under a CO+H2O gas environment. We start with the preadsorbed OH and CO groups (detailed Fig. 1. CuAu surface structural response to CO and H2O gases. (A–G) In situ HRTEM images show CuAu(110) surface structure change upon CO introduction: (A) pristine surface under vacuum \((1 \times 10^{-8} \text{ mbar})\), (B) \(p_{\text{CO}} = 1 \times 10^{-6} \text{ mbar}\), (C) \(p_{\text{CO}} = 1 \times 10^{-4} \text{ mbar}\), and (D) \(p_{\text{CO}} = 1 \times 10^{-2} \text{ mbar}\). The insets in B and C are simulated HRTEM images matching with experimental ones. (E) Schematic atomic models illustrate CuAu surface restructuring and elemental redistribution upon CO introduction. (F–G) In situ HRTEM images show CuAu(110) surface structure change upon H2O introduction at different partial pressures: (F) \(p_{\text{H2O}} = 1 \times 10^{-6} \text{ mbar}\), (G) \(p_{\text{H2O}} = 1 \times 10^{-4} \text{ mbar}\), and (H) \(p_{\text{H2O}} = 1 \times 10^{-2} \text{ mbar}\). The right columns correspond to the boxed areas on the left images. (H) Schematic of H2O adsorption induced structure change on CuAu(110) surface.
structure model in SI Appendix, Fig. S7) in the presence of H on CuAu surface, as shown in the snapshot of 0 s in Fig. 3E. These are three undisputed adsorbates participate in the WGS reaction. The blue dashed boxes highlight the dynamic process of adjacent OH and CO converting to CO2. As the reaction proceeds, OH and CO on adjacent top Cu sites bond together and drag the Cu atom above the surface to generate CO2, followed by its desorption. During this process, the surface atoms largely deviate from their original positions and maintain their positions with continuing gas reaction. Since the adsorption energy of H2O on the Au atom is much smaller than that on the Cu atom (Fig. 2C), the loosely adsorbed H2O can easily move to the adjacent Cu atom, as tracked by the black arrows in Fig. 3E. This critical step highlights the synergetic effect of Cu and Au atoms on the alloy surface that drives WGSR. It is also noted that because of the presence of Au atoms in the CuAu surface layer, the structural activation exhibits a “periodic” characteristic along the [110] direction on the (110) surface, as shown in Fig. 3D and E. We capture a snapshot of the HRTEM image after the CuAu surface is stabilized under the reaction condition, as shown in Fig. 3F, which could reflect a dynamically metastable adsorption status of reactants on the CuAu surface. Then, we compare with the simulated HRTEM image (Fig. 3G) based on the atomic structure after structural relaxation of both CO and OH groups on the CuAu surface (superimposed in Fig. 3H). We could see a good match between the experimentally observed metastable surface atomic structures of activated CuAu and theoretically calculated surface structure. The above structural identification of Au atoms in the “periodic” structural activation on the CuAu surface further illustrates the synergetic effect of Au and Cu atoms under a dynamic reaction condition. The presence of Au atoms on the CuAu surface has a periodic pattern rather than randomly disturbed in the surface results from the interplay between the adsorption of reactants and the trend of minimizing surface energy of CuAu, where Au atoms in the surface layer could lower the total surface energy of CuAu. This is also the essence of the synergetic effect of different metal atoms on the alloy surface from a structural perspective.

In addition, we employed in situ diffusion reflectance infrared Fourier transform spectra of CO adsorption (CO-DRIFTS) to investigate the CO adsorption behavior on CuAu surface before and after exposure to H2O gas at elevated temperature. The sample CuAu thin film was annealed in H2 at 400 °C for 3 h and transferred to the in situ cell, where it was annealed for another hour. Then, 0.053% CO balanced with He was introduced at room temperature. As shown in SI Appendix, Fig. S8,
we can see both Cu$^{0}$-CO and Au$^{0}$-CO adsorption peaks at 2,098 and 2,105 cm$^{-1}$ (31–33). After increasing the temperature to 400 °C, we introduce the H$_2$O through Ar bubbling and we see the emergence of a new peak at 2,154 cm$^{-1}$, which is assigned to Cu$^{2+}$-CO (34, 35). With the attenuation of previous Cu$^{0}$-CO peak, we can see the surface Cu atoms tend to lose electrons and get oxidized, which is in accordance with our ETEM observations in Fig. 1E–G. These observations confirm the reaction route revealed by the above AIMD simulation, i.e., the surface Cu atom bonded with OH group, which attracts the neighboring CO molecules (possibly from neighboring Au sites) to form CO$_2$.

We further investigate the reaction routes of CO and OH on the CuAu surface through AIMD simulation for different configurations of surface species at different Cu and Au sites, as shown in Fig. 4. As shown in Fig. 2, both CO and H$_2$O are more likely adsorbed on Cu-top sites, then we use such a configuration (SI Appendix, Fig. S9) but vary their relative positions with respect to the surface Au atom. When CO is adsorbed on the Cu-top sites near the Au atom (Fig. 4A) it interacts with the OH adsorbed on the adjacent Cu-top site and quickly forms an HOCO intermediate. Then, the HOCO intermediate rotates almost 180° to react with another OH that is adsorbed on the Au sites, resulting in the dehydrogenation of H in HOCO and forming a CO$_2$ product. Finally, the formed CO$_2$ is easily desorbed from the CuAu surface. The whole reaction finishes in 1.08 ps. On the contrary, if CO is adsorbed on the Cu sites that are far away from Au (Fig. 4B), after a prolonged time of 5.73 ps only an HOCO intermediate has been formed on the CuAu surface without the formation and desorption of the CO$_2$ product. This demonstrates the effect of surface Au atoms in the CuAu alloy surface on promoting the WGSR process. The adsorbed OH on CuAu can further dissociate to O and H, and we also compared the reaction process in the presence of O and H.

Fig. 3. Synergetic structural activation of the CuAu surface under WGSR condition. (A–D) HRTEM images of CuAu(110) surface atomic structures under vacuum condition (A), CO+H$_2$O gas pressure of $1 \times 10^{-6}$ mbar (B), $1 \times 10^{-4}$ mbar (C), and $1 \times 10^{-2}$ mbar (D). The right columns are enlarged surface regions. (E) Snapshots of the dynamic reaction between OH and CO on CuAu(110) surface by AIMD simulation. (F) HRTEM image of typical structural basis of activated CuAu surface as shown in D. (G) Simulated HRTEM image of CuAu surface based on the atomic structure after structural relaxation of both CO and OH groups on the CuAu surface. (H) Superimposed HRTEM image and corresponding structure model.
species. Compared with the adsorbed H, the existence of O on the CuAu surface inhibits the production of CO$_2$, as shown in Fig. 4C.

Although an HOCO intermediate is formed initially, the C–O bond in HOCO can break soon to regenerate CO, and CO is desorbed from the CuAu surface. This is probably because the stronger adsorption of O than H on the surface Cu sites weakens the adsorption of HOCO, and the HOCO intermediate could not be maintained and participate the subsequent reactions. The distance (C–O2) changes (Fig. 4D) further confirm the formation of HOCO, and the distance (H–O3) changes and the angle (O1–C–O2) changes (Fig. 4E) show the production of CO$_2$ product on the CuAu$_1$ surface (Fig. 4A). The above simulation results reveal that the synergetic structural activation of the CuAu surface, especially the position of Au atoms on the surface, could have great effect on the reaction process. However, it is the anchoring of Au atoms that is responsible for the periodic surface reconstruction observed in Fig. 3.

![Figure 4](https://doi.org/10.1073/pnas.2120088119)

**Fig. 4.** AIMD calculations of CO and dissociated H$_2$O dynamics on the CuAu surface. (A) CuAu surface (CO adsorbed on the Cu site1). (B) CuAu surface (CO adsorbed on the Cu site2). (C) CuAu surface with dissociated O (CO adsorbed on the Cu site1). (D) The distance change of C–Cu, C–O2, and H–O3. (E) The angle of O1–C–O2 on the CuAu surface (CO adsorbed on the Cu site2) during the AIMD calculations.
In conclusion, the atomic-precise activation of a CuAu surface under WGSR conditions has been identified by ETEM. Compared with the surface segregation and oxidation by inducing CO and H₂O gas, respectively, periodic surface reconstruction on CuAu systems can be visualized upon CO and H₂O gas mixture exposure. The local environment on CuAu surface, as discussed by DFT and AIMD calculations, plays a significant role in adsorbing reactants and intermediate during the WGSR process. Specifically, the adsorption of CO and H₂O is controlled dramatically by tuning the surface Au/Cu ratio, and WGS can be promoted when CO is adsorbed on Cu sites adjacent to Au, demonstrating the synergistic relationships between Cu and Au for WGSR. The activation of local environment on the catalyst surface by reactants observed here may help to understand other catalytic reactions.

**Methods**

**CuAu Thin Film Preparation.** The single crystalline CuAu thin films were prepared through an ultrahigh vacuum e-beam evaporation system (vacuum up to 1 × 10⁻⁶ mbar) through a codeposition process. The substrates were freshly cut single-crystalline NaCl with a (100) orientation and heated to 350 °C upon deposition. The deposition rate was ~1 Å, and the total thickness is ~50 nm. The as-prepared CuAu thin films were stored in a glovebox to prevent surface oxidation. The thin films along with NaCl substrate were cut and immersed in deionized water to remove NaCl. Before loading on the TEM heating grids, the CuAu thin films were washed several times in acetone and methanol.

**ETEM Gas Experiments.** All in situ gas heating experiments were conducted on the FEI Titan aberration-corrected environmental transmission electron microscope with a customized gas delivery system capable of releasing single or mixed gas up to 20 mbar with a precision of ~1 × 10⁻⁶ mbar through a leak valve. A double-tilt heating holder Gatan 652 or a chip-based FEI Nano Ex-iv heating holder were used for loading the CuAu thin films. The gas heating experiments generally follow a heating-stage-gas introduction procedure, i.e., the sample was first heated to a desired temperature (300 °C) and staged for at least 30 min under vacuum in the TEM and then the gases were introduced. The electron beam effect on the gas experiments in ETEM is evaluated in detail in [SI Appendix](#).

**DFT Calculations.** All periodic DFT calculations were conducted using the generalized gradient approximation GGA level within the PW91 exchange correlation functional (33, 34) using the Vienna Ab initio Simulation Package (VASP) (35, 36). A plane wave basis set with a kinetic cutoff energy of 400 eV was used for both total energy calculations and AIMD simulations. Spin polarization was included in the calculations. The detailed modeling process and AIMD simulations parameter are described in [SI Appendix](#).

**Data Availability.** All study data are included in the article and/or [SI Appendix](#).

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