

# Catalyzing the catalyst: Hydrogen dissociation and spillover on Pd impurities in Cu(111) but not in Au(111)

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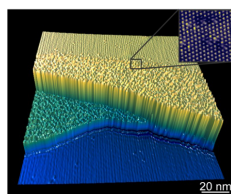
## Introduction

The activation of molecular hydrogen on relatively inert catalysts such as copper is essential to facilitate CO<sub>2</sub> conversion in industrially important reactions such as methanol synthesis. We have demonstrated that single Pd atoms alloyed into a Cu surface dramatically increase the concentration of adsorbed hydrogen on the Cu(111) surface by promoting H<sub>2</sub> dissociation and spillover onto the Cu surface. The same mechanism does not operate on Au(111) surfaces, however, because the spillover is thermodynamically unfavorable with respect to molecular hydrogen desorption. This work reveals that individual Pd atoms can be used to create bifunctional catalyst surfaces in which the isolated Pd atoms promote key steps in hydrogenation reaction networks if they are supported in the correct host.

## Materials and Methods

All experiments were performed in a low-temperature, ultrahigh-vacuum (LT-UHV) scanning tunneling microscope (Omicron). Cu(111) and Au(111) single crystals were cleaned by cycles of argon ion sputtering (1 keV/10  $\mu$ A) and annealing at 820 K. Both crystals were mounted on the same sample plate, allowing both surface alloys to be examined under exactly the same conditions of Pd coverage, H<sub>2</sub> flux and temperature. Pd was deposited on the crystals by resistively heating a Pd wrapped W wire while the Cu(111) and Au(111) samples were held at 420 K. The Pd doser was calibrated from atomic resolution STM images in which the number of both surface Cu and Pd atoms could be quantified. All Pd coverages in this paper are 0.010 $\pm$ 0.001 ML. After depositing Pd, the crystal was dosed with 10 L of H<sub>2</sub> (99.99% purity gas purchased from Airgas) via a leak valve connected to the preparation chamber.

The DFT calculations were all performed with DACAPO [1]. The adsorption energies of hydrogen were modeled in a (3 $\times$ 2) fcc(111) surface unit cell with a slab thickness of 4 layers separated by 10 Å of vacuum space. The Brillouin zone was sampled by an 8 $\times$ 6 $\times$ 1 Monkhorst-Pack grid. The valence electron wave functions were expanded in a plane wave basis set with an energy cutoff of 350 eV. The top two layers and the adsorbate were relaxed until



**Figure 1. Scanning tunneling microscope image of the onset of surface alloying of Pd into Cu(111).**

the maximum force of 0.05 eV/Å was reached. All adsorption energies are relative to gas-phase molecular hydrogen.

## Results and Discussion

We did not observe any Pd-Pd dimers at low Pd coverages; the Pd atoms were always surrounded by Cu or Au neighbors. In a Cu substrate the alloying began at the step edges as shown in Figure 1, suggesting that Pd adatoms were mobile on the terraces until they collide with an ascending step edge where they adsorb and are incorporated into the surface or subsurface [2]. No hydrogen dissociation is observed on Cu(111) surfaces after exposure to 10L of H<sub>2</sub> at 420K. However, when a small amount of Pd (0.01 ML) was alloyed into the Cu(111) surface and exposed to the same amount of hydrogen, large numbers of hydrogen atoms can be seen on the surface with low-temperature scanning tunneling microscopy (Figure 2). In contrast, after the same H<sub>2</sub> exposure no hydrogen atoms were present on Au(111) either before or after Pd alloying.

**Figure 2. Hydrogen atoms on Cu(111) with Pd impurities present.**

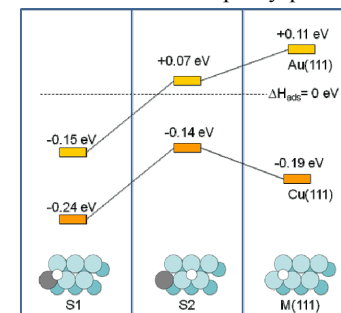
We calculated the stability of hydrogen atoms in the fcc sites of a model Pd impurity surface alloy on both Cu(111) and Au(111) surfaces. Our results show that hydrogen dissociation and spillover is favorable on the Cu surface with Pd impurities. Hydrogen dissociation on the Pd impurity on Au(111) is also favorable, but the spillover is not thermodynamically favorable.

## Significance

Our work shows that a relatively inert catalyst can be promoted by trace impurities via spillover provided that the adsorbates are stable on the inert surface. This work may have important implications in promoting dissociative adsorption of other molecules such as oxygen.

## References

1. DACAPO. [cited; Available from: <http://dcwww.camp.dtu.dk/campos/Dacapo/>.
2. Aaen, A.B., E. Laegsgaard, A.V. Ruban, and I. Stensgaard, Surface Science, 1998. 408(1-3): p. 43-56.



**Figure 3. Density functional calculations of hydrogen adsorption on Pd impurities in Cu (orange) and Au (yellow).**