Hydrogen Dissociation and Spillover on Individual Isolated Palladium Atoms

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Using a combination of low-temperature scanning tunneling microscopy and density functional theory it is demonstrated how the nature of an inert host metal of an alloy can affect the thermodynamics and kinetics of a reaction pathway in a much more profound way than simply a dilution, electronic, or geometric effect. This study reveals that individual, isolated Pd atoms can promote H_2 dissociation and spillover onto a Cu(111) surface, but that the same mechanism is not observed for an identical array of Pd atoms in Au(111).

Metal alloys are unique materials with properties that can stray far from those of their constituent elements. Alloys are often heterogeneous at the atomic scale and a complex electronic and geometric interplay between the atoms of the various elements yields new and useful material properties. In these systems the electronic interactions between the different elements in an alloy (ligand effects), the change in lattice parameters due to alloying (strain effects), and the spatial distribution of atomic sites (ensemble effects) influence the distinctive physical and electronic features which make alloys so appealing [1,2].

Alloying is often used in fields such as catalysis or metallurgy to "dilute" an expensive, reactive material in a cheaper, more inert host. In this way the character of the minority element can still dominate the material properties without the higher cost of a pure metal component. This property is extremely useful in heterogeneous catalysis, where reaction rates and pathways can be altered by tuning the alloy composition [3–5]. A common explanation for such behavior is that the reaction of interest can still be catalyzed by the minority active component; however, mixing in a more passive host allows products to be released more easily. This approach can even lead to enhanced reaction rates and selectivities [3,6,7].

One key reaction step in which alloy catalysts are often employed is the dissociation of molecular hydrogen, which is a crucial part of a number of energy-related technologies including the hydrogenation of CO_2, water gas shift catalysis, and hydrogen separation [8–10]. In methanol synthesis the most common metal used as a catalyst is Cu [11]. H_2 dissociation on pure Cu is activated and occurs very slowly unless high pressures and temperatures are used to drive the reactions [12]. Hydrogen dissociation on Pt-group metals, in contrast, is facile and occurs readily at room temperature and ambient pressures. These observations suggest that a bifunctional catalyst composed of a relatively inert metal such as Cu or Au with a minority Pt-group metal component that can readily dissociate hydrogen may be a superior catalyst when hydrogen is a reactive species, but the catalysis would primarily occur on the host metal.

The atomic-scale geometric and reactive properties of small amounts of Pd alloyed with both Cu and Au(111) host surfaces were investigated in this work using low-temperature scanning tunneling microscopy (STM) and density functional theory (DFT). This study shows how Pd atoms can modify both the ability of these surfaces to dissociate hydrogen and the subsequent hydrogen atom spillover from the Pd sites onto the host surfaces. These results demonstrate that individual, isolated Pd atoms are active for the dissociation of H_2 if supported in the correct host.

Isolated Pd atoms alloyed into Cu(111) and Au(111) hosts were synthesized by physical vapor deposition of small amounts of Pd onto the clean surfaces during controlled annealing. In agreement with previous studies [3,13], no Pd-Pd dimers were observed at low Pd coverages; the Pd atoms were always surrounded by either Cu or Au neighbors. These isolated Pd sites have been shown to be active for catalytic reactions such as vinyl acetate synthesis on Pd/Au(111) [3,14]. In both surfaces it was also possible to distinguish between individual Pd atoms in the surface layer (which appeared as protrusions) and subsurface Pd atoms in the layer below the surface (which appeared as depressions), in good agreement with previous STM studies of similar bimetallic near-surface alloys [13,15,16].

Alloying begins at the step edges in a Cu substrate as shown in Fig. 1(a), suggesting that Pd adatoms are mobile on the terraces until they collide with an ascending step edge where they adsorb and are incorporated into the surface or subsurface [13,16]. Figure 1(b) shows a Au(111) surface with the $22 \times \sqrt{3}$, or herringbone reconstruction, after deposition of Pd. On the Au(111) surface, the elbows of the herringbone reconstruction act as sites for the place exchange of Pd atoms before the Pd disperses into the surface and subsurface layers [inset of Fig. 1(b)]. In order to compare the properties of isolated Pd atoms in both Cu
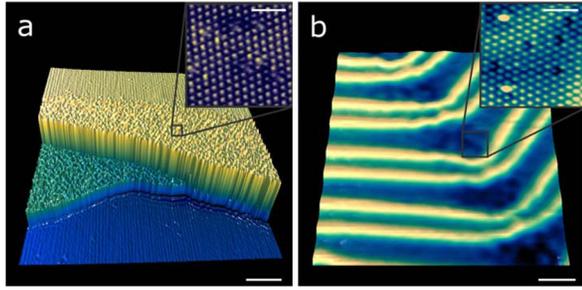
FIG. 1 (color online).   STM images of Pd alloyed surfaces at 78 K. (a) In the Cu(111) surface, Pd alloys preferentially at the step edges and forms "brims" (scale bar = 20 nm, I = 0.1 nA, V_{tip} = 0.4 V). Inset: atomic resolution of the Cu/Pd alloy shows individual Pd atoms in the surface layer appearing as protrusions while subsurface Pd atoms image as depressions (scale bar = 1 nm, I = 0.9 nA, V_{tip} = −0.04 V). (b) Pd incorporation into a Au(111) surface leads to place exchange at the elbows of the herringbone surface reconstruction (scale bar = 4 nm, I = 1.5 nA, V_{tip} = −0.1 V). Inset: atomic resolution of Pd/Au(111) shows a similar appearance of the Pd atoms, where surface Pd atoms image as protrusions and subsurface Pd atoms appear as depressions (scale bar = 1 nm, I = 0.4 nA, V_{tip} = 0.1 V).

and Au, each of the alloy systems was dosed with the same amount of Pd [0.01 monolayer (ML)] at a temperature that yielded ~50% surface and 50% subsurface Pd.

After exposure to 10 L (where 1 L = 1×10^{-6} Torr · s) of H_2 at 420 K, no hydrogen dissociation was observed on the bare Cu(111) surface, which is consistent with previous reports [17]. However, after 0.01 ML Pd was alloyed into the Cu(111) surface and exposed to the same amount of hydrogen at 420 K, a large amount of hydrogen was present on the surface. STM imaging after cooling the sample to 7 K revealed that these H atoms clustered into islands as shown in Fig. 2 [18]. Salmeron and co-workers reported that for H coverages near 1 ML, three vacant sites around a Pd atom are required for hydrogen dissociation on Pd(111) [19]. The results presented here do not contradict the work of Salmeron *et al.*, but show the interesting effect that in the low H coverage regime individual, isolated Pd atoms are very efficient at dissociating molecular hydrogen. Extensive STM imaging revealed a sharp decrease in H coverage further from the Pd atoms, which is consistent with H_2 dissociation occurring at the Pd atom sites. In contrast to the Cu surface, *no* hydrogen atoms were observed on a Au(111) surface containing an identical amount of Pd atoms after exposure to the same H_2 flux.

The stability of isolated Pd atoms in Cu and Au(111) was investigated using density functional theory. The heat of formation was calculated for 21 different clean surface alloy configurations with compositions spanning from pure host (Cu or Au) to a full monolayer of Pd on the surface of the host. The lattice constant of the surface was fixed to the lattice constant of the host, which was also calculated using
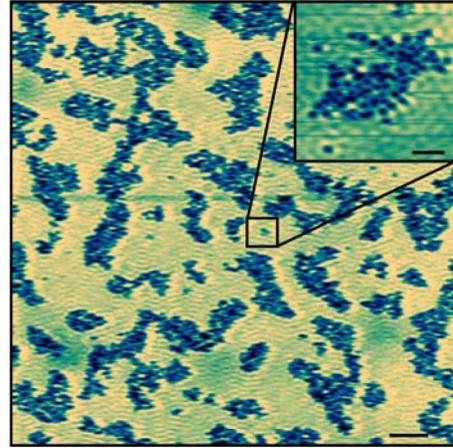

FIG. 2 (color online).   H on Pd/Cu(111) imaged at 7 K. STM image of Pd/Cu(111) after depositing 10 L of H_2 shows islands of H atoms that have spilled over onto pure Cu(111) areas (scale bar = 15 nm, I = 10 pA, V_{tip} = −8 mV). Inset: individual H atoms appear as depressions (scale bar = 5 nm, I = 50 pA, V_{tip} = 20 mV).

density functional theory (Cu 3.67 Å, Au 4.18 Å). Pd exothermically alloys into both Cu and Au(111) surfaces. At coverages below x_{Pd} = 0.4, Pd atoms are most thermodynamically stable when surrounded by Cu or Au atoms, consistent with exothermic alloy formation and maximization of Pd-Cu or Pd-Au bonds. These results are consistent with STM observations in this study and others [13,16].

The Pd alloy surfaces have a distribution of different active sites where hydrogen atoms can adsorb, including sites with and without the Pd atom present. The preferential adsorption site for hydrogen is the threefold fcc hollow site [20,21]. The adsorption energies of hydrogen were modeled on a $(3 \times 2) \times 4$ layer fcc(111) surface. The slab surfaces were separated by 10 Å of vacuum space and the Brillouin zone was sampled by an $8 \times 6 \times 1$ Monkhorst-Pack grid. The stability of hydrogen was calculated in the fcc hollow sites of alloys containing an individual Pd atom in both Cu(111) and Au(111) host surfaces. H atoms located on a Pd fcc site were labeled $S1$, with a H atom on one Pd and two host metal atoms. As the H moved away from the Pd by one fcc site onto the host metal a calculation was performed for this site, labeled $S2$, with the H located on three host metal atoms. Finally the energy was calculated for a site with only the host metal and no Pd contributions, labeled $M(111)$. The Perdew-Wang 1991 (PW91) exchange-correlation functional was utilized to calculate the adsorption energies. The adsorption energies were also calculated using the Perdew-Burke-Ernzerhof (PBE), revised Perdew-Burke-Ernzerhof (revPBE), and alternative revised Perdew-Burke-Ernzerhof (RPBE) functionals non-self-consistently [22] to evaluate the sensitivity of the results to the exchange-correlation functional. The PW91 and RPBE functionals are expected to span the range of expected values with
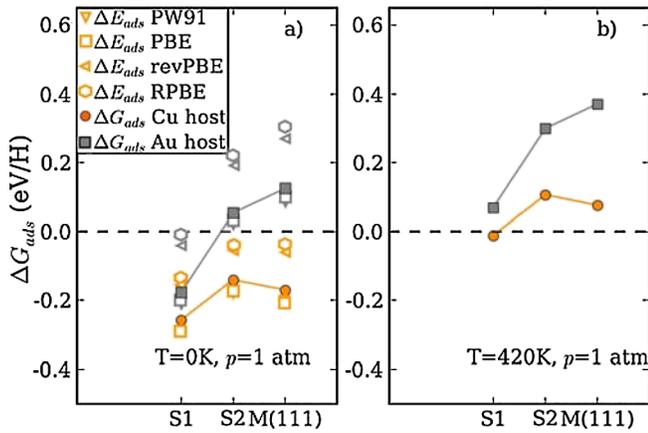
FIG. 3 (color online). Graphical summary of dissociative H adsorption on Pd alloy surfaces (a) at 0 K and (b) 420 K. $S1$ is an fcc site containing an isolated Pd atom, $S2$ is an fcc site near the Pd atom, and $M(111)$ refers to the pure host metal surface. The solid symbols correspond to free energies corrected for zero-point energies, pressures, and temperature. The open circles are DFT adsorption energies at 0 K calculated with the RPBE, revPBE, PW91, and PBE exchange-correlation functionals. H adatoms are stable at Pd sites in both Cu and Au(111), but diffusion away from the Pd atoms is thermodynamically unfavorable on Au(111) at 0 K.

PW91 yielding the most stable energies and RPBE yielding the weaker range of energies [23]. These results are summarized in Fig. 3.

The exchange-correlation functionals all yielded the same trends in adsorption energies with a variation of 0.09–0.16 eV/H between PW91 and RPBE for each site. Here only the PW91 results are discussed. Hydrogen favorably adsorbs on the Pd $S1$ site with an adsorption energy with respect to molecular hydrogen ($\frac{1}{2}H_2 \rightarrow H^*$) of -0.24 eV/H. The adsorption energy on the neighboring $S2$ site is -0.14 eV/H, which is slightly weaker than the adsorption energy of hydrogen on Cu(111).

In contrast to Cu(111), hydrogen dissociation is endothermic on Au(111). Hydrogen favorably adsorbs at isolated Pd atoms in Au(111) ($S1$) with an adsorption energy of -0.15 eV/H, although the RPBE functional suggests the adsorption may be slightly unfavorable at $+0.01$ eV/H. The hydrogen adsorption energy at $S2$ is $+0.07$ eV/H indicating that molecular desorption of H_2 is thermodynamically favorable. It is not surprising in this context that after deposition of H_2 at identical conditions to the Pd/Cu(111) data, no hydrogen spillover was observed on either the Au(111) or the Pd/Au(111) surfaces.

The free energies of adsorption have also been considered to incorporate the effects of zero-point energy, pressure, and temperature using standard atomistic thermodynamics [24,25] and the PW91 adsorption energies discussed above. At 0 K, the free adsorption energies are slightly weaker than the DFT adsorption energies due to the zero-point energies of the adsorbate and the H_2 mole-

cule. At 420 K, however, the adsorption energies are substantially reduced due to entropy in molecular hydrogen, and the calculations suggest that dissociative adsorption of hydrogen is highly unfavorable on the Au host but only slightly unfavorable on the Cu host. Dissociative adsorption on Cu is favorable at temperatures less than 420 K.

The dissociation and diffusion barriers between some of the key adsorption sites were also investigated. The dissociation barrier for H_2 on Cu(111) has been calculated to be 0.5 eV [26], although experimental estimates put the barrier in the range of 0.3–0.4 eV [17,27]. The same method in Ref. [26] has been used to calculate the dissociation barrier over an isolated Pd atom in Cu(111) and a barrier of only 0.02 eV was obtained. Although this method may underestimate the barrier, it suggests the existence of a very low barrier dissociation pathway over the Pd atom, consistent with the experimental observations of efficient dissociative adsorption at 420 K in the presence of individual, isolated Pd atoms.

Nudged elastic band calculations were used to estimate barriers for the adsorbed H atoms to diffuse away from Pd. The calculated barriers were in the range 0.12–0.15 eV from the weaker adsorption energy site to the stronger adsorption energy site. Diffusion barriers were previously reported on late transition metals in the range of 0.12–0.18 eV, and were found to be correlated with adsorption energies of both the initial and final sites [28]. The calculated and estimated dissociation and diffusion barriers are summarized in Fig. 4, where two possible spillover mechanisms are examined. Both mechanisms are feasible, illustrating how dissociative H_2 adsorption can be catalyzed by individual, isolated Pd atoms supported in the correct host.

The understanding that emerges from these results is that hydrogen dissociation is thermodynamically feasible on
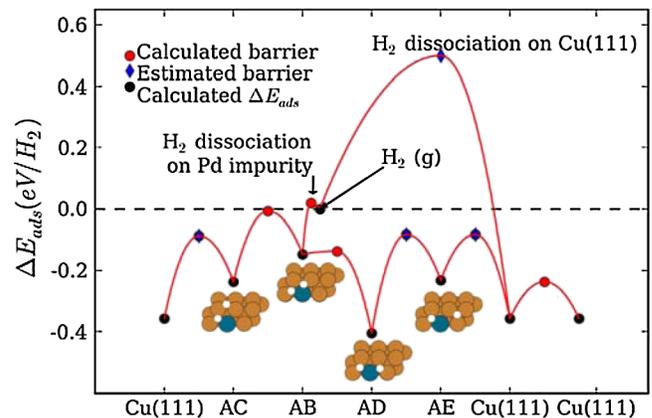

FIG. 4 (color online). Kinetics and thermodynamics of feasible H spillover pathways from individual, isolated Pd atoms to Cu. The lighter circles represent barriers calculated in this work. The darker diamonds are barriers taken from the literature [26,28]. Schematics: The dark (orange) circles represent Cu atoms, the black circle (blue) indicates isolated Pd atoms, and the small white circles are H atoms.

isolated Pd atoms in Cu(111) and Au(111). Spillover is activated and feasible on Cu(111) but thermodynamically infeasible on Au(111) due to desorption of molecular hydrogen. This work also indicates that the hydrogen dissociation barrier is high on Cu(111), where negligible hydrogen dissociation is observed experimentally, and that the barrier is a great deal lower at Pd sites, where significant dissociation and spillover is observed under the same experimental conditions.

These results reveal that small amounts of individual, isolated Pd atoms can efficiently dissociate H_2 and allow it to spill over onto an appropriate host metal. While it is known that H spillover can occur from Pd to Cu sites in the synthesis of methanol [29,30], the results from our study demonstrate that this approach is more general and that multiple alloy combinations can be surveyed theoretically in an identical manner in order to identify potential candidate systems. Careful selection of the host metal and the catalytically active atom in an alloyed system will enable dissociation and spillover of species that typically do not react due to high kinetic barriers (e.g., O_2 on Au). Such bifunctional alloy catalyst surfaces will yield tunable catalytic properties such as stability, adsorption energy, and spillover barrier.

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[1] J. G. Chen, C. A. Menning, and M. B. Zellner, Surf. Sci. Rep. **63**, 201 (2008).
[2] J. A. Rodriguez, Surf. Sci. Rep. **24**, 223 (1996).
[3] M. S. Chen et al., Science **310**, 291 (2005).
[4] M. O. Pedersen et al., Surf. Sci. **426**, 395 (1999).
[5] J. Greeley and M. Mavrikakis, Nature Mater. **3**, 810 (2004).
[6] F. Gao et al., J. Phys. Chem. C **112**, 3362 (2008).
[7] C. J. Baddeley et al., J. Phys. Chem. **99**, 5146 (1995).
[8] K. I. Choi and M. A. Vannice, J. Catal. **131**, 36 (1991).
[9] J. Greeley et al., Chem. Phys. Chem. **7**, 1032 (2006).
[10] P. Kamakoti et al., Science **307**, 569 (2005).
[11] X. M. Liu et al., Ind. Eng. Chem. Res. **42**, 6518 (2003).
[12] B. Hammer and J. K. Norskov, Nature (London) **376**, 238 (1995).
[13] A. B. Aaen et al., Surf. Sci. **408**, 43 (1998).
[14] P. Han et al., J. Am. Chem. Soc. **129**, 14355 (2007).
[15] J. Knudsen et al., J. Am. Chem. Soc. **129**, 6485 (2007).
[16] D. O. Bellisario et al., J. Phys. Chem. C **113**, 5895 (2009).
[17] T. Kammler and J. Kuppers, J. Chem. Phys. **111**, 8115 (1999).
[18] S. Rauber et al., Surf. Sci. **123**, 173 (1982).
[19] T. Mitsui et al., Nature (London) **422**, 705 (2003).
[20] M. F. Luo, G. R. Hu, and M. H. Lee, Surf. Sci. **601**, 1461 (2007).
[21] V. Pallassana et al., Phys. Rev. B **60**, 6146 (1999).
[22] B. Hammer, L. B. Hansen, and J. K. Norskov, Phys. Rev. B **59**, 7413 (1999).
[23] K. Honkala et al., Science **307**, 555 (2005).
[24] J. R. Kitchin, K. Reuter, and M. Scheffler, Phys. Rev. B **77**, 075437 (2008).
[25] K. Reuter and M. Scheffler, Phys. Rev. B **65**, 035406 (2001).
[26] B. Hammer and J. K. Nørskov, Nature (London) **376**, 238 (1995).
[27] K. D. Rendulic and A. Winkler, Surf. Sci. **299–300**, 261 (1994).
[28] A. U. Nilekar, J. Greeley, and M. Mavrikakis, Angew. Chem., Int. Ed. **45**, 7046 (2006).
[29] D. Lee et al., Catal. Today **111**, 373 (2006).
[30] I. Melian-Cabrera et al., Catal. Today **45**, 251 (1998).