Controlling Hydrogen Activation, Spillover, and Desorption with Pd–Au Single-Atom Alloys

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Supporting Information

ABSTRACT: Key descriptors in hydrogenation catalysis are the nature of the active sites for H₂ activation and the adsorption strength of H atoms to the surface. Using atomically resolved model systems of dilute Pd–Au surface alloys and density functional theory calculations, we determine key aspects of H₂ activation, diffusion, and desorption. Pd monomers in a Au(111) surface catalyze the dissociative adsorption of H₂ at temperatures as low as 85 K, a process previously expected to require contiguous Pd sites. H atoms preside at the Pd sites and desorb at temperatures significantly lower than those from pure Pd (175 versus 310 K). This facile H₂ activation and weak adsorption of H atom intermediates are key requirements for active and selective hydrogenations. We also demonstrate weak adsorption of CO, a common catalyst poison, which is sufficient to force H atoms to spill over from Pd to Au sites, as evidenced by low-temperature H₂ desorption.

A key requirement in the efficient use of heterogeneous catalysts, fuel cells, and hydrogen storage devices is the ability to activate, uptake, and release hydrogen easily. Metallic surfaces that bind H weakly can exhibit high catalytic selectivity; however, these surfaces often have high activation barriers for H₂ dissociation, which limits the activity of the catalysts. One viable approach to produce weakly bound H atoms on the surface of catalysts is to use a bimetallic alloy that combines reactive catalytic metals with inert coinage metals. Au nanoparticles have been recently shown to catalyze highly selective hydrogenation and oxidation reactions due to the weak adsorption energy of H and O on Au. The addition of Pd into Au changes the catalytic activity and selectivity for multiple reactions, including vinyl acetate synthesis, hydrogen peroxide synthesis, hydrocarbon hydrogenation, CO oxidation, and oxidation of alcohols to aldehydes. For many of these reactions, the size and dispersion of the Pd atom clusters have an impact on the observed chemistry, the so-called ensemble effect in alloy catalysis. Selective synthesis of vinyl acetate and hydrogen peroxide relies on the inability of Pd monomers to activate O₂, while CO oxidation requires Pd dimers to dissociate O₂. For H₂ activation on Pd–Au, the necessary ensemble size has been debated. Yu et al. and Maroun et al. concluded that contiguous Pd sites are required for H₂ activation. However, density functional theory (DFT) calculations by Venkatachalam et al. indicated that Pd monomers may be capable of H₂ activation. However, so far, no experimental evidence exists demonstrating this single-atom chemistry. Furthermore, CO is a common poison for catalysts. An understanding of CO interaction with adsorbed molecules and competition for active sites is important when designing new catalysts. Hence, an atomic-level understanding of reactive sites for CO adsorption and H₂ activation will elucidate the minimal Pd ensemble capable of activating H₂ and reveal the energetic landscape for uptake, spillover, and release of H and CO.

To probe the ability of Pd monomers in Au to activate H₂ and to induce spillover of H atoms onto Au, we studied the fundamental processes of dissociation, spillover, and desorption using the complementary techniques of scanning tunneling microscopy (STM), temperature-programmed desorption (TPD), and DFT. STM enables direct visualization of the atomic composition of the active sites necessary for H₂
activation, and TPD allows us to elucidate key parts of the energy landscape for activation, spillover, and desorption. By studying dilute concentrations of Pd atoms (≤5%) in Au, we observe facile dissociation and low-temperature recombinative desorption of H₂ from isolated Pd atoms in Au(111). Our Pd–Au single-atom alloy (SAA) data contrast with previous studies that suggested that at least two contiguous Pd atoms are required for H₂ dissociation, although this previous work lacked an atomic-scale characterization of the alloy surface. Furthermore, we have discovered that the coadsorption of CO with H forces H to spill over from the active Pd sites to Au. By comparing H₂ and CO desorption temperatures to calculated adsorption energies of H and CO, we elucidate the energetic pathway for the adsorption, spillover, and desorption of H with and without CO from Pd monomers in Au.

In order to determine if Pd monomers in Au are capable of H₂ activation, we first generated Pd–Au(111) alloys with isolated Pd atoms present in the surface layer (Figure 1). Pd–Au(111) alloys formed by the vapor deposition of Pd on Au(111) have been extensively characterized. Depending on the surface temperature and flux of incoming Pd atoms during alloying, a range of structures can be formed from isolated atoms substituted into the surface and subsurface layers of Au, to Pd-rich nanoparticles on the surface. At low Pd coverages (≤0.05 ML), Pd atoms exist as isolated atoms substituted into the Au lattice. Due to stronger heteroatom bonds, Pd atoms prefer to be surrounded by Au atoms and exist as isolated species at low coverages. At Pd coverages > 0.05 ML, the Pd atoms begin to cluster due to a kinetic limitation on the dispersion of the Pd atoms in Au. In the present study, all Pd–Au(111) alloys were prepared at 380 K, yielding an alloyed surface where Pd atoms predominately exist as monomers in the Au surface at coverages below 0.05 ML.

Using TPD, we investigated the ability of isolated Pd atoms to dissociate H₂ (Figure 2). We prepared Pd–Au(111) SAAs with between 0.01 and 0.05 ML Pd and exposed them to H₂ at 85 K and observed the desorption of H₂ at 110 and 175 K (Figure 2A). The predominant desorption peak at 175 K is due to H₂ desorption from single Pd atoms because increasing the Pd coverage leads to a linear increase in the area of the peak. In the absence of Pd atoms, no desorption of H₂ is observed from bare Au(111) after the same exposure to H₂. The desorption temperature of H₂ at 175 K indicates that H₂ dissociates on the surface because molecular H₂ desorbs from metal surfaces at <30 K. Furthermore, our data show that the desorption of H₂ from Pd monomers is significantly lower than the desorption of H₂ from Pd(111), which occurs at 310 K. The small desorption peak seen in Figure 2A at 110 K is due to desorption of H₂ from Au sites, as previously reported by Pan et al., who adsorbed H atoms onto Au(111) using a H atom source in order to overcome the dissociation barrier. Additionally, in order to determine the desorption order of H₂, we varied the surface coverage of H. With increasing H coverage, the desorption peaks shift to lower temperatures, indicative of second-order desorption, as previously observed for disordered Pd–Au alloys.

Figure 2B shows that in the single-atom regime (≤0.05 ML), the amount of H₂ desorbing from the surface is proportional to the amount of Pd atoms present in the surface, with an average of 1.4 ± 0.1 H atoms per Pd atom. One to three H atoms are predicted by DFT to be thermodynamically stable in the three-fold hollow sites surrounding Pd monomers in Au. Small amounts of H atoms may spill over from the Pd sites to Au, but we are unable to quantify the amount of H₂ desorbing from Au because H₂ begins desorbing at the start of the temperature ramp. With STM, we imaged Pd–Au(111) SAAs exposed to H₂ and observed localized protrusions in the vicinity of edge dislocations where Pd atoms predominately reside.

In accord with our TPD results, we suggest that the enlarged appearance of the Pd atoms is due to the presence of H atoms at the Pd monomer sites. DFT and STM experiments support the suggestion that H atoms are thermodynamically stable on Pd–Au alloys.

**Figure 1.** Pd–Au(111) SAA. Isolated Pd atoms (highlighted by arrows) substituted into the Au(111) surface appear slightly topographically higher than the Au host.

**Figure 2.** H₂ activation on Pd–Au SAAs. (A) TPD spectra of H₂ desorption from a 0.05 ML Pd–Au(111) SAA after exposure to H₂ at 85 K. (B) H₂ coverage on varying concentrations of Pd in the SAA regime. (C) STM image of Pd–Au(111) SAA exposed to H₂ and cooled to 5 K for imaging at −1 V and 1 nA. (D) Desorption traces for m/z 2, 3, and 4 from Pd–Au SAA with equivalent H₂ and D₂ coverages.
To further probe the H₂ activation and H atom mobility on Pd–Au SAAs, we coadsorbed H₂ and D₂ onto Pd–Au SAA (Figure 2D). When H₂ and D₂ were deposited on the SAA, we observed desorption of H–D (m/z = 3). This scrambling provides direct evidence that Pd–Au SAAs are indeed capable of H₂ activation at 85 K. Furthermore, when equal amounts of H₂ and D₂ were activated, the H₂/HD/D₂ product ratio was 1:2:1, demonstrating complete scrambling of H and D. In terms of the energetics of this scrambling, H atoms will diffuse away from Pd sites onto Au by overcoming the diffusion barrier (0.244 or 0.302 eV depending on the diffusion pathway) onto the Au surface (Table S1). Once on Au, H and D atoms move very quickly due to the small diffusion barrier on Au (0.067 eV). At 120 K (i.e., 5 K below the onset of the desorption peak of H₂/HD/D₂ from Pd sites on the surface), the rate of diffusion away from Pd sites is 600 or 2 Hz depending on the diffusion pathway and assuming a pre-exponential factor of 10^13. Therefore, given that the heating rate is 1 K/s, the H and D atoms at Pd sites would be statistically scrambled before desorption of H₂/HD/D₂ and hence the observed 1:2:1 ratio.

As a second probe of the surface chemistry of Pd–Au SAAs, we studied the adsorption of CO, a common catalyst poison. Figure 3 shows that after exposure of a Pd–Au SAA to CO, a catalyst and fuel cell applications in which active site poisoning by CO can be a serious issue.

We discovered that CO can enhance the spillover of H atoms from Pd sites to Au where H₂ predominantly desorbs. Figure 3 shows TPD traces for the coadsorption of H and CO where the desorption temperature of H₂ is dependent on the CO exposure. In the absence of CO, H₂ desorbs from Pd sites at 175 K (Figure 3B). At subsaturation coverages of CO (0.1 L of CO), we observed desorption of H₂ from both Pd (160 K) and Au (110 K) sites (Figure 3C). When the surface was exposed to 1 L of H₂ followed by 1 L of CO, all H₂ desorbed from the surface at 110 K because all of the Pd atoms were saturated with CO (Figure 3D). Thus, it appears that when CO adsorbs on a H-covered SAA surface, CO forces the H atoms on to the Au(111) terraces from where they desorb at a significantly lower temperature than otherwise observed in the absence of CO.

To further understand this desorption behavior, periodic DFT calculations were performed on unreconstructed Au(111) surfaces with the VASP 5.3.3,52,53 code employing the optB86b-vdW code employing the optB86b-vdW exchange–correlation functional, which accounts for dispersion forces within the vdW-DF scheme of Dion et al. (see the Supporting Information for more details of the computational setup and energy definitions). In our DFT calculations, a variety of CO, H, and CO plus H adsorption structures were considered. With regard to the observed tendency of CO to drive H atoms away from the Pd sites of the SAA, our DFT calculations show that there is a strong repulsion between adsorbed CO and H. Specifically, when CO is adsorbed on the atop Pd site and H is in one of the adjacent hollow sites surrounding the Pd atom, there is a 0.56 eV repulsion between CO and H (Table S4). This repulsion can be reduced to only 0.01–0.02 eV if the H atom moves away to a proximal hollow site surrounded by only surface Au atoms. Therefore, despite H atom spillover being unfavorable, when CO adsors to the Pd sites, it becomes favorable for H to move onto Au(111). Furthermore, if CO is adsorbed on the surface prior to H₂, no H₂ is observed desorbing from the surface. Therefore, CO binds to the Pd sites and blocks the adsorption and activation of H₂, which further supports our hypothesis that Pd atoms are the sites responsible for H₂ activation (Figure 3A). For a CO-covered Pd(111) surface, it has previously been shown that CO blocks the dissociative adsorption of H₂. Also, related to these results, previous studies have demonstrated that the adsorption of CO on bimetallic alloys alters the desorption behavior of H₂. For Pd₆₄Au₇₆(110) alloys, the coadsorption of CO and H increases the desorption temperature of H₂ due to a trapping of near-surface H. A similar effect was observed for Pd–Cu alloys where CO selectively binds to the single Pd atoms in Cu and blocks the Pd entrance/exit sites for H₂ adsorption.

Combining our TPD results with DFT calculations (Tables S1–S4), we have elucidated the potential energy landscape for CO desorption peak is observed at 270 K, corresponding to an adsorption energy of ~0.9 eV, assuming a pre-exponential factor of 10^15.45,46 DFT, with various exchange-correlation functionals, is known to overestimate the CO adsorption strength, and likewise, our DFT predicts the adsorption energy to be ~1.34 eV.47,48 Most importantly, this is a significantly lower desorption temperature (270 K) than that observed from pure Pd(111) (~450 K).49 CO is also seen to desorb from Au terraces at <170 K, and from Au step edges at 180 K.50 Low-temperature desorption of CO from Pd–Au alloys has been reported for isolated Pd atoms in Au–Pd(111) and Au–Pd–Mo(110).51 Ruff et al. reported that the low desorption temperature of CO from Pd–Au alloys is due to the size of the Pd ensembles in Au.52 Larger Pd ensembles increase the adsorption energy of CO to the surface. The weak adsorption of CO to Pd–Au SAAs that we observe is important for both
H₂ activation and H adsorption are kinetically and thermodynamically unfavorable, respectively. After dissociation, H binds to Au(111) at 110 K, which infers a barrier significantly lower than when H binds to pristine Pd(111) (0.58 eV) (Figure 4). The facile H₂ activation and weak adsorption of H atoms observed for Pd–Au SAAs are very different from those on monometallic Pd and Au surfaces (Figure 4A). On Au(111), H₂ activation and H adsorption are kinetically and thermodynamically unfavorable, respectively. In order for H₂ to be desorbed from Au(111), it must overcome a large activation barrier, which we calculated to be 1.04 eV, in agreement with other DFT calculations. Additionally, H adsorption on fcc sites of Au(111) is thermodynamically unfavorable with respect to gas-phase H₂ by 0.14 eV, within the current computational setup. H₂ adsorption onto Pd(111), however, is a nonactivated (barrierless) process, with the resulting H atoms adsorbing strongly at fcc sites of Pd(111) with an adsorption energy of −0.58 eV per H atom. With Pd–Au SAAs, we observe facile H₂ activation compared to Au and low-temperature desorption of H₂ from Pd. For dilute concentrations of Pd in Au, we report H₃ dissociation at 85 K, indicating that Pd monomers greatly reduce the activation barrier for the dissociation of H₂ compared to Au(111). Our DFT calculations support a reduction in the activation energy on SAAs because the transition-state energy for H₂ adsorption on Pd–Au SAAs is 0.20 eV compared to 1.04 eV for Au(111). However, it is important to note that the calculated transition-state energies do not account for quantum nuclear effects, which are likely to lower the barriers and make hydrogen dissociation more facile. This is what is observed experimentally as H₂ desorbs from Au(111) at 110 K, which infers a barrier significantly lower than that calculated by DFT. Indeed, previously, we have shown with path-integral-based DFT simulations for atomic and molecular hydrogen that the effective free-energy barrier for adsorption/desorption can be dramatically lowered due to quantum mechanical tunneling. After dissociation, H binds to a Pd–Au fcc site with a computed adsorption energy of −0.11 eV. The negative adsorption energies correspond to exothermic adsorption processes, which are significantly weaker than when H binds to pristine Pd(111) (−0.58 eV) (Figure 4).

The smaller adsorption energy of H on Pd–Au sites compared to Pd(111) occurs mainly because H binds in three-fold hollow sites composed of one Pd atom and two Au atoms. In order to adhere to microscopic reversibility, the adsorption and desorption of H₂ must follow the lowest-energy pathway, which is via the isolated Pd atoms in Au. The total desorption barrier is dependent on the H₂ activation energy and H adsorption energy, which is directly related to the observed desorption temperatures. In order for H₂ to desorb from the Pd–Au SAA, H atoms overcome both the weak adsorption energy of H to the Pd–Au sites and the reduced H₂ activation barrier of Pd monomers (Figure 4B). Due to the thermodynamic instability of H atoms on Au, H atoms adsorb preferentially at Pd–Au sites, but a small quantity of H atoms exist on Au due to spillover from Pd–Au sites. The H atoms that exist on Au desorb directly from Au(111). Though the overall desorption temperature of H₂ from Au is less than the desorption temperature from Pd–Au sites, H₂ predominately desorbs from Pd–Au sites because H₂ adsorbs at Au sites are more strongly bound there.

When we consider the coadsorption of H and CO, we find that the desorption pathway of H₂ from the alloyed surface is altered (Figure 4C). Our DFT calculations reveal a greater thermodynamic stability for CO to occupy Pd–Au sites instead of H atoms. The adsorption of CO (−1.34 eV) on Pd monomers is significantly stronger than the adsorption of H to Pd monomers (−0.11 eV). Therefore, when a H-covered Pd–Au surface is exposed to CO at 85 K, the H atoms are forced from the Pd–Au to Au sites. Although it is thermodynamically unfavorable for H to adsorb on pure Au, the H₂ recombination barrier traps it there until 110 K, at which point, H₂ desorbs from Au sites. CO changes the exit sites for H₂ from Pd atoms to Au sites without violating microscopic reversibility because the addition of CO makes the forward and reverse pathways non-equivalent. Interestingly, CO can force H atoms to spill over from a preferred site to a thermodynamically unstable site and remain trapped on the surface by the recombination barrier.

Figure 4. Schematics of the energy landscapes for H₂ adsorption and desorption. (A) H₂ activation energy (Eₐ) per H₂ molecule and H adsorption energy (ΔE) per H atom in fcc sites on monometallic Au, Pd, and Pd–Au SAAs. Energetics of H₂ desorption for Pd–Au SAAs (B) without and (C) in the presence of CO. The schematic illustrates the preferred active sites for H₂ dissociation as well as the preferred adsorption sites for H and CO. Preferred and minor desorption pathways are displayed in orange and blue, respectively. In (B), the preferred pathway for H₂ desorption is via the Pd site. In (C), the Pd site is blocked by CO; therefore, H atoms spill over to Au and then desorb from there. All energies are reported relative to H₂ in the gas phase, as noted by the dashed horizontal lines. Note that Eₐ for H₂ on Au(111) calculated by DFT (which does not account for quantum nuclear effects) may in fact be a large overestimate of the barrier as, experimentally, H₂ desorbs from Au(111) at 110 K.
By utilizing well-defined Pd–Au model surfaces, we experimentally demonstrate that Pd monomers in a Au(111) surface can activate H₂, a process suggested by other experiments to require two contiguous Pd atoms. We clearly show by coupling high-resolution STM with TPD that low concentrations of individual, isolated Pd atoms can dissociate H₂ because the concentration of adsorbed H atoms is proportional to the surface concentration of Pd atoms in Au. Combining TPD with DFT calculations, we elucidate the energetic landscape for H₂ adsorption, activation, and desorption from isolated Pd atoms, revealing a low-temperature pathway for H₂ activation and release through the Pd atoms with minimal spillover to Au. The coadsorption of H₂ and D₂ leads to complete scrambling of H and D, supporting the dissociation of H₂ and the transient existence of H atoms on Au. Additionally, Pd–Au SAAs bind CO significantly more weakly than Pd(111) (270 vs 450 K), which can potentially improve CO tolerance of the catalysts. The competitive adsorption of CO and H on the Pd atoms forces H atoms to spill over onto the Au surface, altering the desorption pathway to an even lower temperature through Au (110 vs 175 K). Our work demonstrates that individual, isolated Pd atoms in Au allow for facile H₂ activation and weak adsorption of H atoms, a key requirement for efficient and selective hydrogenation catalysis.

ASSOCIATED CONTENT

Supporting Information
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FULL PAPER

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Notes
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