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Published in:
PHYSICAL CHEMISTRY CHEMICAL PHYSICS

Link to article, DOI:
10.1039/c4cp02589j

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Hydrogen adsorption on bimetallic PdAu(111) surface alloys: minimum adsorption ensemble, ligand and ensemble effects, and ensemble confinement

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The adsorption of hydrogen on structurally well defined PdAu–Pd(111) monolayer surface alloys was investigated in a combined experimental and theoretical study, aiming at a quantitative understanding of the adsorption and desorption properties of individual PdAu nanostructures. Combining the structural information obtained by high resolution scanning tunneling microscopy (STM), in particular on the abundance of specific adsorption ensembles at different Pd surface concentrations, with information on the adsorption properties derived from temperature programmed desorption (TPD) spectroscopy and high resolution electron energy loss spectroscopy (HREELS) provides conclusions on the minimum ensemble size for dissociative adsorption of hydrogen and on the adsorption energies on different sites active for adsorption. Density functional theory (DFT) based calculations give detailed insight into the physical effects underlying the observed adsorption behavior. Consequences of these findings for the understanding of hydrogen adsorption on bimetallic surfaces in general are discussed.

1 Introduction

Bimetallic surfaces have been studied intensely using surface science techniques to identify the physical origin of the often superior catalytic properties of bimetallic catalysts as compared to their respective constituents, but also with respect to monometallic supported catalysts in general, on an atomic scale.1 The level of insight gained from these model studies has increased dramatically with the advances in structural characterization, in particular by high resolution scanning tunneling microscopy (STM), e.g., for the resolution and chemical identification of different metal surface atoms2–4 and progress in the theoretical description of adsorbates and surface reactions.5–8 Using tailored nanostructured surfaces with well known concentrations of individual structural elements (‘nanostructures’), one ultimately aims at a qualitative and quantitative understanding of the chemical and catalytic properties of these nanostructures. This, in turn, can be used for designing optimized surfaces and finally optimized catalysts. The power and potential of such approaches has been demonstrated for various reactions.9–11

One example was the vinyl acetate synthesis on PdAu catalysts, which had been investigated in detail by Goodman and coworkers, both on dispersed catalysts and on model surfaces.12–17 For a better understanding of the chemistry of these PdAu surfaces, we had studied the interaction of different, structurally well characterized PdAu surfaces such as Au monolayer island modified Pd(111) surfaces or PdAu–Pd(111) monolayer surface alloys with CO, using this as a probe molecule.18–20

Extending our previous study, we here report on the interaction of hydrogen with bimetallic PdAu–Pd(111) surface alloys. First results were included in an earlier review.21 We are specifically interested in identifying active Pd ensembles for stable hydrogen adsorption, in particular the minimum Pd ensemble size for hydrogen adsorption, but equally in a semi-quantitative understanding of the nature and contributions of the different electronic and geometric effects affecting hydrogen adsorption on these bimetallic surfaces, such as electronic ligand22–24 and strain effects25 as well as geometric ensemble effects.24,26,27

Before presenting and discussing the results, we will briefly summarize earlier findings relevant for this study.

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Received 11th June 2014,
Accepted 22nd September 2014
DOI: 10.1039/c4cp02589j
www.rsc.org/pccp
adsorption on Pd(111) has been studied intensely. Most important for the present study is that hydrogen adsorbs dissociatively with a high sticking coefficient on threefold hollow sites, with adsorption energies differing between 1 eV and 1.48 eV. In addition, a subsurface adsorption site was identified, which can be populated upon adsorption at 120–150 K. Desorption from these sites occurs at around 200 K. For adsorption at low temperatures (≤120 K), the population of this site is kinetically inhibited.

Much less is known about hydrogen adsorption on Au(111), assuming this as a model for the other constituent of the surface alloy. Au is known to be essentially inert towards dissociative hydrogen adsorption, and DFT calculation have shown for Au(111) that this refers both to thermodynamics, where H₂–Au(111) is one of the few chemisorption systems for which H₂ in the gas phase is energetically favored compared to adsorbed atomic hydrogen (Hₐd), and to kinetic effects, because of a pronounced barrier for dissociative adsorption. As a result, atomic hydrogen adsorbed on Au is metastable against instantaneous recombinative desorption.

For CO adsorption on bimetallic PdAu surfaces, we derived the adsorption properties of different Pdₙ ensembles on PdAu–Pd(111) monolayer surface alloys in a combined experimental and theoretical study. Employing temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS) and high resolution STM as well as density functional theory (DFT) based calculations, and correlating the appearance of spectroscopic features with the abundance of certain structural elements, we determined distinct ensemble effects in CO adsorption. A single Pd surface atom surrounded by Au atoms was found to adsorb one CO molecule on the atop site, but with a significantly lower adsorption energy than on Pd(111) (Tdes ≈ 300 K), while a Pd dimer allows for stronger adsorption on a Pd₃ bridge site. The strongest adsorption, which resembles that on Pd(111), was found for CO adsorption on threefold hollow sites above a compact Pd₃ trimer or larger ensembles with Pd₃ sites. These experimental findings were confirmed and rationalized by DFT calculations.

Those results agree well with findings of Goodman and coworkers, who equally investigated this system by CO-TPD and vibrational spectroscopy, using multilayer PdAu alloy films with thicknesses of >10 monolayers deposited on a Mo(110) substrate as a model surface. In their case, the surface composition was quantified by ion scattering spectroscopy (ISS). Ligand and ensemble effects in the adsorption of CO, O and N on PdAu–Pd(111) monolayer surface alloys had been investigated and disentangled in a theoretical study by Liu and Nørskov. A first report on the catalytic activity of PdAu catalysts in different reactions was published by Eley. Baddeley et al. investigated the cyclization of acetylene on PdAu–Pd(111) surface alloys. Vinyl acetate synthesis on PdAu catalysts had been investigated in detail by Goodman and coworkers, both on dispersed catalysts and on model surfaces. The hydrogenation of oxygen on PdAu–Pd(111) surface alloys was investigated by DFT calculations by Ham et al., closely related to the observation of highly selective H₂O₂ formation on supported PdAu catalysts. Neurock and Mei reported results of a combined DFT and Monte Carlo study on the hydrogenation of ethylene on PdAu(111) alloy surfaces with different compositions, focusing on the role of Au in that reaction.

The interaction of bimetallic PdAu surfaces with hydrogen was also investigated by electrochemical methods. In this case, the surfaces were created either by diffusion controlled in situ co-deposition of Pd and Au on a Au(111) substrate, which leads to a PdAu–Au(111) surface alloy, or by electrochemical deposition of a thick (ca. 20 ML) PdAu film on a Ru[0001] substrate and subsequent heating at 700 °C, or by pulse deposition of Pd clusters on Au(111). Based on combined in situ STM and electrochemical measurements, Maroun et al. determined that Pd dimers must be active for underpotential H adsorption, by comparing the abundance of different Pdₙ surface elements and the charge of the Hupd adsorption peak. Pluntke et al. concluded that a Pd monomer on a Au film must be active for H₂ evolution, assuming a similar surface composition as derived by Goodman and coworkers for comparable systems prepared in vacuum. Stimming and coworkers reported that Pd clusters on a Au electrode enhance the H₂ evolution rate by more than 2 orders of magnitude and explained this by thickness dependent strain effects in the Pd structure.

In the following, we will, after a brief description of the experimental set-up and procedures and computational details, first evaluate the structure of the PdAu–Pd(111) surface alloys, as derived from STM imaging (Section 3.1), then present TPD and HREELS measurements on different surface alloys (Section 3.2), and finally the results of the DFT calculations and their correlations with the experimental findings, in particular with the trends in adsorption energies on different PdAu nanostructures and their ability to adsorb hydrogen (Section 3.3). Here we will also discuss consequences of these findings for the understanding of hydrogen adsorption on bimetallic surfaces in general.

2 Experimental and calculational details

2.1 Experimental details

All experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below 10⁻¹⁰ mbar, which was equipped with a variable temperature STM and facilities for surface preparation and characterization. The latter include a differentially pumped mass spectrometer for TPD measurements, as well as spectrometers for HREELS and X-ray photoelectron spectroscopy (XPS), and a low energy electron diffraction (LEED) system. The mass spectrometer was covered by a Au coated snout with an aperture of 2 mm in diameter. The distance between the aperture and the sample was fixed to less
than 1 mm by a spacer. The sample temperature was ramped at 20 K s\(^{-1}\) during TPD measurements. The sample was flushed to 600 K before \(D_2\) exposure at \(\leq 120\) K to remove trace amounts of adsorbates from the residual gas.

The Pd(111) crystal was cleaned by repeated cycles of Ar ion bombardment, annealing in \(O_2\) at 700 K, and annealing to 1250 K. The crystal was judged clean based on XPS and STM measurements. Au was evaporated from a Au droplet on a W wire heated resistively. The amount and purity of evaporated Au were checked by XPS and STM.

Due to technical reasons the interaction with hydrogen was investigated using deuterium adsorption, because of the much lower \(D_2\) background pressure in the UHV system. For \(D_2\) exposure, a tube doser was used to reduce the exposure of the sample surroundings. To avoid confusion with calculations and other studies, we will generally use the term ‘hydrogen’, and only refer to deuterium in the context of experimental details.

### 2.2 Computational details

DFT calculations were based on the DFT-GGA, which was implemented in the DACAPO code.\(^{55}\) The Kohn–Sham one electron valence state was solved on a basis of plane waves with kinetic energies below 25 Ry and an ultra soft pseudopotential.\(^{56}\) The exchange–correlation energy and potential were described by the revised Perdew–Burke–Ernzerhof (RPBE) functional.\(^{57}\) The optimized lattice constants for Pd (3.91 Å) and Au (4.10 Å) bulk agree well with experimental values (3.89 Å for Pd and 4.07 Å). The adsorption energy of hydrogen was defined as

\[
E_{ad} = \frac{1}{n}(E(nH/surf) - E(surf)) - E(H_2),
\]

where \(n\) is the number of H atoms adsorbed on the surface. In all cases, hydrogen was allowed to relax in all directions. The PdAu–Pd(111) systems were described by substituting Pd atoms in the top layer gradually by Au at the lattice position, where the modeling of the surfaces was performed at two different levels. For elucidating trends, in particular for evaluating ligand and ensemble effects, the surface systems were described by using a three-layer slab of Pd(111) with a \((2 \times 2)\) or \((3 \times 3)\) supercell on each layer, while metal atoms were fixed at the lattice position of the substrate. Different sites were selected for hydrogen adsorption (see figures). Further details on such calculation are given in ref. 36. For quantitative calculation of adsorption energies on an absolute scale we additionally performed calculations using a five-layer metal slab in a \((3 \times 3)\) or \((3 \times 4)\) unit cell, where the upper two metal layers were allowed to relax with hydrogen, while the \(k\)-points were kept the same as in the previous calculations. We have checked that the relaxation of the top two layers indeed changes the adsorption energy, but the trend in variation from one system to the next remained the same. In selected cases activation energies for dissociative adsorption were calculated employing the Linear Synchronous Transit (LST) method to bracket the maximum between the reactants and products,\(^{58}\) followed by repeated conjugate gradient minimizations and the Quadratic Synchronous Transit (QST) maximizations until a transition state was identified. The convergence thresholds were set such that the root mean square (rms) forces on the atoms were smaller than 0.01 eV Å\(^{-1}\). Such methods yield results close to those obtained by eigenvector following methods.

### 3 Results and discussion

#### 3.1 Structure of PdAu–Pd(111) surface alloys

The PdAu–Pd(111) surface alloys were prepared by evaporating one to two layers of Au on the Pd(111) surface at room temperature, which grow in a layer-by-layer mode.\(^{54}\) Annealing these samples to 750–850 K, which is just sufficient to start exchange processes at the Au–Pd(111) interface and Au dissolution, leads to the formation of bimetallic Pd–Au surfaces with different surface compositions, where the density of Pd atoms in the topmost layer increases upon increasing the annealing temperature.\(^{20,54}\) It should be noted that neither in this work nor in a preceding study we had any evidence for a surface reconstruction.\(^{20}\) The distribution of the atoms in the surface layer was derived by quantitative evaluation of series of atomic resolution STM images for each surface concentration, which allowed us to distinguish between Pd and Au surface atoms by the so called ‘chemical contrast’.\(^{59}\) Representative STM images, where due to electronic effects Pd surface atoms appear bright and Au surface atoms are dark, are presented in Fig. 1. First of all, these images clearly demonstrate that the two different types of atoms are homogeneously distributed in the topmost layer. For the lowest Pd surface concentration (3.5% Pd, Fig. 1a) in the images in Fig. 1 we find only Pd monomers in the surface layer, while for the next higher concentration (12.5% Pd) Pd monomers and dimers are present (Fig. 1b). Only when reaching

![Fig. 1 STM images of Pd–Au bimetallic surfaces with atomic and chemical resolution with different amounts of Pd in the surface layer: (a) 3.5% Pd, (b) 12% Pd, (c) 23% Pd and (d) 78% Pd (a) 130 Å × 130 Å, 3.3 ML Au, 5 min annealed at 680 K; (b) 135 Å × 135 Å, 2.6 ML Au, 1 min at 700 K; (c) 83 Å × 83 Å, 2.6 ML Au, 1 min at 825 K; (d) 145 Å × 145 Å, 0.3 ML Au, 30 s at 775 K.](image-url)
Pd surface concentrations of above 20% (23% Pd, Fig. 1c), compact and linear trimers also appear, although at rather low concentrations. The high Pd concentration in Fig. 1d (78% Pd) essentially reflects the reverse situation, with largely Au monomers and dimers and some larger Au aggregates.

Based on results of preliminary deuterium adsorption experiments we focused on Pd surface concentrations in the range between 20% and 40%, where not only Pd monomers and dimers are present, but also larger Pd₄ ensembles (see also Section 3.2) and where the differences between different models for the minimum size (‘critical size’) of the adsorption ensemble and its composition will be most pronounced. Quantitative evaluation of the STM images of the surface alloys employed for the adsorption experiments in the present study yielded the distributions of different ensembles and ensemble sizes given in Table 1 and in Fig. 2. Considering that in the end we want to correlate the abundance of different adsorption sites with the TPD spectra, we did not list the relative abundance of specific ensemble sizes, but of specific adsorption sites, such as Pd₁ dimer sites etc., independent of whether they occur in a Pd dimer or in a larger Pd ensemble (Table 1). The same holds true for Pd₃ sites. The quantitative evaluation of sets of STM images obtained for Pd₂Au₇₋₉ Pd(111), for Pd₂₈Au₇₂–Pd(111) and for Pd₃₈Au₆₂–Pd(111) confirmed the qualitative impression derived from the images in Fig. 1 that monomers and dimers are dominant up to Pd surface concentrations of 20%. In addition to Pd₁ sites, we obtain the concentration of Pd₂ bridge sites and of Pd₃ as well as that of Pd₂Au threefold hollow sites, and finally also of compact Pd₄ tetramer sites. PdAu₂ sites were not evaluated, since their surface concentration is much too high to account for the desorption in the low temperature β₁ peak of the D₂-TPD spectra recorded on the PdAu surface alloys (see next section). Furthermore, the calculations (Section 3.3) will show that the adsorption energies on these sites are much too low to stabilize adsorbed hydrogen at the present adsorption temperature. The remaining sites in Table 1 will be discussed later, in combination with the D₂-TPD data and the results of the calculations. The population of other sites with different compositions, up to pentamers, is illustrated in Fig. 2.

It should be noted that within the statistical accuracy in determining the ensemble size distribution for Pd monomers, Pd₁ and PdAu dimers, Pd₄Auₓ₋ₓ trimers, Pd₆Auₓ₋ₓ tetramers and Pd₆Auₓ₋ₓ pentamer sites this essentially corresponds to a calculated statistical (random) distribution of the Pd surface atoms. The latter is indicated by the dashed lines in Fig. 2. While the number of Pd surface concentrations investigated is too low for a conclusive statement, the data provide at least clear evidence that at the freezing temperature of the surface alloy, i.e., at the temperature where surface diffusion becomes too slow to reach the equilibrium configuration during cool down, effective mutual interactions between the different surface species do not significantly affect the distribution of surface atoms.⁶⁰ This result fits well to the miscibility of PdAu alloys, furthermore it allows us to estimate ensemble size distributions also for other Pd surface concentrations in this range of Au surface concentrations assuming a statistical distribution of surface atoms.

Finally, for comparison with the TPD experiments it is important to note that the composition and the ensemble size distribution of the topmost layer showed no change before and after the TPD experiments.

### Table 1

Relative abundance of different adsorption sites evaluated from the sets of STM images for the three Pd surface concentrations used also for the D₂-TPD and HREELS measurements (values relative to Pd(111))

<table>
<thead>
<tr>
<th>No.</th>
<th>Adsorption site</th>
<th>Pd₂Au₇₋₉/%</th>
<th>Pd₂₈Au₇₂/%</th>
<th>Pd₃₈Au₆₂/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd₁ sites</td>
<td>21</td>
<td>28</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>Pd₂ sites</td>
<td>7.4</td>
<td>13.7</td>
<td>25.0</td>
</tr>
<tr>
<td>3</td>
<td>Pd₂ sites without Pd₂ dimers</td>
<td>4.5</td>
<td>10.7</td>
<td>23.4</td>
</tr>
<tr>
<td>4</td>
<td>Pd₂ sites without Pd₂ dimers and Pd₁ trimers</td>
<td>2.5</td>
<td>8.2</td>
<td>22.1</td>
</tr>
<tr>
<td>5</td>
<td>Pd₂ sites without Pd₂ dimers, only pairwise occupation</td>
<td>4.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pd₂ sites without Pd₂ dimers and Pd₃ trimers, only pairwise occupation</td>
<td>2.0</td>
<td>7.1</td>
<td>20.7</td>
</tr>
<tr>
<td>7</td>
<td>Pd₄Au sites</td>
<td>8.1</td>
<td>12.0</td>
<td>30.0</td>
</tr>
<tr>
<td>8</td>
<td>Pd₆Au sites without Pd₂ dimers</td>
<td>5.4</td>
<td>12.0</td>
<td>28.5</td>
</tr>
<tr>
<td>9</td>
<td>Pd₆Au sites without Pd₂ dimers and Pd₁ trimers</td>
<td>2.8</td>
<td>9.2</td>
<td>8.2</td>
</tr>
<tr>
<td>10</td>
<td>Pd₆Au sites without Pd₂ dimers, only pairwise occupation</td>
<td>4.6</td>
<td>11.0</td>
<td>27.1</td>
</tr>
<tr>
<td>11</td>
<td>Pd₆Au sites without Pd₂ dimers and Pd₃ trimers, only pairwise occupation</td>
<td>2.3</td>
<td>8.2</td>
<td>25.4</td>
</tr>
<tr>
<td>12</td>
<td>Pd₃ sites</td>
<td>0.5</td>
<td>0.8</td>
<td>4.5</td>
</tr>
<tr>
<td>13</td>
<td>Pd₃ sites without Pd₂ dimers, trimers</td>
<td>0.3</td>
<td>0.6</td>
<td>4.3</td>
</tr>
<tr>
<td>14</td>
<td>Pd₃ sites without Pd₂ dimers, with pairwise occupation</td>
<td>0.1</td>
<td>0.2</td>
<td>3.0</td>
</tr>
<tr>
<td>15</td>
<td>Compact Pd₄ sites</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>16</td>
<td>D₂ desorption (β₁ peak) from Pd₂ sites without Pd₂ dimers and trimers as calculated from the adsorption sites</td>
<td>3.7</td>
<td>9.9</td>
<td>21.2</td>
</tr>
<tr>
<td>17</td>
<td>D₂ desorption (β₁ peak) from Pd₆Au sites without Pd₂ dimers and Pd₃ trimers as calculated from the adsorption sites</td>
<td>1.9</td>
<td>7.1</td>
<td>19.8</td>
</tr>
<tr>
<td>18</td>
<td>D₂ desorption in β₁ peak</td>
<td>1.2 ± 0.3</td>
<td>5.0 ± 1.0</td>
<td>14.5 ± 1.5</td>
</tr>
</tbody>
</table>

a Concentration of Pd₁ sites is identical to the total concentration of Pd surface atoms. b Concentration of the respective sites without considering those in Pd₂ dimers. c Concentration of the respective sites without considering those in Pd₂ dimers and assuming that only even numbers of H adatoms can be adsorbed from H₂ adsorption (no H₄₉₀ spill-over between ensembles). d Concentration of the respective sites without considering those in Pd₃ trimers, and assuming that only even numbers of H adatoms can be adsorbed from H₂ adsorption (no H₄₉₀ spill-over between ensembles). e Concentration of the respective sites without considering those in Pd₃ trimers, and assuming that only even numbers of H adatoms can be adsorbed from H₂ adsorption (no H₄₉₀ spill-over between ensembles). f Calculation and assumptions see text.
3.2 Adsorption and desorption of hydrogen on PdAu–Pd(111) surface alloys

The interaction of hydrogen with these surfaces was characterized by D₂-TPD measurements. A series of D₂-TPD spectra recorded after increasing D₂ exposures to a Pd₃₇Au₆₃–Pd(111) surface (adsorption temperature 110–120 K) is shown in Fig. 3. The spectra clearly resolve two distinct desorption peaks with a maximum at 235 K ($\beta_1$ peak) and a shoulder at 325 K ($\beta_2$ peak). The additional desorption at higher temperatures (>$450$ K), which is very low on an absolute scale, is attributed to background desorption, e.g., from the sample holder. The origin of the $\beta_1$ and $\beta_2$ states, which in general may arise either from differences in the adsorption energies, or more correctly, in the activation energy for desorption, or from repulsive interactions between the D$_{ad}$ species, will be discussed later. It should also be noted that neither STM imaging nor comparison of TPD spectra before and after such series gave any indication for H$_{ad}$ induced modification of the surface such as Pd segregation in these experiments.

The most important feature in the spectra is the characteristic coverage dependence in the desorption peaks. Different from the second order desorption kinetics normally observed for recombinative hydrogen desorption, the maxima do not shift to lower temperatures with increasing coverage, but remain at essentially constant temperature. This is most easily explained by ‘direct’ desorption from the individual ensembles, where surface diffusion of D$_{ad}$ species between different Pd$_n$ ensembles is inhibited, i.e., the D$_{ad}$ species are confined to the Pd$_n$ ensemble where they were adsorbed. In that case, an increasing D$_{ad}$ coverage results in an increasing number of Pd$_n$ ensembles populated with D$_{ad}$ species, without modifying the local coverage on these Pd$_n$ ensembles. This way, the desorption characteristics remain essentially constant for increasing D$_{ad}$ coverage, only the total intensity increases.

These desorption characteristics also explain a second uncommon feature, namely the population of the low-temperature state before the more stable high temperature state is filled. In fact, the overall shape of the spectra changes very little with increasing D$_{ad}$ coverage, and the low-temperature $\beta_1$ peak is higher in intensity than the $\beta_2$ peak from the lowest coverage on. As described above, in the absence of D$_{ad}$ surface diffusion the respective desorption states are populated for each Pd$_n$ ensemble separately. This also indicates that the states are characteristic for dissociative adsorption of a single D$_2$ molecule per Pd$_n$ ensemble, where only larger ensembles may contain more adsorbed deuterium. It should be noted that a coverage independent peak temperature could also be obtained if desorption is induced by a structural transition of the surface, which, however, is in contrast to STM observations.

Fig. 2 Abundance of compact 2-, 3-, 4- and 5-fold ensembles as a function of Pd-surface concentration. The composition of ensembles is as denoted in the legends, the actual positions of the Pt and Au atoms within the ensembles are not explicitly considered. Symbols result from STM data, lines denote calculated distribution for a purely random distribution.

Fig. 3 Series of D$_2$ TPD spectra recorded upon increasing the D$_2$ exposure up to saturation on the Pd$_{38}$Au$_{62}$ surface alloy (exposures are given in L, with 1 L = $1.33 \times 10^{-6}$ mbar s).
The evolution of the desorption spectra with increasing Pd surface concentration is illustrated in Fig. 4, which shows TPD spectra recorded upon saturation with deuterium for three bimetallic surfaces with different Pd surface contents (21%, 28%, and 38%) and, for comparison, of a Pd(111) surface. The latter TPD spectrum closely resembles Pd(111) saturation spectra reported in earlier studies, with a slightly asymmetric peak shape and a peak temperature of about 325 K.30,61,62 It is important to note that the D$_2$-TPD spectrum recorded on Pd(111) does not show any desorption from subsurface sites, in agreement with expectations for the low adsorption temperature.30,32 The latter would result in a desorption peak at ~200 K, which would interfere with the low-temperature $\beta_1$ peak induced by Au on the surface.

The D$_2$-TPD spectra illustrate that very low D$_{ad}$ saturation coverages are obtained on the bimetallic surfaces despite the significant Pd surface contents. Contributions from background desorption were determined recording a D$_2$-TPD spectrum on a Pd(111) surface fully covered with a Au film and removed by subtraction from the experimental spectra. The spectra recorded on the other bimetallic PdAu surfaces exhibit the same characteristics as described for Pd$_{37}$Au$_{63}$–Pd(111), with a low-temperature peak at 240–250 K and a shoulder at 320 K. For 21% surface Pd content, this peak appears at 250 K; with increasing Pd concentration it shifted to slightly lower temperatures, reaching 235 K for the Pd$_{37}$Au$_{63}$–Pd(111) surface. The D$_2$ exposures were chosen such that the $\beta_1$ peak was saturated.

For gaining more information on the adsorption site and on the critical Pd ensemble size we compare the abundance of different adsorption sites and ensembles as derived from the STM images with the intensity of the $\beta_1$ TPD peak for the different Pd surface concentrations. Normalizing this to the integrated desorption intensity obtained on the Pd(111) surface (1 ML), we obtained saturation coverages of 1.2 ± 0.3% (21% Pd surface atoms), 6.0 ± 1.0% (28% Pd surface atoms), and 15.9 ± 1.5% (38% Pd surface atoms) of the saturation coverage on Pd(111), respectively, on the above surface alloys (Table 1, line 18). Due to the very low intensities in the $\beta_2$ peak after background subtraction, which led to rather large relative errors in the related hydrogen coverage due to uncertainties in the background determination, a similar quantitative evaluation was not pursued for this peak. Already from a simple comparison of the $\beta_1$ desorption peak intensities and the abundance of the different adsorption ensembles on these surfaces (see Table 1, lines 1, 2, 7, 12, 15) it is clear that the concentrations of Pd$_2$ dimer sites and in particular of Pd monomer sites are far too high in the range of lower Pd concentrations to be considered as stable adsorption sites for adsorbed hydrogen. On the other hand, the number of Pd$_3$ threefold hollow sites and especially of compact Pd$_4$ tetramer sites (see Section 3.3) is too low to explain the experimentally observed desorption intensity in the $\beta_1$ peak. Before discussing this in more detail, we will first present additional experimental data.

Further information on the nature of the critical Pd$_n$ ensemble comes from HREEL spectra recorded on the Pd$_{38}$Au$_{62}$ surface after exposure to 4 L of H$_2$ (1 L = 1.33 × 10$^{-6}$ mbar s), which are shown in Fig. 5. A spectrum recorded at 120 K (Fig. 5a) shows vibration losses at 96 and, much weaker, at 131 meV, which are rather close to the loss features at 96 and 125 meV reported by Conrad et al. for hydrogen adsorption on Pd(111).63 Accordingly, these losses are assigned to the parallel and vertical vibrational mode of hydrogen on threefold hollow Pd$_3$ sites. Other loss peaks (227, 237 and 259 meV), whose intensity increased with increasing data acquisition time, are assigned to the C–O stretch mode of CO adsorbed on various Pd sites, which is accumulated from the residual gas.18

Spectra recorded at room temperature (Fig. 5b) also showed a loss peak at 96 meV, indicating that also under these conditions there are H atoms adsorbed on the Pd$_3$ threefold hollow...
sites of the Pd$_3$Au$_{42}$ surface. In addition to the H$_{ad}$ related feature, the spectra showed an additional loss peak at 42 meV (M–CO stretch$^{15}$). The weak signal at 131 meV and the signal at 259 meV do not appear at room temperature. The disappearance of the 259 meV signal is easily explained by the low adsorption energy of CO adsorbed on Pd atop sites, e.g., on Pd monomers.$^{15}$ The absence of the weak signal at 131 meV, which we related to an H$_{ad}$ band, is most easily explained by the lower H$_{ad}$ coverage under these conditions, possibly in combination with a change in the vibrational cross section.$^{63}$

Finally, we performed CO titration experiments on the Pd$_{21}$Au$_{79}$ surface (Fig. 6), exploiting the known adsorption and desorption behavior of CO, with CO adsorbed atop on a Pd monomer desorbing at 330 K, bridge bound CO$_{ad}$ on Pd dimers desorbing at 380 K (Fig. 6a) and CO adsorbed on the threefold hollow sites above compact Pd trimers at 470 K.$^{20}$ For the present experiments, we first exposed the surface to CO at 140 K, and then annealed the sample to defined temperatures. This way, only specific Pd ensembles and sites remained CO$_{ad}$ populated. After cooling the sample to 120 K and exposing it to D$_2$, we monitored the D$_2$ desorption. The CO exposure ($0.5 \times 10^{-6}$ mbar s) was set to the minimum amount that completely suppresses D$_2$ desorption (Fig. 6b, for the $\beta_2$ peak see below). The resulting CO TPD spectrum (Fig. 6a) clearly indicates that only Pd monomer and Pd$_2$ dimer sites are populated on this surface, desorption from Pd$_3$ hollow sites in larger Pd ensembles is absent. Furthermore, the spectra underline that similar to our previous finding (see above), the higher temperature $\beta_1$ desorption peak on this sample is largely due to background desorption, since stepwise removal of CO$_{ad}$ causes little modification of this desorption peak. Removal of the CO$_{ad}$ from the atop sites on Pd monomers by annealing the CO$_{ad}$ covered surface to 330 K before post-adsorption of deuterium causes no change in the D$_{ad}$ population (Fig. 6c), i.e., deuterium adsorption is still completely blocked. Annealing to 360 K, which causes complete desorption of atop adsorbed CO$_{ad}$ species and some desorption of bridge bound CO$_{ad}$, leads to the appearance of the low-temperature $\beta_3$ D$_2$ desorption peak, though only with low intensity. Annealing to higher temperatures before subsequent D$_2$ adsorption causes the $\beta_1$ peak to grow, until after annealing to 400 K it has regained its full intensity. The main points of this sequence are that (i) Pd ensembles leading to bridge bonded CO$_{ad}$ are active for hydrogen adsorption, in contrast to sites allowing only Pd atop adsorption, and that (ii) these hydrogen species desorb in the $\beta_1$ peak, confirming our above assumption.

Based on the experimental findings discussed above we can set up a model for hydrogen adsorption on the bimetallic PdAu–Pd(111) surfaces. First we will assume that adsorbed hydrogen is localized at the Pd$_n$ ensembles upon adsorption,$^{49}$ and that spill-over of H adatoms from one Pd$_n$ ensemble to another one is kinetically inhibited because of the very weak H–Au bond. As will be rationalized and discussed in more detail in Section 3.3, it is energetically more favorable for two H adatoms adsorbed on one Pd$_n$ ensemble to recombine and desorb as H$_2$ rather than that one of them migrates to Au$_n$ sites, which is necessary for the H adatom to get to another, neighbored Pd$_n$ ensemble. Hence, H adatoms are confined to the Pd$_n$ ensemble they were adsorbed at. One important consequence of the confinement of the H$_{ad}$ species to the original Pd$_n$ adsorption ensemble is that each of these ensembles can accommodate only an even number of H adatoms (pairwise adsorption, Table 1, lines 5, 6, 10, 11, 14). Accordingly, we assume that adsorption of a H$_2$ molecule is only possible if two (additional) H adatoms can be accommodated on that ensemble. This means that even if adsorption of one H$_{ad}$ on a Pd$_n$ bridge site or on a Pd$_n$Au hollow site is energetically stable, adsorption would only occur if adsorption of two H$_{ad}$ is sufficiently stable.

Second, it is reasonable to assume that a Pd dimer can stabilize only one H$_{ad}$ either on a Pd$_2$ bridge site or on a Pd$_2$Au hollow site, meaning that occupation of two directly neighbored Pd$_2$Au sites is not possible (see also Section 3.3). This is included in the values given in Table 1. In that case we have to subtract all Pd$_2$ or Pd$_2$Au sites on Pd$_2$ dimers from the total number of Pd$_2$ bridge sites or Pd$_2$Au hollow sites. On the other hand, adsorption on the Pd$_2$Au sites above a linear Pd$_3$ trimer or at both sides of a compact Pd$_3$ trimer would per se be possible. Due to the pairwise adsorption discussed above, a linear Pd$_3$ ensemble can accommodate only two rather than three H$_{ad}$ species on Pd$_3$ or Pd$_3$Au sites. Finally, we may assume that a certain minimum size of the Pd$_n$ ensemble is required for hydrogen adsorption, the critical Pd$_n$ ensemble size. The concentrations of Pd$_1$ or Pd$_4$Au sites on the different surface alloys resulting from the different restrictions described above (no occupation of directly neighbored bridge sites or Pd$_2$Au threefold hollow sites, pairwise adsorption only, and adsorption only on ensembles with a certain minimum size) are listed in the lines 3–6 and 8–11 in Table 1. Similar arguments can also be constructed for adsorption on Pd$_3$ hollow sites, where a compact trimer would be able to accommodate only a single
H$_{\text{ad}}$ species. The resulting concentrations of Pd$_3$ sites are also listed in lines 13 and 14 in Table 1.

Finally, we will consider blocking effects. We can reasonably assume that adsorption on Pd$_3$ hollow sites is more stable than on Pd$_2$ bridge sites or on Pd$_2$Au threefold hollow sites (see also Section 3.3). On the other hand, a H adatom adsorbed on a Pd$_3$ site will block the directly neighboring Pd$_2$Au sites or Pd$_2$ bridge sites for H adsorption, and vice versa. In this case we assume that it is energetically more favorable to adsorb two H$_{\text{ad}}$ on Pd$_2$Au sites (or on Pd$_2$ bridge sites) than one H$_{\text{ad}}$ on a Pd$_3$ site. For adsorption on larger ensembles this would lead to the following consequences: first, recombinative desorption of 2H$_{\text{ad}}$ species on two Pd$_3$ sites in one ensemble occurs in the $\beta_2$ peak, similar to desorption from a Pd(111) surface. Second, the preference for adsorption of more H$_{\text{ad}}$ species means that if a Pd$_n$ surface ensemble contains one or two Pd$_3$ sites which due to site blocking effects are not populated at H$_{\text{ad}}$ saturation coverage, they will become occupied after partial desorption of H$_{\text{ad}}$ by migration of H$_{\text{ad}}$ from weaker bonding sites to strongly bonding Pd$_3$ sites, once site blocking is not effective any more.

Desorption of two H$_{\text{ad}}$ species on two Pd$_3$ sites will not contribute to the $\beta_1$ peak any more. Hence, these H$_{\text{ad}}$ species have to be subtracted from the total amount of adsorbed H$_{\text{ad}}$ when calculating the $\beta_1$ desorption intensity. For instance, if an ensemble would be able to accommodate 4H$_{\text{ad}}$ on Pd$_2$Au sites or alternatively 2H$_{\text{ad}}$ on Pd$_3$ sites, where in the latter case the Pd$_2$Au sites are blocked for H$_{\text{ad}}$, we assume that this Pd$_n$ ensemble would adsorb 4H$_{\text{ad}}$. After desorption of the first H$_2$ molecule, the remaining H$_{\text{ad}}$ species change to the two Pd$_3$ sites and do not contribute to the desorption intensity in the $\beta_1$ peak. If only one Pd$_3$ site is available, one may debate whether desorption from one Pd$_2$Au (or Pd$_2$) site and one Pd$_3$ site occurs in the $\beta_1$ or in the $\beta_2$ peak. We here assume the latter, the number of such cases is, however, so small that they will not cause significant modifications in the $\beta_1$ desorption intensity. These effects were considered in the calculated desorption intensities listed in the last lines 16 and 17 for Pd$_2$ bridge sites and Pd$_2$Au threefold hollow sites, respectively.

Inspection of the resulting concentrations of the different adsorption ensembles and the hydrogen uptake in the $\beta_1$ state at 120 K indicates that even after consideration of these additional restrictions for hydrogen adsorption on the different PdAu bimetallic surfaces the concentration of active and accessible Pd$_3$ and Pd$_2$Au adsorption sites is sufficient to explain the desorption intensity in the $\beta_1$ peak, indicating that the underlying mechanistic ideas of a pairwise adsorption on a Pd$_n$ ensemble and of a certain minimum size of the Pd$_n$ adsorption ensemble are correct. In combination with the conclusions described already above, the experimental findings result in the following model for hydrogen adsorption on a PdAu–Pd(111) surface alloy.

1. Surface diffusion of H$_{\text{ad}}$ species between different Pd$_n$ ensembles is inhibited, while surface diffusion between sites within the individual Pd$_n$ adsorption ensemble is assumed to be facile.

2. The confinement of the H$_{\text{ad}}$ species to the original Pd$_n$ adsorption ensemble results in a pairwise adsorption and desorption behavior on the individual Pd$_n$ ensembles, and in significant deviations from a second order desorption kinetics typical for H$_2$ desorption.

3. Accordingly, adsorption of hydrogen is determined by the size and shape of the individual Pd$_n$ adsorption ensembles. Desorption in the $\beta_1$ state is related to H adatoms adsorbed on sites which allow for bridge bonded CO adsorption, i.e., adsorption on Pd$_2$ sites or on Pd$_2$Au threefold hollow sites. Adsorption on atop sites in general and on Pd monomers in particular is inhibited. Adsorption on Pd$_3$ threefold hollow sites is tentatively associated with desorption in the $\beta_2$ peak.

4. Based on the quantitative comparison between H$_{\text{ad}}$ uptake in the $\beta_1$ state and the concentrations of different adsorption sites and ensembles (Table 1), Pd ensembles with at least 4 Pd atoms seem to be the smallest ensembles to allow dissociative adsorption of hydrogen at 100 K, indicating that the critical Pd cluster size for hydrogen adsorption on dispersed PdAu surface alloys under these conditions is a Pd$_4$ tetramer (see also below). Because of the very low (compact Pd$_4$ ensembles) or even extremely low (compact Pd$_4$ tetramer sites) surface concentrations of compact trimers and tetramers, hydrogen adsorption should be possible on linear or bent Pd$_n$ (with $n \geq 4$) ensembles.

5. Neither from the abundance of the different adsorption sites and their variation with Pd surface concentration nor from the HREELS data can we unambiguously differentiate between adsorption on Pd$_2$ bridge sites or on Pd$_2$Au threefold hollow sites, although based on the general preference of adsorbed hydrogen for threefold hollow sites the latter seems to be more reasonable.

These ideas derived from the experimental data shall be tested and compared with predictions based on theory in the next section.

3.3 Theoretical description of the interaction of hydrogen with PdAu–Pd(111) surface alloys

H adsorption in a (2 x 2) unit cell. For elucidating trends, we calculated the adsorption energies for a variety of adsorption sites on different Pd$_{1-x}$Au$_x$-Pd(111) surface alloys in a (2 x 2) unit cell with 1, 2, or 3 Pd atoms on the surface layer and 1 hydrogen atom per unit cell. For comparison, hydrogen adsorption on a Pd(111) surface was also included. As mentioned earlier, we will focus on trends rather than on absolute values when comparing the calculated adsorption energies. The adsorption sites and the related adsorption energies are illustrated in Fig. 7.

For adsorption on Pd(111), the adsorption energies decrease in the order fcc site > bridge site > atop site (Fig. 7). The difference of ~ 1 eV between the fcc site and the atop site agrees well with the results of recent calculations.64 Going from Pd(111) to the surface alloys, we expect the following trends for adsorption on the Pd surface atoms based on predictions from the d-band model and from the experimental findings for other bimetallic adsorption systems. Due to strain effects (compression of the Pd surface atoms by the larger Au atoms in the pseudomorphic surface layer) we expect bonding on the
Pd surface atoms to be weaker than on Pd(111). On the other hand, due to the chemical interaction with neighboring Au atoms and the weaker Pd–Au interaction as compared to Pd–Pd interaction, we expect the adsorbate–Pd bond to be stronger on the surface alloys than on Pd(111) (‘bond order conservation’). Since these two effects are counteracting, a simple decision on the actual trends is not possible from these qualitative arguments, underlining the need for detailed calculations.

We relate the hydrogen adsorption energy to two properties of the adsorption site. One is the composition of the site, which is associated with the nature of the ensemble (‘ensemble effect’). The other is the surrounding of the site, where the composition of the site remains fixed. This reflects the (lateral) ligand effect. The DFT results show that the hydrogen adsorption on PdAu–Pd(111) is not as strong as that on Pd(111) (Fig. 7), even at the sites with similar compositions, e.g., Pd3 hollow, Pd2 bridge and Pd1 atop sites. The weakened H–Pd interaction can be well explained by the downward shift of the Pd d-band center upon formation of the surface alloy with Au. According to our previous calculations, increasing the Au content in the surface from 0.25 ML to 0.75 ML increases the downshift of the Pd d-band center. As a result, the hydrogen adsorption energy decreases upon going from hollow site 4 to hollow site 18 (Fig. 7). In addition, according to the DFT calculations hydrogen prefers to bind with Pd rather than with Au surface atoms. The higher the Pd content of the adsorption ensemble, the stronger the corresponding hydrogen binding. For the sites involving the same number of Pd atoms, hydrogen favors three-fold hollow sites (Pd3 and Pd3Au sites) rather than bridge and atop sites. Accordingly, in the following calculations for PdAu–Pd(111) containing Pd monomers, dimers and trimers (see below), only hydrogen adsorption at the stable hollow sites (Pd3 and Pd3Au sites) rather than bridge and atop sites was considered. The only exception is the adsorption on the PdAu3 hollow sites, which is slightly less stable than that on Pd–Au bridge site (site 11 vs. 12; site 15 vs. 17, Fig. 7).

**H adsorption in a (3 × 3) unit cell.** In a next step we performed comparative calculations in a (3 × 3) unit cell with a low H_{ad} coverage (θ_H = 0.11 ML) and Pd surface contents of 1, 2, 3 and 4 Pd surface atoms per unit cell. It allows us to model small Pd surface ensembles such as monomers, dimers, trimers and tetramers that are fully surrounded by Au surface atoms, as observed experimentally (see Fig. 8). As evident from
Fig. 8, the adsorption energy increases from PdAu \(_2\) hollow adsorption at a Pd\(_1\) monomer to the Pd\(_2\)Au hollow at a Pd\(_2\) dimer and to finally adsorption on a Pd\(_3\) hollow site on a compact Pd\(_3\) trimer. This increase in adsorption energy reflects the ensemble effect. In this case, the only variable is the composition of the adsorption ensemble, which is fully surrounded by Au in the first shell (Fig. 8). On the other hand, the adsorption on the Pd\(_3\) hollow site on a compact Pd\(_3\) trimer in Fig. 8 is significantly less stable than adsorption on the Pd\(_3\) hollow on a compact Pd\(_4\) tetramer. These two sites differ just by the atoms in the shell around the Pd\(_3\) hollow, where 9 Au atoms surround the Pd\(_3\) trimer compared to 8 Au and 1 Pd surface atoms as for the case of the Pd\(_4\) tetramer (Fig. 8). Accordingly, the corresponding energy difference reflects the influence of electronic ligand effects, as the first shell surrounding of the adsorption site varies from one site to the next, while the composition of the adsorption site (‘adsorption ensemble’) remains identical. According to our calculations, the d-band center of Pd shifts toward the Fermi level from \(-2.74\) eV for a Pd\(_1\) monomer via \(-2.67\) eV and \(-2.61\) eV for a Pd\(_2\) dimer and a compact Pd\(_3\) trimer, respectively, to \(-2.58\) eV for a compact Pd\(_4\) tetramer, where the changes in the initial three values arise from the ensemble effect, and the last one from the decreasing Au coordination in the first ligand shell. In comparison, H adsorption on a threefold hollow site on Pd(111), where all surface atoms in the first ligand shell are Pd atoms and the d-band center of Pd is located at \(-2.16\) eV, is significantly stronger. The stabilization of H\(_{ad}\) with decreasing Au coordination in the first ligand shell means that the (stabilizing) strain effects are dominant, and are stronger than (destabilizing) lateral ligand effects. Similar effects are observed for adsorption on Pd\(_2\) bridge sites or Pd\(_2\)Au hollow sites, where adsorption at an isolated Pd\(_2\) dimer is significantly less favorable than adsorption on a similar site on/aside a string of Pd surface atoms (Fig. 9). These examples further underline the role of electronic ligand effects in hydrogen interaction with PdAu–Pd(111) surface alloys.

Both ligand and ensemble effects result in an approximately linear correlation between the surface composition and the hydrogen adsorption energy, which is illustrated in Fig. 8b. As mentioned before, however, the variation in hydrogen binding energy introduced by the ligand effect is not as significant as that by the ensemble effect.

To assess and further elucidate the influence of strain and vertical ligand effects, we performed similar calculations on a pseudomorphic PdAu surface alloy supported on a Au(111) substrate. According to the simple rules given above we would expect the H–Pd bond to be stronger in this case because of the larger lattice constant of Au compared to Pd(111) via addition of tensile strain on the pseudomorphic PdAu monolayer (strain effect), and because of the weaker Pd–Au interaction compared to the Pd–Pd interaction via directly strengthening the H–Pd bond (vertical electronic ligand effect). The results are also illustrated in Fig. 8b. As expected, the adsorption energies are generally larger than those obtained for PdAu–Pd(111), reflecting the effect of strain and vertical ligand effects. The trends for the (in plane) ensemble effect and the (lateral) ligand effect, which are illustrated by the dashed line, are qualitatively similar to those observed on PdAu–Pd(111), with the energies for adsorption on the three ensembles following a linear relation.
whose slope differs only little from that determined for adsorption on PdAu–Pd(111). We will get back to these results at the end of this section, when comparing with electrochemical experiments performed on PdAu–Au(111) surface alloys.

Overall, the DFT calculations show that at a mixed adsorption site the adsorption energy can be affected by both ensemble and ligand effects, where the effect is more pronounced for the ensemble effect, but the ligand effect is also sizable. These findings agree well with the trends derived for the adsorption of CO, O and N on similar surfaces.36

2 H adsorption in (3 × 3) and (3 × 4) unit cells. In a third step we calculated the adsorption energies for adsorption of 2 H atoms per ensemble for Pd1–4 ensembles, again mostly in a (3 × 3) unit cell, to include the effect of pairwise adsorption discussed above (Fig. 10). A (3 × 4) unit cell was also included to model a linear Pd3 trimer isolated by Au, which was observed using STM. Also here we find a clear trend, with adsorption becoming increasingly more stable on going from a Pd1 monomer to a Pd4 tetramer. Similar to the results for adsorption of a single H atom, the adsorption on atop sites on the Pd4 dimer is significantly less stable than adsorption on the closely neighbored Pd3Au sites (fcc and hcp site). The markedly lower adsorption energy of the latter configuration compared to that on other, larger ensembles, however, fully justifies the assumption made when setting up the adsorption–desorption model from correlating the STM and TPD data in Section 3.2, where we had excluded adsorption of 2 H adatoms on neighbored fcc and hcp sites.

Similar to the case of a Pd2 dimer, the adsorption of 2 H atoms also prefers the two Pd3Au sites of a compact Pd3 trimer, the binding is, however, significantly stronger than on the same sites on a Pd2 dimer (Fig. 10). As discussed above, the difference in adsorption energy at the same Pd3Au site composition reflects the ligand effect, which is associated with the variation in the surrounding of the site. In addition, the repulsion due to the closer proximity of the two H$_{ad}$ species on the Pd3 than on the Pd2 ensemble also contributes to the weaker hydrogen adsorption, since the distance between two H$_{ad}$ atoms is shorter on the Pd3 dimer (1.65 Å) than on the Pd2 trimer (2.81 Å). Finally, a configuration with one H$_{ad}$ located in the central Pd fcc site of the compact Pd3 trimer and the other one in the directly neighbored hcp site is slightly less stable by 0.02 eV than the adsorption on the two Pd3Au sites of that ensemble (Fig. 10). Obviously, the repulsion between the closely spaced H adatoms overcompensates the energy gain from having one H$_{ad}$ adsorbed on the more stable Pd3 site.

The most stable adsorption among the different Pd$_n$ ensembles considered is obtained for adsorption on a compact Pd4 tetramer. In this case, the configuration with 2H$_{ad}$ on the Pd4 sites is the most stable, despite the close proximity of the directly neighbored fcc and hcp adsorption sites (Fig. 10). Obviously, the energy gain upon having two H adatoms located

![Fig. 10](image-url) Adsorption energies for simultaneous adsorption of 2 H adatoms as expected for dissociative adsorption of H$_2$ without spillover of H$_{ad}$ to other Pd$_n$ ensembles (Pd$_2$ dimer, Pd$_3$ compact trimer and Pd$_4$ compact tetramer) on a PdAu–Pd(111) surface alloy as illustrated in the figure. Numbers in brackets denote adsorption energies calculated on relaxed surfaces (see text).
on Pd₃ sites overcompensates the repulsion between the closely neighbored Hₐd species.

For better comparison of the absolute adsorption energies with the experiment, we re-calculated the adsorption energies of some representative configurations using larger slabs and allowing relaxation of the topmost two metal layers (see Section 2.2). The resulting energies are given in brackets for these ensembles in Fig. 10. They essentially confirm the trends derived from the calculations described before, and they furthermore yield adsorption energies which fit reasonably well to the experimental data also on an absolute scale. Interestingly, the adsorption of 2 H atoms on the two Pd₂Au sites of a compact Pd₃ trimer is slightly less stable than that on the Pd₂Au sites above a linear Pd₃ trimer (Fig. 10). In this case, the compositions of the adsorption sites (Pd₂Au) and their surrounding (8 Au and 1 Pd) are identical and 2 Hₐd are packed in a similar position, sharing 1 Pd atom. Our calculations show that the small difference in hydrogen binding (0.15 eV) is associated with different strain in the two Pd₃ ensembles, where the compact Pd₃ introduces a higher compressive strain within the Pd₁ (0.7%) and therefore a weaker hydrogen binding than the linear Pd₃. Different from the experimental data, our calculations suggest that a linear or compact Pd₃ trimer is the smallest Pd ensemble, allowing the dissociative adsorption of hydrogen both energetically (adsorption energy −0.27 eV on a linear Pd₃ ensemble). Calculations of the activation barrier for dissociative H₂ adsorption on a linear Pd₃ trimer yielded a value of 0.4 eV. Possible explanations for the apparent discrepancy between theory and experiment will be discussed below.

Overall, the trends derived from the calculations agree very well with the conclusions from the combined STM and TPD data (see adsorption model in Section 3.2); furthermore they allowed us to distinguish between adsorption sites and configurations where this was not possible from our experimental data: the calculations clearly confirm that adsorption on Pd monomers and dimers as well as on atop sites is unfavorable, justifying the corresponding assumptions we had made for the determination of the adsorbate coverage from the ensemble size distributions (see Table 1). The strongly antibinding adsorption on Au₃ sites fully supports the assumption of pairwise hydrogen adsorption and ensemble confinement of the H adatoms, since it is energetically more favorable for Hₐd to desorb by recombination with a second Hₐd than to move to a Au₃ site, where the latter would be the first step to surface diffusion to another Pdₐ ensemble. Furthermore, the calculations favor the adsorption on Pd₂Au sites as compared to Pd₃ bridge sites, which we had concluded before (see Section 3.2), but where clear proof could not be provided. The only point where experimental finding and calculations seem to disagree is the critical ensemble size, where from calculations Pd₃ ensembles should be sufficient to stabilize hydrogen adsorption, while experimental data tend to favor Pd₄ tetramers as critical ensemble size. Here it should be noted this does not refer to compact Pd₄ tetramers and the tetramer sites, whose number is far too small to explain the intensity in the β₁ peak, but to linear or bent Pd₄ tetramers. This discrepancy may result from two effects: first considering that on an absolute scale the differences in calculated β₁ peak intensity between a Pd₃ and Pd₄ critical ensemble size are still small, experimental errors, e.g., in the coverage determination of the β₁ peak may be possible; second the adsorption energy on the Pd₃ trimers may be too low to populate these sites at 100 K and to stabilize hydrogen adsorption up to the onset of desorption in the β₁ peak at around 150 K. Considering the significant ligand effect determined for this adsorption system (compare, e.g., adsorption on Pd₂Au sites on a Pd₃ dimer and on a Pd₃ chain in Fig. 9) and the higher repulsions between Hₐd on neighbored Pd₂Au sites, the increase in stability for adsorption on Pd₃ and larger ensembles as compared to adsorption on Pd₂ ensembles may indeed be sufficient to stabilize hydrogen adsorption on Pd₄ and larger Pdₐ ensembles under the present experimental conditions, while stable adsorption on linear or bent Pd₃ ensembles would be inhibited. Furthermore, the calculated barrier for dissociative adsorption on a linear Pd₃ trimer of 0.4 eV means that the sticking probability is so low (s₀ < 10⁻¹⁷ at 110 K) that during a normal adsorption experiment these sites would not be populated.

Finally it should be noted that the present findings and interpretation agree very well also with findings from an electrochemical study, investigating hydrogen adsorption on a PdAu–Au(111) surface alloy, which was prepared in situ by diffusion limited codeposition of Pd and Au on a Au(111) substrate to yield a mixed AuPd monolayer of defined composition. In that study, Pd₂ dimers (or Pd₂Au trimers) were identified as a smallest Pd ensemble which is able to adsorb hydrogen. For electrochemical experiments in acidic solution (hydrogen underpotential deposition – Hₐpd), hydrogen is supplied by H⁺ species from the electrolyte, and therefore the need for locally accommodating 2Hₐd species does not exist. Furthermore, the observation that hydrogen adsorbed on Pd₀Au sites is stable against desorption as H₂ (from adsorption ensembles with more than 1Hₐd) also at room temperature, in contrast to the onset of desorption from these sites at <200 K on PdAu–Pd(111) (see Fig. 3), can at least partly be explained by the different substrate (Au(111) rather than Pd(111)). The different lattice constants and the different chemical nature of the two substrates result in tensile rather than compressive strain and weaker vertical ligand effects, which in turn lead to a stabilization of the metal–hydrogen bonds (see Fig. 8b). Furthermore, recombinative desorption from Pd₂ dimers (with one adsorbed hydrogen atom) would not be possible. Desorption as H⁺, in contrast, is mainly controlled by the adsorption potential.

In a more general sense the present findings for hydrogen adsorption and desorption on PdAu–Pd(111) can be considered as representative for adsorption and reaction on bimetallic surfaces where one surface species shows a very low adsorption energy for the respective adsorbate and where ensemble effects are dominant, but ligand effects are still effective. In that case, the activity of the surface will rapidly decrease with increasing surface concentration of the weakly binding surface species. On the other hand, the large variety of different adsorption sites on different ensembles means that the surface activity is tunable.
According to the Sabatier principle, there will always be an ensemble, which can provide the optimal adsorption for maximizing their activity for a catalytic reaction. In that case, careful optimization of the surface composition opens the possibility to optimize the activity of the bimetallic catalyst.

4 Conclusions

The structure and local hydrogen adsorption properties of disordered PdAu–Pd(111) surface alloys were studied in a combined experimental and theoretical approach, aiming at a quantitative description of the overall adsorption properties in a coherent microscopic picture, in terms of local chemisorption properties of individual metal nanostructures. Employing high resolution STM imaging and TPD as well as HREELS measurements on the one hand and periodic density functional theory calculations on the other hand, we arrive at the following conclusions.

(1) In the PdAu–Pd(111) surface alloys, which were formed by annealing a (partly) Au covered Pd(111) surface, Pd and Au surface atoms are homogeneously distributed over the surface, and their distribution follows essentially a random distribution, indicative of weak net interaction energies between the two species. For up to 20% Pd surface concentration, Pd surface atoms are arranged predominantly as monomers and dimers, and only at higher Pd surface concentration larger ensembles contribute measurably.

(2) Correlation of desorption intensities in TPD spectra with the abundance of different adsorption ensembles and adsorption sites for different Pd surface concentrations indicates that Pd₄ trimers are the smallest ensemble (‘critical ensemble’) that can adsorb hydrogen via dissociative adsorption of H₂, with H adsorption taking place on Pd₃Au threefold hollow sites under present adsorption conditions (UHV, 120 K). Calculations find stable adsorption already on the same sites on Pd₃ trimers, but the adsorption energy may be too low to allow adsorption at 120 K, in addition, adsorption on these sites is hindered by a sizable activation barrier.

(3) Hydrogen adsorption on PdAu–Pd(111) surface alloys exhibits a pronounced ensemble effect, with H₆ ad being most stable on Pd₃ threefold hollow sites, less stable on Pd₄ bridge sites and least stable on Pd monomers. HREELS measurements as well as DFT data indicate that adsorption on Pd₃Au sites is more favorable than adsorption on Pd₄ bridge sites. Lateral (in-plane) ligand effects in contrast are smaller due to two opposing effects: increasing the number of Pd atoms in the surface alloys reduces the tensile strain which should increase the local adsorption strength, but it also increases the interaction with neighboring Pd atoms which decreases the local reactivity of the respective Pd surface atom. Both effects partly cancel each other for PdAu–Pd(111) surface alloys.

(4) The formation of 2 desorption peaks at 235 K and 325 K, respectively, which is observed for H₂ desorption from surfaces with Pd surface concentrations of 20–40%, is attributed to desorption from a weakly bound state where the H adatoms are not adsorbed in a Pd₃ threefold hollow site, but on a Pd₄Au site, or where the two Pd₃ sites are directly neighbored fcc and hcp Pd₃ sites, e.g., for compact tetramers. Accordingly, the higher temperature desorption peak is tentatively attributed to desorption from 2 Pd₃ sites with at least 1 lattice constant separation.

(5) Surface diffusion of H adatoms between isolated Pdₙ ensembles is inhibited due to the high energy of H₆ adsorbed on Auₙ surface sites, i.e., the H adatoms are confined to the original Pdₙ adsorption ensemble. As a consequence, dissociative adsorption of H₂ molecules is only possible if both H₆ species can be stably adsorbed on the same Pdₙ ensemble, and hydrogen adsorption occurs pairwise.

Overall, these results illustrate the detailed insight into the chemistry of bimetallic surfaces accessible from such kind of combined experimental and theoretical model studies on structurally well defined surfaces, and we expect these trends to be valid in a more general sense for comparable adsorption systems. Applying similar approaches to reaction studies will be the next task.

Acknowledgements

We gratefully acknowledge a fellowship of the Alexander von Humboldt Foundation (AvH) for N.T. and financial support from the Deutsche Forschungsgemeinschaft via the Research Unit 1376 (Be 1201/18-2). The DFT calculations were performed with support from the Danish Center for Scientific Computing through grant no. HDW-1101-05.

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