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Strain-Modulated Hydrogen-Deuterium Exchange over Au-Pd Core-Shell Nanocatalysts

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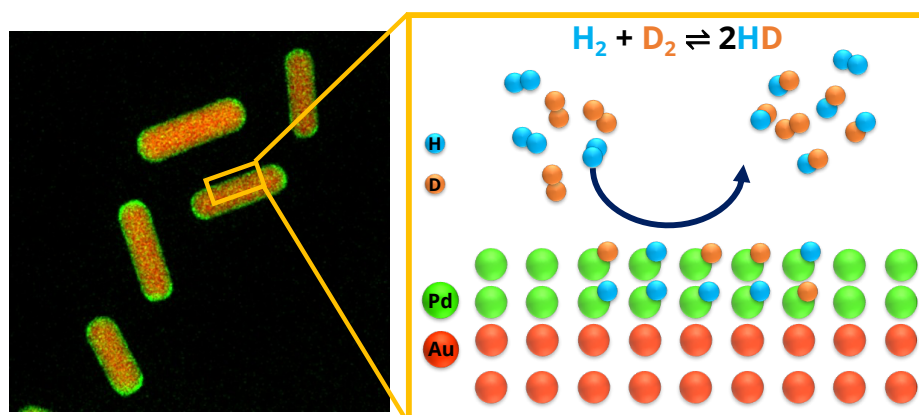
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Abstract

Hydrogen dissociation is an essential step in hydrogenation catalysis and critical to catalyst performance. Recently, Au-Pd core-shell nanoparticle catalysts have emerged as a highly promising class of materials for hydrogenation catalysis. Yet, fundamental understanding on the origin of bimetallic synergy in these core-shell catalysts and their interaction with hydrogen is largely unknown. Here, we investigate the kinetics of hydrogen dissociation and recombination over Au-Pd core-shell catalysts using the hydrogen-deuterium (HD) exchange reaction. We employed colloiddally prepared core-shell nanorod catalysts and used 4D scanning transmission electron microscopy to assess the degree and directionality of the strain in the Pd-shell. This revealed that even relatively thick Pd-shells are highly strained in the direction parallel to the surface. Catalytic testing showed that the HD exchange rate increases with increasing Pd-shell thickness and drastically decreases upon alloying. Interestingly, the core-shell nanorods showed temperature-dependent apparent activation energies and pre-exponential factors, indicating the presence of hydrides in the Pd-shell at the lower temperatures and gradual hydrogen release upon heating. Density functional theory (DFT) calculations indicate that subsurface hydrogen plays a major role in accelerating the hydrogen-deuterium exchange reaction by providing a lower energy pathway for recombinative desorption of hydrogen and deuterium, which is the rate limiting step. Altogether, our combined experiment-theory approach revealed that lattice strain and hydride formation can significantly influence the hydrogenation behavior of Au-Pd core-shell nanoparticles, and is relevant to further advance the design of core-shell materials for hydrogenation catalysis.



Introduction

Pd-based alloys are widely studied for hydrogenation catalysis.^{1,2} The addition of coinage metals like Au, Ag and Cu can substantially improve the selectivity of Pd-based catalysts towards the desired, semi-hydrogenated products, while usually drastically decreasing the activity.²⁻⁵ This well-studied activity-selectivity compromise can be surpassed through careful design of the metal distribution in the nanoparticle, specifically by departing from the conventionally used alloyed structures and tailoring the metal distribution towards a core-shell configuration.^{6,7} Au-Pd core-shell nanoparticles (NPs) can be up to 50 times more active in the selective hydrogenation of butadiene than alloyed analogues, while maintaining high selectivity.⁷ In core-shell systems, the catalytic activity largely depends on shell thickness. For example, Au-Pd core-shell nanorods (NRs) showed an optimal performance at a shell thickness of 6 atomic Pd layers for the selective hydrogenation of butadiene.⁷ However, the optimal Pd-shell thickness depends on the reaction.⁸⁻¹² For example, in the selective oxidation of benzyl-alcohol the optimum was at ~3 Pd-shell layers for <10 nm Au-Pd core-shell NPs.^{8,12} Thus, the Pd-shell thickness is an important parameter in regulating the catalytic performance of core-shell nanoparticle systems.

The enhanced performance of core-shell NPs arises from ligand and geometric effects that modify the binding energies of the reactants, reaction intermediates and products.^{13,14} The ligand effect refers to the interaction of the d-bands of the core metal with those of the shell metal. This ligand effect decays quickly and lasts only up to 2 monolayers from the Au-Pd interface.^{8,13} Strain arises from a lattice mismatch between the core and shell metal,¹⁵ leading to an upshift of d-band center for the tensile strain present in Pd overlayers epitaxially grown on Au,¹⁶ giving rise to stronger reactant binding on the Pd surface.^{7,17} Strain in the Pd-shell is considerably influenced by the shell thickness and, in contrast to the ligand effect, also persists in thicker shells. Rapid lattice relaxation occurs within the first few layers of Pd deposited on a Au surface, followed by a progressively slower strain release until full relaxation is achieved after 30 monolayers.^{18,19} The strain can be retained by controlling the nanoparticle morphology, and Pd-shells can adapt to the Au lattice up to a thickness of 10.5 nm when grown on flat Au surfaces.²⁰

Incorporation of hydrogen into the Pd lattice can occur in hydrogen-rich environments, leading to the formation of Pd hydrides (PdH_x), which alters the catalytic properties of Pd-based hydrogenation catalysts.²¹⁻²³ Palladium hydride exhibits a phase transition upon increasing hydrogen concentration from the low hydrogen content α -phase to the hydrogen-rich β -phase.^{24,25} The β -PdH_x is stable at room temperature for bulk Pd, and its stability decreases upon increasing temperatures and decreasing nanoparticle size.²⁶⁻³⁰ The formation of a subsurface hydride decreases the stability of surface-adsorbed hydrogen,³¹ thereby affecting the hydrogenation rates.²¹ Recent modeling work revealed that the Pd-shell of Au-Pd core-shell nanoparticles can also accommodate subsurface hydrogen in the form of PdH_x.³² As a result, hydrogen binding on Au-Pd core-shell catalysts is not only impacted by ligand and geometric effects but also by the incorporation of hydrogen into the Pd lattice.

The hydrogen-deuterium exchange reaction ($\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$) is a powerful experimental tool to measure the interaction of hydrogen with a catalyst.^{21,33} Through this isotope-exchange reaction one can assess the hydrogen dissociation and recombination steps on a catalyst surface. These elementary steps are critical in hydrogenation reactions and largely influence the catalytic performance both in terms of activity and selectivity.³⁴ This reaction has been used to study dilute Pd-in-Au alloys, showing that both the isotope exchange rate and rate limiting step are strongly influenced by the Pd ensemble size.^{5,33} However, the interaction of hydrogen with core-shell structured Au-Pd systems has not yet been studied, and the kinetics of hydrogen dissociation and recombination over Au-Pd core-shell NPs are still unknown.

Here, we investigate Au-Pd core-shell nanoparticle catalysts in the hydrogen-deuterium exchange reaction for the first time and assess hydrogen dissociation and recombination as a function of Pd-shell thickness. For a set of well-defined Au-core Pd-shell NRs with different shell thicknesses we characterized the degree and

directionality of strain with sub-nm resolution using 4D scanning transmission electron microscopy. We assessed the temperature-dependent reaction kinetics of HD exchange over these core-shell catalysts and compared them to their alloyed counterparts. Complementing with DFT calculations allowed evaluation of the hydrogen binding at the surface and in the subsurface of the Pd-shell and to link the experimental results to strain and hydride formation.

Results

Preparation of the Au-Pd core-shell nanorod catalyst system

Au-Pd core-shell nanorods (NRs) with varying Pd-shell thicknesses coated with a mesoporous silica shell were prepared using a multi-step colloidal synthesis approach.^{7,35} The Au NRs were single-crystalline and had a face-centered cubic lattice with the {110} and {100} facets exposed along their long flat sides, while the tips possessed a mix of facets.³⁶ The NR shape and mesoporosity of the silica shell is clearly visible in the annular dark field scanning transmission microscopy (ADF-STEM) images in Figure 1a. This ~18 nm thick mesoporous silica shell ensures the thermal stability of the nanorod shape, and the mesopore diameter of 2.5 nm allows access to the metal surface during catalysis.^{35,37} The Pd content was varied from 4 to 32 atomic %, as determined by inductively coupled plasma (ICP), giving rise to rods with 1-6 Pd layers (xL Pd) in the Pd-shell, as described in Table 1.⁷ The core-shell structure of the 5L Pd-shell NRs is clearly seen in the EDX maps in Figure 1b, that shows that the Pd signal extends over the Au signal, and the EDX map in Figure 1c shows the mesoporous silica shell over the Au-Pd core-shell nanorods. The final catalyst consisted of the mesoporous silica shell coated Au-core Pd-shell NRs supported on SiO₂ (Figure S1).

Table 1. Properties of the Au-Pd core-shell catalysts. ICP was used to obtain the composition, and TEM was used to determine sizes of the nanorods.

Sample	Pd content (X _{Pd})	Length (nm)	Diameter (nm)	Metal loading on SiO ₂ (wt%)
1L Pd	0.04	71 ± 8	22 ± 2	0.20
2L Pd	0.08	69 ± 7	21 ± 3	0.20
5L Pd	0.21	66 ± 6	18 ± 4	0.20
6L Pd	0.32	72 ± 8	24 ± 3	0.20
Au reference	0	68 ± 11	21 ± 2	1.00
Pd reference	1	20 ± 2	20 ± 2	0.15

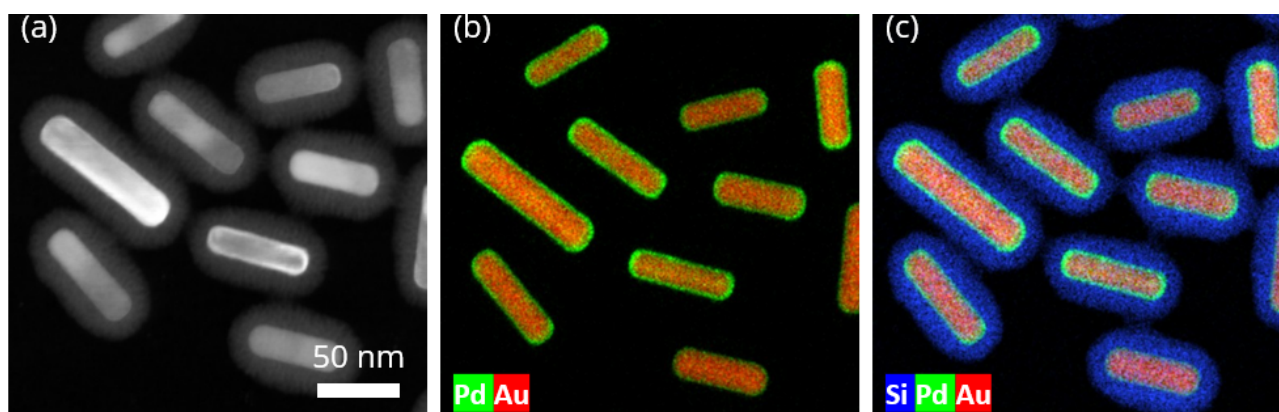


Figure 1. Au-Pd core-shell nanorods protected with a mesoporous silica shell. (a) Annular dark field scanning transmission electron microscopy (ADF-STEM) images of the NRs with 5L Pd, showing the mesopores of the silica shell. (b) Energy dispersive X-ray STEM (EDX-STEM) maps showing the Au-core Pd-shell structure and the (c) mesoporous silica shell. Prior to TEM analysis, the nanoparticles deposited on the TEM grid were heated at 200 °C for 1 h in H₂.

Measuring lattice strain in Au-Pd core-shell nanorods with 4D-STEM

Lattice strain can strongly impact the binding of adsorbates,¹⁴ and can be characterized using 4D scanning transmission electron microscopy (4D-STEM). This technique uses an electron probe to scan over a sample and simultaneously acquiring the annular dark field signal and a nanobeam electron diffraction (NBED) pattern, producing a 4D dataset where each pixel in the 2D ADF image contains a 2D NBED pattern.³⁸ The inverse relationship between the lattice parameter and the distance between diffraction disks in the NBED patterns allows to map strain, as the NBED pattern at each pixel can be compared with a NBED pattern of a reference region.³⁸

We employed 4D-STEM to characterize the amount and directionality of strain in the Au-Pd core-shell NRs. The ADF image of the 4D-STEM dataset is shown in Figure 2a. The Z-contrast allows distinguishing the Au-core from the Pd-shell, which can be used for masking the different regions (Figure S2). A section of the Au-core (blue rectangle overlaid in Figure 2a), which lattice parameter measured with high-resolution STEM (HR-STEM) corresponded to the bulk Au lattice (407 pm), was used as reference for strain mapping. The NBED pattern at each pixel of the image was compared to the NBED pattern at this reference region (Figure S3). Strain was computed in the direction perpendicular and parallel to the NR long edge surface, yielding the ϵ_{xx} and ϵ_{yy} strain maps, respectively (Figure 2b, c). This was achieved by following the 200 and 020 diffraction disk across the NR. The bottom part of the NR was slightly off zone axis, and the diffraction disks on the y-direction were less bright and defined, resulting in noise in the ϵ_{yy} strain map. The resulting strain maps in Figure 2b and c show that while the Au is mostly unstrained and exhibits little lattice parameter variation across the particle, some parts of the Pd-shell show compressive strain, meaning that the lattice parameter in the Pd-shell is smaller than in the Au-core and approaching that of bulk Pd.

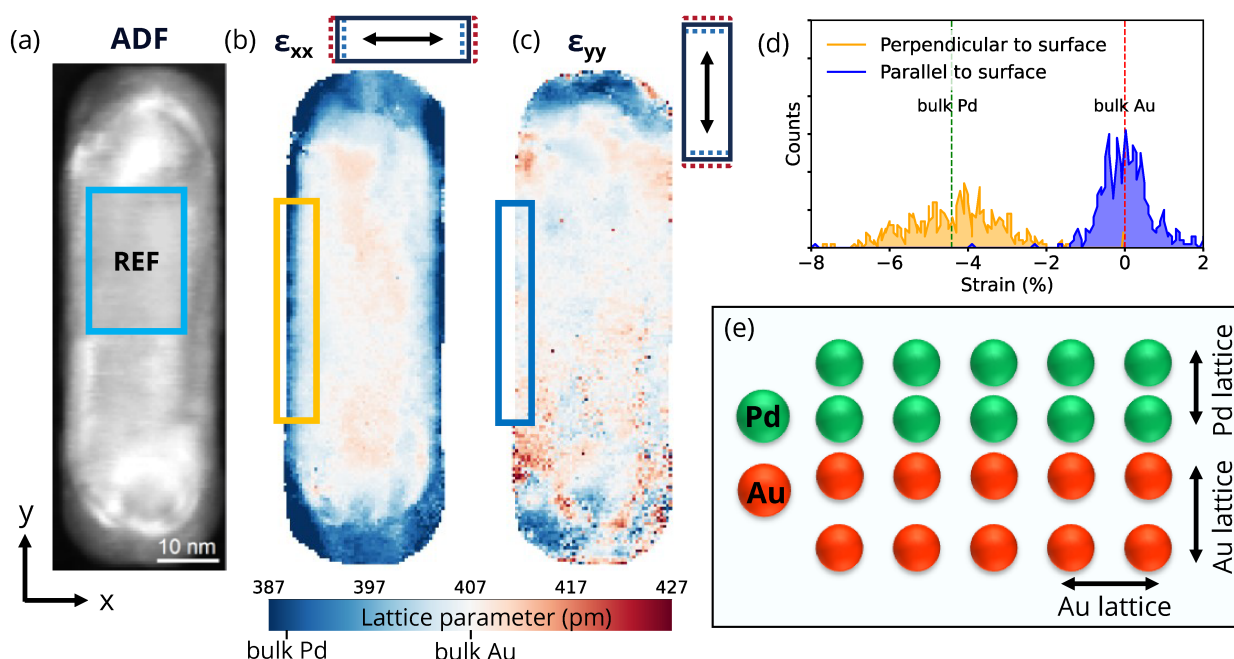


Figure 2. 4D-STEM strain mapping of an Au-Pd core-shell nanorod. (a) Annular dark field (ADF) image of the Au-Pd core-shell nanorod. On the long edges the Pd-shell thickness was of 1.6 nm, therefore 5 Pd layers, while in the tips it was of 2.4 nm. The area marked as REF was used as reference for the strain mapping. Each pixel contains a nanobeam electron diffraction (NBED) pattern. (b) Strain map in the x- and (c) y-direction. The color scale is shown at the bottom, with red and blue corresponding to tensile and compressive strain, respectively. The corresponding lattice parameters in pm are written underneath: white is close to the Au lattice and blue close to the Pd lattice. Note that the noisy pixels in the bottom of the nanoparticle correspond to noisy NBED patterns, where the diffraction spots are not well-defined and therefore strain quantification is inaccurate. (d) Histogram of the strain values of the Pd-shell in the regions marked in orange and blue in (b) and (c), with the vertical lines indicating the expected values for bulk Au and bulk Pd. (e) Schematic representation of the change of interatomic distances in the core-shell interface. In the direction parallel to the surface, the Pd (green) adapts the Au (red) lattice parameter and does not relax, while in the direction perpendicular to the surface the Pd relaxes to close to the bulk Pd lattice.

Interestingly, clear differences between strain perpendicular and parallel to the surface are observed. Along the long edges of the nanorods, the ϵ_{xx} map in Figure 2b shows compressive strain in the Pd-shell, while almost no strain is observed in the ϵ_{yy} map in Figure 2c. The strain values of the Pd-shell along the long edge of the nanorod, marked in blue and yellow in Figure 2b and c are summarized in Figure 2d, which shows that in the direction perpendicular to the surface Pd is relaxed to almost its bulk lattice parameter, but parallel to the surface the Pd adapts to the gold lattice parameter and does not relax. Figure S4 shows the strain values of the whole nanoparticle. Note that some regions of the Pd-shell have smaller lattice parameters than bulk Pd (Figure 2d), which is probably due to the Poisson effect.²⁰ In the curved tips of the nanorod the differences in strain in ϵ_{xx} and ϵ_{yy} directions are less pronounced, indicating relaxation of the Pd lattice closer to its bulk lattice parameter. A schematic of the positioning of the atoms in the Pd shell is shown in Figure 2e. Along the length of the nanorod, the Pd adapts to the Au lattice parameter parallel to the Au surface, while perpendicular to the surface the Pd atoms relax to the bulk Pd lattice parameter. This is different in the curved nanorod tips of the nanorods, where strain relaxation happens in both directions.

We complimented the strain analysis with both HR-STEM and x-ray diffraction (XRD), as the 0.5 nm probe size used in 4D-STEM is too large for studying thin Pd-shells. HR-STEM images of the NRs with 6L Pd-shell layers support the 4D-STEM findings (Figure S5), as a relaxed Pd lattice (389 ± 3 pm) was observed in the perpendicular direction and a strained (401 ± 7 pm) lattice parallel to the surface (Table S1). Epitaxial growth was observed in the direction parallel to the surface for all samples, and the average lattice parameter measured in the Pd shell was 398, 397 and 395 pm (Table S1), respectively for the 2L, 5L and 6L, which is between the Au and Pd bulk lattice parameter. This shows that the strain relaxation in the direction perpendicular to the surface occurs in thicker Pd-shells, as expected from literature.^{18,19} On the other hand, HR-STEM did not show a difference in lattice parameter between the Au-core and Pd-shell for a shell thickness of 1L Pd, but due to the rounded nature of the nanorods and the possibility of Au intermixing in the shell the difference in contrast is not enough to distinguish the 1L Pd-shell clearly. With XRD, only one diffraction peak at each reflection was observed for the 1L NRs, whereas for the 6L NRs a shoulder appeared at higher 2 θ values, indicating that a portion of the crystallite had a smaller lattice parameter (Figure S6). Thus, our XRD, HR-STEM and 4D-STEM results show that with increasing Pd content the strain in the direction parallel to the surface is maintained but relaxes perpendicular to the surface to bulk-like Pd.

Pd-shell thickness dependent hydrogen-deuterium exchange rates

Hydrogen-deuterium exchange experiments were performed on the Au-Pd core-shell NR catalysts. During this reaction, isotope exchange rates were monitored by quantitative mass spectrometry (MS).³³ The degree of HD exchange was dependent on the reaction temperature: an increase in temperature led to a decrease in H₂ and D₂ signal and an increase in HD signal in a 1:1:2 ratio, as shown in Figure 3a for the Au-Pd core-shell catalysts with a 2L Pd-shell. The conversion of the 2L Pd catalyst calculated at the isothermal steps is shown in Figure 3b. The raw data and conversion profiles of the Au-Pd nanorods with 1L, 5L and 6L Pd are shown in Figure S7. The catalyst loading was varied to reach similar conversion levels (~15%) at 225 °C for all catalysts and to avoid approaching equilibrium conversion, which is 50% for this reaction and corresponds to a 1H₂/1D₂/2HD mixture. The catalysts showed no signs of deactivation, as the heating and cooling conversion profiles were nearly identical (Figure 3b), indicating the absence of irreversible structural changes. Indeed, EDX mapping of the used catalyst confirmed that no atomic redistribution had taken place (Figure S8a). The 6L NR catalyst showed a reaction order of 1 both in H₂ and D₂ (Figure S9). In contrast to the Au-Pd core-shell catalysts, monometallic Pd and Au references showed no conversion at low temperatures and isotope scrambling only started to occur well above 150 °C as shown in Figure S10.

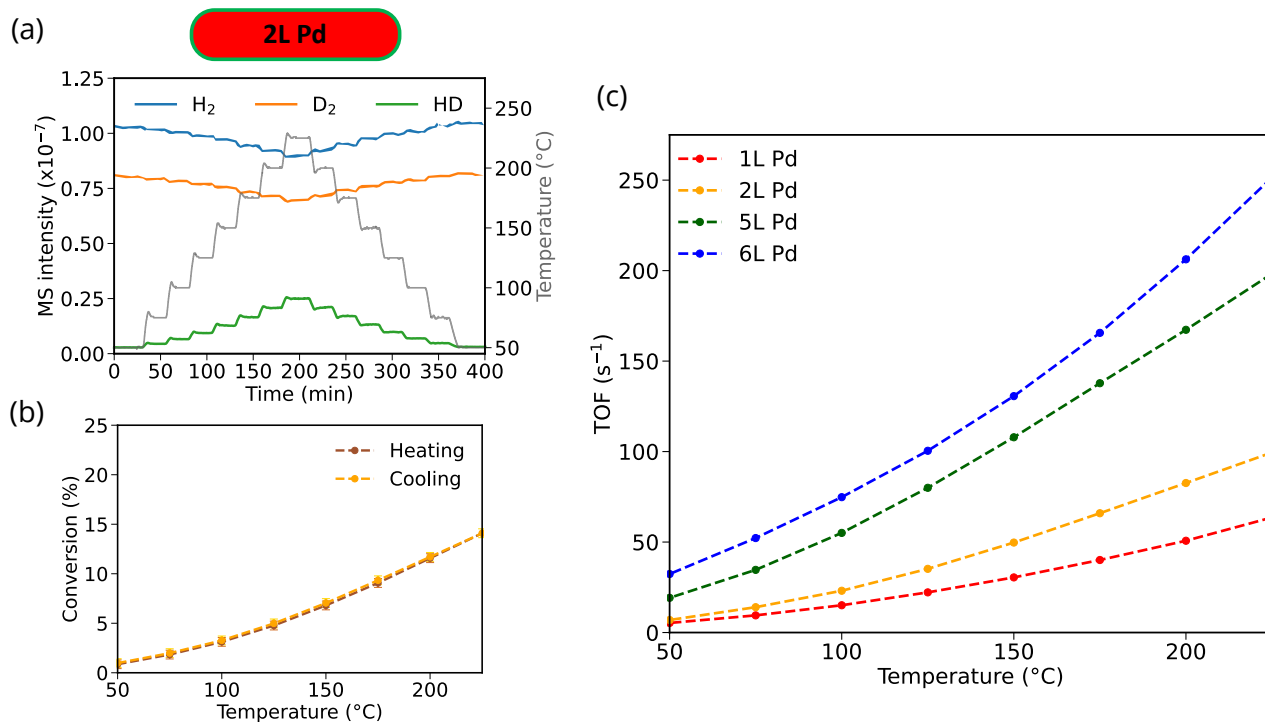


Figure 3. HD exchange activities of the Au-core Pd-shell catalysts (a) Mass spectrometry data as a function of time of catalyst with 2L Pd ($X_{\text{Pd}} = 0.08$), showing H_2 ($m/z = 2$) in blue, HD ($m/z = 3$) in green, and D_2 ($m/z = 4$) in orange. The stepwise temperature profile is shown on the right axis and plotted in grey. (b) H_2 conversion versus temperature on heating (brown) and cooling (orange) of the 2L Pd catalyst. (c) Turnover frequencies (TOF) of the nanorod catalysts with different layer thicknesses. TOF is expressed in molecules of HD converted per metal surface atom per second and were measured on cooling. Reaction conditions: total flow of 40 mL/min 10% H_2 and 10% D_2 diluted in Ar; ~5-20 mg of catalyst (0.2 wt %, sieve fraction 90-212 μm) diluted with 100 mg of SiC (>212 μm).

The turnover frequencies (TOFs) increased with the Pd-shell thickness (Figure 3c). The catalysts are compared by TOFs to exclude nanoparticle size differences and the various catalyst loadings in the reactor. At 50 °C the catalysts with 1L and 2L Pd show negligible conversion, while the catalyst with 5L and 6L Pd readily convert H_2 at this temperature. The TOFs increase with temperature for all the catalysts. Over entire conversion range, NRs with 5L Pd show more than double the activity of the 2L catalyst. One reason of the lower activity of the 1L and 2L Pd samples is likely the partial intermixing of Au in these thin Pd-shells. To verify this, we studied the influence of pretreatment temperature on the 1L catalyst (Figure S11). Pretreating this catalyst at lower temperatures (100 °C) significantly increased the activity, while pretreating at higher temperature (250 °C) decreased the activity. This suggest that Au intermixing in thin Pd-shells is temperature dependent and did occur to some extent upon pretreatment at 225 °C, while thicker Pd-shells are known to be more stable against alloying.⁷ Another reason of the lower activity of the 1L and 2L Pd samples linked with the low stability of subsurface hydrogen atoms in the thinner shells will be developed in the modelling section. Note that our NRs are single crystalline (Figure S5) and thus we do not expect defects of the crystal lattice to play a big role in the activity or kinetics identified in this work.

Metal distribution affects catalyst performance in HD exchange

The metal distribution within the nanorod largely affected the activity of the nanorod catalysts. Upon alloying at 450 °C for 12 hours in H_2 , the activity of the 5L NRs with $X_{\text{Pd}} = 0.21$ was significantly lower than the pristine 5L core-shell NRs that had only been reduced at 225 °C, as evident from the TOFs displayed in Figure 4a. EDX confirmed that the treatment at 450 °C led to an alloyed distribution (Figure S8b). The alloyed NRs showed negligible conversion at 50 °C. The conversion increased at higher temperatures, but only reached half of the activity of the core-shell catalyst at 225 °C, the highest temperature in our tests.

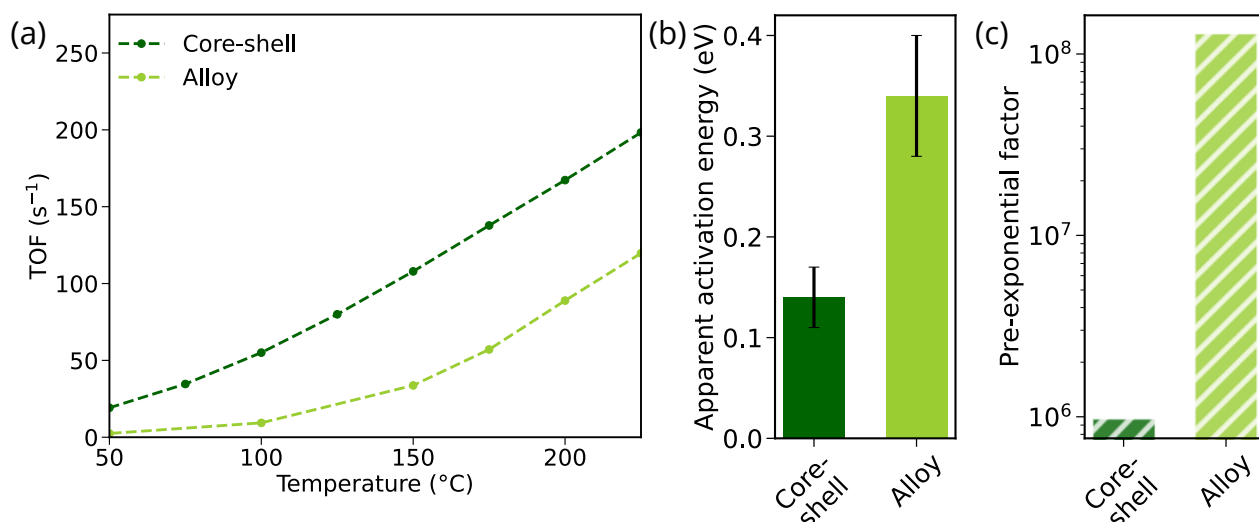


Figure 4. HD exchange activity of core-shell versus alloyed AuPd NRs. (a) Turnover frequencies expressed in HD molecules converted per metal surface atom per second of 5L core-shell nanorods (dark green) and alloyed nanorods (light green) with $X_{Pd} = 0.21$. (b) Apparent activation energies and (c) pre-exponential factors ($\mu\text{mol}_{HD} \text{g}^{-1} \text{s}^{-1}$) of the core-shell and alloyed nanorods (5L Pd, $X_{Pd} = 0.21$). Apparent activation energies and pre-exponential factors were calculated at similar conversion levels (10-15%).

Alloying resulted in an increase in apparent activation energies and pre-exponential factors (Figure 4b and 4c). These parameters were calculated by constructing Arrhenius plots using the isothermal steps between 1 and 20% conversion. Data below 1% conversion were excluded because of the measurement error, which arises from the baseline correction, and at low conversions small errors in the baseline result in large errors in activity. Data above 20% conversion were excluded to stay away from equilibrium conditions (50% conversion), where the reverse reaction $2\text{HD} \rightarrow \text{H}_2 + \text{D}_2$ would take place, which would result in lower activation energies. Upon alloying, the apparent activation energy increased from 0.14 ± 0.03 eV to 0.34 ± 0.06 eV, with the pre-exponential factor showing an even more pronounced increase, rising by approximately two orders of magnitude from 9.71×10^5 to 1.28×10^8 for the core-shell and alloyed catalysts, respectively.

Temperature-dependent apparent activation energies

The apparent activation energy and pre-exponential factor of the Au-Pd core-shell catalysts were dependent on temperature, as indicated by the non-linear Arrhenius plots (Figure 5a). To assess this behavior, we selected different temperature windows, each including three datapoints, and calculated the apparent activation energies and pre-exponential factors. The results are summarized in Table 2 and visualized in Figure 5b and 5c for a lower (75-125 °C) and higher (175-225 °C) temperature range.

Both the apparent activation energies and pre-exponential factors decreased with increasing temperature, suggesting a temperature-dependent reaction mechanism. The apparent activation energy at higher temperature was ~ 0.06 eV lower for both catalysts, and the catalysts with 2L Pd showed slightly higher apparent activation energies in both temperature regimes (~ 0.02 eV). The differences in pre-exponential factor were notably larger, decreasing by a factor of $\sim 5\times$ from the lower to higher temperatures. The 5L Pd catalyst exhibited a larger pre-exponential factor at all temperatures, with the difference being more pronounced in the 75-125 °C range. This behavior is not observed for the catalyst with 1L Pd which shows a linear Arrhenius plot over the entire temperature range (Figure S12).

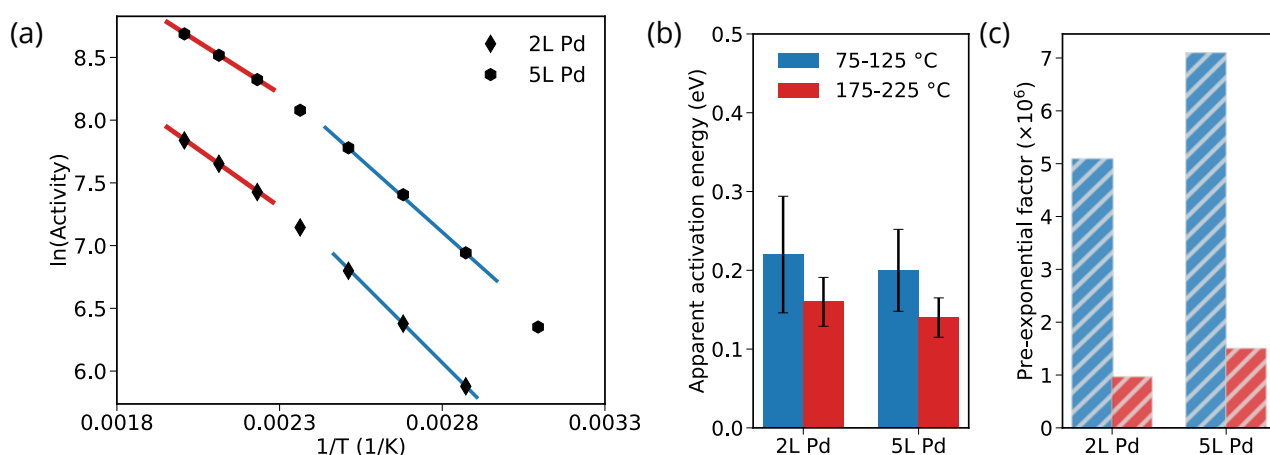


Figure 5. Temperature-dependent apparent activation energy and pre-exponential factor. (a) Arrhenius plots for the Au-Pd core-shell catalysts with 2 (diamond shape) and 5 (hexagon) Pd-shell layers. (b) Temperature-dependent apparent activation energy in eV and (c) apparent pre-exponential factors ($\mu\text{mol}_{\text{HD}} \text{g}^{-1} \text{s}^{-1}$) of the Au-Pd core-shell nanorods with 2L Pd (left) and 5L Pd (right) measured from the cooling data. The Arrhenius parameters were calculated in two temperature ranges: 75-125 °C (blue) and 175-225 °C (red).

Table 2. Temperature-dependent apparent activation energies and pre-exponential factors for the Au-Pd core-shell nanorods with 2 and 5L Pd, based on the conversion data during cooling. The highlighted rows correspond to the data used to make Figure 5.

2L Pd			5L Pd	
Temperature range (°C)	Activation energy (eV)	Pre-exponential factor ($\mu\text{mol}_{\text{HD}} \text{g}^{-1} \text{s}^{-1}$)	Activation energy (eV)	Pre-exponential factor ($\mu\text{mol}_{\text{HD}} \text{g}^{-1} \text{s}^{-1}$)
50-100	No sufficient conversion at 50 °C		0.21 ± 0.08	1.2×10^7
75-125	0.22 ± 0.07	5.1×10^6	0.20 ± 0.05	7.3×10^6
100-150	0.21 ± 0.05	3.5×10^6	0.18 ± 0.04	4.4×10^6
125-175	0.19 ± 0.04	2.3×10^6	0.17 ± 0.03	2.9×10^6
150-200	0.18 ± 0.04	1.4×10^6	0.15 ± 0.03	1.9×10^6
175-225	0.16 ± 0.03	9.7×10^5	0.14 ± 0.03	1.5×10^6

Influence of subsurface hydrogen revealed by density functional theory

For an in-depth understanding of the stability and effects of subsurface hydrogen in the HD exchange reaction, we performed DFT calculations. Our model consisted of a 3x3 periodic slab with 5 Pd layers on top of 3 Au layers with a (111) surface termination. The lattice parameter used is that of Au and the in-plane lattice parameters of the slab are kept fixed. The relaxed epitaxial structure shows a release of the Pd-shell strain perpendicular to the surface, with Pd-Pd distances quickly converging to the bulk values when moving away from the interface, in agreement with experimental observations for the dominant surface of the NR shown in Figure 2. We examined the stability of subsurface hydrogen in a temperature range of 50-250 °C with 0.2 atm hydrogen pressure to allow a direct comparison to the experimental results. Under reaction conditions the fcc hollow (fcc) surface sites are always fully covered with hydrogen. Only when the surface is fully occupied with hydrogen, the occupation of the subsurface octahedral (oct) sites starts being favorable. In our calculations, we initially assumed that each interlayer of oct positions between two Pd-shell layers is either

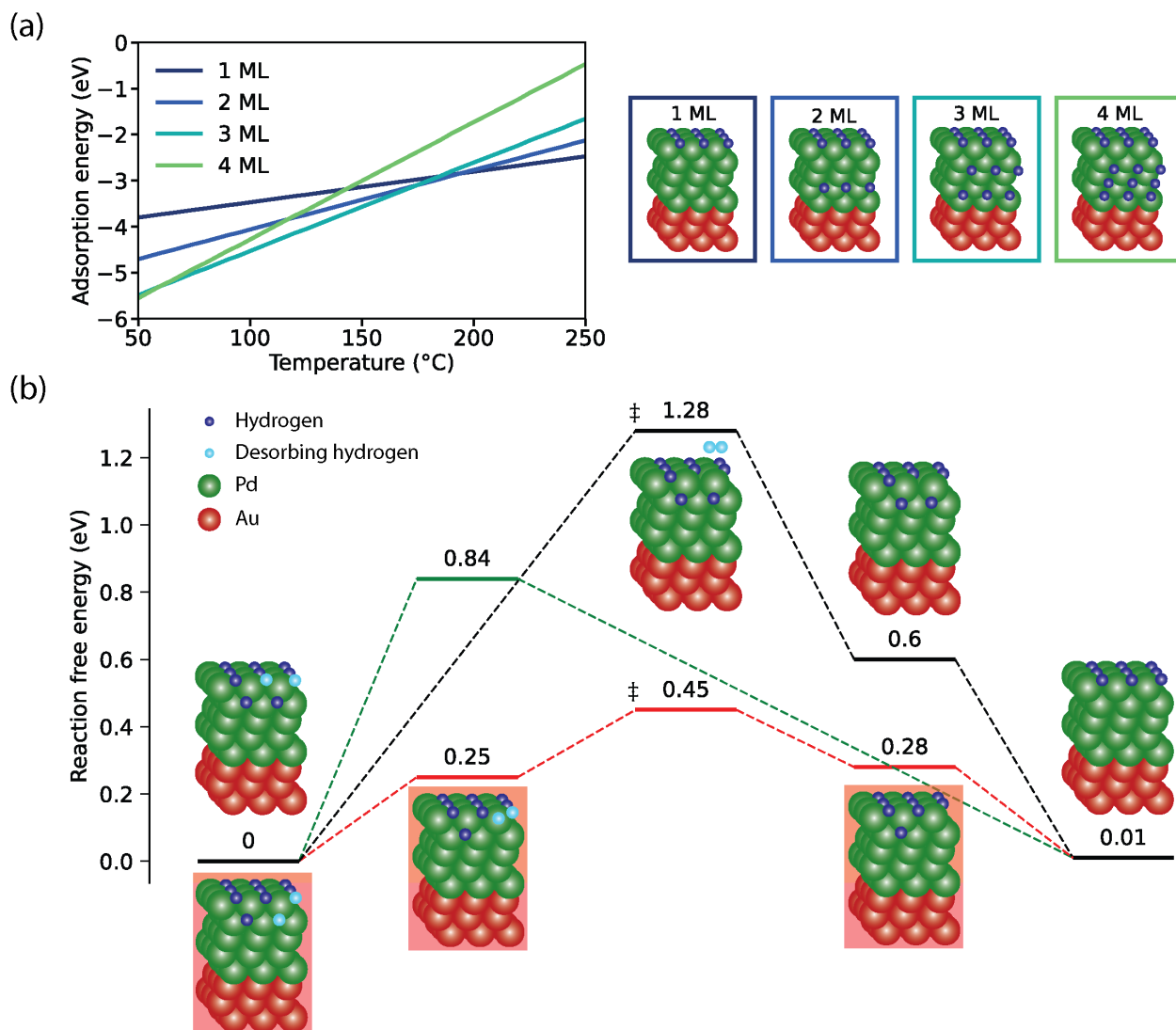


Figure 6. DFT calculations evaluating the stability of subsurface hydrogen in a 5L Pd-shell on Au-core model, and the mechanism of hydrogen desorption. (a) The stability of the subsurface hydrogen changes with temperature. Adsorption free energy diagram of different hydrogen monolayers at different temperatures. The schematics on the right depict the most favorable conformation. (b) DFT-computed Gibbs free energy profile for the hydrogen desorption process in the presence of subsurface hydrogen. Three possible pathways are shown. In black: recombination of two surface hydrogen atoms, in red: migration of a subsurface hydrogen to the surface upon which recombination and desorption occur, in green: migration of two subsurface hydrogens to the surface and subsequent desorption of those. The structures corresponding to the red and black pathways are shown in the schematics. Transition states are indicated by ‡. The reaction pathways shown were calculated at 200 °C and 0.2 atm of hydrogen pressure.

fully occupied with hydrogen or empty. The stability of subsurface hydrogen decreases with temperature. The stability of fully occupied hydrogen interlayers is shown in Figure 6a, and the corresponding structures are shown in the schematic. Four distinct temperature regimes can be distinguished. In the low temperature regime from 50 °C to 60 °C the structure with 4 monolayers (ML) of hydrogen is most favorable. This structure consists of a hydrogen surface layer and 3 subsurface hydride interlayers. The lowest energy configuration of interlayer occupation is shown in Table S2 and Figure S13, and consist of the surface occupied, the first Pd-Pd interlayer vacant and the second, third and fourth interlayer occupied. In the second regime, from 60 °C to approximately 175 °C, the 3 ML structure is the most energetically favorable. Increasing the temperature above 175 °C leads to destabilization of the subsurface hydrides, and the 2 ML structure becomes the most stable conformation until 195 °C, with hydrogen occupying the surface layer and 3rd interlayer. Note that replacing the fully occupied interlayer with two partially occupied interlayers (2nd and 3rd interlayer) results in a negligible energy difference (Table S2). The fourth regime lies at temperatures above 195 °C. In this regime,

the 1 ML structure is most stable, having a surface that is occupied with hydrogen but no full subsurface layer of hydrogen. Partial subsurface occupation is still possible in this regime. Thus, the calculations indicate that the amount of subsurface hydrogen decreases with increasing temperature, with substantial subsurface hydrogen being present up to 195 °C. Consequently, we expect that under our experimental conditions, the surface of the catalyst is always occupied with hydrogen and the hydrogen occupancy in the subsurface is variable, decreasing with temperature.

To understand the impact of subsurface hydrogen on the experimentally measured HD exchange rates, we investigated how subsurface hydrogen can participate in the hydrogen desorption mechanism via transition state modeling using DFT calculations. The reaction free energies of the intermediates and transition states of three plausible mechanisms were evaluated at 200 °C and 0.2 atm of hydrogen pressure for the 5L epitaxial Pd-shell model and are shown in Figure 6b. The starting point for all mechanisms was a fully covered surface of a 3x3 slab (9 surface hydrogens at the fcc sites) and two subsurface hydrogen atoms at the oct sites. The calculated reaction barriers show that the involvement of subsurface hydrogen substantially lowers the desorption barrier compared to the case where only surface hydrogens are considered, which is important since this desorption step is known to be the rate-limiting step in the HD exchange reaction over Au-Pd core-shell systems.⁵ The overall thermodynamics of the desorption step in presence of subsurface hydrogen is approximately zero, meaning that hydrogen desorption in the presence of subsurface hydrogen is not thermodynamically limited. This is different in a 1L Pd system, where subsurface hydrogen cannot be present, resulting in a final structure after desorption which is 0.61 eV higher in energy under the same conditions (Figure S14). DFT calculations showed that hydrogen penetration into the Pd-Au interlayer drastically destabilized the system by approximately 2 eV for the complete occupation of the surface and subsurface of the 3x3 unit cell (0.22 eV per surface atom), compared to surface adsorption only, signaling that the subsurface occupation in the 1L Pd model is not accessible.

The three distinct pathways in Figure 6b show significant differences in energy barriers. The mechanism in black involves direct recombination and desorption of surface hydrogen atoms followed by the migration of the two subsurface hydrogen atoms to the surface. This mechanism has an overall energy barrier of 1.28 eV, and the reaction intermediate with two vacancies at the surface is 0.6 eV higher than the initial state. The mechanism in green first allows the two subsurface hydrogens to migrate to the hcp hollow (hcp) sites at the surface, increasing the surface hydrogen coverage above 1 ML, followed by recombination and desorption of H₂. The migration of two hydrogen atoms from the subsurface to the already fully covered surface comes with a large energy penalty of 0.84 eV. In the mechanism in red, one subsurface hydrogen migrates to a hcp surface site (with an energy cost of 0.25 eV), subsequently it combines with a surface fcc hydrogen and H₂ desorbs. The single empty surface fcc site is then filled by migration of the other subsurface hydrogen. This combined (migration, recombinative desorption, migration) pathway involving subsurface hydrogen provides a highly efficient path for H₂ desorption with an overall free energy barrier of 0.45 eV. The H-H recombination step occurs with a barrier of only 0.2 eV. The pathway can also be taken backward, leading to an easy adsorption of H₂, producing two subsurface hydrogens. The subsurface hydrogen atoms therefore play a major role in accelerating the hydrogen-deuterium exchange and provide pathways compatible with the high rate measured (160 s⁻¹ under these conditions). In addition, our DFT calculations demonstrated that additional subsurface hydrogen atoms can potentially act as spectators and further reduce the desorption barrier. The transition state may benefit from the stabilization effects of the spectator subsurface H. With 9 oct subsurface hydrogen atoms, the fcc- and hcp-covered structures have a desorption barrier of 0.28 eV and 0.39 eV, respectively, both lower than that of 9fcc+2oct structure, at 200 °C (Figure S15).

To compare with experimental Arrhenius analysis, we now focus on enthalpy barriers for H₂ desorption, instead of free energy barriers. At 200 °C, a full coverage of subsurface hydrogen atoms is unstable, and the desorption process will occur from structures that present a small number of subsurface hydrogen atoms, for example from 9fcc + 2oct to 9fcc, which presents an enthalpy barrier of 0.42 eV (Table S3). When lowering the temperature to 100 °C, two effects with an opposite effect on the enthalpy barrier can occur. The first

effect is related to the temperature dependency of the enthalpy. If the number of subsurface hydrogen is kept constant, the enthalpy barrier increases from 0.42 eV at 200 °C to 0.45 eV at 100 °C. The second effect is related to the temperature dependent number of subsurface hydrogen atoms in the Pd-shell. At 100 °C, the subsurface hydrogen atoms become stable, so that their number increases. This results in a decrease of the enthalpy barrier at 100 °C, but this effect is small, much smaller than the previously discussed change of the free energy barrier. If we consider a full coverage of subsurface hydrogen atoms and include fact that surface hydrogens prefer a hcp site in this case, calculations show a decrease of the enthalpy barrier at 100 °C to a value of 0.43 eV (Table S3). Determining which effect dominates for the barrier, temperature dependent enthalpy or subsurface H coverage, is not safely possible from calculations due to limited accuracy. In experiment, we observed a small increase in apparent activation energy at low temperatures, suggesting that the temperature dependent enthalpy effect may dominate. Yet, in both experiment and theory the variations with temperature are small.

Discussion

Our findings demonstrate that the hydrogen dissociation capability of the core-shell Au-Pd NRs is strongly related to the Pd-shell thickness, as an increased Pd-shell thickness resulted in increased TOFs in the HD exchange reaction (Figure 3). This layer thickness effect can in part be ascribed to Au intermixing in the thin Pd-shells, while the thicker Pd-shells are more pure core-shell systems. Although STEM-EDX reveals a core-shell structure also for the 1L and 2L Pd catalysts after pretreatment at 200 °C (Figure S16), some Au intermixing in the thin 1L and 2L Pd-shell cannot be excluded.⁷ By testing the 1L Pd catalysts after different pretreatment temperatures, we indeed confirmed partial alloying upon pretreatment at 225 and 250 °C (Figure S11). The catalyst shows higher activities and more core-shell like HD exchange behavior when using a pretreatment temperature of 100 °C. Thus, while the 1L Pd-shell is highly strained, partial intermixing causes lower catalytic activities than expected, which is in line with previous work on selective hydrogenation.⁷ The same catalysts showed higher activity with thicker Pd-shells in the selective hydrogenation of butadiene.⁷ It is generally accepted that the rate limiting step in hydrogenation reactions over Au-Pd or Pd catalysts is hydrogen dissociation or the addition of hydrogen to the unsaturated hydrocarbon.^{34,39,40} The similar behavior of the Au-Pd core-shell NRs in the hydrogen-deuterium exchange reaction and selective hydrogenation of butadiene highlights the important role of hydrogen dissociation activity in the hydrogenation mechanism.

Alloying of the core-shell structure resulted in a large drop in isotope exchange rate, which is in line with previous research showing significant loss of activity after alloying of core-shell structures in hydrogenation reactions.^{7,41} The decrease in activity upon alloying is associated with a doubling in the apparent activation energy and a 100-fold increase in the pre-exponential factor. The resulting values ($E_{\text{act}} = 0.34$ eV and $A = 1.28 \times 10^8 \mu\text{mol}_{\text{HD}} \text{g}^{-1} \text{s}^{-1}$) are comparable to those obtained for dilute Pd-in-Au alloys with Pd monomers in the Au surface reported in literature.^{5,33} While larger Pd ensemble sizes might be expected from the higher Pd content in our alloy ($X_{\text{Pd}} = 0.21$),⁴² it is likely that the alloying treatment in hydrogen at 450 °C drove most of the Pd into the subsurface, leaving only a small percentage of isolated Pd atoms on the surface. Indeed, only Pd monomers were observed in CO-DRIFTS after alloying core-shell nanoparticles ($X_{\text{Pd}} = 0.35$) in hydrogen.⁴³ While for a Pd-on-Au monolayer hydrogen desorption is known to be the rate-limiting step in the HD exchange reaction, hydrogen dissociation is rate-limiting for Pd monomers in an Au surface.⁵ This change of rate-limiting step can explain the large increase in pre-exponential factor upon alloying of the core-shell structure, that is probably not linked to the number of active sites but to a change in apparent activation entropy.³³

Strain mapping with 4D-STEM on the Au-Pd core-shell nanorods confirmed that the lattice parameter in the Pd-shell is larger than bulk Pd, and thus that strain is present in our system. From surface science studies, we expected a strained surface up to 30 monolayers of Pd on Au, with some degree of strain release.¹⁹ The HR-STEM data reveals that the average lattice parameter in the Pd-shell follows this expected strain relaxation trend (Table S1). Our 4D-STEM mapping showed that in the flat long surface of the nanorods the Pd adapts to the lattice parameter of the Au in the direction parallel to the surface, but is relaxed in the perpendicular

direction (Figure 2). This is in line with recent literature that showed epitaxial growth in the direction parallel to the surface but strain release in the perpendicular direction.^{8,12} However, in the curved tips of the nanorod strain release in both directions was observed. Similarly, 4D-STEM mapping of Au-Pd core-shell nanocubes showed that strain can be preserved up to a 10.5 nm Pd-shell thickness, as long as no rounded edges were present, as strain release was only observed in curved surfaces.²⁰ 4D-STEM can therefore give direct insight of the variation of lattice parameter in a nanoparticle, not possible to obtain from bulk or surface techniques where only average strain is observed.

Our DFT calculations demonstrate that the presence of subsurface hydrogen facilitates the rate-limiting desorption of hydrogen from the surface by participating in the desorption mechanism. This is in line with studies that showed how subsurface hydrogen can participate in the HD exchange reaction on Pd nanoparticles^{44–46} and with the higher catalytic activity usually associated with the formation of a Pd hydride phase in hydrogenation reactions.^{22,23} The inaccessibility of subsurface hydrogen in the 1L Pd core-shell catalyst is contributing to the low reactivity observed in the experiments compared to its counterparts with thicker Pd layers. In our 5L Pd core-shell system, the presence of subsurface hydrogen makes hydrogen desorption thermodynamically neutral, and the participation of subsurface hydrogen in the hydrogen desorption mechanism lowers the hydrogen desorption barrier by 0.83 eV (Figure 6b). The results of our calculations explain the low experimental apparent activation energies for the core-shell NRs. We find only a small difference in apparent activation energies between the 2L and 5L Pd catalysts as both systems can have subsurface hydrogen present.³² The slightly higher apparent activation energy of the 2L Pd NRs may be caused by the higher energy cost for subsurface hydrogen occupying the first layers compared to occupation of the 2nd and 3rd interlayer in the 5L Pd-shell system (Table S2). Besides, recent calculations on a 2L Pd system show that the energy barrier for hydrogen desorption (0.53 eV) is slightly higher for 2L Pd in the presence of subsurface hydrogen than in our case of 5L Pd.³² Finally, we observe that additional subsurface hydrogen content that does not directly participate in the desorption mechanism can help lower the free energy barrier of hydrogen desorption (Figure S15). Recent work of Chu *et al.* shows that the near-surface hydrogen species can alter the preferred pathway of H₂ dissociation and enhance the selectivity of the COOH pathway in CO₂ hydrogenation on β -Ga₂O₃(100) catalyst.⁴⁷ However, further investigation on the electronic structures is required to fully understand the influence of spectator hydrogen in the reaction.

The Au-Pd core-shell catalysts exhibited temperature-dependent apparent activation energies and pre-exponential factors (Figure 5), which may in part be linked to hydride stability (Figure 6a). It is well-known that Pd can intercalate hydrogen in the subsurface forming Pd hydride at room temperature, which gradually desorbs at higher temperatures.^{26–29} While it is difficult to provide experimental proof for the different amounts of hydrogen present at different temperatures in the Pd-shell of our catalysts, the DFT calculations in Figure 6a show that the stability of the subsurface hydrogen in the Pd-shell decreases upon increasing the temperature from 50 to 250 °C. Recent modelling work has shown that subsurface hydride stability is Pd-shell thickness dependent: while the 2L Pd-shells only form an hydride phase up to 62 °C, subsurface hydrogen is stabilized in thicker 4L Pd-shells up to 154 °C,³² Our work extends the calculations to a 5L Pd system and shows that fully occupied subsurface hydrogen interlayers are expected up to 190 °C, and that the stability of the subsurface hydrogen decreases upon increasing the temperature from 50 to 250 °C (Figure 6a). Figure 6c shows that at 200 °C, the 5L model with the surface fully occupied by adsorbed H and with 2 subsurface hydrogen atoms is 0.01 eV more stable than the surface-only adlayer which has no subsurface hydrogen, indicating that it is possible to have partial occupancy for the 5L model up to 200 °C. Although the 2L and 5L models both present Pd₆ subsurface octahedral sites for hydrogen, the subsurface hydride exhibits very different stabilities. In the range of considered temperature, subsurface H is not stable for the 2L model, while it is stable for the 5L model. Subsurface H atoms enable a low barrier for desorption and adsorption of hydrogen and a high rate for H₂/D₂ exchange. This explains the observed reactivity difference, with the 5L core-shell catalysts showing a much higher TOF than that of the 2L catalyst (Figure 3c). While our experimental work does not show major differences in the temperature-dependent behavior of the catalysts with 2L and

5L Pd, the high pre-factor at low temperatures indicates an increased number of active sites at low compared to high temperature which can be linked to the amount of subsurface hydrogen present in the Pd-shell. This is further substantiated by the absence of this temperature dependent behavior in the 1L catalysts where no hydrides can be present (Figure S12). Together, theory and experiment show that subsurface hydrogens impact the reaction mechanism and thus affect the HD exchange performance of Pd-shell Au-core catalysts.

The Pd-shell thickness dependent HD exchange activity of the Au-Pd core-shell nanorods observed in experiment is likely related to both lattice strain in the Pd-shell, as tensile strained Pd has a stronger interaction with hydrogen, and intermixing effects.⁷ The high activity of the 5L and 6L Au-Pd core-shell nanorods in the HD exchange reaction can be ascribed to lattice strain, as our 4D STEM data clearly shows that strain is retained at even in these thick Pd-shells. Our DFT calculations also showed that the strain in the Pd layers made the subsurface hydrogen adsorption more favorable, and the alloying effect of the Au substrate was very minimal (Table S4). The presence of the strain on Pd is critical to stabilize subsurface hydrogen configurations at the considered reaction temperature. In the absence of strain, subsurface hydrogen only occurs at low temperature and no subsurface hydrogen is present under reaction conditions (Figure S17). Additionally, our previous work shows that the hydrogen penetration into the subsurface layers is more exergonic and has a smaller effective barrier when strain is applied.³² Therefore, the subsurface hydrogen is both more thermodynamically favorable and kinetically accessible when Pd layers are strained in the surface plane to the Au lattice. If instead the ligand effect was dominant, a volcano-plot would be expected with an activity optimum around 2-3 Pd-layers, which has previously been observed in literature for oxidation reactions.^{8,12} Due to the low weight loading of our catalyst samples we could not assess the possible charge transfer between Au and Pd, but based on previous studies ligand effects are not expected in shells thicker than 2-3 Pd layers.^{8,13,47} While a larger presence of subsurface hydrogen might be expected in the thicker Pd-shells, it is unlikely that hydrides alone can explain the Pd-shell thickness dependent catalytic activity, as also in low amounts subsurface hydrogen facilitates the mechanism of hydrogen desorption. The thinner 1L and 2L Pd-shell systems are highly strained, but less active as they are more prone to intermixing of Au in the thin Pd-shell upon pretreatment (Figure S11).

Conclusion

Our study shows that the activity in HD exchange over Au-Pd core-shell catalysts strongly depends on the Pd-shell thickness, and that thick shells still maintain significant strain parallel to the surface as evidenced by our 4D-STEM measurements. Increasing the Pd shell thickness results in higher TOFs, in line with selective hydrogenation butadiene studies of the same nanoparticles indicating the relevance of the hydrogen reactivity in hydrogenation reactions. Alloying leads to a pronounced decrease in TOFs accompanied by an increase in apparent activation energy and pre-exponential factor, which can be attributed to a change in the rate-limiting step from desorption limited on the core-shell system to dissociation limited on the alloy. Moreover, the core-shell systems exhibited a temperature-dependent activation energy and pre-exponential factor, likely caused by the higher stability of subsurface hydrogen in the Pd-shell at the lower temperatures of our test. With DFT calculations, we showed that the subsurface hydrogen plays a crucial role in reducing the energy barrier for hydrogen desorption, which is the limiting step in the HD exchange reaction in core-shell systems. Altogether, our work shows that strain in Pd-based catalyst can be used to modulate the interaction with hydrogen at the surface and in the subsurface, which can be exploited to control the catalytic performance of core-shell systems in selective hydrogenation reactions.

Methods

Catalyst synthesis: Silica supported Au-Pd core-shell nanorods coated with a mesoporous silica shell

The synthesis and further sample details of the Au-Pd core-shell nanorods coated with a mesoporous silica shell and supported on Aerosil OX50 is described in detail in ref.⁷ In short, the Au-Pd core-shell nanorods were

synthesized through a multi-step colloidal synthesis consisting of four steps: gold NR synthesis, mesoporous silica shell growth, Pd overgrowth and deposition on the silica support.

First, the Au NRs were synthesized according to the protocol of Ye *et al.*⁴⁸. The synthesis was performed at 500 mL scale using a growth solution containing 7.0 g CTAB, 1.24 g NaOL, 250 mL MQ H₂O and 250 mL 1.0 mM HAuCl₄, 4.8 mL 10 mM AgNO₃, 2.10 mL concentrated HCl (37 wt%), 1.25 mL 64 mM ascorbic acid and 0.8 mL seed solution. Preparation of the seeds was done using 10 mL 0.10 M CTAB, 51 μ L 50 mM HAuCl₄ and 1.0 mL 6.0 mM NaBH₄. The NRs were washed with water once and stored in 5.0 mM CTAB H₂O.

Second, the AuNRs were coated with a 18 nm thick mesoporous silica shell following the procedure of Gorelikov *et al.*³⁷ The coating was performed using 200 mL of Au NR dispersion (2.5x concentrated with respect to the original synthesis solution) with a CTAB concentration of 1.5 mM in water. To the NR dispersion 2.0 mL 0.10 M NaOH were added and, 3 times 0.60 mL 0.90 M TEOS in ethanol (EtOH) with a 30 min time interval between the additions. The generated Au@SiO₂ NRs were washed with water and ethanol. Subsequently, the CTAB ligands were removed from the mesopores through washing with an acidified ethanol solution (0.1 M HCl in ethanol). The acidified Au@SiO₂ NR dispersion was sonicated for 30 min at room temperature (RT) and washed three times with EtOH. In order to accommodate a 6L Pd-shell one batch of rods were etched prior to palladium overgrowth by adding 1.0 mL concentrated HCl and 1.0 mL 20 mM H₂O₂ in methanol (MeOH) to Au@SiO₂ NRs in MeOH which was allowed to react for 20 minutes.

Third, the palladium overgrowth was performed according to the procedure of van der Hoeven *et al.*³⁵. For the 1L Pd NRs, 250 mL Au@SiO₂ NR dispersion in water was used to which 2.0 mL 0.1 M HCl, 2.5 mL 1.5 mM Na₂PdCl₄ and 2.5 mL 6.0 mM ascorbic acid were added. For the 2L Pd NRs, 200 mL Au@SiO₂ NR dispersion in water was used to which 2.0 mL 0.1 M HCl, 2.0 mL 2.25 mM Na₂PdCl₄ and 2.0 mL 9.0 mM ascorbic acid were added. For the 5L Pd NRs, 240 mL Au@SiO₂ NR dispersion in water was used to which 2.4 mL 0.1 M HCl, 2.4 mL 5.5 mM Na₂PdCl₄ and 2.4 mL 22 mM ascorbic acid were added. For the 6L Pd NRs, 145 mL Au@SiO₂ NR dispersion in water was used to which 1.45 mL 0.1 M HCl, 1.45 mL 8 mM Na₂PdCl₄ and 1.45 mL 32 mM ascorbic acid were added. The resulting Au-Pd core-shell NRs were washed with H₂O and EtOH and stored in EtOH at 4 °C in the dark to prevent oxidation of the Pd-shell.

Finally, the Au-Pd core-shell NRs were deposited on a commercial Aerosil OX50 silica support (Evonik, BET surface area: 50 m²/g) through an anti-solvent deposition approach using toluene.⁷ The Pd and Au concentrations were determined prior to deposition by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES). To 1.0 g Aerosil support an amount of mesoporous silica coated Au-Pd core-shell NRs in ethanol was added to yield a catalyst with a metal weight loading of 0.2 wt% on silica. The mixture was sonicated for 30 minutes after which 14.0 mL of toluene was added followed by a few minutes of sonication. After centrifugation, the supernatant was removed and the supported NRs were dried in a N₂-flow and subsequently overnight at 60 °C in air.

Pd nanocubes from previous work^{29,41} were used as a monometallic Pd references, synthesized according to a literature protocol.⁴⁹ As monometallic gold reference Au@SiO₂ NR on Aerosil OX50 were used.

Characterization

Characterization of the size and metal distribution of the silica coated Au-Pd core-shell nanorods was performed on a TFS Talos F200X electron microscope operated at 200 kV. The free-standing nanorods were dropcasted onto a 200-mesh Cu grid coated with a Formvar film (Ted Pella) and pretreated at 200 °C during 1 h under H₂ (50 mL/min) in a Thermolyne 79300 tube furnace to mimic the pretreatment performed before catalysis. The microscope was operated in (high-angle) annular dark-field (HAADF-STEM or ADF-STEM, with collection angles of 35-200 and 14-33 mrad, respectively) with a camera length of 160 mm, 2048x2048 pixels and 2 μ s dwell time. Energy Dispersive X-ray Spectroscopy (EDX-STEM) mapping was performed with a screen current of 1.68 nA, a dwell time of 5 μ s per pixel, a pixel size of 516.2 pm and 512x512 pixels per map. The

Super-XTM EDX detector was used to collect the EDX signal, which was quantified with the Velox software by using the L-lines of both Au and Pd.

High resolution images and 4D-STEM strain maps of the NRs were obtained on a double aberration-corrected TFS Spectra300 microscope operated at 300 kV. High-resolution images were acquired with a convergence angle of 21.5-22.0 mrad, camera length of 146 mm, collection angle 40-200 mrad, a screen current of 0.11-0.18 nA, 2048x2048 pixels of 2-40 pm size acquired as 10-20 frames of 100-200 ns dwell time and combined with the DCFI algorithm in the Velox software. Before measuring the nanorods, an AuPd Cross Grating Replica was measured, to allow for precise determination of the lattice parameters. All lattice parameters were corrected by a factor 1.0125 arising from a slight error in calibration. The 4D-STEM dataset consisted of an annual dark field (ADF) image with a nanobeam electron diffraction pattern at every pixel with a step of 0.5 nm. A convergence angle of 2.5 mrad, a camera length of 29 mm and a screen current of 3 pA was used. NBED patterns were collected in a CCD camera with 512x512 pixels and 0.2 s exposure time placed after the Gatan Continuum energy filter, operated with a slit of 5 eV centered in the zero-loss peak. The data was analyzed using the Gatan Digital Micrograph strain mapping module⁵⁰ by selecting a 13x27.5 nm reference area placed on the Au and following the 200 and 020 diffraction disks up to the 2nd order of diffraction.

X-ray diffraction was performed on a Bruker D2 Phaser with a CoK α -source ($\lambda = 0.17902$ nm). Measurements were performed from 42-56 2 θ with a step size of 0.2 and a measurement time of 1 second per step. The signal-to-noise ratio was improved by measuring over this range for 16 hours.

Pd layer thickness calculations

The thickness of the Pd shell was calculated starting from the NR sizes in Table 1. The NR volume was obtained by assuming that the rods possess a spherocylindrical shape. Using the Pd fraction measured with ICP, an average density and molar mass was calculated for each Pd fraction and the moles of metal per NR were calculated. Next, the theoretical expected amount of Au was calculated for different layer thicknesses by using the NR sizes and subtracting the lattice parameters of Pd, assuming that the rods have sides containing a 50:50 ratio of (110) and (100) facets, and (111) facets at the tips. The difference between the theoretical expected and measured amount of metals were compared to the Pd fraction to obtain an estimate of the layer thickness in the samples. The nanorods with 6L Pd had Au-cores that were etched prior to Pd-shell growth to create space in the SiO₂ shell to accommodate a larger amount of Pd. As the etching predominately occurs at the tips of the Au NRs, most space for Pd to grow is at the tips. Therefore, the 6L sample has a thicker Pd-shell at the tips than at the sides of the NRs. As a consequence, the calculation used for the 1L, 2L and 5L rods does not yield a good estimate of the layer thickness for the 6L sample. We measured the layer thickness of the 6L sample from the HR-STEM images, which gives a layer thickness of 6L for the sides and 9L for the tips. Note that small deviations in the NR sizes lead to large effects in layer thickness, therefore this is only an estimation of the layer thickness.

Catalysis: Hydrogen-deuterium exchange reaction

HD exchange experiments were conducted in a cylindrical reactor tube with an inner diameter of 4 mm monitoring the temperature with a thermocouple inside the reactor. Typically, 5-20 mg of sieved (90-212 μ m) catalyst of 0.2 wt% was diluted with 100 mg SiC (>212 μ m) to achieve a reactor bed height of approximately 1 cm. The amount of catalysts loaded was adapted (5-20 mg) to reach similar conversion at 225 °C for all layer thicknesses. The catalytic tests consisted of three parts which are also schematically depicted in Figure S18: first the catalysts were pretreated in H₂ (40 mL/min) *in situ* at 225 °C for 60 minutes with a ramp of 5 °C/min to ensure a smooth and homogenous and reduced Pd-shell. Secondly, the MS signal was allowed to stabilize for a minimum of 4 hours at a flow of 8.0 mL/min H₂ and 32 mL/min Ar while the reactor was kept at 50 °C. Thereafter, isotope scrambling experiments were performed. The reactor was heated to 225 °C with a ramp of 5 °C/min holding the temperature for 20 minutes every 25 °C to collect data in isothermal steps, both on heating and cooling. During these experiments a flow of 32 mL/min Ar, 4 mL/min H₂ and 4 mL/min D₂ was

used. Reaction order experiments were performed by varying the amount of H₂ and D₂ keeping the total flow at 40 mL/min by adapting the amount of Ar. Isotope exchange rates were monitored using quantitative MS,³³ where m/z of 2 for H₂, 3 for HD, 4 for D₂ and 40 for Ar were scanned using a Hidden analytical QGA gas analyzer. Settle and scan times of H₂, D₂ and HD were set 1000 and 750 ms respectively to obtain sufficient signal-to-noise ratio. Deuterium 2.8, hydrogen 5.0 and argon 5.0 were purchased from Linde.

HD exchange data analysis

Quantitative Mass Spectrometry Analysis. Quantification of the measured mass spectrometry intensity to calculate conversion from the highest signal-to-noise HD m/z = 3 signal was performed as follows. First, a baseline for the hydrogen signal was determined by forming a regression line with the average of the last 10 minutes of the stabilization step before catalysis and 10 minutes after the stabilization step after catalysis. An additional baseline for the HD signal was calculated using an average of the HD values at 50 °C, and the H₂ signal was correlated to the HD signal. This correlation allowed measuring the amount of HD at each time point, as the amount of H₂ (in mL/min) flown during the stabilization time is known. The resulting signal overlaps with the hydrogen signal but shows significant improvement in data quality, as the signal-to-noise is much higher for the HD signal when compared to the H₂ signal. Conversions were calculated from averages over 10 minutes on isothermal steps to ensure steady-state conditions. The error indicated in the conversion was calculated from a combination of the standard deviation in the baselines and the error in the correlation between the H₂ and HD data.

TOF calculations. TOFs were expressed as number of H₂ molecules converted per surface atom per second. The amount of surface atoms was calculated assuming rods with a 1:1 ratio of {110} and {100} facets at the sides of the rods and {111} facets at the tips.^{7,36} The atomic density of the facets was calculated to be 1.03 × 10¹⁵ atoms/cm² along the sides and 1.39 × 10¹⁵ atoms/cm² at the tips of the NRs, based on the geometry of the surface facets and assuming the Au lattice parameter shown in the following equations:⁵¹

$$d_{111} = \frac{4}{a^2\sqrt{3}} \quad d_{100} = \frac{2}{a^2} \quad d_{110} = \frac{2}{a^2\sqrt{2}}$$

Where d is the surface atomic density of the different facets and a is the gold lattice parameter, assuming Pd grows epitaxially in the Au lattice as shown in the 4DSTEM strain map in Figure 2.

The surface area was calculated assuming a spherocylindrical shape with the surface of the sides as $\pi \times D \times L$ and the surface of the tips as $4 \times \pi \times (D/2)^2$, where D is the diameter of the nanorods and L the length obtained from TEM size distribution. The nanoparticle volume, approximated to be $\frac{\pi}{12} \times D^2 \times (3L - D)$ and nanoparticle density $NP_{\text{density}} = \rho_{\text{Au}} \times \text{at\%}_{\text{Au}} + \rho_{\text{Pd}} \times \text{at\%}_{\text{Pd}}$, where X_{Au} and X_{Pd} are the atomic fraction of Au and Pd and ρ_{Au} and ρ_{Pd} are the Au and Pd density (19.3×10^{-21} and 12.0×10^{-21} g/nm³) were used to calculate the weight of a single nanorod. The amount of nanoparticles #NP loaded in the reactor was calculated by:

$$\#NP = \frac{\text{mass loaded metal}}{\text{mass of a nanoparticle}} = \frac{\text{mass loaded metal}}{NP_{\text{volume}} \times NP_{\text{density}}}$$

Using this, the number of Pd surface atoms was calculated assuming only Pd atoms at the surface by multiplying the number of nanoparticles by the amount of surface atoms in a nanoparticle.

$$\#Surface\ Atoms = \#NP \times \#Surface\ atoms\ per\ NP$$

We assume that for the core-shell particles the surface is fully covered with Pd, and thus the TOF per surface metal is the same as the TOF per Pd surface metal. In the alloy we also calculate the TOF per surface metal atom and count both gold and palladium.

Calculation of apparent activation energy and pre-exponential factors. For the calculation of the Arrhenius parameters, H₂ conversion data of isothermal steps between 1 and 20% conversion were taken into account to plot ln(activity) in micromoles HD per gram of metal per second versus the inverse of temperature in Kelvin. Errors were calculated by taking the standard deviation of the baselines combined with the error in the correlation of H₂ and HD data. These data were fitted linearly with a weighted fit taking into account the relative higher errors at lower conversion as shown in Figure S19. These fits were performed in different temperature windows, including three isothermal points to observe temperature dependent behavior. The apparent activation energies and pre-exponential factors were extracted from the slope and intercept of these fits. The error in the activation energies was calculated by using the average of the minimum and maximum slope obtained by fitting the errors. Pre-exponential factors were obtained using:³³

$$b = \ln(A_{\text{app}}) + (n_{\text{H}_2} + n_{\text{D}_2})\ln(P_{\text{H}_2})$$

where b is the intercept of the Arrhenius plot, A_{app} the apparent pre-exponential factor, $n_{\text{H}_2} + n_{\text{D}_2}$ the reaction order and P_{H_2} the partial pressure of hydrogen. The reaction order for the 6L Pd NRs was determined to be 1, and it was assumed that this reaction order holds for all layer thicknesses of Pd. The molar volume of gas (0.024465 $\mu\text{mol/mL}$) was used for conversion of mL to moles as pre-exponential factors are expressed in $\mu\text{mol}_{\text{HD}}\text{g}^{-1}\text{s}^{-1}$.

DFT calculations

We carried out DFT calculations using the projector augmented-wave (PAW) method and plane-wave basis sets in the Vienna Ab Initio Simulation Package (VASP).^{52,53} We set the plane-wave kinetic energy cutoff at 450 eV. We employed the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with the dDsC dispersion correction to take van der Waals interactions into account.^{54–56} The Methfessel-Paxton smearing scheme was employed with a broadening value of 0.2 eV.⁵⁷ Structure optimizations were done via ionic relaxation, with the total energy and forces converged to 10^{-6} eV and 0.05 eV/Å, respectively. Two types of Pd/Au(111) slabs were created, one with 5 Pd layers and the other with 1 Pd layer. Both slabs were separated by 12 Å of vacuum along the direction normal to the surface (z-direction) to avoid spurious interactions between any two adjacent unit cells. The Brillouin zone was sampled using a gamma-center 5x5x1 k-point grid for a 3x3 unit cell of the (111) facet. The bottom two Au layers were fixed, and all other layers were allowed to relax during the optimization. The free energy calculations included the vibration of hydrogen in both adsorbate states and the gas-phase. In this work, we chose to use a model with a (111) facet for DFT calculations, different from the experimental observations. Previous studies showed that the surface and subsurface hydrogen adsorption on Pd(111), Pd(100), and Pd(110) were similar, in terms of adsorption energies.^{58,59} Besides, the (111) surface is known to have a minor lattice relaxation and to be more resistant to hydrogen-induced restructuring.⁶⁰

Supporting Information

Characterization data including TEM, HR-STEM, 4D-STEM, STEM-EDX, XRD; catalytic performance data; DFT calculations including energy barrier and enthalpy profile calculations; supplementary figures and tables

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Data Availability

The raw catalytic data, EM images and 4D-STEM data will be available at the DataverseNL repository upon publication.

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