

UCLA

UCLA Previously Published Works

Title

Atomistic Landscape of Pt Nanoparticles via Machine Learning: How Size Effect and Hydrogen Adsorption Govern Structural Ensembles and Catalytic Activity

Permalink

<https://escholarship.org/uc/item/9xt3z631>

Journal

Angewandte Chemie, 138(2)

ISSN

0044-8249

Authors

Chen, Dongxiao

Sautet, Philippe

Publication Date

2026-01-09

DOI

10.1002/ange.202519209

Copyright Information

This work is made available under the terms of a Creative Commons Attribution-NonCommercial-NoDerivatives License, available at

<https://creativecommons.org/licenses/by-nc-nd/4.0/>

Peer reviewed

Atomistic Landscape of Pt Nanoparticles via Machine Learning: How Size Effect and Hydrogen Adsorption Govern Structural Ensembles and Catalytic Activity

Dongxiao Chen¹, Philippe Sautet^{1,2,3*}

¹*Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, California 90095, United States*

²*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States*

³*California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California 90095, United States.*

ABSTRACT: Understanding the atomistic structure and fluxionality of Pt nanoparticles under reactive conditions is essential for rational design of effective catalysts, yet their structural complexity presents a great challenge. In this work, we combine grand canonical global optimization methods and machine learning potentials to explore the atomistic landscape of nanometer-sized (1 ~ 2 nm) Pt nanoparticles under a pressure of hydrogen, resulting in a comprehensive library of Pt_xH_y nanoparticles with over one million low-energy metastable structures. We found that hydrogen adsorption drives a size-dependent transformation from an amorphous to a crystalline structure, leading to sharp phase transitions for smaller nanoparticles and smooth transformations for larger ones. This behavior is governed by a competition between distinct core configurations, as well as the formation of rigid and fluxional local domains, where stability is dictated by specific surface motifs at low H coverage and by the crystalline core at high H coverage. We uncover general rules for the coverage-dependent structure of surface Pt hydrides, which are analyzed and compared with the experiments. By applying this structural library for reactivity modeling of methane dehydrogenation and ethylene hydrogenation, we show a marked discrepancy between the abundance of a surface site and its catalytic contribution, indicating that the active sites are rare, structurally distinct motifs, not the most common sites. This study provides a foundational understanding of Pt nanocatalysts under hydrogen and highlights a paradigm shift in nanoparticle computational catalysis research: from using a single model catalyst to the screening of vast, realistic structural ensembles to identify the active sites.

Introduction

The structural identification of noble metal nanoparticles (NPs) is crucial for understanding nanoscale effects and has broad applications in heterogeneous catalysis^[1–3]. While experimental

techniques like the combination of high-resolution electron microscopy^[4–6] and X-ray spectroscopy^[7,8], paired with theoretical calculations^[9,10], can determine the structure of metal NPs in a vacuum, the scenario is more complex in catalytic applications. Under reactive environment and temperature, NP catalysts interact extensively with their surroundings, which alters their configuration^[11–15]. A key example is the structural mobility of Pt NPs. Their morphology dramatically changes upon adsorbing molecules like CO or H₂, affecting their ordering, surface mobility, metal-support interaction, and the ratio of low-coordinated surface sites. These phenomena have been demonstrated through both experimental characterization and theoretical modeling^[16–24], and similar behaviors are observed in other metal NPs such as Pd^[25,26] and Au^[27,28]. However, the precise structure of NPs when adsorbing these molecules is highly sensitive to NP size and adsorbate coverage, making the detection of metal NPs under realistic reactive conditions a significant challenge for catalytic studies.

To clearly reveal the structures of metal NPs with adsorbates, one major challenge is the adsorbate-mediated evolution of NPs^[29]. For instance, under typical dehydrogenation or hydrogenation conditions (with a wide range of temperature between 300 ~ 900 K)^[30–33], H₂ dissociatively adsorbs onto the Pt surface. These surface hydrogen species modify the structure of small Pt NPs (1 ~ 2 nm), leading to a more ordered structure, which is observed on various supports (e.g., γ -Al₂O₃, C)^[22]. Experimental findings for the H₂/Pt system indicate the coexistence of ordered and disordered Pt NPs, suggesting a noncrystalline-to-crystalline transition zone that is sensitive to external conditions^[22]. Extended X-ray absorption fine structure (EXAFS) spectroscopy reveals that a H₂ environment increases both the average Pt coordination number (CN) and the Pt-Pt first-neighbor distance, confirming a significant morphological influence^[18]. These trends are supported by Density Functional Theory (DFT) calculations, which model Pt clusters (e.g., Pt₇, Pt₁₃, Pt₄₄) and predict a cuboctahedral shape for hydrogenated Pt clusters at high H coverage^[20,21,23].

In addition to the structural evolution of the Pt atoms, the variation of surface species under H₂ exposure, especially the Pt hydrides, is also critical for understanding active sites in heterogeneous catalysis. Infrared (IR) spectroscopy is widely used to detect Pt hydrides in-situ. For example, using operando FT-IR, Carosso et al.^[34] observed various top-site H species on supported Pt NPs in an H₂/N₂ flow at 393 K. The replacement of H₂ by N₂ leads to the quick decrease of a frequency peak at 2100 cm⁻¹ associated with strongly adsorbed top-site H, and to an increase of peaks around 2000 cm⁻¹, being weakly adsorbed top-site H. Their findings support the 'three-site' model^[35], which classifies Pt hydrides as top-site H, multi-fold H (2-fold or 3-fold), and coexisting (top-site and multi-fold H on the same Pt) species, where the coexisting species with strongly adsorbed top-site H appears only after the formation of the other two species. To detect all Pt-H vibrational modes, Vottero et al.^[19] employed inelastic neutron scattering (INS) spectroscopy, which identified bridge- and hollow-site H signals below 1600 cm⁻¹. By fitting these spectra with various supported Pt_xH_y NPs, they confirmed the coexistence of ordered and disordered Pt NPs and suggested a cuboctahedral Pt shape at high H coverage.

Despite this partial understanding of hydrogenated Pt NPs, accurate models for real-size Pt catalyst (1 ~ 2 nm) are lacking due to the high computational cost of DFT calculations. Importantly, the gap between experimental characterization and theoretical modelling also hinders the understanding of size-dependence and adsorbate-effect on the structures of Pt NPs. For example, the spectroscopic experiments only give an average picture, over large amounts of configurations among structural ensembles. The exploration of one or several models typically cannot depict the overall behavior of a NP^[36], especially for a system with good atomic mobility as Pt NP^[37]. On the other hand, Pt NPs are typically deposited on various supports (e.g. Al₂O₃, C, SiO₂, TiO₂, zeolite) as the real catalyst^[30,38–41], and metal-support interaction also affect the behavior of Pt NPs. However, theoretical calculations have shown that the adsorption of hydrogen actually weakens the metal-support interaction by partly detaching NP from the support, so that metal-support interactions become less important at high H coverage^[19,20]. It is therefore essential to first decouple the intrinsic behavior of Pt NP under H adsorption from metal-support interaction effect, by modelling Pt NPs in vacuum and exploring their structural ensembles with the variation of NP size and H-coverage.

Recently, the development of machine-learning potential (MLP) offers a promising solution, accelerating energy and force evaluations by several orders of magnitude compared to DFT without sacrificing accuracy^[42,43]. For instance, it has enabled thousands-of-atoms or nanosecond-scale molecular dynamics (MD) simulations, revealing shape changes in Pt surface or unsupported Pt NPs interacting with H₂ molecules^[44,24]. Our previous work also combined neural network potential (NNP) with global optimization to identify the structures of unsupported Pt₁₃ clusters at various H coverages, focusing on both the global minima (GM) and the low-energy metastable ensembles (LEME)^[21], defined as the ensemble of metastable structure for a given composition with an energy higher than the GM by 0.5 eV or less. The present work aims to extend NNP-based theoretical modeling to realistic catalyst sizes (1 ~ 2 nm), which enables a direct comparison with experimental data, bridging the gap between small Pt clusters and bulk-truncated Pt surfaces for our understanding of the response to H adsorption for Pt catalysts.

This paper is organized as follows. All the computational methods that introduce our Pt_xH_y structure database (x ranging from 46 to 210 and y ranging from 0 to 192), comprising over one million GM or LEME configurations, are placed in Supporting Information (SI) Section 1. To be brief, this is achieved by extensive potential energy surface (PES) sampling, accelerated by an NNP that mimics DFT energies and forces with the optPBE-vdW functional. Then, we use the GM from this database to construct thermodynamic formation free energy profiles and analyze their geometries. Next, we investigate the fluxionality of LEME structures, detailing the mobile rearrangement of the Pt core, the Pt local environment and the surface hydride species. Finally, we apply these findings to two catalytic case studies, methane activation and ethylene hydrogenation, to demonstrate how the evolution of Pt NPs under H₂ generates active sites. We will conclude by discussing how Pt nanoparticle size and H coverage control the final NP structure, which is critical

for their application in heterogeneous catalysis. The complete structure database is publicly available via the link in the Data Availability Section.

Results and Discussion

In this work, we modeled three primary sizes of Pt NPs: Pt₅₀ (~1.1 nm), Pt₁₀₀ (~1.4 nm), and Pt₂₀₀ (~1.8 nm). To ensure the results were not dependent on the exact atom count, we also investigated adjacent sizes (Pt_{46/54}, Pt_{95/105}, and Pt_{190/210}), corresponding to a $\sim\pm 2\%$ size variation for each model. For each of these nine Pt NPs, we added H atoms until the surface was nearly saturated and further H-addition was unfavorable even under typical hydrogenation reaction conditions (323 K, 1 bar H₂). The maximum number of H are Pt₄₆H₈₃, Pt₅₀H₈₈, Pt₅₄H₉₂, Pt₉₅H₁₂₈, Pt₁₀₀H₁₂₈, Pt₁₀₅H₁₂₈, Pt₁₉₀H₁₉₂, Pt₂₀₀H₁₉₂, Pt₂₁₀H₁₈₄, with a Pt:H ratio decreasing with size from 1:2 to 1:1. To generate the structural database, we employed a multi-step procedure for each Pt_xH_y composition. For each composition, we first performed global optimizations to get GM and collect all local minima. The resulting GM then underwent a grand canonical expansion to enumerate hydrogen addition or removal actions to obtain structural generations for other compositions. Finally, all the collected structures were used in an iterative LEME exploration until convergence was achieved. All calculations were efficiently performed using the NNP models trained on the energy and forces of DFT calculations (see SI Section 1.1). The framework, training procedure, and validation of these NNP models are detailed in SI Section 1.2 and Figures S1-S3, together with the details of the structure sampling methods (SI Section 1.3). This rigorous process yielded a database of over one million distinct Pt_xH_y NPs, which were used for the following structural analysis (Figures 1 to 5).

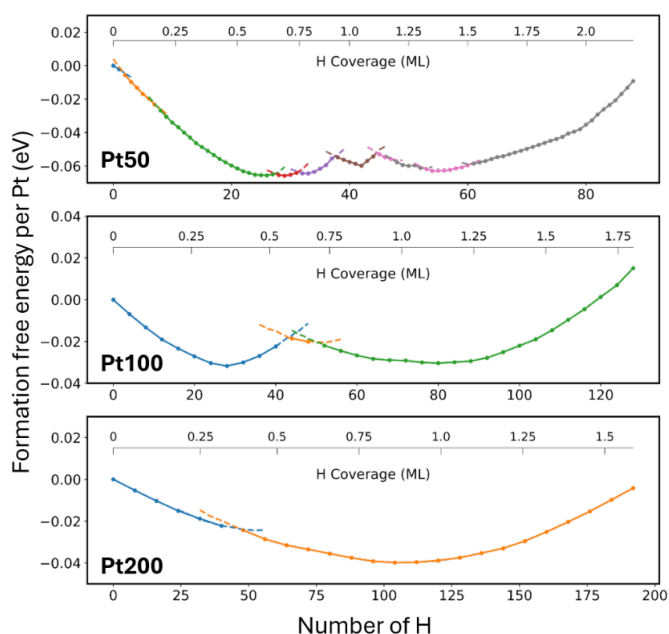


Figure 1. Formation free energy for Pt_{50}H_x , $\text{Pt}_{100}\text{H}_x$, and $\text{Pt}_{200}\text{H}_x$ NPs as a function of the number of H or of the H surface coverage in monolayer (ML). Each point represents a GM, with the colors denoting distinct classes of Pt configuration (see SI Section 1.5 for classification). Solid lines connect the neighboring GM, while dashed lines connect structures that share the same Pt configuration across adjacent compositions (but are not GM). The hydrogen chemical potential for formation free energy calculations corresponds to conditions of 1 bar H_2 under 460 K.

Thermodynamic scheme

We first analyzed the formation free energy (see SI Section 1.5 for equation) of the GM structures to understand the thermodynamic behavior of Pt NPs under H_2 atmosphere. Figure 1 shows representative results for Pt_{50}H_x , $\text{Pt}_{100}\text{H}_x$, and $\text{Pt}_{200}\text{H}_x$. Under the given conditions (1 bar of H_2 , 460 K), all NPs favor a moderate hydrogen coverage (with surface H coverage of 0.3 to 1.4 ML), but the stability landscape strongly depends on the NP size. Locally stable H contents correspond to minima of the formation free energy. The energy profile for the small Pt_{50}H_x NP is complex, with three distinct convex hulls of similar stability at H coverages of 0.5 ~ 0.75 ML, 1.0 ML, and 1.25 ~ 1.5 ML. The medium $\text{Pt}_{100}\text{H}_x$ NP is simpler, showing two stable convex hulls at around 0.35 ML and 1.0 ~ 1.25 ML. In contrast, the large $\text{Pt}_{200}\text{H}_x$ NP exhibits a smooth, parabolic energy curve with a single, well-defined stable convex hull around 0.8 ML of H coverage.

These different energy landscapes dictate the thermodynamic behavior of the NPs. As shown in the phase diagrams in SI Figures S4 ~ S6, the complex profiles for Pt_{50}H_x and $\text{Pt}_{100}\text{H}_x$ lead to phase gaps between low and high H coverage phases at ~ 460 K with 1 bar H_2 , with abrupt jumps from $\text{Pt}_{50}\text{H}_{29}$ to $\text{Pt}_{50}\text{H}_{56}$ and from $\text{Pt}_{100}\text{H}_{28}$ to $\text{Pt}_{100}\text{H}_{80}$, respectively. Conversely, the smooth energy curve for $\text{Pt}_{200}\text{H}_x$ results in a continuous phase diagram. We have verified these thermodynamic trends by reoptimizing some NNP-predicted GM directly by DFT (SI Section 2.2 and Figures S7-S10), also demonstrating a small influence of different DFT functionals on these trends (SI Section 2.3 and Figures S11-S13). This trend is also general for other Pt sizes: for small and medium sizes of Pt NPs, like Pt_{46} , Pt_{54} , Pt_{95} , Pt_{105} , their formation free energy curves are not parabolic (SI Figures S14, S15), showing multiple convex hulls and corresponding phase gaps in the phase diagrams (SI Figures S17, S18), while larger NPs (Pt_{190} , Pt_{210}) exhibit parabolic curves in formation free energy landscapes and smooth transitions in phase diagrams (SI Figures S16, S19). Intriguingly, for all small and medium size NPs (< 1.5 nm), the conditions for phase gaps consistently occur between 400 ~ 500 K at 1 bar H_2 (or 300 ~ 350 K at 1 mbar H_2). This suggests the existence of an ideal window for observing hydrogen mass transfer between the gas phase H_2 and small Pt nanoparticles, which is indeed the typical experimental conditions in some previous works^[22].

In the next step, we classified the GM structures by their underlying Pt configuration (see SI Section 1.5 for classification), with each color in Figure 1 representing an ensemble of similar Pt configurations, with variable H coverage. The non-parabolic profiles for Pt_{50}H_x and $\text{Pt}_{100}\text{H}_x$ are

a direct result of hydrogen-induced changes in the underlying Pt configurations. While each individual Pt configuration follows its own simple parabolic energy curve as H is added or removed, the system's true GM switches between these configurations to maintain the lowest energy. The $\text{Pt}_{100}\text{H}_x$ NP provides a clear example of this. Its overall energy curve is the lower envelope of three distinct parabolic curves (blue, orange, and green). The blue configuration is the most stable one at low H coverage (< 0.5 ML), but as coverage increases, the orange ($0.55\text{--}0.7$ ML) and then the green (> 0.7 ML) configurations become the GM. These transitions create the non-parabolic shape of the overall formation free energy profile. This behavior is even more pronounced for the Pt_{50}H_x NP, which traverses eight different Pt configurations, resulting in a highly complex energy profile. Note that even the smooth curve of the $\text{Pt}_{200}\text{H}_x$ NP is a composite of two separate Pt configurations, although they possess similar formation energies where they intersect. These results show that H adsorption strongly influences the nanoparticle's core structure, with smaller NPs undergoing more frequent configurational changes as hydrogen coverage increases. The geometries of these Pt configurations will be analyzed in more details in the next section.

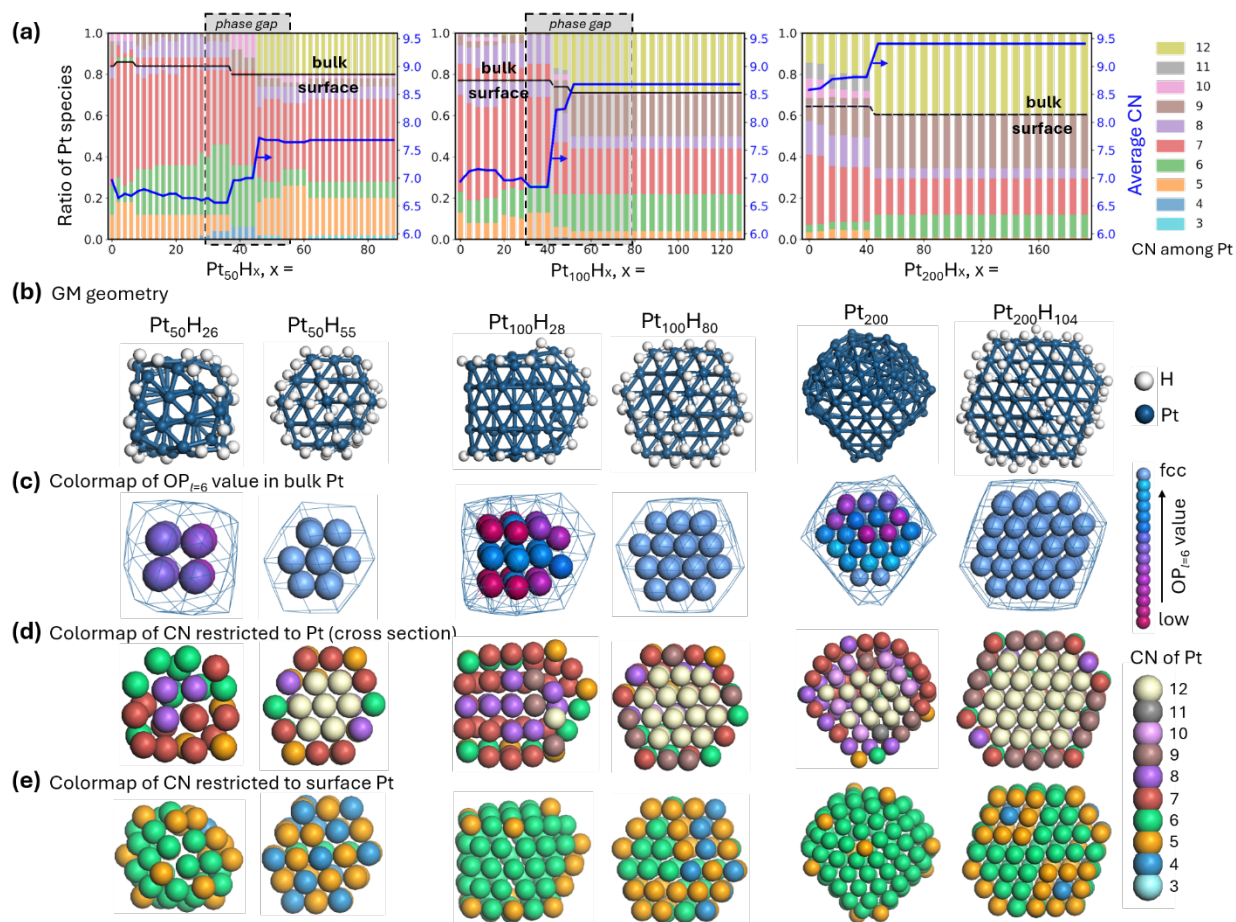


Figure 2. (a) The distribution of Pt CN (restricted to Pt atoms) for the GM structures of Pt_{50}H_x , $\text{Pt}_{100}\text{H}_x$, $\text{Pt}_{200}\text{H}_x$ NPs, with x ranging from 0 to the maximum by the step of 2, 4, 8, respectively. The colored areas represent the proportion for each Pt CN occurrence. The blue line tracks the average Pt CN, while the black line separates surface and bulk Pt atoms. (b-e) Detailed geometric views for representative structures ($\text{Pt}_{50}\text{H}_{26}$, $\text{Pt}_{50}\text{H}_{55}$, $\text{Pt}_{100}\text{H}_{28}$, $\text{Pt}_{100}\text{H}_{80}$, Pt_{200} , $\text{Pt}_{200}\text{H}_{104}$), including (b) snapshot of GM geometry, (c) atomic order parameter value with $l = 6$ to measure the intensity of the hexagonal symmetry, (d) a cross-section of each Pt configuration colored by Pt CN, and (e) Pt configuration colored by CN restricted to surface atoms, CN_{surf} .

Pt geometries of all global minima

The formation free energy profiles tell us that the addition of hydrogen atoms significantly impacts the configuration of Pt NPs, leading to new Pt configurations that are stable at high H coverage. In this section, we focus on the geometry of these Pt configurations. Figure 2(a) first illustrates the change in Pt coordination number (CN, restricted to Pt atoms) for the GM structures of Pt_{50}H_x , $\text{Pt}_{100}\text{H}_x$, $\text{Pt}_{200}\text{H}_x$ NPs with different number of H. The average Pt CN shown with the blue line increases with higher H coverage across all NP sizes. For example, the medium Pt_{100} NPs show the largest increase (from 7.0 to 8.6), while the Pt_{50} and Pt_{200} NPs exhibit more modest increases from 6.6 to 7.6 and 8.6 to 9.5, respectively. This increase is not gradual but occurs in sudden leaps at specific compositions (e.g., $\text{Pt}_{50}\text{H}_{44}$ to $\text{Pt}_{50}\text{H}_{46}$, $\text{Pt}_{100}\text{H}_{40}$ to $\text{Pt}_{100}\text{H}_{44}$, $\text{Pt}_{200}\text{H}_{40}$ to $\text{Pt}_{200}\text{H}_{48}$), which is in line with the finding of sudden changes in Pt configurations. Before the leap, both Pt_{50}H_x and $\text{Pt}_{100}\text{H}_x$ structures indicate a fluctuation in the average Pt CN, while such the fluctuation disappears after the leap. Analysis of the individual CN species in Figure 2(a) reveals that these jumps are caused by an increase amount of Pt bulk atoms with $\text{CN}=12$, and Pt surface atoms with CN being 8 or 9, a potential signal of the formation of face-center cubic (fcc) crystal. The change in average Pt CN is consistent with experimental EXAFS data^[34], where a 7.0 to 8.4 increase of Pt CN was found on supported Pt NPs with the size of 1.4 ± 0.4 nm.

Actually, the increase of average Pt CN with the adsorption of more H atoms is not immediately obvious to understand, since a simple application of the bond order conservation principle would imply that upon H adsorption Pt-Pt bonding would be weakened. It is thus essential to also analyze the Pt-Pt bond lengths with the variation of H coverage. SI Figures 20~28 plot the radial distribution functions (RDF) of Pt-Pt interaction for GM structures among all sizes of Pt NPs and various numbers of H. In all sizes of Pt NPs, although the number of overall Pt-Pt bonds (peak intensity in RDF) is increasing, there is an obvious elongation (peak shift) of Pt-Pt bond length with an increase of H coverage, revealing a weakened Pt-Pt interaction. By classifying the Pt-Pt bonds based on Pt location (surface or bulk), we can see that Pt-Pt bonds among surface Pt atoms elongate gradually from approximately 2.7 to 2.8 Å, indicating a direct competitive effect from H adsorption. In contrast, Pt-Pt bonds within the bulk part exhibit more abrupt changes, with a small shift (from 2.70 to 2.75 Å) in one sudden elongation for the large NPs ($\text{Pt}_{190} \sim \text{Pt}_{210}$), and

a large shift (from 2.6 to 2.8 Å) in several elongation steps for the small NPs ($\text{Pt}_{46} \sim \text{Pt}_{54}$). This suggests that changes of Pt-Pt bond length in the bulk part of NP are an indirect result of structural rearrangements induced by surface hydrogenation. Previous EXAFS experiments^[34] on supported Pt NP (1.4 ± 0.4 nm) show an average Pt-Pt bond length increase from 2.702 Å to 2.737 Å after exposure to a H_2 atmosphere, which corresponds well with our theoretical results for large NPs.

It should be noted that not all GM shown here are stable in real conditions. There are phase gaps in Pt_{50}H_x and $\text{Pt}_{100}\text{H}_x$ NPs shown in previous section, the locations of which are indicated in Figure 2(a). These gaps correspond precisely to the compositions where the Pt CN undergoes dramatic changes, indicating that these transition zones are thermodynamically unstable. A key difference across these phase gaps is the emergence of bulk Pt atoms with CN of 12. For the case of the $\text{Pt}_{200}\text{H}_x$ NP that lacks a phase gap, this type of bulk Pt atoms can already be found in its bare state (without H). This suggests that the emergence of an ordered, bulk-like core (containing Pt atoms with CN of 12) is the critical factor driving this phase transition, together with the appearance of phase gap. Similar behaviors are also found across the other Pt models (SI Figures S29 ~ S31), with one minor exception on Pt_{46}H_x NPs, where a $\text{Pt}_{46}\text{H}_{46}$ phase without bulk-like core is a stable transition phase that interrupts the phase gap.

We now focus on the geometric differences between the structures before and after the phase gap, as illustrated in Figure 2(b-e). For the $\text{Pt}_{200}\text{H}_x$ series, which does not have a phase gap, we select Pt_{200} and $\text{Pt}_{200}\text{H}_{104}$ as representative examples of the two different Pt configurations labeled in Figure 1.

$\text{Pt}_{50}\text{H}_{26}$ versus $\text{Pt}_{50}\text{H}_{55}$. The GM geometry of $\text{Pt}_{50}\text{H}_{26}$ is less ordered in its Pt arrangement compared to $\text{Pt}_{50}\text{H}_{55}$, as shown in Figure 2(b). Regarding the bulk atoms in Figure 2(c), $\text{Pt}_{50}\text{H}_{55}$ has a clear fcc core, with Pt atoms in perfect hexagonal symmetry, matching standard fcc bulk atoms. In contrast, $\text{Pt}_{50}\text{H}_{26}$ has low hexagonal symmetry, though it still possesses some order, evidenced by the similar order parameter value (with $l = 6$ only, see SI Section 1.5) among its bulk Pt atoms. Figure 2(d) indicates the Pt CN in $\text{Pt}_{50}\text{H}_{26}$ are diverse, ranging from 5 to 8, with CN=7 being the dominant coordination. For $\text{Pt}_{50}\text{H}_{55}$, all bulk Pt atoms have a CN of 12, while its surface Pt ranges from 5 to 8, again with the main Pt species with CN=7, indicating a high ratio of (110)-surface like sites on the surface of such a small NP. When the CN is restricted to only surface Pt atoms (CN_{surf}), Figure 2(e) shows a slight decrease from $\text{Pt}_{50}\text{H}_{26}$ (5 or 6) to $\text{Pt}_{50}\text{H}_{55}$ (4 or 5), different from the changing trend of average Pt CN (6.6 for $\text{Pt}_{50}\text{H}_{26}$ versus 7.7 for $\text{Pt}_{50}\text{H}_{55}$).

$\text{Pt}_{100}\text{H}_{28}$ versus $\text{Pt}_{100}\text{H}_{80}$. The GM geometry of $\text{Pt}_{100}\text{H}_{28}$ in Figure 2(b) has a rather unique order, with a low bulk coordination of mainly 8, arranged by six coplanar atoms forming a hexagonal ring, and two atoms in the axial positions above and below the plane. In contrast, the geometry of $\text{Pt}_{100}\text{H}_{80}$ has characteristics that are similar to $\text{Pt}_{50}\text{H}_{55}$, with all Pt atoms in a fcc lattice. In Figure 2(c), all bulk Pt atoms in $\text{Pt}_{100}\text{H}_{80}$ are perfect fcc atoms, while only a medium strength (blue color) of hexagonal symmetry is found in the middle layer of bulk Pt atoms in $\text{Pt}_{100}\text{H}_{28}$, demonstrating the lack of fcc symmetry for it. Regarding the Pt CN in Figure 2(d), CN=7 and

CN=8 Pt species mainly occupy the surface and bulk parts of $\text{Pt}_{100}\text{H}_{28}$, respectively, which has an average CN higher than $\text{Pt}_{50}\text{H}_{26}$. The bulk of $\text{Pt}_{100}\text{H}_{80}$ is fully occupied by Pt with CN=12, and its surface is largely occupied by Pt atoms with CN=9, indicating the formation of regular (111) fcc surfaces. The CN_{surf} situation shown in Figure 2(e) is similar to the Pt_{50}H_x case, with a decrease of CN_{surf} with increased H coverage, opposite to the change for average Pt CN.

Pt₂₀₀ versus Pt₂₀₀H₁₀₄. In the low H coverage case of the $\text{Pt}_{200}\text{H}_x$ series, unlike $\text{Pt}_{50}\text{H}_{26}$ and $\text{Pt}_{100}\text{H}_{28}$, the bare Pt_{200} NP already exhibits an fcc lattice in its lower half, although the upper half remains disordered. This partial crystallinity is demonstrated by its GM geometry, high order parameter value with CN=12 in the lower half of bulk Pt, as shown in Figure 2(b-d). Figure 2(d) also shows that the disordered part of the NP lowers the CN of some bulk Pt species to 10 or 11, and makes Pt surface atoms with CN=7 dominant. Despite the partial formation of an fcc lattice, the CN_{surf} values in Pt_{200} are still 6 or 5, without exposing a (100)-like facet, which is similar to the cases of $\text{Pt}_{50}\text{H}_{26}$ and $\text{Pt}_{100}\text{H}_{28}$. In contrast, the $\text{Pt}_{200}\text{H}_{104}$ structure forms a nearly perfect cuboctahedral NP. This is evident from its fcc-lattice geometry, with order parameter values similar to perfect fcc atoms, its CN=12 for all Pt bulk atoms, and regular (111) and (100) surfaces, as shown in Figure 2(b-e), respectively. The structure has only one surface Pt vacancy on the edge of two (111) surfaces when comparing with the magic number for a cuboctahedral NP, Pt_{201} .

In general, the GM geometries of the Pt NPs reveal several key trends. For Pt NPs with low H coverage, regardless of size, the surface is dominated by Pt atoms with CN_{surf} of 5 and 6, indicating the high stability of these specific surface sites. In contrast, after sufficient H adsorption, all NPs converge to a structure with a crystallized fcc core and a generally cuboctahedral shape. The mechanism governing these geometric changes is a competition between surface stability and bulk stability. The surface stability dominates for NPs where adsorbate is insufficient, favoring Pt configurations that maximize surface bonding, even at the cost of a less-ordered core or a lower CN in bulk atoms. When adsorbate like H is introduced, it stabilizes the undercoordinated Pt surface sites, allowing bulk stability to be the dominant factor. Consequently, the Pt atoms in bulk rearrange to form a more dense, crystalline fcc core. This strong adsorbate effect drives a significant evolution of the Pt configurations. It leads to the phase gaps and the formation of intermediate configurations (like $\text{Pt}_{50}\text{H}_{42}$ and $\text{Pt}_{100}\text{H}_{44}$ in Figure 1), where the final structure is determined by the competition between surface stability and bulk stability.

This framework also explains the observed size effect in Pt nanoparticles. Larger NPs have a higher proportion of bulk atoms (see Figure 2(a)) and thus inherently favor bulk stability more than smaller NPs. This clarifies the observation that bare Pt_{200} is already partially crystalline, and that Pt_{50}H_x requires a higher H coverage than $\text{Pt}_{100}\text{H}_x$ to achieve full crystallization. Furthermore, the fcc crystals formed by smaller NPs typically present a higher density of low-coordination surface sites (e.g., (100) facets, kinks, vacancies), which also require a higher H coverage to be fully stabilized. This model explains key experimental findings, such as the coexistence of non-crystalline and crystalline Pt NPs, and the higher proportion of ordered structures observed for larger Pt particles or under H_2 atmosphere^[22].

It is important to explore the kinetics of NP transformation, to address the accessibility of certain GM configurations in experimental conditions. To this end, we take the $\text{Pt}_{100}\text{H}_x$ series as an example, which is an ideal model for studying the kinetics of the noncrystalline-to-crystalline transformation without going through many intermediate Pt configurations. The dissociation barrier of H_2 is first explored as a function of H coverage and discussed in SI Figure S32, the main finding being that accessible barriers (< 0.7 eV) exist in a wide range of H coverage ($\text{Pt}_{100} \sim \text{Pt}_{100}\text{H}_{112}$), covering all the considered transformations between Pt configurations.

The kinetic feasibility of the noncrystalline-to-crystalline transformation was also explored on the example of the $\text{Pt}_{100}\text{H}_x$ NPs. At 1 bar H_2 and 460 K, this transformation is slightly endergonic and occurs around $\text{Pt}_{100}\text{H}_{44}$. The transition coverage does not significantly change with temperature, while the transformation becomes exergonic below 450 K (SI Figure S33). By adding H atoms on the GM of $\text{Pt}_{100}\text{H}_{40}$ while fixing this noncrystalline Pt configuration, we obtained metastable $\text{Pt}_{100}\text{H}_{50}$, $\text{Pt}_{100}\text{H}_{60}$, and $\text{Pt}_{100}\text{H}_{80}$ structures (extrapolating the blue line on Figure 1) that represent the quick response of Pt NP under H_2 rich conditions in a H coverage region where the crystalline fcc structure is more stable. MD simulations at different temperatures (300 K, 500 K, 700 K) were then conducted starting from these initial structures. The results and detailed discussions shown in SI Figures S34~S36 indicate the successful observation, even in the short time scale of the MD (1 ns), of phase transition under moderate MD temperature or H coverage, as identified by the snapshots and evolution of Pt CN. Already with $\text{Pt}_{100}\text{H}_{50}$ at 500 K (resp $\text{Pt}_{100}\text{H}_{60}$ at 300K), we observe a transition towards a partial fcc crystalline structure after 150 ps (resp 350 ps). At higher H coverage with $\text{Pt}_{100}\text{H}_{80}$, only 60 ps is required to form the complete fcc core at simulation temperature of 300 K. This demonstrates the clear kinetic feasibility for H-driven NP transformation. If a metastable non-crystalline structure with a H coverage higher than the transition threshold can be populated, it will quickly rearrange into crystalline structure. The noncrystalline-to-crystalline transformation should happen at intermediate temperature where the thermodynamics is favorable and the H coverage can reach high values (SI Figure S33), while the kinetics is fast. Note that a thermodynamic barrier is also present at high temperature, significant above 400 K, rendering energetically difficult the increase in H coverage above the 44 H threshold on Pt_{100} . Although these preliminary kinetics studies support the accessibility of the thermodynamic structures explored here, further studies are still required to fully understand the dynamic behaviors of Pt NPs under H_2 , such as the influence of size on NP kinetics.

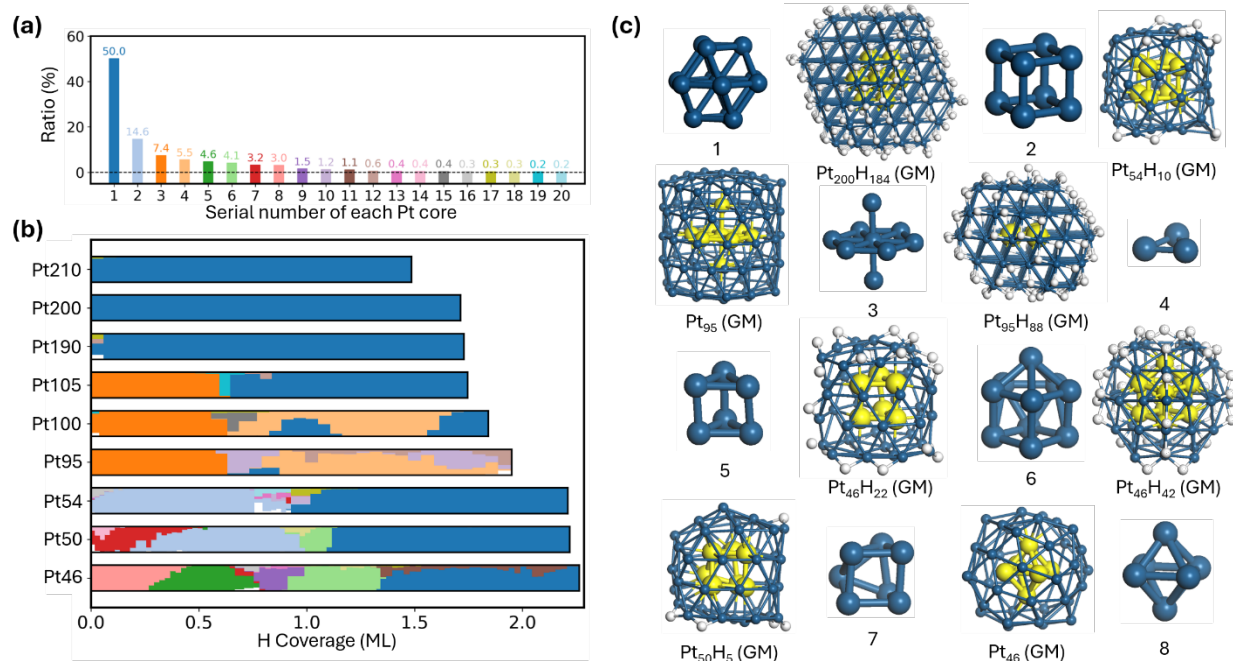


Figure 3. (a) Occupation ratios of the top 20 most frequent Pt core configurations (coded by color) among all LEME structures of all compositions. (b) The distribution of these Pt cores (with the same color codes as in (a)) among LEME structures of each composition, as represented by the number of Pt atoms and the H coverage. Within the zone of one composition, the area of each color is proportional to the occupation ratio of that specific Pt core within the LEME structures of that composition. The white color indicates the Pt core that does not belong to the top 20 cores. (c) Geometric views of the top 8 most frequent Pt cores (with the same serial numbers as in (a)) and their representative examples. The geometric views of all other Pt cores can be found in SI Figure S37.

Fluxionality of Pt core in the LEMEs

Having analyzed the GM structures, we now investigate the fluxionality within the LEME structures from a thermodynamic perspective, i.e. identifying the variation of structure motifs within the LEME structures. This analysis is crucial because at finite temperatures, the behavior of one NP is determined by the ensemble average of all its thermally accessible isomers, not solely by the GM. In this section, we first identify the fluxionality of the Pt core, as determined by the most central Pt atoms in a NP (see SI Section 1.5 for details).

Our analysis began by extracting the Pt core from each structure in all of the explored LEME structures. As shown in Figure 3(a), although there are more than one million distinct LEME structures, the diversity of Pt cores is surprisingly limited. Only 20 distinct Pt core configurations have an occupation ratio above 0.1%, and the top 8 of them account for over 90% of all LEME structures. Remarkably, the most frequent Pt core, core 1 (in deep blue color), is found

in half of all LEME structures. Figure 3(b) and 3(c) shows the distribution of these Pt cores among LEME structures of each NP size and composition, and the detailed geometries of core 1 to core 8, while geometries of the remaining Pt cores are shown in SI Figure S37. It is shown that core 1 is actually a Pt₁₃ cuboctahedral cluster, the smallest unit representing an fcc core. This Pt₁₃ core is dominant under two main conditions: at high H coverages for small and medium-sized NPs (Pt₄₆ to Pt₁₀₅), and across nearly all H coverages for large NPs (Pt₁₉₀ to Pt₂₁₀). This aligns with our previous analysis linking H coverage and Pt size to crystallization. In the cases of large NPs, the overwhelming occupation by core 1 among not only GM but also LEME structures indicates a quenching of the Pt core's fluxionality, where the structural change of the Pt core is highly thermodynamically unfavorable.

We now focus on the zones in Figure 3(b) where the Pt core is not restricted to core 1. For medium Pt particles (Pt₉₅ to Pt₁₀₅) with low H coverage (0 ~ 0.5 ML), the Pt core is also quenched, but to a unique configuration, core 3, which is not seen in any other cases. As shown in Figure 3(c), this core (of composition Pt₉) is centered on an octa-coordinated Pt atom with D_{6h} symmetry, generating a stable, barrel-shaped Pt₉₅ NP. This foundational shape is stable and relatively insensitive to the addition of Pt and small amount of H atoms, an example of which is Pt₁₀₀H₂₈ shown previously in Figure 2(b). At higher hydrogen coverages, competition among cores 1, 4, and 10 is observed in Pt₁₀₀H_x and Pt₉₅H_x. This phenomenon does not imply an absence of fcc crystallization within the LEME structures. For instance, in core 4 (as seen in Pt₉₅H₈₈), although the Pt atoms are arranged in an fcc lattice, the NP lacks a center of symmetry. Instead, a triangular Pt₃ unit forms the NP's core. Because core 4 does not fully occupy this zone and competes with other cores like core 10, it suggests that Pt atoms are not fully quenched even within a crystallized lattice structure.

The most complex region in Figure 3(b) is the lower-left corner, which corresponds to small NPs (Pt₄₆ ~ Pt₅₄) at low-to-moderate H coverage (0–1.0 ML). For Pt₅₄ and a large portion of the Pt₅₀ structures, core 2, a perfect Pt₈ cube, is the dominant internal motif. As exemplified by the Pt₅₄H₁₀ structure in Figure 3(c), these nanoparticles are formed by this cubic core enveloped by a surface Pt-H layer. Similar core-shell structures are found for other configurations in this region, possessing cores 5 to 8 that contain 6, 10, 7, and 6 Pt atoms, respectively. These Pt cores have been identified in the GM or low-energy isomers of small Pt NPs in previous theoretical works^[45]. Despite the variety of these metastable Pt cores, a unifying feature is that their surfaces are consistently covered by triangular Pt₃ motifs, with H atoms on bridge sites, preferentially formed by two undercoordinated Pt atoms, thereby maximizing the surface stability. This suggests that at low H coverage, the small Pt NPs first arrange its surface atoms into a uniform shell, and the remaining Pt atoms then assemble to form the core. Consequently, for ~1.1 nm NPs, the Pt core structure is highly sensitive to the precise number of Pt atoms but weakly sensitive to H coverage or choice of structure among the LEME structures. This explains why only a limited number of distinct core configurations were observed for the specific numbers of Pt atoms that we investigated.

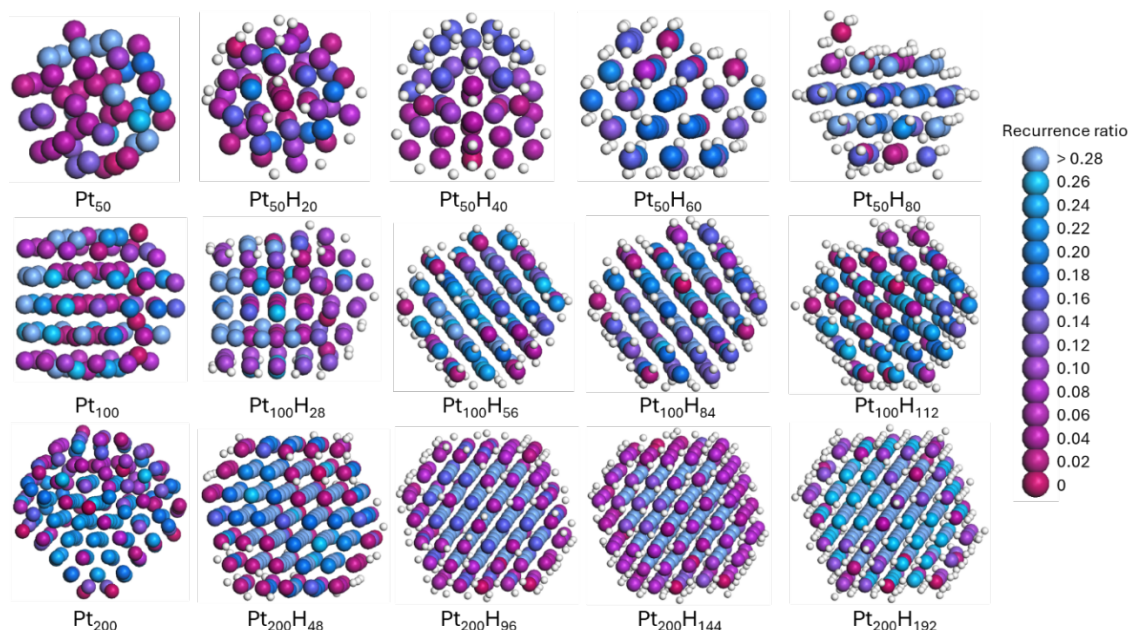


Figure 4. Recurrence ratio of Pt atomic environments for representative GM structures. The recurrence ratio for a given Pt atom in the GM is defined as the fraction of LEME structures that contain at least one atom with a nearly identical local environment, as measured by the small difference (< 0.05) in their order parameter values (see SI Section 1.5). This analysis provides a measure of how frequently the local structure around each GM atom reappears within the LEME structures.

Fluxionality of local Pt environment in the LEMEs

In this section, we assess structural fluxionality from a thermodynamic viewpoint by analyzing the existence of specific local atomic environments within the LEME. The recurrence ratio is defined for each atom in a given GM structure, as the fraction of the LEME structures that contain at least one atom with a nearly identical local environment. A low recurrence ratio signifies a "fluxional" environment for the Pt atom, while a high ratio indicates a stable, rigid environment.

Figure 4 visualizes these recurrence ratios for several representative compositions in Pt_{50}H_x , $\text{Pt}_{100}\text{H}_x$, and $\text{Pt}_{200}\text{H}_x$, following the order of H coverage from low to high. Focusing on the bulk atoms in Figure 4, we can see that at high H coverage (e.g., $\text{Pt}_{50}\text{H}_{60-80}$, $\text{Pt}_{100}\text{H}_{56-112}$, $\text{Pt}_{200}\text{H}_{48-192}$), the atoms within the crystallized fcc core exhibit high recurrence ratios. This indicates these environments are rigid and largely unaffected by surface rearrangements. In contrast, at low H coverage (e.g., $\text{Pt}_{50}\text{H}_{0-40}$, $\text{Pt}_{100}\text{H}_{0-28}$), the core atoms show very low recurrence ratios (deep red color). Although from the last section we know that $\text{Pt}_{100}\text{H}_{0-28}$ share the same Pt core, the results shown here indicate that the local atomic environments of a non-fcc core, including bond lengths

and angular arrangements, are easily perturbed by variations in surrounding atoms among the LEMEs. Such perturbations demonstrate the intrinsic flexibility and responsiveness of the non-fcc core structure to external atomic rearrangements.

Turning to the surface atoms in Figure 4, we observe some high-recurrence regions, indicating the existence of energetically-favored local surface patterns. For example, in $\text{Pt}_{50}\text{H}_{40}$, the high-recurrence region is the upper half, which corresponds to a specific surface pattern saturated with H. Conversely, in $\text{Pt}_{100}\text{H}_{28}$, the surface pattern with high recurrence ratio is on the left half, a metallic pattern that resists H adsorption and surface rearrangement compared with Pt_{100} . For Pt_{200} , the surface atoms with high recurrence ratios are those in the lower part of the NP, anchored by the underlying fcc lattice. These results highlight the heterogeneous nature of surface fluxionality at low H coverage. Specific surface patterns, whether metallic or hydrogenated, form rigid domains (the blue areas in the figure), while the remainder of the NP stays fluxional, permitting atomic rearrangements to adapt to the environment.

For the NPs where the fcc lattice is well-formed, some surface atoms still remain fluxional. Structural defects such as vacancy sites (e.g. lower-right corner of $\text{Pt}_{200}\text{H}_{192}$), ad-atom sites (e.g., the top Pt atom of $\text{Pt}_{50}\text{H}_{80}$), and missing-row defects (e.g. top-left corner of $\text{Pt}_{100}\text{H}_{112}$) consistently exhibit low recurrence ratios (red color in Figure 4). The inherent mobility of these defect sites from one LEME structure to another introduces a persistent fluxionality to the nanoparticle surface, a behavior that contrasts sharply with that of magic-number clusters like Pt_{13} ^[21]. For the regular, well-ordered facets of these crystalline NPs, such as $\text{Pt}_{200}\text{H}_{48-192}$, the recurrence ratio is also dictated by the diversity of H adsorption sites. For example, the (111) sites of $\text{Pt}_{200}\text{H}_{48}$ are mostly empty, leading to low diversity and a high recurrence ratio (blue), while H begins to populate the (111) sites in $\text{Pt}_{200}\text{H}_{96}$ and $\text{Pt}_{200}\text{H}_{144}$, generating multiple occupation patterns and thus lowering the recurrence ratio. At higher H coverage in $\text{Pt}_{200}\text{H}_{192}$, the saturated adsorption of H on (111) sites once again reduce the configurational diversity, leading to the even larger recurrence ratio (blue (111) sites in Figure 4). In all $\text{Pt}_{200}\text{H}_{48-192}$ NPs, the (100) and edge sites are consistently more fluxional (i.e., have lower recurrence ratios) than the (111) sites, which reflects their ability to host a greater variety of metastable H adsorption patterns. This demonstrates that fluxionality on crystalline facets is driven by both surface defects and the statistical diversity of H adsorption.

Pt framework is quenched into a stable fcc lattice, often resembling an ideal cuboctahedron. This provides a fixed structural template upon which we can systematically analyze the formation of surface hydrides. Considering the first-neighbor environment on surface atoms of an ideal Pt cuboctahedron, there are five distinct types of surface sites. Based on their location and CN_{surf} , these are: two terrace (t) sites on a (111) facet ($CN_{surf}=6$) or (100) facet ($CN_{surf}=4$), two edge (e) sites at a (111)/(111) junction ($CN_{surf}=6$) or a (111)/(100) junction ($CN_{surf}=5$), and one kink (k) site at a (111)/(111)/(100) junction ($CN_{surf}=5$). These five Pt surface species, namely Pt_{6t} , Pt_{4t} , Pt_{6e} , Pt_{5e} , Pt_{5k} , can be identified based on calculating CN_{surf} and the number of planes between Pt and its neighbors. The evolution of surface hydrides on these specific sites will be analyzed as a function of the number of H on the NP.

The $Pt_{200}H_x$ series serves here as an excellent representative example because the NP adopts a nearly perfect cuboctahedral shape at moderate to high H coverage. Figure 5(a) first tracks the population of these five Pt surface sites across the LEME distribution for all $Pt_{200}H_x$ NPs, revealing the significant fluctuation of their population ratios at low H coverage ($Pt_{200}H_{0-40}$) and the constant population in the high H coverage regime ($Pt_{200}H_{48-192}$). This indicates that the LEME structures conform to the ideal cuboctahedral shape after $Pt_{200}H_{48}$, with all Pt atoms being quenched into the fcc lattice. This transformation leads to the decreased number of Pt sites with $CN_{surf}=6$, and the increase or emergence of Pt sites with low CN_{surf} (4 or 5), which is consistent with our previous analysis. For an ideal Pt_{201} cuboctahedral NP, the ratio of these Pt species should follow $Pt_{6t} : Pt_{6e} : Pt_{5e} : Pt_{5k} : Pt_{4t} = 48 : 12 : 24 : 24 : 6$. The slightly different values in $Pt_{200}H_x$ NPs at high H coverage is the result of a stable vacancy on one Pt_{6e} site, removing also two Pt_{5k} and four Pt_{6t} sites.

The plots in Figure 5(a) also detail the H coordination environment for each of the five Pt surface types, with the results averaged over the entire LEME structures of one composition. From this data, we can infer the intrinsic H affinity for each site. The trend follows the order $Pt_{4t} \sim Pt_{5k} \sim Pt_{5e} > Pt_{6e} > Pt_{6t}$, which is determined by the population of bare sites in the figure. Pt sites that remain bare longer, like Pt_{6t} , have the lowest affinity for H. However, the H affinity does not directly correlate with the maximum H storage capacity, which obeys the order $Pt_{5k} > Pt_{4t} \sim Pt_{5e} \sim Pt_{6e} > Pt_{6t}$. The Pt_{5k} site exhibits the highest capacity, capable of forming up to a PtH_5 hydride (purple zone). In contrast, the Pt_{6t} has the lowest capacity, reaching a maximum of only PtH_3 hydride (yellow zone).

Figure 5(b) displays representative snapshots of the H coordination environment for each of the five Pt surface types, illustrating the most abundant configuration at each stage of hydrogenation. Supported by these visualizations, we can understand the detailed distinction between top-site, bridge-site, and hollow-site H in Figure 5(a), revealing that each Pt site has a strong and distinct preference for certain H coordination environment (top, bridge, or hollow). For example, the Pt_{6t} site exclusively adsorbs H in top or hollow positions, avoiding bridge sites entirely across all H coverages. In contrast, the Pt_{4t} site shows an overwhelming preference for bridge-site H. The edge and kink sites, including Pt_{6e} , Pt_{5e} , Pt_{5k} , are all initially populated by bridge-site H. However, as the number of H increases, hollow-site H begins to either replace (on

Pt_{6e}) or concurrently appears with the bridge H (on Pt_{5e} and Pt_{5k}). This site-specific behavior is rooted in the local Pt geometry visible in Figure 5(b): the triangular Pt₃ motifs on (111) facets favor top-site H or hollow-site H, while the edge sites themselves and square-like Pt₄ motifs on (100) facets favor bridge-site H. Notably, the unique PtH₅ hydride that forms on the Pt_{5k} kink site at high H coverage is the only environment observed to simultaneously accommodate all three H coordination types.

The data in Figure 5(a) also explains the diversity of LEME structures at a given composition. At an intermediate H coverage of ~0.8 ML as in Pt₂₀₀H₁₀₄, for example, the Pt_{6t} site exists as a statistical mixture of bare site, Pt_{6t}-H(top), Pt_{6t}-H(hollow) in roughly a 2 : 1 : 1 ratio, while one edge site, Pt_{6e}, shows a 3 : 1 mixture of Pt_{6e}-H₂(bridge) and Pt_{6e}-H₄(hollow). The combinatorial possibilities arising from these local mixtures across the surface generate a vast number of distinct LEME configurations. Similarly, at high coverage as in Pt₂₀₀H₁₈₄ (~1.5 ML), the competition between PtH₄ and PtH₅ geometries on Pt_{5k} is another major source of structural diversity.

Despite the diversity of the LEMEs, we can nevertheless identify a general occupation order of various surface hydrides when increasing the H coverage. Top-site H first preferentially occupies the Pt_{6t} sites, dominating the LEME distributions for compositions from approximately Pt₂₀₀H₆₄ to Pt₂₀₀H₁₆₀. At higher H coverage, this top-site H shifts to the Pt_{5k} sites as part of the more complex PtH₅ hydride. This observed order, whereby a complex site (PtH₅ hydride) containing both top-H and bridge/hollow-H appears only after the appearance of simpler sites (PtH hydride with H in a single type of sites), provides a detailed atomic picture of the 'three-site' model previously proposed^[35] and supported by experimental IR spectroscopy^[19].

Figure 5(c) enables us to compare the overall population of different hydrogen species as a function of H coverage across Pt₂₀₀H_x, Pt₁₀₀H_x, and Pt₅₀H_x NPs. For the Pt₂₀₀H_x series, H adsorption occurs almost exclusively at bridge sites before 0.5 ML, then hollow-site and top-site H begin to appear (on Pt_{6t} sites). At ~1.2 ML, a sharp increase in hollow-H corresponds with a decrease in top-H, indicating a transition from top-H to hollow-H occurring on Pt_{6t} sites. After ~1.4 ML, the population of top-H increases again, which corresponds to its occupation on Pt_{5k} sites. A similar behavior is found for Pt₁₀₀H_x NPs, except for the decrease in strength of the first top-H peak. However, the small Pt₅₀H_x NPs show a distinct tendency, featuring a much larger proportion of top H at low H coverages and, conversely, a higher proportion of bridge H at high H coverages compared to the larger NPs. We also compared the results of six other Pt models (Pt₄₆H_x, Pt₅₄H_x, Pt₉₅H_x, Pt₁₀₅H_x, Pt₁₉₀H_x and Pt₂₁₀H_x, see SI Figures S38 ~ S40) with the models selected for Figure 5 (Pt₅₀H_x, Pt₁₀₀H_x, Pt₂₀₀H_x), which indicates that the results are intrinsic and not modified significantly by a small variation in Pt NP sizes.

The average hydrogen CN (the number of neighboring H atoms), CN(H), for the Pt atoms bonded to each H type are analyzed in Figure 5(d) for Pt₂₀₀H_x, Pt₁₀₀H_x, and Pt₅₀H_x NPs, and in SI Figures S41 ~ S43 for the other six Pt models. We observe remarkably similar trends across all

sizes of NP. The behavior of hollow and top H is characterized by a dramatic transition, where the CN(H) for the bonded Pt atom(s) undergoes a sharp increase. For example, the CN(H) of top H in $\text{Pt}_{200}\text{H}_x$ NPs shifts from 0.5 to 4 at ~ 1.3 ML, corresponding to the transition from H-Pt on Pt_{6t} to H-PtH₄ on Pt_{5k} . The existence of this trend for all sizes of Pt further indicates a general occupation order of surface hydrides, which is independent on the sizes of Pt NP or the ratio of different H species. In the case of bridge H, the CN(H) for the bonded Pt atoms increases continuously and regularly across the entire range of H coverage. This indicates that bridge-H atoms progressively activate the H capacity of the preferred sites (mainly edges and kinks) in the whole hydrogenation process, which is a key driving force for the structural rearrangements of the Pt NP under an H_2 atmosphere.

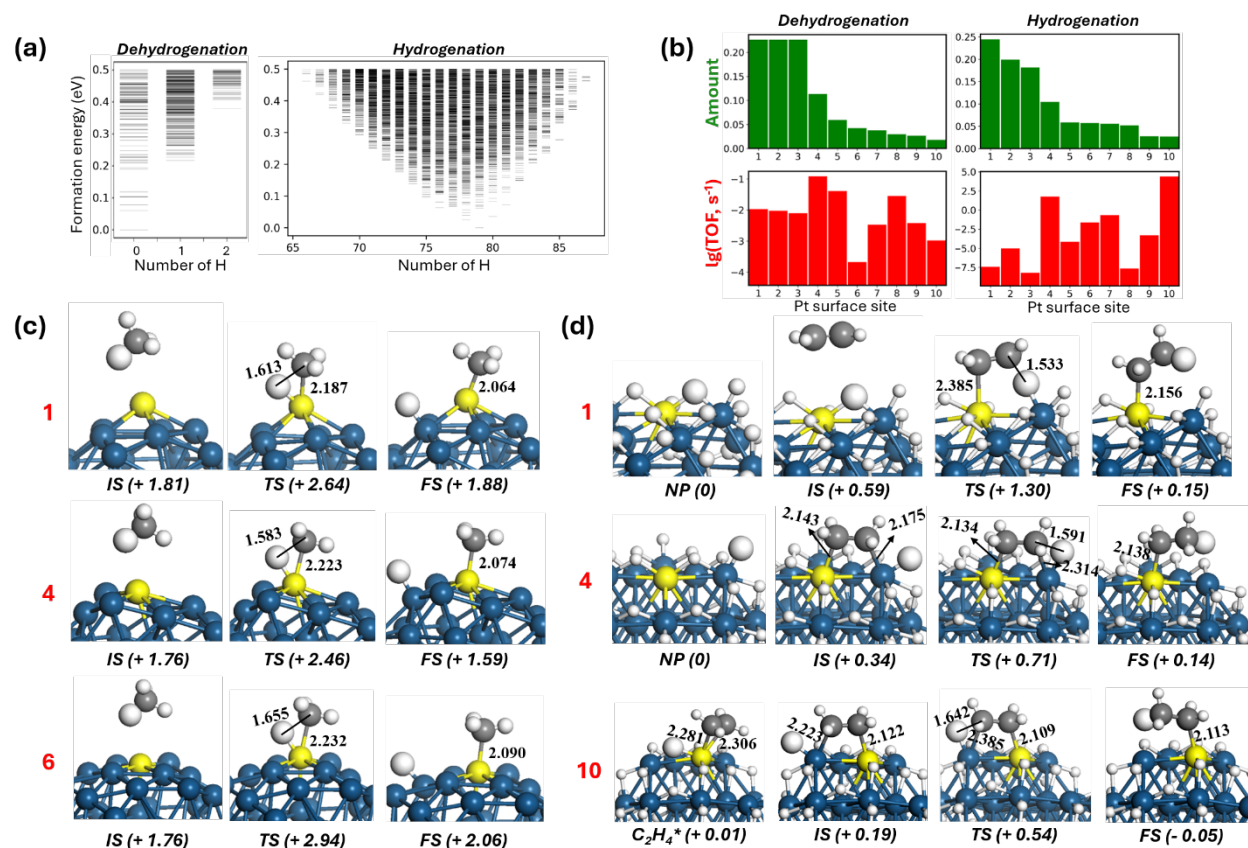


Figure 6. (a) LEME distributions as a function of the number of H atoms for Pt_{50}H_x NPs in the conditions typical for dehydrogenation reactions (873 K, 1 bar H_2) and hydrogenation reaction (323 K, 1 bar H_2). Each bar represents a distinct configuration. (b) Comparison between normalized abundance of 10 Pt surface sites and their calculated turnover frequencies (TOFs) for methane dehydrogenation and ethylene hydrogenation. (c) Snapshots of the initial states (IS), final states (FS), and transition states (TS) for methane dehydrogenation on sites 1, 4, 6, and (d) IS, FS,

TS for ethylene hydrogenation on sites 1, 10, 4. In ethylene hydrogenation, we further show the snapshots of the ethylene adsorption state with π -bonded mode (if present) or only NP. Yellow atoms represent the reactive Pt atom of each site, and large white balls are reactive H. The bond lengths of all bonding Pt-C and C-H in TS are marked, and the Gibbs free energies are labeled relative to NP and gaseous CH_4 (873 K, 0.1 bar) or C_2H_4 (323 K, 0.01 bar). All the reaction pathways on other Pt sites are shown in SI Figure S48, S49.

Application to Catalysis: Active Sites in Pt_xH_y Nanoparticles

To develop an application of our Pt_xH_y structure database in chemical reactivity, we now apply it to investigate the active sites for heterogeneous catalysis. Two representative probe reactions, that operate under distinct conditions, are selected i.e. (i) methane dehydrogenation^[46–48], a high-temperature reaction (873 K, 1 bar H_2) where conditions are chosen to maximize product yield and suppress coking, and (ii) ethylene hydrogenation^[32,33,49], a low-temperature reaction (323 K, 1 bar H_2) where conditions are set to thermodynamically favor the forward reaction. The rate-determining step (RDS) in both reactions is their corresponding first step, i.e. $\text{CH}_4 \rightarrow \text{CH}_3^* + \text{H}^*$ and $\text{C}_2\text{H}_4 + \text{H}^* \rightarrow \text{C}_2\text{H}_5^*$. Both of these two elemental reactions involve only a single Pt atom that adsorbs the carbon species of the products (CH_3^* and C_2H_5^*), which allows us to approximate a reaction site as a single surface Pt atom to accept the product. To investigate the active sites for these two probe reactions, we use Pt_{46}H_x , Pt_{50}H_x , Pt_{54}H_x NPs as computationally feasible models to represent Pt catalyst, corresponding to NP catalyst with ~ 1.1 nm in size.

First, we determined the relevant LEME for each reaction condition. Because the Pt NP continuously interacts with the H_2 atmosphere in a real system, the relevant ensemble includes structures with varying numbers of H. To enable a direct thermodynamic comparison across these different compositions, we calculated the LEME distribution using the formation free energy (without normalizing to each Pt) instead of the total energy. The resulting distributions for the Pt_{50}H_x series are shown as a representative example in Figure 6(a), while that for the Pt_{46}H_x and Pt_{54}H_x series are shown in SI Figures S44, S45. Under dehydrogenation condition, H adsorption is hindered by high temperature. Consequently, the GM of bare Pt_{50} NP is the most stable structure in this condition, and the accessible ensemble is narrow, comprising only 770 distinct LEME structures primarily from the LEME structures of Pt_{50} , Pt_{50}H_1 and Pt_{50}H_2 . In contrast, the hydrogenation condition under low temperature favors H adsorption. The most stable structure shifts to the GM of $\text{Pt}_{50}\text{H}_{79}$, and the accessible ensemble becomes vast and diverse, containing 13,845 distinct LEME structures, with the compositions ranging from $\text{Pt}_{50}\text{H}_{66}$ to $\text{Pt}_{50}\text{H}_{87}$. This vast increase in the number of LEME structures also highlights the fluxionality of surface Pt hydrides.

To accurately model the catalytic activity, all surface sites should be evaluated, even those on metastable LEME structures. This is because an active site with high intrinsic activity on a metastable structure can compensate the stability of its host NP and contribute significantly to the overall reaction rate^[21]. This presents a formidable computational challenge. For the ~ 1.1 nm NPs

studied here, the number of distinct surface Pt environments across the LEMEs is 43,491 for the dehydrogenation condition and 97,758 for the hydrogenation condition, making a full analysis of each site impossible in this paper. To select representative active sites for analysis, all unique surface Pt sites within the LEME structures were classified using the mean-shift clustering algorithm. This process identified structurally distinct site classes. For both hydrogenation and dehydrogenation conditions, the 10 most abundant Pt sites representing distinct classes were chosen for the catalytic activity analysis (see SI Figures S46, S47). This selection ensures the chosen sites are both abundant and structurally diverse.

Figure 6(b) plots the turnover frequency (TOF) of each representative Pt site against its normalized abundance among these sites. The calculation of the TOF requires the identification of TS and IS (see SI for details) that contains hydrocarbon species, which are calculated directly by DFT. For both methane dehydrogenation and ethylene hydrogenation, a clear discrepancy emerges between site abundance and catalytic activity. For methane dehydrogenation, the three most abundant sites (1, 2, 3) exhibit a TOF of approximately 0.01 s^{-1} , an order of magnitude lower than the less abundant site 4 (0.1 s^{-1}). The site-dependency is even more pronounced for ethylene hydrogenation. Here, site 10, which constitutes only $\sim 2\%$ of the selected sites, overwhelmingly dominates the catalytic activity. Its TOF is roughly 100 times greater than the second-most active site (site 4) and approximately 10^{12} times greater than the most abundant site (site 1).

Figure 6(c) and SI Figure S48 details the geometries for the methane dehydrogenation pathway of these 10 sites. In all cases, the reaction begins with weak CH_4 physisorption ($-0.10 \sim -0.16 \text{ eV}$), a thermodynamically unfavorable process that increases the Gibbs free energy by approximately 1.8 eV , due to the large entropy loss of CH_4 . The CH_4 molecule then proceeds through a TS where the breaking C-H bond interacts with a single Pt atom. Following dissociation, the resulting methyl group remains adsorbed on the original Pt site, while the dissociated H atom migrates to a neighboring surface Pt atom.

The differing catalytic activities on sites 1, 4, 6 shown in Figure 6(c) arise primarily from their TS geometries. For example, the most active site 4 is a six-coordinate kink site, with a geometry of the six surface Pt neighbors resembling a chair conformation. It exhibits a low electronic energy barrier (0.70 eV) and overall Gibbs free energy barrier (2.46 eV). This unique topology facilitates C-H activation by shortening the C-H bond in the TS ($1.583 \text{ \AA}$) and stabilizing the FS at $+1.59 \text{ eV}$ in free energy. In contrast, the most abundant site 1, a penta-coordinated Pt atom, is less active, with energy and free energy barriers of 0.83 eV and 2.64 eV , respectively. The least active site, site 6, resembles a flat Pt(111) terrace, which has a high energy and free energy barriers (1.18 and 2.94 eV) and features the longest Pt-C and C-H bond in the TS (2.232 and $1.655 \text{ \AA}$). These results indicate that protruding sites are more active for dehydrogenation than planar terrace sites, although the latter will become numerically dominant on larger NPs.

The structure-activity relationship for ethylene hydrogenation is more complex, as shown in Figure 6(d) and SI Figure S49. The dramatic differences in performance among sites 1, 4, and

10 originate from local defects, since their positions can all be attributed to $\text{Pt}_{5\text{e}}$ site in a perfect, vacancy-free cuboctahedral NP. Site 1 represents the ideal, fully hydrogen-saturated $\text{Pt}_{5\text{e}}\text{H}_4$ environment with two $\text{Pt}_{5\text{k}}\text{H}_5$ neighbors, making it the most abundant site on small NPs under reaction conditions. However, this saturation lowers its reactivity, with a high energy barrier of 0.71 eV. In contrast, site 4, which has two H vacancies ($\text{Pt}_{5\text{e}}\text{H}_2$) plus two $\text{Pt}_{5\text{k}}\text{H}_5$ neighbors, and site 10, two adjacent PtH_4 kink sites ($\text{Pt}_{4\text{k}}\text{H}_4 + \text{Pt}_{5\text{k}}\text{H}_4$), formed by the missing of one neighboring $\text{Pt}_{5\text{k}}$ and the top-H of the other neighbor, are far more active, with energy barriers being 0.37 eV and 0.35 eV, respectively. This trend is amplified when coupling with ethylene adsorption. The free energy barrier, considering the entropy loss of C_2H_4 during adsorption, is 1.30 eV for the inactive site 1, which drops to 0.71 eV for site 4 and just 0.54 eV for site 10. This reveals that local H vacancies are crucial for lowering the reaction barriers, while Pt vacancy further increases the activity of the site by favoring ethylene adsorption.

The different activities of each site can be understood by examining their ethylene adsorption modes and TS geometries in Figure 6(d). On site 1, the high local H coverage only allows for a weak physisorption of ethylene (-0.19 eV), making the adsorption endothermic by 0.59 eV in free energy. Even in the TS structure, the neighboring, already hydrogen-saturated $\text{Pt}_{5\text{k}}\text{H}_5$ site also repels the incoming H atom for hydrogenation, which is reflected by a long Pt-C bond (2.385 versus ~ 2.1 Å) and a short C-H bond (1.533 versus ~ 1.6 Å) compared to the other two sites. In contrast, the H vacancy on site 4 allows for strong chemisorption of ethylene as a di- σ bonded species, a process resulting in only a 0.34 eV increase in free energy and two short Pt-C bonds (2.143 and 2.175 Å). From this stable configuration, the ethylene molecule reacts with the top H on neighboring $\text{Pt}_{5\text{k}}$ to form an ethyl group, which goes through a TS containing still two Pt-C bonds (2.134 and 2.314 Å).

In more advanced, the exceptional activity of site 10 is due to a neighboring Pt vacancy, creating an ideal kink-like center for ethylene adsorption. Initially, ethylene adsorbs in a very stable π -bonded configuration, where two carbon atoms attach to the same Pt atom with Pt-C length close to about 2.3 Å. This state is highly favorable, with an adsorption energy of -0.77 eV and nearly no free energy loss upon adsorption. The chemisorption nature of ethylene is confirmed by a 0.057 Å elongation of the C-C bond upon adsorption, indicating a weaker C-C double bond. To proceed hydrogenation, C_2H_4 must first shift its binding from π -bonded mode to a reactive di- σ -bonded configuration, together with the movement of reactive H from bridge site to the top of $\text{Pt}_{5\text{k}}$. This rearrangement has a small energy cost of 0.18 eV. Once this active configuration is achieved, the subsequent C-H bond formation step proceeds via a low-barrier pathway similar to that on site 4.

Our findings on ethylene adsorption are consistent with extensive surface science experiments and theoretical calculations on model single crystal surfaces^[50,51], which confirm that both π -bonded and di- σ -bonded species exist on Pt surfaces and that the π -bonded state is more stable under hydrogen-rich conditions^[50]. Our calculations on realistic NP models, however, provide new atomic-level insights into the active site, highlighting the critical role of surface vacancies. Specifically, we find that an ideal active center requires a combination of features: a

local H vacancy is necessary to allow ethylene to adopt its reactive di- σ configuration, while a neighboring Pt vacancy is also highly beneficial to stabilize the initial π -bonded state and lowers the overall free energy barrier. Two adjacent PtH₄ kink sites, are thus an ideal motif for achieving exceptionally high catalytic activity of ethylene hydrogenation.

Now we compare our calculated TOF with the experimental data. For methane dehydrogenation, Pt supported by metal carbides was tested to provide a TOF of 0.2~0.6 s⁻¹ at 1023 K and 0.01 atm CH₄^[47], while a Pt catalyst on ZSM-5 zeolite had a TOF of ~ 0.05 s⁻¹ with 0.1 atm CH₄ at a lower temperature (923 K)^[48]. By summing the TOF of each site normalized by its site proportion, we get a total TOF of 0.02 s⁻¹ at 873 K and 0.1 bar CH₄, in good agreement with the experimental value. For the TOF of ethylene hydrogenation, Somorjai group found that silica-supported Pt NPs (1.7 ~ 7.1 nm) have a TOF of ~ 1 at room temperature^[52] while ~ 10² s⁻¹ at 403 K^[53], both under 0.013 bar of C₂H₄ and 0.13 bar of H₂. Our estimated total TOF of 574 s⁻¹ (323 K, 0.01 bar C₂H₄) is notably higher than values reported in experiments. We attribute this to the lack in the experiment of the extremely active double PtH₄ kink sites (site 10), which should be found only on small (~1.1 nm) NPs. Indeed, if we only count sites 1 ~ 9 for their activity contributions, our calculated TOF drops to 5.4 s⁻¹, a value that aligns well with the experimental data, where the primary active site is a common Pt_{5c} edge site with H vacancy (site 4). Additionally, experimental data suggest that the apparent activation energy of this reaction is little affected by the conditions or type of catalysts, being in the range of 0.36 ~ 0.47 eV^[54-56]. We have checked the sensitivity of our calculated TOF on temperature, which is shown in SI Figure S50. The obtained apparent activation energy is 0.46 eV, consistent with the upper bound experimental values, thus confirming the adequacy of our models and calculations. These findings highlight the exceptional catalytic potential of ~ 1 nm Pt NPs for ethylene hydrogenation, and underscore that investigating only the most abundant site may be insufficient to identify the true minority species that often govern overall catalytic performance.

The results in this section highlight a significant inconsistency between the abundance of a surface site and its actual contribution to the overall catalytic activity. This inconsistency arises from the conflicting structural requirements for nanoparticle stability versus catalytic reactivity. The majority of surface sites on a catalyst are configured for maximum stability, often featuring Pt atoms with well-coordinated environment. However, catalytic reactions frequently favor more unstable or "active" sites, such as kinks or vacancies. Consequently, a small fraction of rare, metastable sites can contribute the majority of activity. While the exploration of the LEMEs via NNP has allowed us to identify tens of millions of surface sites, it also presents a new challenge: identifying the handful of truly active sites within this vast ensemble. Therefore, the next frontier of the work should be the development of high-throughput screening methods, likely based on machine learning, to rapidly assess the reactivity of these surface sites and pinpoint the true origins of catalytic activity.

Conclusion

In this study, we leveraged the combination of grand canonical global optimization methods and machine-learning potentials to construct and analyze a vast atomistic landscape of unsupported, nanometer-sized Pt NPs under a hydrogen atmosphere. The atomistic models encompass bare and hydrogenated Pt NPs with sizes in the 1 ~ 2 nm size range and with H coverages from 0 to 2 ML, allowing for the investigation of intrinsic properties of realistic Pt catalysts, separate from the effects of a support, across a wide variety of catalytically relevant conditions. By generating and analyzing an ensemble of over one million structures, our findings offer several key insights into the structure, fluxionality, and reactivity of these complex systems.

(i) Hydrogen interaction is a primary driver of nanoparticle structure. H promotes a size-dependent crystallization, leading to sharp, complex phase transitions from a non fcc to a fcc structure for smaller NPs (< 1.5 nm) and smoother transformations from partly fcc to full fcc structure for larger ones. This behavior arises from a competition between surface stability (high CN_{surf} sites) and core stability (fcc), which are selectively combined at different H coverages. The atomistic model shown here provides an explanation and understanding of the noncrystalline-to-crystalline transformation observed in previous TEM experiments.

(ii) The fluxionality of NPs within the LEMEs, in a thermodynamic view, is contributed by the fluxionality of Pt core, local Pt environments, and surface hydrides. The Pt NP is best described as a dynamic mosaic of rigid and fluxional regions. At low H coverage, rigid regions are dictated by specific surface motifs, where the environments of the Pt core (for smaller NPs) and other Pt atoms are highly fluxional. At high H coverage, a rigid crystalline core and fcc lattice dominates the location of Pt atoms, but fluxionality of Pt atoms persists, governed by inherent structural Pt surface defects. The primary source of the system's fluxionality is the vast statistical diversity of possible H adsorption patterns. However, underlying this complexity, we identify the sequential appearance of different surface hydrides upon increased H coverage, which strongly depends on the local environment of surface Pt atom but is only slightly affected by particle size.

(iii) By coupling the structural library with reactivity modeling for methane activation and ethylene hydrogenation, we have uncovered that for NP catalysts the abundance of a surface site does not correlate with its activity. Despite their vastly different reaction conditions, dehydrogenation and hydrogenation reactions favor kink sites as their active centers, while ethylene hydrogenation on fully hydrogenated Pt NP requires a more complex active motif that includes specific local defects to achieve maximum activity. These active sites are rare, structurally distinct motifs, not the most stable and common sites on the Pt NPs at relevant conditions. This finding is extending the dynamic picture of the active sites proposed in recent years for small clusters (about 10 atoms)^[37] to the regime of NP catalysts. Comparisons of the calculated TOF with the experimental values highlight the importance of considering both the abundance and the intrinsic activity of each catalytic site. Our findings reveal that the maximum performance of a catalyst is dictated by a small population of rare, highly active sites. Conversely, the more

numerous but less active sites actually lower the overall performance by diluting these key active centers.

Overall, this work highlights a paradigm shift in computational catalysis. With the power of machine learning potentials and PES sampling methods, the challenge is no longer limited to predicting a single ground-state structure on model catalyst. The new frontier is to develop high-throughput methods to screen vast structural ensembles for the modelling of real catalyst in reaction conditions and the identification over these ensembles of active sites that govern the performance of a working catalyst.

Supporting Information

Computational methods, including DFT calculations, training of neural network potential, potential energy surface sampling methods, zero-point energy corrections, structure analysis, and catalytic activity evaluation; Details in thermodynamic scheme; Pt-Pt radial distribution functions for Pt nanoparticles; Distribution of Pt CN among different size of Pt nanoparticles; Geometric views of Pt cores; Variations of surface hydrides for other sizes of Pt nanoparticles; LEME and site distributions under catalytic relevant conditions; Geometries along reaction pathways.

Data Availability

The training dataset of three NNP models, and the XYZ coordination, calculated order parameters, and NNP-predicted energies of ~ 1 million Pt_xH_y NPs are available via the following Zenodo link: https://zenodo.org/records/16621963?preview=1&token=eyJhbGciOiJIUzUxMiIsImlhdCI6MTc1MzkxMjA1NiwiZXhwIjoxNzY0NTQ3MTk5fQ.eyJpZCI6IjZiMzkwYjBhLTMwMGItNDFIYi1iMjczLTU0M2FhNW12ZDQxYSIsImRhdGEiOnt9LCJyYW5kb20iOiJiNDkyOGMyY2JjYjVhOWZjNDIwMjhhZmJiNjQ3OGUwNiJ9.iEi0Umj_weJa2WV7zlZWmPRudTX33aZe_jMoDdsImL SgguWAfuu9__RV6d60Fg_yQZ_XhblOW6jO0p5ai09BAQ

Acknowledgement

This work was supported by the National Science Foundation CDS&E grant 2152767. Computations in this work were performed on the Hoffman2 cluster at UCLA Institute for Digital Research and Education (IDRE), and the Bridges2 cluster through allocation CHE170060 from the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) supported by the National Science Foundation.

Notes

The authors declare no competing financial interest.

Keywords

Heterogeneous catalysis; Pt nanoparticle; Adsorbate effect; Machine learning potential; Metastable configurations

References

- [1] Y. Shi, Z. Lyu, M. Zhao, R. Chen, Q. N. Nguyen, Y. Xia, “Noble-Metal Nanocrystals with Controlled Shapes for Catalytic and Electrocatalytic Applications” *Chem. Rev.* **2021**, *121*, 649–735.
- [2] L. Liu, A. Corma, “Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles” *Chem. Rev.* **2018**, *118*, 4981–5079.
- [3] X. Wang, A. Ruditskiy, Y. Xia, “Rational design and synthesis of noble-metal nanoframes for catalytic and photonic applications” *Nat. Sci. Rev.* **2016**, *3*, 520–533.
- [4] D. Llorens Rauret, A. Garzón Manjón, J. Arbiol, “Advances in *in situ* and *operando* TEM: From basic catalysis to industry-relevant reactions and future directions” *Matter* **2025**, *8*, 102139.
- [5] H.-Y. Chao, K. Venkatraman, S. Moniri, Y. Jiang, X. Tang, S. Dai, W. Gao, J. Miao, M. Chi, “In Situ and Emerging Transmission Electron Microscopy for Catalysis Research” *Chem. Rev.* **2023**, *123*, 8347–8394.
- [6] S. W. Chee, T. Lunkenbein, R. Schlögl, B. Roldán Cuenya, “Operando Electron Microscopy of Catalysts: The Missing Cornerstone in Heterogeneous Catalysis Research?” *Chem. Rev.* **2023**, *123*, 13374–13418.
- [7] M. Salmeron, R. Schlögl, “Ambient pressure photoelectron spectroscopy: A new tool for surface science and nanotechnology” *Surf. Sci. Rep.* **2008**, *63*, 169–199.
- [8] L. Nguyen, F. F. Tao, Y. Tang, J. Dou, X.-J. Bao, “Understanding Catalyst Surfaces during Catalysis through Near Ambient Pressure X-ray Photoelectron Spectroscopy” *Chem. Rev.* **2019**, *119*, 6822–6905.
- [9] J. Greeley, “Theoretical Heterogeneous Catalysis: Scaling Relationships and Computational Catalyst Design” *Annu. Rev. Chem. Biomol.* **2016**, *7*, 605–635.
- [10] B. Hammer, J. K. Nørskov in *Advances in Catalysis*, Academic Press, **2000**, pp. 71–129.
- [11] P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen, H. Topsøe, “Atom-Resolved Imaging of Dynamic Shape Changes in Supported Copper Nanocrystals” *Science* **2002**, *295*, 2053–2055.
- [12] S. Helveg, C. López-Cartes, J. Sehested, P. L. Hansen, B. S. Clausen, J. R. Rostrup-Nielsen, F. Abild-Pedersen, J. K. Nørskov, “Atomic-scale imaging of carbon nanofibre growth” *Nature* **2004**, *427*, 426–429.
- [13] F. Tao, M. E. Grass, Y. Zhang, D. R. Butcher, J. R. Renzas, Z. Liu, J. Y. Chung, B. S. Mun, M. Salmeron, G. A. Somorjai, “Reaction-Driven Restructuring of Rh-Pd and Pt-Pd Core-Shell Nanoparticles” *Science* **2008**, *322*, 932–934.

- [14] H. Frey, A. Beck, X. Huang, J. A. van Bokhoven, M. G. Willinger, “Dynamic interplay between metal nanoparticles and oxide support under redox conditions” *Science* **2022**, 376, 982–987.
- [15] M. Duan, J. Yu, J. Meng, B. Zhu, Y. Wang, Y. Gao, “Reconstruction of Supported Metal Nanoparticles in Reaction Conditions” *Angew. Chem., Int. Ed.* **2018**, 57, 6464–6469.
- [16] Y. Lei, H. Zhao, R. D. Rivas, S. Lee, B. Liu, J. Lu, E. Stach, R. E. Winans, K. W. Chapman, J. P. Greeley, J. T. Miller, P. J. Chupas, J. W. Elam, “Adsorbate-Induced Structural Changes in 1–3 nm Platinum Nanoparticles” *J. Am. Chem. Soc.* **2014**, 136, 9320–9326.
- [17] O. A. Yakovina, A. S. Lisitsyn, “Probing the H₂-Induced Restructuring of Pt Nanoclusters by H₂-TPD” *Langmuir* **2016**, 32, 12013–12021.
- [18] Y. Lei, J. Jelic, L. C. Nitsche, R. Meyer, J. Miller, “Effect of Particle Size and Adsorbates on the L₃, L₂ and L₁ X-ray Absorption Near Edge Structure of Supported Pt Nanoparticles” *Top Catal* **2011**, 54, 334–348.
- [19] E. Vottero, M. Carosso, A. Ricchebuono, M. Jiménez-Ruiz, R. Pellegrini, C. Chizallet, P. Raybaud, E. Groppo, A. Piovano, “Evidence for H₂-Induced Ductility in a Pt/Al₂O₃ Catalyst” *ACS Catal.* **2022**, 12, 5979–5989.
- [20] C. Mager-Maury, G. Bonnard, C. Chizallet, P. Sautet, P. Raybaud, “H₂-Induced Reconstruction of Supported Pt Clusters: Metal–Support Interaction versus Surface Hydride” *ChemCatChem* **2011**, 3, 200–207.
- [21] G. Sun, P. Sautet, “Metastable Structures in Cluster Catalysis from First-Principles: Structural Ensemble in Reaction Conditions and Metastability Triggered Reactivity” *J. Am. Chem. Soc.* **2018**, 140, 2812–2820.
- [22] L. Li, L.-L. Wang, D. D. Johnson, Z. Zhang, S. I. Sanchez, J. H. Kang, R. G. Nuzzo, Q. Wang, A. I. Frenkel, J. Li, J. Ciston, E. A. Stach, J. C. Yang, “Noncrystalline-to-Crystalline Transformations in Pt Nanoparticles” *J. Am. Chem. Soc.* **2013**, 135, 13062–13072.
- [23] G.-F. Wei, Z.-P. Liu, “Restructuring and Hydrogen Evolution on Pt Nanoparticle” *Chem. Sci.* **2015**, 6, 1485–1490.
- [24] C. J. Owen, N. Marcella, Y. Xie, J. Vandermause, A. I. Frenkel, R. G. Nuzzo, B. Kozinsky, **2023**, arXiv preprint, DOI: 10.48550/arXiv.2306.00901.
- [25] M. Khanuja, B. R. Mehta, P. Agar, P. K. Kulriya, D. K. Avasthi, “Hydrogen induced lattice expansion and crystallinity degradation in palladium nanoparticles: Effect of hydrogen concentration, pressure, and temperature” *J. Appl. Phys.* **2009**, 106, 093515.
- [26] D. S. Dolling, J. Chen, J.-C. Schober, M. Creutzburg, A. Jeromin, V. Vonk, D. I. Sharapa, T. F. Keller, P. N. Plessow, H. Noei, A. Stierle, “Probing Active Sites on Pd/Pt Alloy Nanoparticles by CO Adsorption” *ACS Nano* **2024**, 18, 31098–31108.
- [27] K. P. McKenna, A. L. Shluger, “Shaping the Morphology of Gold Nanoparticles by CO Adsorption” *J. Phys. Chem. C* **2007**, 111, 18848–18852.
- [28] Y. He, J.-C. Liu, L. Luo, Y.-G. Wang, J. Zhu, Y. Du, J. Li, S. X. Mao, C. Wang, “Size-dependent dynamic structures of supported gold nanoparticles in CO oxidation reaction condition” *Proc. Natl. Acad. Sci.* **2018**, 115, 7700–7705.
- [29] E. Groppo, S. Rojas-Buzo, S. Bordiga, “The Role of In Situ/Operando IR Spectroscopy in Unraveling Adsorbate-Induced Structural Changes in Heterogeneous Catalysis” *Chem. Rev.* **2023**, 123, 12135–12169.

- [30] O. A. Bariås, A. Holmen, E. A. Blekkan, “Propane Dehydrogenation over Supported Pt and Pt–Sn Catalysts: Catalyst Preparation, Characterization, and Activity Measurements” *J. Catal.* **1996**, *158*, 1–12.
- [31] S. Chen, X. Chang, G. Sun, T. Zhang, Y. Xu, Y. Wang, C. Pei, J. Gong, “Propane dehydrogenation: catalyst development, new chemistry, and emerging technologies” *Chem. Soc. Rev.* **2021**, *50*, 3315–3354.
- [32] A. S. Crampton, M. D. Rötzer, F. F. Schweinberger, B. Yoon, U. Landman, U. Heiz, “Ethylene hydrogenation on supported Ni, Pd and Pt nanoparticles: Catalyst activity, deactivation and the d-band model” *J. Catal.* **2016**, *333*, 51–58.
- [33] T. D. Shittu, O. B. Ayodele, “Catalysis of semihydrogenation of acetylene to ethylene: current trends, challenges, and outlook” *Front. Chem. Sci. Eng.* **2022**, *16*, 1031–1059.
- [34] M. Carosso, E. Vottero, A. Lazzarini, S. Morandi, M. Manzoli, K. A. Lomachenko, M. J. Ruiz, R. Pellegrini, C. Lamberti, A. Piovano, E. Groppo, “Dynamics of Reactive Species and Reactant-Induced Reconstruction of Pt Clusters in Pt/Al₂O₃ Catalysts” *ACS Catal.* **2019**, *9*, 7124–7136.
- [35] M. K. Oudenhuijzen, J. A. van Bokhoven, J. T. Miller, D. E. Ramaker, D. C. Koningsberger, “Three-Site Model for Hydrogen Adsorption on Supported Platinum Particles: Influence of Support Ionicity and Particle Size on the Hydrogen Coverage” *J. Am. Chem. Soc.* **2005**, *127*, 1530–1540.
- [36] Z. Zhang, B. Zandkarimi, A. N. Alexandrova, “Ensembles of Metastable States Govern Heterogeneous Catalysis on Dynamic Interfaces” *Acc. Chem. Res.* **2020**, *53*, 447–458.
- [37] G. Sun, P. Sautet, “Active Site Fluxional Restructuring as a New Paradigm in Triggering Reaction Activity for Nanocluster Catalysis” *Acc. Chem. Res.* **2021**, *54*, 3841–3849.
- [38] A. Zadick, L. Dubau, N. Sargent, G. Berthomé, M. Chatenet, “Huge Instability of Pt/C Catalysts in Alkaline Medium” *ACS Catal.* **2015**, *5*, 4819–4824.
- [39] Q. Sun, N. Wang, Q. Fan, L. Zeng, A. Mayoral, S. Miao, R. Yang, Z. Jiang, W. Zhou, J. Zhang, T. Zhang, J. Xu, P. Zhang, J. Cheng, D.-C. Yang, R. Jia, L. Li, Q. Zhang, Y. Wang, O. Terasaki, J. Yu, “Subnanometer Bimetallic Platinum–Zinc Clusters in Zeolites for Propane Dehydrogenation” *Angew. Chem., Int. Ed.* **2020**, *59*, 19450–19459.
- [40] N. Zhang, X. Li, Y. Guo, Y. Guo, Q. Dai, L. Wang, W. Zhan, “Crystal Engineering of TiO₂ for Enhanced Catalytic Oxidation of 1,2-Dichloroethane on a Pt/TiO₂ Catalyst” *Environ. Sci. Technol.* **2023**, *57*, 7086–7096.
- [41] S. Kattel, B. Yan, J. G. Chen, P. Liu, “CO₂ hydrogenation on Pt, Pt/SiO₂ and Pt/TiO₂: Importance of synergy between Pt and oxide support” *J. Catal.* **2016**, *343*, 115–126.
- [42] J. Behler, “Perspective: Machine learning potentials for atomistic simulations” *J. Chem. Phys.* **2016**, *145*, 170901.
- [43] J. Behler, “Four Generations of High-Dimensional Neural Network Potentials” *Chem. Rev.* **2021**, *121*, 10037–10072.
- [44] J. Vandermause, Y. Xie, J. S. Lim, C. J. Owen, B. Kozinsky, “Active learning of reactive Bayesian force fields applied to heterogeneous catalysis dynamics of H/Pt” *Nat. Commun.* **2022**, *13*, 5183.
- [45] A. Sebetci, Z. B. Güvenç, “Energetics and structures of small clusters: Pt_N, N=2–21” *Surf. Sci.* **2003**, *525*, 66–84.

- [46] P. Tang, Q. Zhu, Z. Wu, D. Ma, “Methane activation: the past and future” *Energy Environ. Sci.* **2014**, 7, 2580–2591.
- [47] Z. Li, Y. Xiao, P. R. Chowdhury, Z. Wu, T. Ma, J. Z. Chen, G. Wan, T.-H. Kim, D. Jing, P. He, P. J. Potdar, L. Zhou, Z. Zeng, X. Ruan, J. T. Miller, J. P. Greeley, Y. Wu, A. Varma, “Direct methane activation by atomically thin platinum nanolayers on two-dimensional metal carbides” *Nat. Catal.* **2021**, 4, 882–891.
- [48] Y. Xiao, A. Varma, “Highly Selective Nonoxidative Coupling of Methane over Pt-Bi Bimetallic Catalysts” *ACS Catal.* **2018**, 8, 2735–2740.
- [49] A. S. Crampton, M. D. Rötzer, C. J. Ridge, F. F. Schweinberger, U. Heiz, B. Yoon, U. Landman, “Structure sensitivity in the nonscalable regime explored via catalysed ethylene hydrogenation on supported platinum nanoclusters” *Nat. Commun.* **2016**, 7, 10389.
- [50] P. S. Cremer, X. Su, Y. R. Shen, G. A. Somorjai, “Ethylene Hydrogenation on Pt(111) Monitored in Situ at High Pressures Using Sum Frequency Generation” *J. Am. Chem. Soc.* **1996**, 118, 2942–2949.
- [51] V. Pallassana, M. Neurock, “Electronic Factors Governing Ethylene Hydrogenation and Dehydrogenation Activity of Pseudomorphic PdML/Re(0001), PdML/Ru(0001), Pd(111), and PdML/Au(111) Surfaces” *J. Catal.* **2000**, 191, 301–317.
- [52] R. M. Rioux, H. Song, J. D. Hoefelmeyer, P. Yang, G. A. Somorjai, “High-Surface-Area Catalyst Design: Synthesis, Characterization, and Reaction Studies of Platinum Nanoparticles in Mesoporous SBA-15 Silica” *J. Phys. Chem. B* **2005**, 109, 2192–2202.
- [53] R. M. Rioux, R. Komor, H. Song, J. D. Hoefelmeyer, M. Grass, K. Niesz, P. Yang, G. A. Somorjai, “Kinetics and mechanism of ethylene hydrogenation poisoned by CO on silica-supported monodisperse Pt nanoparticles” *J. Catal.* **2008**, 254, 1–11.
- [54] U. Jung, A. Elsen, Y. Li, J. G. Smith, M. W. Small, E. A. Stach, A. I. Frenkel, R. G. Nuzzo, “Comparative in Operando Studies in Heterogeneous Catalysis: Atomic and Electronic Structural Features in the Hydrogenation of Ethylene over Supported Pd and Pt Catalysts” *ACS Catal.* **2015**, 5, 1539–1551.
- [55] J. Grunes, J. Zhu, M. Yang, G. A. Somorjai, “CO Poisoning of Ethylene Hydrogenation over Pt Catalysts: A Comparison of Pt(111) Single Crystal and Pt Nanoparticle Activities” *Catal. Lett.* **2003**, 86, 157–161.
- [56] J. Grunes, J. Zhu, E. A. Anderson, G. A. Somorjai, “Ethylene Hydrogenation over Platinum Nanoparticle Array Model Catalysts Fabricated by Electron Beam Lithography: Determination of Active Metal Surface Area” *J. Phys. Chem. B* **2002**, 106, 11463–11468.

Table of Contents

The nature and structure of Pt nanoparticles under a pressure of hydrogen is studied using machine learning potential guided grand-canonical global optimization, generating more than one million stable and metastable Pt_xH_y structure candidates for analysis. A noncrystalline-to-crystalline transformation of Pt configurations is revealed at the atomic level, driven by the adsorption of hydrogen or the increased size of the nanoparticle.

