Evolution of Metastable Structures in Bimetallic Surfaces from Microscopy and Machine-Learning Molecular Dynamics

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Abstract

Restructuring of interface plays a crucial role in materials science and heterogeneous catalysis. Bimetallic systems, in particular, often adopt very different composition and morphology at surfaces compared to the bulk. For the first time, we reveal a detailed atomistic picture of long-timescale restructuring of Pd deposited on Ag, using microscopy, spectroscopy, and novel simulation methods. Experimental observations indicate that encapsulation of Pd by Ag always precedes layer-by-layer dissolution of Pd, resulting in significant Ag migration out of the surface and extensive vacancy pits. These metastable structures are of vital catalytic importance, as Ag-encapsulated Pd remains much more accessible to reactants than bulk-dissolved Pd. The underlying mechanisms are uncovered by developing and performing accelerated machine-learning molecular dynamics, followed by automated discovery and characterization of key surface restructuring mechanisms. This approach is broadly applicable to complex multimetallic systems and enables the previously intractable mechanistic investigation of restructuring dynamics at atomic resolution.

Dynamic restructuring of complex interfaces is ubiquitous in multicomponent materials. In particular, elemental segregation at grain boundaries, dislocations, and surfaces can have a significant impact on a range of functional properties, such as fracture strength, plastic deformation, corrosion resistance, and catalytic activity.¹⁻³ In heterogeneous catalysis, surface composition and morphology often differ dramatically under reaction conditions, compared to the original synthesized state.⁴⁻⁸ Such restructuring has recently been shown to play a central role in catalytic performance of several nanoparticle systems, such as nanoporous AgAu,⁹ single-atom Pt/TiO₂,¹⁰ and Pd/Al₂O₃.¹¹ Therefore, fundamental understanding of surface restructuring is crucial to enabling accurate prediction and engineering of catalyst performance.¹²

However, mechanistic and kinetic studies of surface restructuring at the atomic level have remained scarce and challenging.^{17,21-26} Experimentally, it is very difficult to probe fast atomic motions with sufficient temporal resolution, even with techniques that possess surface

and chemical sensitivities. Computationally, density functional theory (DFT) enables exploration of reaction pathways on model surfaces,²⁷ but its high computational cost precludes its use for dynamical simulation of realistic systems beyond tens of picoseconds. Furthermore, exploration of large configurational space underlying restructuring processes quickly becomes intractable with brute force approaches. In this work, we overcome all of these limitations by combining microscopy, spectroscopy, and novel simulation methods. Fast and large-scale machine-learning molecular dynamics (MD) is performed using our recently developed Gaussian process force field,¹³ spanning microseconds at first-principles accuracy. Furthermore, a new automated analysis method is used to discover and characterize key surface restructuring mechanisms (Fig. 1). Our streamlined approach enables an efficient

Figure 1: Automated characterization of surface restructuring events. (a) Gaussian process (GP) machine-learning force field is trained on DFT data.¹³ (b) The GP model is used to perform fast, large-scale, and long-timescale MD simulation of surfaces. (c) The raw MD trajectory is first "clamped" by assigning all atoms onto discrete FCC lattice sites.^{14–16} Then, an event is detected whenever the z -coordinate (normal to the surface) of any atom changes irreversibly over 1–2 ps.¹⁷ (d) The events are sorted into seven main classes¹⁷ based on changes in the atomic layer and the coordination number. (e) The event pathways are detailed using transition state modeling.^{18–20}

and unbiased characterization of restructuring dynamics in complex multimetallic systems.

Surface restructuring of late-transition metals can be classified into three categories: (1) relaxation involving localized atomic displacements;²⁸ (2) reconstruction involving intralayer atomic site changes;²⁹ (3) segregation in alloys involving interlayer atomic site changes.³⁰ All three processes aim to reduce the surface free energy arising from reduced surface atom coordination. Bimetallic systems, of particular interest for selective hydrogenation, possess additional complexity due to elemental variations in surface energy. In general, elements with fuller *d*-shells have lower surface energy and segregate to the surface in the absence of adsorbates, forming e.g. core@shell nanostructures.³¹

The quasi-chemical approximation³² can be used to model surface and subsurface species, assuming a chemical equilibrium. The main energetic contributions have been established as the "three effects' rule"³⁰ (surface energy; strain energy; alloying energy) and the "chemical pump effect"³³ (adsorption energy). The last component refers to adsorbate-induced reverse segregation, where strongly bound adsorbates such as CO and O stabilize, for example, catalytically active Pd on the surface of a more inert Ag host.^{34,35} These observations suggest pretreatment as a promising way of activating or deactivating bimetallic catalysts.⁸

Based on prior studies using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and *ab initio* thermodynamics, Pd dissolves into the Ag bulk after mild heating because of the higher surface energy of Pd.⁸ However, the underlying mechanism and timescale have remained unclear. To our best knowledge, the work herein provides the first direct atomistic observation and characterization of the long-timescale restructuring of a bimetallic surface. After annealing, monatomic Pd islands on Ag(111) evolve into a dramatically different state involving Ag-encapsulated Pd islands, surrounded by extensive vacancy pits. In contrast to the thermodynamically favored state where Pd is dispersed in the Ag bulk, these structures are metastable and prevail at mild temperatures. They are of vital catalytic importance, as Ag-encapsulated Pd remains much more accessible to reactants than bulk-dissolved Pd. As such, our results provide an important foundation for

engineering surface ensemble distributions toward optimal activity-selectivity balance.³⁶

Four distinct stages have been established for the restructuring of Pd islands on Ag (Fig. 3): (1) Pd-Ag place exchange; (2) formation of PdAg alloy layer; (3) Ag pop-out and vacancy pit growth; (4) layer-by-layer Pd dissolution. Surprisingly, the first three stages produce nontrivial metastable structures that result from encapsulation of the Pd deposit by Ag and the growth of extensive vacancy pits, as observed in STM images (Fig. 2). As such, these stages comprise a kinetically distinct metastable dissolution mode, previously named "surfactant" mode in the literature³⁷ due to the similarity to semiconductor growth. This mode precedes the direct layer-by-layer dissolution of Pd into the thermodynamically favored subsurface. Fig. 3 shows the evolution of a hexagonal Pd₉₁ island on Ag(111) at 500 K over 2 μ s of our simulation. In addition, Table 1 shows four main types of microscopic restructuring events discovered by our automated scheme (Sec. 2, SI).

Figure 2: STM images demonstrate the restructuring of Pd islands deposited on Ag(111). Metastable structures form prior to complete dissolution of Pd into the Ag bulk. Schematic height profiles along the blue horizontal lines are depicted above the images, labeled by the layer heights: level -1 (subsurface); level 0 (surface); level 1 (deposit); level 2 (capping). (a) Pd islands, deposited at 300 K, consist mostly of monolayers at level 1 . (b) After mild annealing at 400-450 K, the difference in the elemental surface energy results in encapsulation of the Pd islands by capping layers at level 2 , along with extensive vacancy pits at level -1 .

Figure 3: Frames of MD simulation showing the evolution of a Pd₉₁ island on Ag(111) at 500 K over 2 μ s. The system reaches a quasi-equilibrium after 2 μ s. As depicted in the bottom schematic, Pd atoms are green, and Ag atoms are colored by the layer height, from red (level -2) to blue (level 2). The bottommost layer (level -3) is fixed in the simulation and hence omitted. (a) As-deposited hexagonal Pd₉₁ island on Ag(111). (b) Pd undergoes a series of place exchange with the underlying Ag atoms around the island edges. (c-d) A few Ag atoms climb on top of the deposit and attempt to pull Pd atoms up to level 2. (e-f) PdAg alloy layer forms at level 2. (g-h) In the second half of the simulation, more Ag atoms migrate out of the surface to further encapsulate the cluster, resulting in a vacancy pit. See video [here](#).

Table 1: Four main classes of restructuring events underlying the restructuring of a Pd island on Ag(111): (a) Pd-Ag direct exchange; (b) Ag pop-out; (c) Ag hopping ascent; (d) Pd exchange ascent. The structures (IS = initial state; TS = transition state; IMS = intermediate state; FS = final state) and the corresponding energy level diagrams are fully optimized by the GP model. Slab atoms are semi-transparent for clarity.

In the beginning, Pd undergoes a series of place exchange with the underlying Ag atoms around the island edges [Fig. 3(b)]. Such Pd-Ag direct exchange [Table 1(a)] is the predominant mechanism by which Pd atoms are incorporated into the Ag surface in the earlier stages. First, a Ag atom migrates out of the surface layer into a kink or a corner site present at the island edge. As seen by a modest energy barrier of 0.4 eV, such edge vacancies facilitate the otherwise constrained exchange process. The Ag pop-out creates a vacancy in the surface layer, which is quickly filled by a neighboring Pd atom. This Pd insertion has an energy barrier of only 0.1 eV, due to a large thermodynamic driving force (over 1.2 eV stabilization).

Next, some of the Ag atoms, now occupying the edge sites, become mobile and climb on top of the Pd deposit [Fig. 3(b)]. These Ag atoms are mobilized around kinks and corners, allowing the island edges to be rather fluxional. Adatom diffusion along the step edges of close-packed surfaces has been investigated extensively in the computational literature for homoepitaxial cases.³⁸ For example, our previous work has shown facile edge & corner diffusion of both Ag & Pd adatom on Ag, with energy barriers below 0.4 eV in all cases.¹⁷

Step ascent & descent are well-established in the context of island growth, where the growth mode is determined by the Ehrlich-Schwoebel barrier^{39,40} associated with step descent.⁴¹ There are two main mechanisms: (1) simple hopping over the edge [Table 1(c)], or (2) exchange involving an insertion into the edge through the displacement of an edge atom [Table 1(d)]. In our simulation, exchange ascent & descent, followed by their hopping counterparts, comprise the majority of the observed restructuring events (Fig. S6). Interestingly, Ag atoms ascend primarily via hopping in the earlier stages, whereas exchange ascent occurs only when a sufficient number of Ag atoms are already present on the top to participate in the exchange. It is important to note that descent is easier than ascent in general, due to the larger coordination present at the lower edge than at the upper edge. However, an ascending Ag atom is capable of being stabilized by Ag atom(s) that may already be present on the top. Such extra coordination can lower the energy barrier by up to 0.3 eV (Table S4). In all

cases, the energy barriers for Ag ascent are below 0.6 eV (Table S4-5).

Surprisingly, the top Ag atoms pull up the underlying Pd atoms, ultimately forming a PdAg alloy layer in the second level [Fig. 3(c)]. This Pd ascent occurs primarily through a series of exchange involving the Ag atoms over a relatively short period of 0.2 μ s, with energy barriers below 0.5 eV [Table 1(d)]. The process is accompanied by a distinct relaxation of the deposit layer upon becoming coordinated by this second layer (Sec. 7, SI). Mechanistically, Pd hopping ascent occurs much less frequently, in contrast to Ag hopping ascent. In general, Pd atom experiences a larger energetic cost than Ag atom undergoing a given restructuring event, unless it is driven by a significantly large thermodynamic stabilization (e.g. Pd insertion into the surface).¹⁷

In the second half of the simulation, more Ag atoms migrate out of the surface to further cover the bilayer structure around its edges, resulting in a vacancy pit [Fig. 3(d)]. Our previous work found that Ag pop-out is very unfavorable on clean terraces, with energy barriers over 1.0 eV in all scenarios.¹⁷ Surprisingly, a single-atom Ag pop-out next to an island edge has a modest energy barrier of 0.5 eV [Table 1(b)], which is attributed to the stabilization of the transition state by the edge atoms. The resulting vacancy pits create double steps through which facile Ag migration occurs, as proposed in previous experiments of rapid vacancy island decay.^{42,43} Remarkably, the thermodynamic driving force underlying this Ag transport becomes even more pronounced at higher Pd coverages (Sec. 6.3, SI). For example, at 0.75 ML coverage, the surface area of the exposed Ag is less than that of the deposited Pd. Consequently, additional Ag migration starts to occur out of the subsurface layers, resulting in multiple-height steps and significant surface coarsening (Fig. S18).

At a relatively moderate temperature, the system has evolved into a completely different structure from the as-deposited Pd monolayer in a period of microseconds. At 500 K, the system reaches an apparent quasi-equilibrium after 2 μ s in this metastable structure, as opposed to the thermodynamically favored state with Pd dispersed in the bulk. In particular, the exposed Pd clusters in the second layer are now much smaller and interspersed by Ag

atoms. The observed structure is consistent with low-temperature CO-probe experiments comprised of XPS, high resolution electron energy loss spectroscopy (HREELS), low energy ion scattering spectroscopy (LEISS), and temperature programmed desorption (TPD) that collectively demonstrate significant reduction in CO binding after annealing at 450 K (Sec. 4, Methods; Sec. 9, SI). These experiments are also supported by DFT calculations showing a systematic reduction in CO adsorption energy, by up to 0.8 eV on an isolated Pd monomer in Ag(111) compared to an extended Pd(111) surface⁴⁴ (Sec. 8, SI). Furthermore, our simulation predicts $\sim 7\%$ of exposed Pd after annealing, in good agreement with $\sim 12\%$ determined experimentally from quantifying CO adsorption before and after annealing. Overall, these results demonstrate the predictive power of our method, complementary to experimental techniques with surface and chemical sensitivities.

At higher temperatures (Sec. 6.1, SI), the bilayer structure becomes further encapsulated by a third Ag capping layer, followed by layer-by-layer dissolution of Pd over a longer period of time (Fig. S12; See video [here](#)). The dissolution consists of multiple interlayer transfer events (Table S6), starting at the edges and moving toward the center of the island. A subsurface Ag atom first ascends into a pre-existing surface vacancy, after which a neighboring Ag-Pd pair descends into the resulting subsurface vacancy. As Pd dissolves layer-by-layer, it is no longer thermodynamically favorable for the Ag atoms to remain in the capping layer. As such, they migrate back into the surface, resulting in a gradual decay of vacancy pits. In the end, all pits are refilled, and almost all Pd remains dissolved in the subsurface, with a small amount of Pd resurfacing transiently as isolated atoms. Such surface-subsurface equilibrium is in direct agreement with the thermodynamic model of the quasi-chemical approximation.³²

The formation of metastable Ag-encapsulated Pd is predominant at moderate temperatures islands and always precedes layer-by-layer dissolution of Pd. Such behavior has vital implications for catalysis. Our previous work showed that Pd resurfaces at moderate temperature and pressure of CO or O₂.⁸ This reverse segregation allows the catalytically active

element to be present on the surface of an inert host metal under reaction conditions. Our results suggest that such activation of the catalyst would be enabled by metastable structures, where Pd remains largely accessible to the reactants in the form of Ag-encapsulated Pd rather than bulk-dissolved Pd. Evolution of these metastable structures would play a central mediating role in engineering of catalytic activity through various pretreatment strategies.^{45–48} Our automated modeling strategy within machine-learning molecular dynamics, in combination with surface science experiments, allows complex surface restructuring dynamics to be mapped out at atomic resolution, a task that would otherwise be intractable with a brute-force static approach. Investigation of other bimetallic systems as well as various adsorbate-induced (H_2 , O_2 , CO) surface restructuring phenomena is underway.

Experimental Section

Automated characterization of surface restructuring events: A fully automated workflow for surface restructuring event characterization has been developed (Fig. 1), building upon our previous framework.¹⁷ All of our interactive Jupyter Notebook files are publicly available.⁴⁹ Density functional theory data is used to train a Gaussian process machine-learning force field,¹³ which allows us to perform large-scale and long-timescale molecular dynamics (MD) at first-principles accuracy (Sec. 1, SI). From preliminary visual inspections, we find that most restructuring events occur over 1-3 ps, with atoms transitioning between well-defined face-centered cubic (FCC) lattice sites. To better follow the events, we first "clamp" the raw MD trajectory: All atoms are assigned onto discrete FCC lattice sites, frame by frame^{14–16} (Sec. 3, SI). The resulting clamped trajectory is automatically scanned to detect restructuring events. A frame is flagged as an event point if the z -coordinate (normal to the surface) of any atom changes irreversibly over 1-2 ps. The flagged frames within 2 ps of each other are clustered into distinct events. Then, the events are automatically sorted into seven main classes,¹⁷ based on changes in the atomic layer and coordination number (Sec. 4, SI).

Finally, pathways for representative events of each class are optimized using transition state modeling^{18–20} (Sec. 2, SI).

Surface science experiments: The experimental measurements are performed with three different Ag(111) crystals mounted in three separate ultrahigh vacuum (UHV) chambers, described in detail elsewhere.^{8,50} Scanning tunneling measurements are performed in a UHV chamber using a beetle-type scanner (RHK UHV VT STM).⁸ X-ray photoelectron and ion scattering measurements are performed in a UHV chamber using an X-ray source (Perkin Elmer 04-548/32-095 with RBD 20-042) with (non-monochromatized) Mg K α radiation, a 1.5 eV 4He⁺ ion beam (SPECS IQE 12/38) with a Wien mass filter (SPECS WF-IQE), and a hemispherical analyzer (SPECS Phoibos 100 equipped with a 5-channel electron multiplier).⁸ The high-resolution electron energy loss measurements are performed in a UHV chamber using an electron energy loss spectrometer (LK 2000) with a primary energy of 4.5 eV at 60° specular geometry.⁵⁰ The Ag(111) crystals are cleaned by repeated cycles of Ar⁺ sputtering (1-2 kV) and annealing (750-800 K) in UHV. The PdAg surface alloys are formed by depositing Pd (99.99%) at room temperature on clean Ag(111) using an electron-beam evaporator. CO adsorption experiments use a mixture of 20% CO (99.9% purity) in Ar.

Additional information

Supplementary information is available in the online version of the paper.

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Competing financial interests

The authors declare no competing financial interests.

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