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Atomic Control of Active Site Ensembles in Ordered Alloys to Enhance Hydrogenation Selectivity

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Abstract

Intermetallic compounds offer unique opportunities for atom-by-atom manipulation of catalytic ensembles through precise stoichiometric control. The [Pd, (M), Zn] γ -brass phase allows for controlled synthesis of Pd-M-Pd catalytic sites (M = Zn, Pd, Cu, Ag and Au) isolated in an inert Zn matrix. These multi-atom heteronuclear active sites are catalytically distinct from Pd single atoms and fully coordinated Pd. We quantify the unexpectedly large effect of active site composition (i.e., identity of M atom in Pd-M-Pd sites) on ethylene selectivity during acetylene semi-hydrogenation. Subtle stoichiometric control demonstrates Pd-Pd-Pd sites are active for ethylene hydrogenation, whereas Pd-Zn-Pd sites show no measurable ethylene to ethane conversion. Agreement between experimental and density functional theory predicted activities and selectivities demonstrates precise control of Pd-M-Pd active site composition. The diversity and well-defined structure of intermetallics can be utilized to design active sites assembled with atomic-level precision.

Introduction

Advances in heterogeneous catalyst active site design are limited by our ability to exert atomically-precise synthetic control over active site ensembles.¹ Tailoring the electronic and geometric structure of the active site has mainly been accomplished by carefully tuning bimetallic alloys, in which the addition of the second metal modifies the electronic and structural properties of the primary reactive metal. Development of model bimetallic catalysts has traditionally relied on vapor deposition of a second (minority) metal onto a single crystalline form of the host metal, followed by annealing treatment to form a bimetallic surface.²⁻⁵ Vapor deposition methods lead to a distribution of ensemble sizes of ill-defined geometry and composition, and large uncertainty in surface composition due to redistribution of the deposited metal between the surface and subsurface post annealing.

A more recent application of this approach, in which low loadings of a second metal are physically deposited on a well-defined surface of a second metal, has led to a class of “single atom alloy” (SAAs) catalysts.⁶⁻⁸ As the name implies, SAAs may possess well-defined active sites consisting of isolated metal atoms in an inert or less active host metal. Sykes and co-workers demonstrated the enhanced reactivity of Cu single crystals for acetylene hydrogenation after doping with single Pd atoms.⁷ The authors proposed Pd enabled facile dissociation of hydrogen (compared with activated dissociation of H₂ on Cu). The atomic H bound to Pd subsequently spilled over to Cu, catalyzing the hydrogenation of acetylene. Single atom catalysts (SACs) are a related class of catalysts in which individual metal atoms are isolated on refractory or reducible oxides.⁹⁻¹¹ A major limitation of both SAAs and SACs is their inherent limitation to mononuclear assemblies (i.e., single atoms) because site isolation is accomplished through low surface densities.

Therefore, SAAs and SACs do not offer the ability to create well-defined homomultinuclear (M_n , $n > 1$) or heteromultinuclear (M_nM' , $n > 1$) assemblies.

Goodman and co-workers controlled the coverage of Pd atoms on Au single crystals to demonstrate precise spacing of monomer ‘pairs’ that facilitated synthesis of vinyl acetate monomer (VAM).⁶ They deposited a low-coverage of Pd atoms on Au(111) and Au(100) single crystals, which have different surface interatomic Au spacing, to control spacing between the deposited Pd atoms. The spacing of Pd atoms on Au(100) was sufficient to allow the Pd atoms to act as a monomer ‘pair’ capable of synthesizing VAM, while Pd atoms on Au(111) were too distant to catalyze VAM formation. This study controlled nuclearity and spacing of active metal atoms (Pd) within a relatively inert host (Au) to provide active and selective catalytic sites. These sites, however, were prepared through a statistical distribution of low coverage Pd atoms rather than targeted synthesis of a specific active metal atom arrangement.

We demonstrate the intermetallic γ -brass phase of Pd-Zn can be used to directly synthesize both well-defined homomultinuclear and heteromultinuclear active sites. Intermetallic compounds contain at least two metals with a well-defined crystal structure with fixed atom positions and site occupancies, leading to long range order; this offers distinct advantages over SACs and SAAs for controlling active site ensembles beyond single, isolated atoms. The well-defined crystal structure and long-range atomic ordering of intermetallic compounds offer consistent site isolation throughout the catalyst, as well as control over the number of atoms per active site. Beyond this exquisite control over site nuclearity ($n > 1$), homo- and hetero- multinuclear sites can also be prepared with high density on the surface; no comparable synthetic methods exist for SAAs or SACs.

Intermetallics demonstrate distinct catalytic properties from their corresponding monometallic catalyst. Pd-Ga intermetallics have high acetylene semi-hydrogenation selectivity compared to monometallic Pd.^{12,13} Li et al. studied MgO supported Ni-Ga intermetallics and found their selectivity towards phenylacetylene semi-hydrogenation was much higher than pure Ni.¹⁴ Intermetallic β -Pd-Zn catalysts expose a checkerboard arrangement of alternating Pd and Zn atoms, with distinct selectivity toward acetylene semi-hydrogenation.¹⁵ These examples demonstrate intermetallics offer more precise control over active site local composition than vapor-deposited bimetallic systems. In the referenced studies, however, control over the geometry and composition of the active site ensembles was limited to isolated single Pd or Ni atoms. Previous work has demonstrated active assemblies of n atoms ($n = 3$, trimers) in Pd₃In(111),¹⁶ Pt₃Sn(111) and Pt₂Sn(111),¹⁷ but these “trimer” active sites are interconnected rather than being isolated by In or Sn atoms. A combined surface science-computational examination of PdGa($\bar{1}\bar{1}\bar{1}$) demonstrated the presence of isolated Pd trimers, but their reactivity and selectivity during semi-hydrogenation were not reported.¹⁸ To date, there has been no demonstration of the ability to synthesize isolated active site ensembles composed of more than one catalytic active metal.

Here, we utilize the intermetallic [Pd, Zn] γ -brass phase to control the geometry of isolated, active catalytic ensembles dispersed within an inert matrix, as well as the composition of isolated multi-nuclear active sites. The γ -brass structure is a 52 atom unit cell with four symmetry inequivalent positions – outer tetrahedral (OT), inner tetrahedral (IT), octahedral (OH) and cuboctahedral (CO) (Figure S1).¹⁹ This precise and homogeneous metal ensemble distribution is maintained at the surface, exposing isolated OT-OH-OT catalytic ensembles. The occupation of the OT-OH-OT ensemble is determined by the composition of the γ -brass phase. The [Pd, Zn] binary γ -brass phase exposes single-atom Pd₁ monomers where Pd atoms are separated by zinc

(Pd-Zn-Pd) and elongated Pd₃ trimer (Pd-Pd-Pd) ensembles (see insets in Figure 1a, b) through simple and subtle stoichiometric tuning (15.4-19.2 at % Pd). Similarly the [Pd, (M), Zn]_{M=Au,Ag,Cu} γ -brass phase exposes Pd-M-Pd ensembles through introduction of a heterometal atom during solid-state synthesis.

The compositional control of the catalytic active site within the γ -brass Pd-Zn phase tunes ethylene hydrogenation activity across orders of magnitude, which has important consequences for selectivity during acetylene semi-hydrogenation. Consistent with the observed activity for ethylene hydrogenation, Pd₁ monomers display high selectivity to ethylene, while Pd₃ trimers over-hydrogenate ethylene to ethane. The extent of over-hydrogenation can be controlled by breaking up Pd₃ trimers through the introduction of a third metal (M = Cu, Ag, Au) during synthesis to create Pd-M-Pd trimers with ethylene selectivity intermediate to Pd₁ monomers and Pd₃ trimers. The isolated active site with precise compositional control renders these intermetallic catalysts amenable to direct comparison with computational predictions. Density functional theory (DFT) calculations predict the experimental hydrogenation activity and selectivity as the Pd-M-Pd site composition is varied.

Results and Discussion

Ethylene Hydrogenation Activities on Pd-Zn Binary γ -brass Intermetallics

Unsupported Pd-Zn γ -brass catalysts were synthesized using a well-established bulk synthesis technique and characterized by inductively-coupled plasma – optical emission spectroscopy (ICP-OES), scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffraction (XRD) to ensure phase purity and bimetallic composition. BET surface area was determined to calculate and compare normalized reaction rates. Small changes in

Pd-Zn ratio result in enormous differences in ethylene hydrogenation activity, which we establish below is due to transition from inactive Pd₁ monomers to active Pd₃ trimers. As shown in Figure 1a, a Pd-Zn catalyst with 17.3 Pd atomic % (25.4 wt%) shows a measurable ethylene hydrogenation activity. This activity doubles upon increasing to 19.2 Pd atomic % (27.9 Pd wt%); both 17.3% and 19.2% samples have the same activation barrier (Figure 1b). However, a Pd-Zn γ -brass catalyst with 15.4 Pd atomic % (22.8 Pd wt%) shows no measurable activity for ethylene hydrogenation. Based on a conservative flame ionization detection limit, the hydrogenation rate over the 15.4 Pd atomic % catalyst was less than 10^{-13} mol m⁻² s⁻¹, at least four orders of magnitude lower than the rate measured over the 17.3 Pd atomic % catalyst at 307 K.

DFT calculations indicate Pd₁ sites are inactive for ethylene hydrogenation whereas Pd₃ sites demonstrate measurable activity. Figure 1c reports DFT calculations of the ethylene hydrogenation barrier and desorption energies on the γ -brass (1 $\bar{1}$ 0) Pd₈Zn₄₄ (Pd₁ monomers, 15.4 Pd atomic%), Pd₉Zn₄₃ (Pd₁ monomers and Pd₃ trimers, 17.3 Pd atomic%), Pd₁₀Zn₄₄ (doubling of Pd₃ trimer density, 19.2 Pd atomic%), and extended Pd(111) surfaces. We will refer to these three γ -brass phase compositions as 8-Pd, 9-Pd, and 10-Pd, leaving off the remaining Zn stoichiometry that completes the 52 atom unit cell. The Pd₁ monomer site, exposed on the surface of all three γ -brass compositions, does not provide a sufficient Pd ensemble to bind ethylene, activate H₂, and form the ethylene hydrogenation transition state. This leads to a hydrogenation barrier significantly exceeding the ethylene desorption energy, a reliable descriptor for ethylene hydrogenation activity.²⁰ In contrast the Pd₃ trimers in 9-Pd and 10-Pd provide a sufficient active site ensemble and, therefore, the hydrogenation barrier is similar to the desorption energy and the catalyst is active for ethylene hydrogenation.

The lack of ethylene hydrogenation activity on the 8-Pd catalyst is due to the complete isolation of all Pd atoms as Pd₁ monomers, surrounded by all Zn nearest neighbors. This catalyst exposes “single atom” Pd sites despite a relatively high 15.2 Pd atomic % due to the intermetallic nature of the γ -brass Pd-Zn structure. The π -bound ethylene on Pd₁ monomers blocks H co-adsorption and formation of the hydrogenation transition state. The drastic increase in ethylene hydrogenation activity at 9-Pd occurs due to the formation of Pd₃ trimers, also isolated from other surface Pd atoms by Zn nearest neighbors. Further increasing the Pd content to 10-Pd doubles the ethylene hydrogenation rate without changing the apparent activation barrier (Figure 1b), suggesting the doubling of Pd₃ ensembles doubles the surface density of active sites. Hydrogenation rates over Pd-Zn catalysts are four orders of magnitude lower than Pd foil, indicating a distinct active site of the Pd-Zn catalysts. We confirm below through XRD and computational modeling that the varying site occupations in the Pd-Zn ratio γ -brass intermetallic structure generate isolated Pd₁ monomers in 8-Pd, Pd₃ trimers in 9-Pd, and a doubling of the Pd₃ trimer surface density in 10-Pd, showing unprecedented control of the nuclearity of Pd active sites.

Figure 1. Hydrogenation of ethylene over γ -brass [Pd, Zn] catalysts. (a) Ethylene hydrogenation activity at different temperatures (34°C, 40°C, 47°C, 55°C) on $\text{Pd}_8\text{Zn}_{44}$, $\text{Pd}_9\text{Zn}_{43}$, $\text{Pd}_{10}\text{Zn}_{42}$ and Pd foil with $\text{C}_2\text{H}_4:\text{H}_2 = 1:40$. (inset) Corresponding DFT calculated most stable

surface of $\text{Pd}_8\text{Zn}_{44}$, (b) Arrhenius plot for ethylene hydrogenation over $\text{Pd}_9\text{Zn}_{43}$ (square) and $\text{Pd}_{10}\text{Zn}_{42}$ (triangle) in the temperature range 34-55°C with 5 Torr ethylene, 200 Torr hydrogen and balance He. (inset, left) DFT calculated most stable surface facet of $\text{Pd}_9\text{Zn}_{43}$ exposing Pd_3 trimer ensemble. (inset, right) DFT calculated most stable surface facet of $\text{Pd}_{10}\text{Zn}_{42}$ exposing double Pd_3 trimer ensemble. (c) DFT calculated ethylene hydrogenation barrier and desorption energy on $\text{Pd}_8\text{Zn}_{44}(1\bar{1}0)$, $\text{Pd}_9\text{Zn}_{43}(1\bar{1}0)$, $\text{Pd}_{10}\text{Zn}_{42}(1\bar{1}0)$ and $\text{Pd}(111)$ surfaces.

Synthesis and Characterization of [Pd, Zn] and [Pd, M, Zn] γ -brass Intermetallics

The [Pd,Zn] intermetallic compound allows us to systematically vary Pd content and thus the ensemble size of the active site. At the lower solubility limit of 8-Pd ($\text{Pd}_8\text{Zn}_{44}$), Rietveld refinement of XRD data revealed all 8 Pd atoms occupy the OT site. This has important consequences for the surface structure of the catalyst, as the Pd atoms are isolated from one another by Zn (Section S3 and Table S2).²¹ Increasing the Pd fraction beyond $\text{Pd}_8\text{Zn}_{44}$ leads to Pd occupation of the OH site (Table S2 and Figures S3 and S4); forming either 1 Pd_3 (9-Pd) or 2 Pd_3 (10-Pd) trimers per unit cell, which are exposed on the $(1\bar{1}0)$ facet (Figure 2a) of the material.

A first-principles based cluster expansion method (CEM)²² was employed to confirm the lowest-energy configuration among all the independent configurations (the total number of configurations is 2^{26} or 6.7×10^7) of 8-Pd and 10-Pd γ -brass phase using a 26-atom sublattice model of $(\text{Pd}, \text{Zn})_4^{\text{OT}}(\text{Pd}, \text{Zn})_4^{\text{IT}}(\text{Pd}, \text{Zn})_6^{\text{OH}}(\text{Pd}, \text{Zn})_{12}^{\text{CO}}$ ²⁰ (Figure 2b, for more details see Section S10). The CEM demonstrated the lowest energy configuration for 8-Pd places all 8 Pd in OT sites, whereas for 10-Pd, 8 Pd occupy OT sites and 2 Pd occupy OH sites. These results agree with our DFT calculations (Figures S3 and S4) and XRD Rietveld refinement results. In contrast to our previous research on the Ni-Zn γ -brass phase,²³ DFT calculations for the Pd-Zn γ -brass phase indicate a trimer containing $(1\bar{1}0)$ surface termination is energetically stable (Tables S4 and S5) and substantially (~ 50 % area basis) exposed in the Wulff particle construction (Figure 2c) for Pd-Zn γ -brass materials.

DFT was also used to consider the possibility of surface reconfiguration in which Pd surface aggregation (Pd monomers exchanged with Zn to expand the Pd trimer ensemble), and subsurface-to-surface exchange (sub-surface Pd atoms exchanged with Zn to expand the Pd trimer

ensemble) were considered. All reconfigurations were found to have highly unfavorable formation energies because these restructuring events require Pd atoms to reside in Zn-occupied surface lattice positions - an inherently unstable local atomic composition (Figure 2d). Thus, the combined experimental, CEM and DFT calculations demonstrated the Pd-Zn intermetallics with composition ranging from 8-Pd to 10-Pd could be synthesized with high phase purity and well-defined lattice siting. DFT calculations further confirmed Pd₃ trimers were stable and present on (1 $\bar{1}$ 0), a predominant exposed facet.

Figure 2. X-Ray Diffraction and Density Functional Theory results show the location of Pd atoms in the bulk and surface of [Pd, Zn] γ -brass structures. (a) XRD (black line) with Rietveld refinement fit (red dash) for Pd₉Zn₄₃. (inset, left) Rietveld refinement derived γ -brass crystal structure showing trimer Pd-M-Pd (in this case M = Pd) sites along the {110} orientation in the crystal lattice. (inset, right) Corresponding SEM-EDS showing homogenous distribution of Pd and Zn. (b) The formation enthalpies of Pd-Zn γ -brass configurations at 0 K are referenced to FCC Pd and HCP Zn. The black line is the convex hull determined by DFT calculations, the red triangles are the CEM results for Pd₈Zn₄₄ and Pd₁₀Zn₄₂ configurations. (c) DFT surface energies of low index facets for Pd₉Zn₄₃ along with the most favored termination for each orientation and

the corresponding Wulff construction. Numbers in the bar diagram represent relative exposure of respective terminations in the Wulff construction. The $\{110\}$ facet has two equally stable terminations (depicted here as $(1\bar{1}0)$ and (110) by virtue of the 4-fold crystal symmetry of the γ -brass phase) one having Pd_3 sites and the other only Pd_1 sites. From a Wulff construction of a particle, $\sim 45.5\%$ of the exposed surface area contains trimer sites (in addition to monomer sites which decrease in number per unit cell with Pd addition) (Tables S4 and S5). (d) Relative energies of restructured $\text{Pd}_9\text{Zn}_{43}$ $(1\bar{1}0)$ surfaces relative to the bulk-terminated, Pd_3 trimer containing surface. Pd_4 is constructed by swapping a sub-surface Pd with a Zn in the surface. Pd_5 is constructed by swapping 2 Pd monomers on the surface with Zn atoms adjacent to the Pd_3 trimer. Pd_6 is constructed by swapping Pd from the sub-surface and 2 Pd monomers on the surface with Zn atoms adjacent to the Pd_3 trimer.

Influence of Active Site Nuclearity (Pd-M-Pd trimer) on Catalytic Semi-Hydrogenation

Acetylene hydrogenation serves as a probe reaction to demonstrate how the relative density of isolated Pd sites impacts both hydrogenation activity and selectivity. Our experimental studies indicate Pd₁ monomers hydrogenate C-C triple bonds at a rate two orders of magnitude slower than Pd₃ trimers. Computational studies demonstrate the central atom of the Pd-M-Pd active ensemble plays a controlling role in governing catalyst performance. DFT calculations predict that, just as for Pd₉Zn₄₃, replacement of a single Zn atom in Pd₈Zn₄₄ by a coinage metal atom results in the formation of stable Pd-M-Pd ensembles (M = Cu, Ag, Au) both in the bulk and, more importantly, at the surface. Further, the catalytic performance (acetylene-ethylene competitive hydrogenation) of Pd-M-Pd ensembles is between Pd₁ and Pd₃.

Experiments confirm these predictions. As shown in Figure 3(a), acetylene hydrogenation activity increased by over two orders of magnitude from 8-Pd to 9-Pd, indicating a distinct change in active site morphology, which we attribute to the transition from Pd₁ to Pd₃ active sites. From 9-Pd to 10-Pd the areal rate doubles, due to the doubling of Pd₃ sites (as for ethylene hydrogenation) that overshadows any kinetic impact of the corresponding decrease in the number of Pd₁ sites. Pd foil exhibits an order of magnitude higher rate per area than 10-Pd and significantly lower ethylene selectivity. 8-Pd, consisting of only Pd₁ monomers on the surface, demonstrates high selectivity towards ethylene, due to its inactivity to hydrogenate ethylene, as previously discussed.

DFT calculations provide elementary reaction energetics that agree with the experimentally observed impact of Pd_n nuclearity on acetylene hydrogenation *activity*. On the 8-Pd surface, acetylene adsorbs in a di- σ mode across Pd₁-Pd₁ monomer sites (Pd₁ sites are spaced by 4.42 Å), whereas on the 9-Pd surface, acetylene adsorbs at Pd₃ hollow sites. Such adsorption configurations are consistent with literature.^{13,14,18} DFT energetics (Figure 3b, for more details see Figure S10

and Table S6) indicate both Pd₁ and Pd₃ sites have surmountable barriers for acetylene hydrogenation to ethylene. The di- σ binding mode of acetylene leaves room for H co-adsorption and hydrogenation transition state formation on Pd₁ sites. Pd₃ sites, however, have significantly lower C-H bond formation barriers than Pd₁ sites. Acetylene and hydrogen adsorption energies on the Pd(111) surface are significantly stronger than 8-Pd and 9-Pd, as shown in Figure 3b, indicating higher surface coverage of acetylene and hydrogen, and thus higher hydrogenation rate. DFT predictions agree with experimental observations that 8-Pd, 9-Pd, 10-Pd, and extended Pd surfaces are active for acetylene hydrogenation, with increasing activity as the Pd content increases.

DFT calculated elementary reaction energetics also predict the observed acetylene semi-hydrogenation *selectivity* for 8-Pd, exposing Pd₁ active sites. The DFT calculated ethylene hydrogenation barrier is significantly higher than the desorption energy on Pd₁ sites, indicating high selectivity towards ethylene formation. However, on the Pd₃ sites, the ethylene hydrogenation barrier is similar to the desorption energy, and hydrogenation becomes kinetically preferred on Pd(111). The difference between ethylene hydrogenation barrier and desorption energy on Pd₁ sites, Pd₃ sites and Pd(111) is in agreement with the experimental observation of decreasing ethylene selectivity with increasing Pd content.

The central atom of the Pd-M-Pd active ensemble plays a controlling role in governing ethylene hydrogenation activity because it controls the apparent barrier for C-H bond formation. With the middle atom of the trimer active ensemble replaced with a coinage metal (both in the bulk and more importantly on the surface) to form Pd-M-Pd ensembles (M=Cu, Ag, Au), activation barriers intermediate to Pd₁ and Pd₃ are calculated for both ethylene and acetylene hydrogenation, as shown in Figure 3c. The difference between ethylene hydrogenation and desorption barriers can be tuned between 0.51 eV on Pd-Zn-Pd to 0.11 eV on Pd-Pd-Pd, with the Pd-M-Pd series giving

intermediate values (0.32 eV on Pd-Au-Pd, 0.28 eV on Pd-Ag-Pd and 0.24 eV on Pd-Cu-Pd, Figure 3d). The acetylene hydrogenation barrier is similarly tunable as shown in Figure 3c. DFT results, therefore, predict addition of coinage metals in Pd-M-Pd sites will lead to acetylene hydrogenation activity and selectivity values intermediate to 8-Pd and 9-Pd. DFT calculation of reaction energies clearly demonstrate the nuclearity of the Pd-M-Pd active site can finely tune activity and selectivity. We demonstrate these predictions can be confirmed experimentally utilizing a synthetic approach with precise control of active site composition.

Figure 3: Experimental study of acetylene hydrogenation on Pd-Zn intermetallics and Pd foil and DFT reaction energy diagrams for acetylene hydrogenation on Pd-M-Pd (M = Zn, Pd, Au, Ag, Cu) sites. (a) Acetylene hydrogenation results at 160°C using $C_2H_2:H_2 = 1:100$. (b)-(c) Acetylene hydrogenation energy diagram on Pd-M-Pd. (d) Ethylene desorption energy and hydrogenation barrier on Pd-M-Pd. Structures with further details are presented in Table S6 and Figure S10.

Solid state diffusion, in a flame-sealed and evacuated quartz ampoule, at 800 °C was used to prepare ternary γ -brass intermetallics. XRD confirms phase pure [Pd, M, Zn] (M = Cu, Ag, Au) γ -brass materials can be synthesized (Figure S2). Using similar Rietveld refinement and DFT calculations, as described earlier (Section S3-6, Tables S3-S5 and Figure S5-S9) for [Pd, Zn], it is further confirmed Pd-M-Pd active sites form in [Pd, M, Zn] γ -brass materials because (i) M preferentially replaces Zn from OH sites and (ii) exposure of Pd-M-Pd trimers at the surface is energetically favorable in all these materials.

We used $^{13}\text{C}_2$ -ethylene and $^{12}\text{C}_2$ -acetylene to independently track conversion and allow for rigorous quantification of semi-hydrogenation selectivity during the hydrogenation of acetylene in excess ethylene (Section S9). $\text{Pd}_8\text{Zn}_{44}$, $\text{Pd}_9\text{Zn}_{43}$ and $\text{Pd}_8\text{AuZn}_{43}$ had comparable *intrinsic* ethylene selectivity ($= \frac{^{12}\text{C}_2\text{H}_4}{\Delta^{12}\text{C}_2\text{H}_2}$, Figure 4a) similar to ethylene selectivity for non-competitive acetylene hydrogenation (Figure 3a). More importantly, the *net* semi-hydrogenation selectivity ($= \frac{^{12}\text{C}_2\text{H}_4 - ^{13}\text{C}_2\text{H}_6}{\Delta^{12}\text{C}_2\text{H}_2}$, Figure 4a) on Pd_3 trimers on $\text{Pd}_9\text{Zn}_{43}$ is far below its intrinsic value because of the simultaneous hydrogenation of $^{13}\text{C}_2$ -ethylene. Net ethylene selectivity for $\text{Pd}_8\text{Zn}_{44}$ is within ~15% of its intrinsic value (and far superior to $\text{Pd}_9\text{Zn}_{43}$) even at ~100% acetylene conversion (Figure 4b). The single Pd atoms cannot supply hydrogen to C-C double bonds because π -bound ethylene blocks H_2 dissociative adsorption, H co-adsorption and C=C hydrogenation, whereas di- σ acetylene binding across a Pd monomer “pair” allows H co-adsorption and C $\equiv$ C hydrogenation. $\text{Pd}_8\text{AuZn}_{43}$ demonstrates an intermediate net ethylene selectivity between $\text{Pd}_8\text{Zn}_{44}$ and $\text{Pd}_9\text{Zn}_{43}$, due to the trimer ensemble modification as predicted by DFT calculations. Figures S11 and S12 demonstrate $\text{Pd}_8\text{Ag}_3\text{Zn}_{41}$ and $\text{Pd}_8\text{Cu}_3\text{Zn}_{41}$ have intermediate activities and selectivities between 8-Pd and 9-Pd catalysts.

Figure 4. Competitive hydrogenation of $^{13}\text{C}_2$ -ethylene and $^{12}\text{C}_2$ -acetylene mixed feed over γ -brass [Pd, (Au) Zn] catalysts. (a) ^{13}C (black) $_2$ -ethylene and ^{12}C (grey) $_2$ -acetylene reaction path and definition of intrinsic and net selectivity. Note the net selectivity can take on negative values if the rate of ^{13}C -ethylene hydrogenation is greater than the rate of ^{12}C -acetylene hydrogenation. (b) Net and intrinsic ethylene hydrogenation selectivity of Pd₈Zn₄₄ (red and black square, respectively), Pd₉Zn₄₃ (red and black triangle, respectively) and Pd₈AuZn₄₃ (red and black circle, respectively) at 160 °C, $^{12}\text{C}_2\text{H}_2$: $^{13}\text{C}_2\text{H}_4$: H_2 = 1:31:18.

As a final proof of precise control over these model catalytic systems, we correlate DFT performance descriptors ($\exp(-\frac{E_{C_2H_2}^{act}^{hydro}}{RT})$ for activity and $E_{C_2H_4}^{act}^{hydro} - E_{C_2H_4}^{des}$ for selectivity) with experimental performance (Figure 5). The first acetylene C-H formation barrier is a reasonable descriptor for acetylene hydrogenation activity given the strong adsorption of acetylene. The difference of ethylene hydrogenation barrier and desorption energy is used as a selectivity descriptor, as applied previously.^{20,24} Both activity and selectivity show strong agreement between experimental kinetics and DFT, thus providing evidence of excellent control of these multi-nuclear-heteroatomic active ensembles through subtle stoichiometric tuning and introduction of an additional metal atom.

Figure 5. Experimental and computational comparison of acetylene semi-hydrogenation on γ -brass [Pd, (M), Zn] (M = Zn, Pd, Cu, Ag, Au). Qualitative agreement between experimental activity (a) and selectivity (b) with corresponding DFT descriptors to evaluate catalyst performance for acetylene semi-hydrogenation.

In conclusion, we demonstrate the [Pd, (M), Zn] γ -brass crystal structure can be manipulated to reliably access well-defined, isolated, catalytically relevant 3-atom active sites of the form Pd-M-Pd which are distinct amongst themselves and from fully coordinated Pd sites. These model surfaces demonstrate the impact of active atom nuclearity on catalytic performance in Pd-catalyzed hydrogenation chemistry. These precise Pd-M-Pd ensembles are experimentally easy to access and convenient for DFT modeling due to their single crystal-like nature to enable probing the impact of active site nuclearity on catalytic activity and selectivity. From this work, the use of intermetallic compounds can be extended to create active sites that are potentially tuned to the molecular footprint of any hydrocarbon reactant/product of interest. Such materials will be key in the pursuit of atomically precise active site generation for selective conversion with high atom efficiency.

Methods

The γ -brass phase materials were synthesized using a solid-state diffusion method.^{21,25-27} X-ray diffraction (XRD) was performed on a PANalytical X'pert Pro instrument using constant wavelength Cu K α radiation. A graphite monochromator was used on the detector side to cut off K β peaks that can interfere with refinement. Rietveld refinement was conducted using the EXPGUI interface of the General Structure Analysis System (GSAS) software package.^{28,29} Ethylene hydrogenation experiments were performed in a fritted glass tube (10 mm ID, ChemGlass) operating as a plug-flow reactor. Catalysts were reduced for 8 h at 250°C in hydrogen and then held for 20 min at that temperature under He flow before being cooled under He flow to the desired reaction temperature. The product stream was analyzed with an online Hewlett Packard 5890 Series II GC. All conversions were below 10% and may be considered differential. Competitive acetylene and isotopically-labeled ethylene hydrogenation was performed in a home-made batch

reactor similar to that used by Spanjers et al.²⁶ The reactor tube had an outer diameter of 5 mm. The batch reactor was evacuated to 180 mTorr before filling with reactant gases. The catalyst was initially reduced for 4 h at 250°C by evacuating the set-up and back-filling to ~850 Torr hydrogen. It was then cooled to room temperature, evacuated, and filled with 550 Torr 1% acetylene, 170 Torr ¹³C₂-ethylene (99%, Sigma Aldrich), 100 Torr hydrogen (UHP, Praxair) and 20 Torr Ar (UHP, Praxair) and subsequently heated up to the reaction temperature. Gases were sampled via a 100 µL gas-tight syringe (Hamilton Company) and the products analyzed with a Shimadzu 2010 QP Ultra GC-MS. The Ar signal ($m/z = 40$) is used as an internal standard to correct for fluctuations in sample injection volume. Details on the synthesis, characterization, and reactivity studies of the [Pd, (M), Zn] γ -brass intermetallics are available in the Supplementary Information.

All DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP).³⁰⁻
³² The Perdew–Burke–Ernzerhoff (PBE) generalized gradient approximation was applied with a plane wave basis set with energy cutoff of 450 eV.³³ The Methfessel-Paxton (MP) smearing method was applied in all calculations with a broadening value of 0.2 eV.³⁴ Structural optimizations were carried out until forces on all atoms were less than 0.05 eV/Å. A $6 \times 6 \times 6$ Monkhorst–Pack k-point mesh sampling was used for bulk (Pd₈Zn₄₄, Pd₉Zn₄₃, Pd₁₀Zn₄₂, Pd₈AgZn₄₃, Pd₈CuZn₄₃ and Pd₈AuZn₄₃) optimization.³⁵ The nudged elastic band (NEB) method was applied to locate transition states as the highest energy image with tangential force to the reaction coordinate less than 0.05 eV/Å, and each transition state was verified through the existence of a single imaginary vibrational frequency.³⁶ Further details on the DFT calculations and CEM are available in the Supplementary Information.

Data Availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code Availability

All computational codes/algorithms utilized in this study were performed with either commercially available or open-source software.

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Author Contributions

These authors contributed equally: Anish Dasgupta, Haoran He.

A. D., E. K. Z., and R. M. R. planned, executed, and analyzed the experimental work. H. H. and M. J. J. performed and analyzed the density functional theory computational work. R. G., S. S., and Z. L. performed and analyzed the cluster expansion method work. R. J. M, M. J. J, and R. M. R. conceived the work and supervised the research. A. D. and H. H. wrote the paper with contributions from all authors.

Competing Interest

The authors declare no competing financial interests.

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Figure 1

Figure 2

See manuscript for full figure caption.

Figure 3

Experimental study of acetylene hydrogenation on Pd-Zn intermetallics and Pd foil and DFT reaction energy diagrams for acetylene hydrogenation on Pd-M-Pd (M = Zn, Pd, Au, Ag, Cu) sites. (a) Acetylene hydrogenation results at 160°C using $\text{C}_2\text{H}_2:\text{H}_2 = 1:100$. (b)-(c) Acetylene hydrogenation energy diagram on Pd-M-Pd. (d) Ethylene desorption energy and hydrogenation barrier on Pd-M-Pd. Structures with further details are presented in Table S6 and Figure S10.

Figure 4

Competitive hydrogenation of $^{13}\text{C}_2$ -ethylene and $^{12}\text{C}_2$ -acetylene mixed feed over γ -brass [Pd, (Au) Zn] catalysts. (a) ^{13}C (black) $_2$ -ethylene and ^{12}C (grey) $_2$ -acetylene reaction path and definition of intrinsic and net selectivity. Note the net selectivity can take on negative values if the rate of ^{13}C -ethylene hydrogenation is greater than the rate of ^{12}C -acetylene hydrogenation. (b) Net and intrinsic ethylene hydrogenation selectivity of $\text{Pd}_8\text{Zn}_{44}$ (red and black square, respectively), $\text{Pd}_9\text{Zn}_{43}$ (red and black

triangle, respectively) and Pd₈AuZn₄₃ (red and black circle, respectively) at 160 °C, 12C₂H₂:13C₂H₄:H₂ = 1:31:18.

Figure 5

Experimental and computational comparison of acetylene semi-hydrogenation on γ-brass [Pd, (M), Zn] (M = Zn, Pd, Cu, Ag, Au). Qualitative agreement between experimental activity (a) and selectivity (b) with corresponding DFT descriptors to evaluate catalyst performance for acetylene semi-hydrogenation.

Supplementary Files

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