Bimetallic Nanoparticles: Synthesis, Characterization, and Applications in Catalysis

By

Alexandra Marcela Landry

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Committee in charge:

Professor Enrique Iglesia, Chair
Professor Alexander Katz
Professor Andrew Minor

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Abstract

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Bimetallic nanoparticles can lead to catalysts with improved turnover rates and selectivities, but many synthetic protocols, such as impregnation or precipitation, typically form particles of non-uniform size and composition. Colloidal methods may be able to improve their uniformity, but often require reagents that poison catalytic surfaces (ex. S, B, P). Such compositional non-uniformity and ubiquitous impurities have prevented rigorous conclusions about the consequences of alloying on reactivity and selectivity. Herein, we describe a sequential galvanic displacement-reduction (GDR) colloidal synthesis method using precursors containing only C, H, O, and N, that leads to bimetallic AuPt and PtPd nanoparticles narrowly distributed in size and composition.

Au<sup>3+</sup> or Pt<sup>4+</sup> precursors were added to monometallic Pt or Pd clusters, respectively, whose surface atoms are thermodynamically driven to reduce and deposit the solvated cations onto cluster surfaces due to the lower reduction potentials (E<sub>0</sub>) of the seed metal relative to the precursor cations (E<sub>0</sub> Au < E<sub>0</sub> Pt < E<sub>0</sub> Pd); oxidized Pt and Pd surface atoms subsequently return to cluster surfaces upon reduction by the solvent, a reductant (ethanol or ethylene glycol, respectively). Such methods have been previously used to synthesize AuPd clusters from Pd seed clusters.

TEM micrographs confirm that initial seed cluster sizes increase monotonically with increasing Au<sup>3+</sup> or Pt<sup>4+</sup> content, with final bimetallic cluster dispersity values near unity indicating a narrow size distribution. UV visible spectroscopy of AuPt cluster suspensions show no plasmon resonance features characteristic of Au nano-sized surfaces, indicating the presence of Pt atoms at bimetallic surfaces, as expected for GDR processes. Elemental analysis using EDS confirmed the formation of strictly bimetallic particles with the mean composition of the synthesis mixture.

The GDR model requires that bimetallic growth be proportional to the initial seed surface area, with the number of precursor atoms deposited per surface metal atom of the seed constant and independent of seed metal size. Elemental analysis using EDS supports this hypothesis for thermodynamically favorable alloys such as PtPd and AuPd, but not for AuPt, an unfavorable alloy. These differences appear to reflect the segregation of metals within AuPt clusters during synthesis, placing the metal with the lower surface energy, Au, at cluster surfaces, and
decreasing the availability of Pt$^0$ surface atoms for GDR. Consequently, autocatalytic Au$^{3+}$ reduction on Au$^0$ sites becomes a competitive Au$^{3+}$ reduction pathway during the synthesis of AuPt clusters.

Polymers such as polyvinylpyrrolidone (PVP)—which bind to metal surfaces during synthesis via charge-transfer interactions—were required in colloidal suspensions to prevent particle agglomeration in solution, but must be removed prior to catalysis. We show that after depositing clusters on SiO$_2$, PVP can be removed from particle surfaces by post-synthetic treatments at mild temperatures (≤ 423 K) in reductants such as H$_2$ and/or EtOH without significant particle agglomerations. Reductants compete with the polymer at the metal surface, thus breaking the polymer-metal bond. The absence of surface residues was confirmed by the similar cluster sizes derived from O$_2$ chemisorption and TEM measurements. Larger cluster sizes and surfaces that chemisorb oxygen more weakly—such as Pt relative to Pd—were found to facilitate the removal of PVP from metal particles due to weaker metal-polymer bonds.

The model catalytic materials prepared in this study are of both fundamental and practical interest to probe the effects of alloying. Using AuPd and AuPt, we investigate the consequences of alloying with Au on the reactivity of catalyst surfaces saturated with either chemisorbed CO* (CO oxidation) or O* (H$_2$ oxidation) that bind strongly to Pt and Pd surfaces and inhibit rates. Singleton Pt-CO* bond energies, reflected in vibrational CO* stretches, were decoupled from dipole-dipole coupling effects using isotopic dilution methods, and were shown to decrease with increasing catalyst Au content. Despite lower CO* binding energies, CO oxidation turnover rates (normalized per metal surface atom) on AuPt catalysts decreased with increasing Au content. These results show that CO oxidation rates depend weakly on CO* binding energy—consistent with the reported structured insensitivity of this reaction—and that Au acts primarily as an inert diluent of the active Pt ensembles required for catalysis.

In contrast, H$_2$ oxidation turnover rates (normalized per metal surface atom) on AuPt and AuPd catalysts increase with increasing Au content (up to 11 % at. Au content on AuPt and up to 67 % at. Au content on AuPd), indicating that the reactivity of O* saturated surfaces is more sensitive to changes in adsorbate binding energy than surfaces saturated in CO*, consisted with the reported structure sensitivity of reactions on O* saturated surfaces. Reconstruction of CO* adlayers is facile due to highly mobile CO* molecules, thus allowing CO* adlayers to access configurations that help mitigate strong CO* binding and introduce vacancies. O* adlayers, meanwhile, are more strongly bound to Pt and Pd metal surfaces and less mobile. H$_2$ oxidation rates thus depend more strongly on adsorbate binding energy than CO oxidation rates.
Table of Contents

Chapter 1: *Introduction to Bimetallic Nanoparticle Synthesis and Catalysis Catalysts* 1
   References 5

Chapter 2: *Synthesis of Bimetallic AuPt Clusters with Clean Surfaces via Sequential Displacement-Reduction Processes* 6
   2.1 Introduction 6
   2.2 Methods 9
   2.3 Results and Discussion 13
   2.4 Conclusions 31
   2.5 Acknowledgements 31
   2.6 Supporting Information 32
   2.7 References 37

Chapter 3: *Displacement-Reduction Strategies for the Synthesis of Uniform PtPd Clusters with Clean Surfaces and Mechanistic Guidance for Other Bimetallic Systems* 39
   3.1 Introduction 39
   3.2 Methods 41
   3.3 Results and Discussion 44
   3.4 Conclusions 57
   3.5 Acknowledgements 58
   3.6 Supporting Information 59
   3.7 References 63

Chapter 4: *Consequences of Alloying Pt or Pd with Au on CO Oxidation and H₂ Oxidation Turnover Rates* 65
   4.1 Introduction 65
   4.2 Methods 67
   4.3 Results and Discussion 70
   4.4 Conclusions 85
   4.5 Acknowledgements 85
   4.6 References 86
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Chapter 1

Introduction to Bimetallic Nanoparticle Synthesis and Catalysis

Supported bimetallic clusters are used ubiquitously as catalysts for a number of applications including naptha reforming\textsuperscript{[1]} and the conversion of noxious gases in automobile exhaust,\textsuperscript{[2]} and are also studied extensively as possible cost effective materials for the electrodes of hydrogen fuel cells.\textsuperscript{[3]} Bimetallic catalysts are used because they can increase turnover rates, enhance selectivity, and/or improve catalyst stability;\textsuperscript{[1, 4]} the consequences of alloying are attributed to changes in the electronic properties of the catalyst surface (ligand effect), dilution of monometallic ensembles of surface atoms (geometric effect), or a combination of ligand and geometric effects.\textsuperscript{[4]} The interaction between two metals is complex and often not well understood, however, grounding the study of bimetallic catalysis in empirical, rather than fundamental, knowledge. A pervasive obstacle to developing such fundamental understanding of the structure-function relationship of alloys is the confounding effects from other catalyst properties—such as particle size, support interactions, and surface impurities—that also influence catalytic behavior and vary widely between samples. Clusters within a single sample may also vary broadly in cluster size and composition. Such variability stems from imprecise synthesis methods. Here, we discuss the controlled synthesis of bimetallic AuPt, AuPd, and PtPd nanoparticles uniform in both size and composition using reagents with no poisonous heteroatoms; after dispersing clusters onto an inert support, we describe how metal surfaces can be cleared of synthetic residues, exposing the surface metal atoms required for catalysis. Such materials are ideal model catalysts for studying the effects of alloying Au, Pt, and Pd, and are used here to show how combining Au with Pt or Pd influences CO oxidation rates and H\textsubscript{2} oxidation rates.

The most commonly used technique to synthesize bimetallic catalysts is incipient wetness impregnation of the support with a solution of the metal precursors.\textsuperscript{[5]} Although this technique is simple to execute, the two metals are not coerced to interact with one another, resulting in clusters that vary widely in composition and often include monometallic clusters. In addition, particle size distributions are broad, further complicating the study of the catalytic behavior of such samples.\textsuperscript{[6]} As such, correlations between catalyst performance and composition become difficult to resolve.

The synthesis of bimetallic clusters via electroless deposition (ED) is an attractive alternative to incipient wetness impregnation.\textsuperscript{[7]} ED involves first preparing a monometallic catalyst by traditional impregnation methods, and subsequently treating it in a carefully regulated solution of the second metal precursor such that the second metal selectively deposits on the initial clusters. Such techniques, however, limit the bimetallic compositions that can be achieved, as the selective deposition of the second metal is impeded once the surface of the initial seed clusters is obscured by the deposited metal.

Synthesizing bimetallic clusters within zeolites has been shown to yield highly dispersed and uniform clusters, often with intimate contact between the two metals.\textsuperscript{[8]} However, the zeolite pore structure can impose unwanted steric effects, confounding the consequences of alloying. The deposition of molecular bimetallic precursors containing preformed metal-metal bonds onto
a support and their subsequent treatment to form bimetallic clusters has also shown promise for the preparation of bimetallic catalysts,[9] although the protocols required to ensure that metals remain mixed, that clusters do not aggregate, and that the coordinating ligands are removed are challenging.

In contrast, the preparation of bimetallic clusters via colloidal methods is simple and highly reproducible.[10] Such techniques produce highly dispersed metal particles while avoiding problematic metal-support interactions during cluster formation. They are also easily and precisely tuned—by changing the temperature, the reductant, the protecting agent, and other parameters—to obtain the desired cluster properties.[11] Although colloidal methods have shown promise to form compositionally uniform bimetallic clusters, they frequently require the use of protecting agents and/or reductants with strongly-binding heteroatoms (ex. S, P, B) that are difficult to remove after synthesis and can alter catalytic activity.[12] Here, we use colloidal methods and reagents containing only C, H, O, and N to synthesize bimetallic nanoparticles uniform in size and composition that can be dispersed onto an inert support (SiO$_2$) and cleaned of remaining surface residues via treatment at mild temperatures in a reductive environment.

Clusters were prepared using galvanic displacement-reduction (GDR) protocols previously shown to selectively deposit solvated Au cations onto pre-made Pd seed clusters to yield bimetallic AuPd clusters (Scheme 1).[13] GDR exploits the relative reduction potentials ($E^0$) of the two metals to ensure metal mixing: surface atoms of seed clusters composed of the metal with the lower $E^0$ are thermodynamically driven to reduce the solvated cations of the more noble metal (step 2a). As the solvated metal species are reduced, the surface metal atoms get oxidized and dissolve into solution. Oxidized surface atoms are subsequently reduced back onto growing bimetallic cluster surfaces by the solvent, a reductant (step 2b). Growth of the seed particles via GDR is proportional to the initial seed surface area, with the number of precursor atoms deposited per surface metal atom of the seed constant and independent of seed metal size. Thus, all seed clusters increase in diameter by a constant value ($\Delta d$), irrespective of initial size.

![Scheme 1](image)

Scheme 1 Galvanic displacement-reduction synthesis involves metal surface atoms of pre-made seed particles ($\bullet$, [M$_A$]) reducing solvated metal cations ($\bullet$, M$_B^{n+}$) of the more noble metal due to a positive $\Delta E^0_{\text{redox}}$ (step 2a, M$_B > \{M_A\}$). The solvent, a reductant, re-reduces the oxidized seed surface atoms (step 2b) back onto growing bimetallic cluster surfaces. Nucleation of M$_B$ (path 1) must be avoided to ensure a uniform bimetallic sample.

We discuss the required modifications of the GDR protocols developed for AuPd clusters, a thermodynamically favorable alloy, to synthesize AuPt clusters, a thermodynamically unfavorable alloy, in Chapter 2. Endothermic alloys such as AuPt tend to phase segregate, and the synthesis of such samples favors the formation of monometallic clusters or clusters enriched in one of the metals (Scheme 1.1). The synthesis of AuPt samples without heterogeneous or homogeneous nucleation of Au cations—which lead to the formation of large Au-rich clusters that compromise the size and compositional uniformity that we seek—requires a slower addition of the Au precursor and higher synthesis temperatures relative to AuPd synthesis. The former maintains low concentrations of Au species in solution that can nucleate, while the latter
promotes the entropic contributions of mixing—that dominate at higher temperatures—to decrease Gibbs free energies.

AuPt clusters were characterized using transmission electron microscopy, UV-visible spectroscopy, high angle annular dark-field imaging, and energy dispersive X-ray spectroscopy (EDS), which confirm that clusters are bimetallic and uniform in size and composition. Particle-by-particle elemental analysis by EDS reveals that the growth of the Pt seed clusters (∆d) increases with increasing seed particle size, in contrast to the expectation for GDR growth. These differences appear to reflect size-dependent intra-cluster diffusion during synthesis—a consequence of the enthalpic unfavorability of AuPt—which determines the composition of cluster surfaces and the availability of Pt metal surface atoms for reducing solvated Au cations via GDR.

In contrast, the seed clusters of thermodynamically favorable alloys such as AuPd and PtPd, discussed in Chapter 3, all grow by a constant value ∆d regardless of initial seed diameter, consistent with the growth of seed particles via GDR processes. Seed clusters of varying sizes that all increase in diameter by the same amount (∆d) via addition of a second metal results in bimetallic clusters with a distribution of compositions: larger seed clusters ultimately contain relatively less of the second metal than smaller clusters due to smaller surface-to-volume ratios. Thus, the breadth of the initial seed cluster size distribution governs the breadth of the final bimetallic cluster composition distribution.

Prior to their use as catalysts, clusters within colloidal suspensions are dispersed onto a support (SiO₂) and their protecting polymers (polyvinylpyrrolidone, PVP), which were required to prevent particle agglomeration in solution, are removed. PVP binds to metal surfaces via charge-transfer interactions; reductants compete with the polymer at the metal surface, thus breaking the polymer-metal bond. We show that adsorbed PVP can be removed from Pt (Ch. 2), PtPd, and Pd (Ch. 3) cluster surfaces by low temperature treatment (≤ 423 K) in H₂ or EtOH without significant particle agglomeration. The absence of surface residues or sintering was confirmed by the similar cluster sizes derived from O₂ chemisorption and TEM measurements. PVP binds to Au atoms more weakly than Pt or Pd atoms; thus, the strategies developed here for Pt and Pd should also be effective for Au-containing alloys.

In Chapter 4, we explore how Au alters the catalytic reactivity of Pt and Pd catalysts for reactions limited by the high binding energies of adsorbates. Specifically, we examine the effects of alloying with Au on CO oxidation turnover rates on Pt surfaces saturated in CO*, and on H₂ oxidation turnover rates on Pt and Pd surfaces saturated in O*. Au atoms, which have a higher electronegativity than Pt or Pd, are expected to withdraw electron density away from neighboring active metals, potentially decreasing the strength of the M-CO* and M-O* bonds (ligand effect). Au atoms may also interrupt Pt or Pd surface ensembles (geometric effect), thus disrupting the dense, stable, and unreactive adlayer that leads to lower rates, similar to the effect of C* on Pt surfaces saturated in CO* during CO oxidation rates in H₂-CO mixtures.

We show that CO oxidation turnover rates (per metal surface atom) on AuPt catalysts at 443 K decreases with increasing catalyst Au content, in spite of AuPt catalysts having lower apparent activation energy barriers and weaker Pt-CO* binding energies—as determined by isotopic
dilutions studies that isolate the singleton vibrational frequency of CO* bound to Pt in the absence of dipole-dipole coupling. These results are consistent with the structure insensitivity of CO oxidation catalysis on Pt,\cite{15c} which is a consequence of the weak dependence of CO oxidation turnover rates on CO* adsorbate binding strength. The ligand effects proffered by Au that decrease Pt-CO* binding energies are thus outweighed by its role as an inert diluent of the Pt ensembles required for catalysis. In contrast, H₂ oxidation turnover rates are higher on AuPt and AuPd catalysts than on their monometallic counterparts. Au decreases the binding energy of M-O* via a ligand effect and/or geometric effect that decreases the strength of the M-O* bond, thus rendering surface O* more reactive and aiding in generating the vacancy sites required for turnovers. The present study is consistent with O* saturated surfaces being more sensitive than CO* saturated surfaces to changes in particle size and, thus, in changes to adsorbate binding energies.

This dissertation discusses the synthesis strategies essential to forming uniform bimetallic nanoparticles of both thermodynamically unfavorable (AuPt; Ch. 2) and favorable (PtPd; Ch.3) alloys via GDR processes, and how such clusters, upon deposition onto a support, can be cleaned of synthetic residues without compromising particle uniformity. The insights developed here can be extended to other bimetallic systems of interest, and is crucial to developing the materials necessary for rigorous mechanistic studies of the effect of composition on reactivity and selectivity. Using AuPt and AuPd catalysts prepared by the protocols described herein, we gain insight into the consequences of alloying Au, Pd, and Pt on reaction rates limited by O* and CO* saturated surfaces (Ch. 4).
References

Chapter 2

Synthesis of Bimetallic AuPt Clusters with Clean Surfaces via Sequential Displacement-Reduction Processes

Abstract

We report the synthesis of bimetallic AuPt nanoparticles (3.3 - 4.3 nm diameter) uniform in size and composition using colloidal methods and reagents containing only C, H, O, and N. Clusters were dispersed onto SiO$_2$ and treated at low temperatures ($\leq$ 423 K) in the presence of a reductant (H$_2$ and 1:1 by volume H$_2$O:EtOH) to remove all surface residues without particle agglomeration, thus yielding model bimetallic catalysts ideal for rigorous mechanistic studies that examine the structure-function relationships of Au-Pt alloys. Clusters were prepared using a galvanic displacement-reduction (GDR) protocol previously developed to synthesize AuPd clusters that promotes metal mixing by exploiting the relative standard reduction potentials of the alloyed metals. Several key parameters of the previously proposed protocols were modified in order to avoid the formation of large (> 5.5 nm) Au-rich clusters that compromise both the size and compositional uniformity of bimetallic AuPt samples. In doing so, we extend the GDR protocols developed for an exothermic alloy (AuPd) to an endothermic one (AuPt). The successful formation of uniform clusters was probed by UV-visible spectroscopy, transmission electron microscopy, high angle annular dark-field (HAADF) imaging, and energy-dispersive X-ray spectroscopy (EDS). Particle-by-particle elemental analysis using EDS in tandem with HAADF imaging was used to show that size-dependent intracluster diffusion—driven by the unfavorable thermodynamics of AuPt alloys—alters the surface composition of the growing bimetallic nanoparticles during synthesis, thereby altering the available pathways for bimetallic growth on cluster surfaces. In the case of AuPt, surfaces become enriched in Au, replacing the surface Pt atoms required for GDR synthesis, and instead promoting fast autocatalytic reduction of Au precursors that renders the controlled formation of uniform clusters more challenging. The insights developed here are valuable for the synthesis of other bimetallic systems of interest using the GDR approach.

2.1 Introduction

The combination of two metals within a small crystallite of nanometer dimensions can lead to marked consequences for turnover rates and selectivities in the practice of heterogeneous catalysis.$^{[1]}$ Bimetallic catalysts are known to increase rates and improve selectivity of Fischer-Tropsch synthesis;$^{[2]}$ they are also used for NO$_x$ reduction and CO oxidation reactions,$^{[3]}$ as well as in electrodes for methanol and H$_2$ fuel cells.$^{[4]}$ The development of rigorous mechanistic descriptions of the effects of atomic metal mixing and their applications in predictive catalyst design criteria require the preparation of bimetallic clusters that are uniform in both size and chemical composition, but which also expose surfaces free of residual synthetic detritus. Conventional catalyst synthesis protocols, such as incipient wetness impregnation, seldom deposit the two metals within the same cluster, thus failing to provide the intimate metal mixing required for bimetallic synergies.$^{[5]}$ Also, the broad particle size distributions typical of such techniques convolute the consequences of bimetallic mixing and cluster size.$^{[6]}$ Colloidal synthesis methods, in contrast, provide greater control of the final particle size and
composition,\textsuperscript{[1b, 7]} but typically require reagents containing heteroatoms (e.g. S or B) that block active structures at catalyst surfaces. Non-uniformity in cluster composition and size, together with these ubiquitous surface impurities, have frequently led to ambiguous and imprecise interpretations of bimetallic effects in catalysis.

Our recent studies have provided evidence for sequential galvanic displacement-reduction (GDR) processes in the formation of AuPd clusters.\textsuperscript{[8]} These synthetic protocols use weakly-coordinating reagents containing only C, H, O, and N atoms, and form clusters uniform in size and composition. Reagents can be readily removed, without marked consequences for the size or composition of clusters, using oxidants such as O$_3$.\textsuperscript{[8]} or by carrying out treatments at low temperatures in reducing environments, as the current study demonstrates. GDR synthesis protocols start with colloidal suspensions of pre-formed seed clusters of the element (M$_A$) with the lower standard reduction potential (E$^0$); these suspensions are then mixed with a solution of cations of the precursor of the second element (M$_B$; Scheme 1). The surface metal atoms in the seed clusters reduce the metal cations in solution, driven by the favorable thermodynamics inherent in the positive $\Delta E_{\text{redox}}^0$ values ($\Delta E_{\text{redox}}^0 = E^0_{\text{red. (M}_A) - E^0_{\text{ox. (M}_B)$ > 0) for the overall redox reaction (Scheme 1.2a). Such reactions lead to the deposition of the second metal onto the seed clusters, while surface atoms of the seed clusters are oxidized and brought into solution as solvated cations. The solvent also acts as a reductant, subsequently reducing the solvated M$_A$ cations formed from the initial seed clusters back onto the growing bimetallic cluster surfaces (Scheme 1.2b) at rates proportional to the surface area of each cluster.\textsuperscript{[8]}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\end{scheme}

\textbf{Scheme 1} Galvanic displacement-reduction synthesis processes: surface atoms of seed particles composed of M$_A$ (●) reduce M$_B$ cations (○) due to a positive $\Delta E_{\text{redox}}^0$, and are concurrently oxidized into solution (step 2a). The reductant (ethanol or ethylene glycol) subsequently re-reduces the oxidized seed surface atoms back onto growing bimetallic particle surfaces (step 2b). Heterogeneous or homogeneous nucleation of Au (step 1) must be avoided to ensure size and compositional uniformity.

These GDR steps were previously shown to form AuPd nanoparticles starting from Pd seed clusters.\textsuperscript{[8]} The mechanistic details of such synthesis protocols led us to infer that similar approaches would succeed for other bimetallic combinations, provided that the suspensions initially contained clusters of the element with the lower standard reduction potential (Table 1). We show here that, with minor modifications in synthesis protocol, this is the case for AuPt particles formed from Pt seed particles; we also confirm the relevant mechanistic details for both AuPt and AuPd systems by means of rigorous statistical analysis of the size and composition of individual bimetallic clusters using electron microscopy. Specifically, we use energy-dispersive X-ray spectroscopy (EDS) and high-angle annular dark-field (HAADF) imaging to determine the size and composition of a large number (> 100) of AuPd and AuPt clusters (< 5.5 nm) prepared using these methods. The small size of such clusters is essential for their function as catalysts,
but requires state-of-the-art methods to accurately assess the composition of each particle, thus requiring the sensitivity of the advanced EDS detectors used here.

**Table 1** Standard reduction potentials of metals of catalytic interest.

<table>
<thead>
<tr>
<th>Element</th>
<th>E° = Standard Reduction Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au^{3+}</td>
<td>1.52</td>
</tr>
<tr>
<td>Pt^{2+}</td>
<td>1.18</td>
</tr>
<tr>
<td>Pd^{2+}</td>
<td>0.99</td>
</tr>
<tr>
<td>Ir^{3+}</td>
<td>0.92</td>
</tr>
<tr>
<td>Ag^{+}</td>
<td>0.80</td>
</tr>
<tr>
<td>Rh^{3+}</td>
<td>0.60</td>
</tr>
<tr>
<td>Ru^{2+}</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>-0.26</td>
</tr>
<tr>
<td>Co^{2+}</td>
<td>-0.28</td>
</tr>
</tbody>
</table>

The data obtained and reported here confirm that seed clusters of M_A act as reductants during bimetallic formation; the rate of M_B reduction (and of M_A oxidation) is proportional to the seed cluster surface area for AuPd.\[^{[8]}\] This is in contrast to AuPt, for which the larger seeds consume more Au than expected from their surface area alone. Unlike Au-Pd, Au and Pt atoms mix endothermically (ΔH_{AuPt} = +2.3 kJ mol⁻¹ vs. ΔH_{AuPd} = -6.7 kJ mol⁻¹),\[^{[11],[12]}\] thus driving metal atoms to segregate within clusters by placing the metal with the lower surface energy (Au)\[^{[13]}\] preferentially at cluster surfaces.\[^{[14],[15]}\] Larger clusters with larger bulk reservoirs of Au maintain the thermodynamic driving force for Au surface enrichment by mitigating the depletion of Au from the bulk upon segregation, consequently increasing their Au⁰ surface contents.\[^{[16]}\] The Au-rich cluster surfaces of the larger AuPt clusters impede GDR reduction routes by minimizing accessible Pt⁰ atoms and instead promoting the fast autocatalytic reduction of Au cations on Au⁰ atoms\[^{[17]}\] that scavenge solvated Au cations, thus preventing their ultimate deposition onto smaller clusters.

The smaller ΔE°_{redox} driving force for displacement reactions (Scheme 1.2a), the stronger (competing) reductant required as the solvent (ethylene glycol for AuPt; ethanol for AuPd), and the enrichment of bimetallic surfaces with Au⁰ impose additional hurdles in the synthesis of uniform AuPt clusters relative to AuPd clusters. As a result, more precise protocols become essential to avoid the enrichment of the larger Pt seed clusters with Au and the homogeneous nucleation of pure Au clusters (illustrated in Scheme 1.1), both of which detract from the size and compositional uniformity that we seek in these bimetallic materials. In the synthetic protocols that we report here, the continuous addition of low concentrations of solvated Au precursors is used to inhibit homogeneous nucleation, while higher synthesis temperatures are used to compensate for the unfavorable mixing enthalpies through mixing entropies that become more consequential for Gibbs free energies as temperature increases.
2.2 Methods

2.2.1 Synthesis of Monometallic and Bimetallic Nanoparticles

Scheme 2 Colloidal synthesis protocol via sequential galvanic displacement-reduction processes. a) Metal precursor \( \text{M}_A \) and the protecting polymer ( ) are combined in a reductive solvent ( ) and heated to form a suspension of polymer-protected seed clusters. b) Metal precursor \( \text{M}_B \) is added to the suspension and c) subsequently reduced and incorporated into the monometallic seed clusters to form bimetallic clusters. d) Clusters are dispersed onto a support and e) the polymer removed prior to catalytic studies.

2.2.1a Monometallic Pd clusters protected by polyvinyl-alcohol (PVA)

The synthesis of the parent Pd clusters has been described elsewhere.[8] Briefly, \( \text{Pd(NO}_3\text{)}_2\cdot2\text{(H}_2\text{O)} \) (5·10⁻⁴ M, Sigma Aldrich, ~40% Pd basis) was dissolved in a solution of 1:1 by volume ethanol (EtOH, Sigma Aldrich, >99.5%) and deionized water (H₂O; resistivity ~0.06 µS cm⁻¹) containing PVA (0.02 M PVA, monomeric unit basis; 31,000-51,000 amu, Sigma Aldrich). The solution was treated in ambient air at 368 K (Scheme 2a) for 0.5 h, which led to a color change from yellow to black, indicative of the reduction of the metal precursors and the formation of metal clusters. UV-visible spectra of the suspension did not show any residual features of the Pd complexes, confirming their complete reduction.

2.2.1b Monometallic Pt clusters protected by polyvinylpyrrolidone (PVP)

\( \text{H}_2\text{PtCl}_6 \) (Sigma Aldrich, 8 wt % in H₂O) was dissolved in a solution of ethylene glycol (EG, Fischer Scientific) containing PVP (0.02 M, monomeric unit basis; 40,000 amu, Sigma Aldrich). Heating the solution in ambient air at 423 K (Scheme 2a) for 0.5 h led to a color change from yellow to brown, indicative of the reduction of the metal precursors and the formation of metal clusters. UV-visible spectra of the suspension did not show any residual features of the Pt complexes, confirming their complete reduction.

EG, and not the EtOH/H₂O mixtures used to synthesize Pd clusters (Section 2.2.1a), was required to stabilize Pt seed clusters. Pt clusters synthesized in EtOH/H₂O flocculated, forming large aggregates visible as precipitates and as deposits on glass surfaces of containers.

2.2.1c Monometallic Au clusters protected by PVP

HAuCl₄·(H₂O)₃ (5·10⁻⁴ M, Sigma Aldrich) was dissolved in a solution of EG (Fischer Scientific) containing PVP (0.02 M, monomeric unit basis; 40,000 amu, Sigma Aldrich). Heating the solution in ambient air at 423 K (Scheme 2a) for 0.5 h led to a color change from yellow to red, indicative of the reduction of the metal precursors and the formation of metal clusters. UV-visible spectra of the suspensions did not show any residual features of the Au complexes, confirming their complete reduction.
2.2.1d AuPd clusters protected by PVA

The procedures used for the synthesis of AuPd clusters have been described elsewhere. Briefly, a solution of HAuCl₄·H₂O₃ (5·10⁻⁴ M, Sigma Aldrich) in a solution of 1:1 by volume EtOH (Sigma Aldrich, >99.5%) and deionized H₂O (resistivity ~0.06 μS cm⁻¹) was added to the monometallic Pd cluster suspension (5·10⁻⁴ M, Pd atom basis; prepared as described in Section 2.2.1a) and allowed to stir (310 rpm) for 2 h at ambient temperature in air (Scheme 2b). Unless otherwise noted, equal volumes of the Au precursor solution and Pd seed cluster suspension were combined to form clusters with mean bulk (Au/Pd)ₜₚ of unity. Other compositions were prepared by changing the volumetric ratio of the Au precursor solution and Pd seed cluster suspension.

2.2.1e AuPt clusters protected by PVP

A Pt cluster suspension (5·10⁻⁴ M, Pt atom basis; prepared as described in Section 2.2.1b) was heated while stirring (310 rpm) for 0.17 h in a two-neck round-bottom flask placed within an oil bath held at 423 K. A solution of HAuCl₄·H₂O₃ (5·10⁻⁴ M, Sigma Aldrich) in EG was added at 16.7 nmol s⁻¹ using a syringe pump (KD Scientific KDS 100); the resulting mixture was allowed to stir (310 rpm) for 0.5 h at 423 K. Unless otherwise noted, equal volumes of the Au precursor solution and the Pt seed cluster suspension were combined to form clusters with mean bulk (Au/Pt)ₜₚ of unity. Other compositions were prepared by changing the volumetric ratio of the Au precursor solution and Pd seed cluster suspension.

2.2.2 Elemental Analysis of Bimetallic Clusters

High angle annular dark-field (HAADF) imaging and energy-dispersive X-ray spectroscopy (EDS) were used to determine the diameter and composition, respectively, of individual bimetallic nanoparticles. EDS measurements were obtained using an FEI Titan microscope operated at 200 kV and equipped with an FEI Super X-Quad windowless detector based on silicon drift technology. EDS data were analyzed using Bruker Esprit software calibrated against mineral standards for quantitative accuracy, and with Cliff-Lorimer k-factors for quantification. Scanning transmission electron microscopy (STEM) images were acquired using a HAADF detector with a convergence semi-angle (α) of 10 milliradians and an inner semi-angle (β) of 50 milliradians. Cluster diameters were obtained from HAADF images using ImageJ software. Over 100 individual particles were analyzed for each bimetallic sample (Au/M_A)ₜₚ = 0.5, 1, or 2; M_A = Pt or Pd). The volume-weighted mean atomic fraction (X_Mₜₚ,Mₚ) of metal M (Au, Pt, or Pd) within a bimetallic particle was calculated using the equation:

\[
\langle X_M \rangle_{\text{at.}} = \frac{\sum X_{M,i} d_i^3}{\sum d_i^3}
\]  

where \(X_{M,i}\) is the atomic fraction of metal M in particle \(i\), and \(d_i\) is the diameter. Equation 1 accounts for the greater atomic contribution of the larger particles to the total metal content.

Samples were prepared for microscopy by placing a drop of a suspension containing the clusters onto holey-carbon Cu grids (Ted Pella Inc.). AuPd samples were deposited directly from their EtOH/H₂O synthesis media, which evaporated at ambient temperature. AuPt nanoparticles
suspended in EG were first re-dispersed in a more volatile solvent, EtOH (Sigma Aldrich, >99.5%), by adding acetone (10 cm³, Fisher Scientific) to a suspension of AuPt clusters in EG (2 cm³) to flocculate the clusters, collecting precipitates by centrifugation (133 Hz, 0.6 ks), and re-dispersing clusters in 1 cm³ of EtOH. The solvent was then removed by evaporation without thermal treatments that could affect cluster size and composition.

2.2.3 Ultraviolet-Visible Spectroscopy

Ultraviolet-visible (UV-visible) spectra of cluster suspensions were measured using quartz cuvettes (10 cm³, Agilent) and a two-beam spectrophotometer (Varian Cary 400 Bio). Spectra were collected at 5 nm s⁻¹ scan rates in the 200-800 nm spectral range. Time-dependent spectra obtained during the synthesis reaction were measured by quenching the synthesis mixture using an ice bath at designated time intervals and collecting spectra of the dispersions at ambient temperature. The intensities of the ligand-to-metal charge transfer (LMCT) band of HAuCl₄ (323 nm) and of the localized surface plasmon resonance (LSPR) band of Au-covered surfaces (530 nm) were used to monitor the reduction of Au³⁺ (to Au⁺ or Au⁰) and the nucleation of Au particles, respectively. The absorbance in a spectral range free of detectable features, the background (410 nm), was used to monitor the total mass of suspended particles.

The LMCT and LSPR bands were deconvoluted for more accurate analysis using previously reported procedures. The spectra are first regressed to an exponential function excluding the LMCT (300-500 nm) and/or LSPR (400-650 nm) spectral regions. The regressed background curve was subtracted from the spectra, and the intensity of the LMCT/LSPR bands were used to determine qualitative amounts of Au³⁺ in solution and Au⁰ at cluster surfaces, respectively.

2.2.4 Dispersion of Polymer-Protected Particles onto SiO₂

Clusters were dispersed onto fumed SiO₂ (0.510 g for AuPt, 0.507 g for Pt; Sigma Aldrich, 7 nm particle size, 395 m² g⁻¹ surface) by suspending SiO₂ in deionized water (0.052 L, resistivity ~ 0.06 µS cm⁻¹) and adding the colloidal suspension dropwise (0.052 L, ~0.2 cm³ s⁻¹). The mixed slurry was stirred (310 rpm) at ambient temperature for 1 h, and the solids recovered by centrifugation (133 Hz, 0.6 ks; Scheme 2d). The complete dispersion of all clusters on the silica support was confirmed by the absence of any background intensity in its UV-visible spectra. The SiO₂-supported clusters were stirred (310 rpm) in deionized water (0.052 L, resistivity ~ 0.06 µS cm⁻¹) for 1 h and collected by centrifugation two more times before treating samples overnight at 356 K in ambient air. These procedures led to metal loadings of ~1 % wt.

2.2.5 Transmission Electron Microscopy (TEM)

Bright-field transmission electron micrographs were obtained using a JEOL 1200 EX microscope at an accelerating voltage of 80 kV, and were used to measure the surface-averaged mean cluster diameters (〈d〉) of each sample using a minimum of 200 clusters and the equation:

\[
〈d〉 = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}
\]  

(2)
where \( n_i \) is the number of clusters with diameter \( d_i \). Particle uniformity was quantified by calculating the dispersity index \( (D_A) \):\(^{[18]} \)

\[
D_A = \frac{\sum \pi d_i^2 n_i}{(\sum \pi d_i^2 n_i)^2}
\] (3)

Unsupported clusters were prepared for microscopy as described in Section 2.2.2. SiO\(_2\)-supported clusters were placed onto holey-carbon Cu grids after suspending the samples in acetone.

### 2.2.6 Removal of Protecting Polymers and Assessment of Surface Accessibility by \( \text{O}_2 \) Chemisorption Uptakes

#### 2.2.6a Removal of the protecting polymer via treatment in \( \text{H}_2 \) at low temperatures

SiO\(_2\)-supported Pt clusters (1 \% wt., prepared as described in Sections 2.2.1b and 2.2.4) were treated in flowing \( \text{H}_2 \) (Praxair 99.999\%, 0.25 cm\(^3\) s\(^{-1}\) g\(^{-1}\)) at 348 K for 1 h followed by 423 K for 1 h (0.033 K s\(^{-1}\)). Immediately afterwards, the sample was treated as described in Section 2.2.6c to measure \( \text{O}_2 \) chemisorption uptakes.

#### 2.2.6b Removal of the protecting polymer via treatment in \( \text{EtOH/} \text{H}_2\text{O and } \text{H}_2 \) at low temperatures

SiO\(_2\)-supported Pt clusters (1 \% wt., prepared as described in Sections 2.2.1b and 2.2.4) were stirred (310 rpm) for 20 h in 50 cm\(^3\) g\(^{-1}\) 1:1 by volume EtOH (Sigma Aldrich, >99.5\%) and deionized \( \text{H}_2\text{O} \) (resistivity \( \approx \)0.06 \( \mu \)S cm\(^{-1}\)) heated to 351 K. The solids were recovered by centrifugation (133 Hz, 0.6 ks) and maintained at 353 K in stagnant air overnight before treating the samples in flowing \( \text{H}_2 \) (Praxair 99.999\%, 0.25 cm\(^3\) s\(^{-1}\) g\(^{-1}\)) at 423 K (0.033 K s\(^{-1}\)) for 1 h. Immediately afterwards, the sample was treated as described in Section 2.2.6c to measure \( \text{O}_2 \) chemisorption uptakes.

#### 2.2.6c \( \text{O}_2 \) chemisorption uptakes

The chemically accessible surface atoms of SiO\(_2\)-supported Pt clusters treated as described in Section 2.2.6a or 2.2.6b were titrated by the dissociative chemisorption of \( \text{O}_2 \). \( \text{O}_2 \) uptakes consistent with TEM-derived surface-averaged mean diameters were considered definitive evidence for clean surfaces and full polymer removal. Au surfaces, which do not chemisorb \( \text{O}_2 \) effectively,\(^{[19]} \) cannot be used to obtain an accurate measure of particle size. Consequently, monometallic Pt/SiO\(_2\) samples, not AuPt/SiO\(_2\) samples, were used in all polymer removal experiments.

Chemisorption uptakes were measured using a volumetric adsorption apparatus equipped with a Baratron gauge and a turbomolecular pump (Pfeiffer Vacuum, <1 Pa dynamic vacuum). SiO\(_2\)-supported Pt clusters (1 \% wt., prepared as described in Sections 2.2.1b and 2.2.4) were treated as described in Sections 2.2.6a or 2.2.6b, and subsequently evacuated for 1 h at 423 K before cooling to 298 K. Isotherms were measured between 0.013 kPa and 101.3 kPa \( \text{O}_2 \) (Praxair,
99.999%) using an equilibration time of 0.24 ks. O₂ uptakes were estimated by extrapolation to zero O₂ pressure. Metal dispersions were calculated using an adsorption stoichiometry of one O-atom per Pt surface atom.[20] Particle diameters were calculated using:

\[ \langle d \rangle = \frac{C}{D} \]  

(4)

where \( \langle d \rangle \) is the mean diameter in nm, \( D \) is the dispersion, and \( C \) is a function of the metal identity (1.13 nm for Pt), calculated assuming a spherical geometry and using the density of the bulk metal.[21]

2.3 Results and Discussion

2.3.1 Transmission Electron Microscopy

Figure 1 Particle size distributions and sample transmission electron micrographs for a) Pt clusters and bimetallic clusters with nominal (Au/Pt)₅₅ ratios of b) 0.5, c) 1, and d) 2.
Table 2 Surface-averaged mean particle diameters, expected AuPt mean diameters, dispersity indices, and relative standard deviations

<table>
<thead>
<tr>
<th>(Au/Pt)$_{at}$</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM-derived surface-averaged diameter, $\langle d \rangle \pm $STD$\cdot N^{-0.5}$ (nm, Eq. 2)</td>
<td>2.7 ± 0.03</td>
<td>3.3 ± 0.04</td>
<td>3.5 ± 0.05</td>
<td>4.3 ± 0.07</td>
</tr>
<tr>
<td>Expected diameter, $d_{AuPt}$ (nm, Eq. 5)</td>
<td>--</td>
<td>3.3</td>
<td>3.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Dispersity index, $D_A$ (Eq. 3)</td>
<td>1.10</td>
<td>1.15</td>
<td>1.25</td>
<td>1.31</td>
</tr>
<tr>
<td>Relative standard deviation (%)</td>
<td>14.7</td>
<td>18.2</td>
<td>21.9</td>
<td>22.8</td>
</tr>
</tbody>
</table>

Cluster size distributions obtained from transmission electron micrographs were used to calculate surface-averaged mean diameters of Pt and AuPt samples ((Au/Pt)$_{at}$ = 0.5, 1, and 2; Fig. 1) using Equation 2 (Table 2). Mean cluster sizes increased monotonically with increasing Au content of each sample (3.3 nm, 3.5 nm, and 4.3 nm, respectively), consistent with the incorporation of Au atoms into the starting Pt seed clusters (2.7 nm). The mean AuPt diameters ($\langle d_{AuPt} \rangle$) of samples with different nominal (Au/Pt)$_{at}$ ratios were accurately described by the equation: \[ \langle d_{AuPt} \rangle = \langle d_{Pt} \rangle \left(1 + \frac{V'_{Au}N_{Au}}{V'_{Pt}N_{Pt}}\right)^{1/3} \] (5)

Here, $\langle d_{Pt} \rangle$ is the surface-averaged mean diameter of the initial Pt seed clusters, $V'_{Au}$ and $V'_{Pt}$ are the atomic volumes of Au and Pt in their bulk zero-valent state, and $N_{Au}$ and $N_{Pt}$ are the number of Au and Pt atoms in each sample. Equation 5 is derived based on the premise that solvated Au cations are reduced and dispersed across all Pt clusters uniformly, and do not nucleate heterogeneously on the surfaces of a few select seed clusters that grow at the expense of the majority or nucleate homogeneously in solution to form the large (~10-100 nm) broadly-distributed clusters typical of monometallic Au particles prepared under similar conditions. Both heterogeneous and homogeneous nucleation of Au would result in a bimodal particle size distribution containing the parent Pt seed initial cluster distribution and larger Au-rich clusters; the presence of such large particles would skew surface-averaged diameters (Eq. 2) to values larger than those predicted by Equation 5. The observed agreement between the values measured by TEM and those predicted by Equation 5 (Table 2) is consistent with uniform Pt seed cluster growth via addition of Au.

A more rigorous assessment of size uniformity is the calculation of dispersity indices ($D_A$, Eq. 3), which we report in Table 2, together with the more commonly reported, but less precise, relative standard deviation of the cluster diameters (ratio of the mean to the standard deviation). $D_A$
values are near unity (< 1.5), consistent with clusters of uniform size, as defined by IUPAC. Relative standard deviations (14.7-22.8%) are typical of colloidal clusters prepared using NaBH₄ reductants and thiol-based protecting agents, but were obtained here without protecting agents or the use of reductants containing S and B heteroatoms, which irreversibly titrate the surface atoms required for the catalytic function intended for such clusters.

2.3.2 UV-Visible Spectroscopy

UV-visible spectra were used to probe the extent of Au-Pt mixing within clusters. UV-visible spectra of Au clusters (prepared by the procedures in Section 2.2.1c) exhibit a localized surface plasmon resonance (LSPR) band at 500-700 nm (Fig. 2) that is typical of nano-sized Au clusters larger than 2 nm in diameter. Pt clusters, in contrast, do not exhibit detectable LSPR features, which become evident only in the presence of pure Au clusters in physical mixtures of monometallic Pt and Au clusters (Fig. 2). Undesired Au-rich clusters formed from the homogeneous or heterogeneous nucleation of Au during synthesis (Scheme 1.1) would therefore be detected from their UV-visible spectra, even when such clusters co-existed with monometallic Pt particles.

![Figure 2 UV-visible absorption spectra of a) Pt clusters (---), b) bimetallic AuPt clusters (--- (Au/Pt)ₐₜ = 1), c) a physical mixture of Pt and Au clusters (---), and d) Au clusters (- - - -).](image)

Bimetallic clusters ((Au/Pt)ₐₜ = 1; synthesized as described in Section 2.2.1e) do not show a plasmon resonance, indicating that monometallic Au clusters and core-shell particles with PtₜₜₜₜAuShell arrangements did not form. The Pt-like UV-visible spectra of these AuPt clusters indicate that particle surfaces contain a significant number of Pt atoms—which would dampen the surface plasmon oscillations of Au atoms—a conclusion similar to that reached from the Pd-like spectrum of AuPd particles prepared from Pd seed clusters. As proposed in the case of AuPd, the prevalence of seed cluster metal atoms (Pt or Pd) at bimetallic cluster surfaces suggests that Au cations replace surface Pt or Pd atoms via galvanic displacement reactions.
and that they are subsequently covered by Pt or Pd atoms that return upon re-reduction of their solvated cations by solvent molecules (Scheme 1.2b).

2.3.3 Elemental Analysis of Individual Particles by EDS

The uniformity of bimetallic mixing and its mechanistic implications are most accurately examined through particle-by-particle elemental analysis using EDS; such methods also allow us to confirm the exclusive presence of bimetallic clusters, as well as to rigorously assess how the size of the parent seed (Pt or Pd) relates to its ultimate Au content. The mean atomic fraction of Pt or Au in a bimetallic sample was calculated using data from more than 100 bimetallic particles and Equation 1. Mean EDS-derived compositions agree with those predicted from the reagent mixtures used (Fig. 3a), thus confirming the full recovery of metals and of their cationic precursors as part of the colloidal particles. Data obtained via EDS analysis of AuPd clusters are also included in Figure 3; they similarly show that the expected compositions were achieved. No monometallic clusters were detected in any of the AuPt or AuPd bimetallic samples.

![Figure 3](image-url)

**Figure 3** Parity plots of the measured and expected mean Au to M₂ atomic ratio ($\langle \text{Au}/\text{M}_2 \rangle_{\text{at.}}$) of a) AuPt and b) AuPd particles. Experimental $\langle \text{Au}/\text{M}_2 \rangle_{\text{at.}}$ values were determined via particle-by-particle elemental analysis of over 100 particle per sample using EDS.

Next, we examine how the chemical composition of individual particles changes with cluster size to assess the compositional uniformity of each sample and to infer the synthesis routes by which they form. (Au/Pt)ₜₐt ratios increased with increasing cluster size (Fig. 4a), indicating that larger AuPt particles within a given AuPt sample contain relatively more Au atoms than smaller ones. Such Au enrichment in larger particles becomes more evident in samples with higher nominal (Au/Pt)ₜₐt ratios. As a result, the omission of a few undetected particles with high Au content in the calculation of the mean atomic fraction of Au (Eq. 1) for such samples would lead to underestimates of Au content and, thus, also to underestimates of mean (Au/Pt)ₜₐt; this appears to be the case for the sample with mean (Au/Pt)ₜₐt ratio of 2, for which the EDS-derived (Au/Pt)ₜₐt ratio falls below the parity line in shown Figure 3a.
In contrast with the trends observed for AuPt clusters, the (Au/Pd)\text{at.} ratios of individual AuPd clusters decreased with increasing cluster size (Fig. 4b). M\textsubscript{B} seed clusters grow via the addition of Au atoms; thus, dissimilar trends in the effects of cluster size on bimetallic composition for AuPd and AuPt systems suggest, in turn, dissimilar growth mechanisms, consistent with the different synthetic protocols required to achieve size and compositional uniformity in AuPd and AuPt samples (discussed later in Section 2.3.4).

![Figure 4](image_url)

**Figure 4** a) Changes in mean Au to Pt atomic ratio (\(\langle\text{Au/Pt}\rangle\text{at.}\), from EDS data) with AuPt particle diameter (\(d_{\text{AuPt}}\), from HAADF imaging) and b) changes in mean \(\langle\text{Au/Pd}\rangle\text{at.}\) with \(d_{\text{AuPd}}\). Greater than 100 particles analyzed for each bimetallic sample. Samples with bulk (Au/M\textsubscript{A})\text{at.} of 0.5 (○), 1 (■), and 2 (▲) shown. Particles binned by particle diameter (bin width of 0.5 nm), with bins containing less than 3 particles omitted for clarity, and 74-87\% of particles located within 4 bins.

Next, we derive the equations that govern cluster growth via GDR to determine the relevant parameters that influence the amount of Au added to each parent seed cluster and their sensitivity to cluster size. The mechanistic features of GDR, the proposed growth mechanism for AuPd clusters,\textsuperscript{[8]} are that:

(a) seed particle surface atoms (M\textsubscript{A} = Pt or Pd) act as reductants for solvated cations of the more noble metal species (M\textsubscript{B} = Au; Scheme 1.2a),
(b) oxidized seed atoms brought into solution by step (a) are subsequently reduced by the solvent and return to the surface of the growing bimetallic clusters (Scheme 1.2b), and
(c) atoms of M\textsubscript{A} are replenished at the cluster surface in step (b) and thus continue to serve as reductants of solvated M\textsubscript{B} cations.

Such growth pathways require that solvated M\textsubscript{B} cations encounter—and are therefore reduced by—M\textsubscript{A} atoms instead of M\textsubscript{B} atoms at cluster surfaces. The growth rate of a spherical particle, \(i\), is therefore proportional to its surface area \(A_i\), as expressed by:
\[ \frac{dN_i}{dt} = A_i k \]  

(6)

where \( N_i \) is the moles of atoms in a growing cluster and \( k \) is the areal rate constant for the galvanic displacement reaction. \( N_i \) and \( A_i \) in Equation 6 were expressed as functions of the cluster diameter, \( d_i \), and the resulting differential equation was solved to give the thickness by which each seed cluster grows (\( \Delta d_i \)) as a result of the addition of Au atoms (derivation in SI Section 2.6.1):

\[ \Delta d_i = 2V_i' k t \]  

(7)

Here, \( V_i' \) is the atomic volume of the particle and \( t \) is time. Equation 7 shows that the diameter of each parent seed cluster increases by a value (\( \Delta d_i \)) that does not depend on the size of the initial seed cluster.\[^{[8, 27]}\] Consequently, seed particles with distributed diameters that all grow by the same amount (\( \Delta d \)) via addition of Au atoms lead, in turn, to AuMA clusters with distributed compositions; larger seed particles give rise to bimetallic clusters with lower (Au/MA)\(_{\text{at.}}\) ratios (Scheme 3), as shown by rearranging Equation 5 for an individual cluster, \( i \):

\[
\left( \frac{N_{Au}}{N_{MA}} \right)_i = \left[ \left( 1 + \frac{\Delta d}{d_{MA,i}} \right)^3 - 1 \right] \frac{V'_{MA}}{V'_{Au}}
\]  

(8)

where \( d_{AuMA} \) in Equation 5 was replaced by:

\[ d_{AuMA,i} = d_{MA,i} + \Delta d \]  

(9)

The expected inverse dependence of (Au/MA)\(_{\text{at.}}\) on particle size was evident for AuPd but not for AuPt particles (Fig. 4), suggesting that Pt seed clusters grow by a thickness (\( \Delta d \)) that depends on the parent seed cluster diameter; thus, the requirements for GDR (a-c) stated above may not be fully met for AuPt compositions, and additional Au cation reduction routes may contribute to cluster growth during the synthesis of AuPt clusters.

Scheme 3 GDR processes result in MA seed particles that grow at rates proportional to their surface areas, and, thus, by an amount (\( \Delta d \)) that is independent of the size of the initial seed particle (\( d_{MA} \)).\[^{[8]}\] Monometallic seed clusters that are heterogeneous in size but all grow by the same amount, \( \Delta d \), result in bimetallic clusters whose (Au/MA)\(_{\text{at.}}\) ratios decrease with increasing \( d_{MA} \).
The dependence of $\Delta d$ on the initial Pt or Pd seed size was determined using particle-by-particle EDS elemental analysis and HAADF imaging to measure the atomic fraction of $M_A$ ($X_{M_A,i}$) and the particle diameter ($d_{AuM_A,i}$), respectively, of each bimetallic cluster, $i$. These data were used to calculate the number of Pt or Pt atoms within each bimetallic cluster and, accordingly, the diameter of the parent Pd or Pt seed cluster from which each bimetallic cluster, $i$, was formed (derivation in SI Section 2.6.2). Seed cluster diameters were subtracted from $d_{AuM_A,i}$ to determine the thickness by which each Pd or Pt seed grows ($\Delta d_i$) via the addition of Au atoms:

$$\Delta d_i = d_{AuM_A,i} \left[ 1 - \left( \frac{x_{M_A,i}V'M_A}{x_{M_A,i}V'_M + x_{Au,i}V'_{Au}} \right)^{1/3} \right]$$

(10)

Here, $V'_M$ and $V'_{Au}$ are the atomic volumes of $M_A$ and Au. Equation 10 is valid when $M_A$ surface atoms removed via oxidation and dissolution from cluster surfaces (Scheme 1.2a) return to cluster surfaces at rates that are strictly proportional to their respective surface areas (requirement (b); Scheme 1.2b). In such cases, the number of $M_A$ atoms removed equals the number returned to each cluster, thus rendering them available for galvanic displacement when solvated Au ions again reach those surfaces (requirement (c); Scheme 1.2a).

Figure 5 shows the effects of seed cluster size on $\Delta d$ values for different nominal AuPd and AuPt compositions. The $\Delta d$ values of AuPd clusters did not vary monotonically with seed size (Fig. 5b), thus exhibiting the behavior expected for GDR processes, for which deposition and re-reduction rates are both proportional to surface area and Au cations arriving at cluster surfaces find Pd surface atoms (instead of Au atoms) with a probability that is independent of seed cluster size. The expected $\Delta d$ values for each composition can be calculated using the TEM-derived size distribution of the initial seed particles and distributing Au atoms among them based on particle surface area (derivation in Section 2.6.3 of SI). The calculated $\Delta d$ values for the AuPd samples agree well with EDS-derived values (Fig. 5b; dashed line indicates calculated $\Delta d$ values), consistent with GDR processes during synthesis.
**Figure 5** Effects of initial seed cluster diameter ($d_{MA}$) on the growth ($\Delta d$) of a) Pt and b) Pd seeds. Horizontal dashed lines in b) denote expected $\Delta d$ values assuming GDR growth, calculated from TEM-derived Pd seed particle size distributions. At least 100 particles analyzed for each bimetallic sample using EDS and HAADF imaging. Samples with nominal (Au/M)$_{at}$ of 0.5 (●), 1 (■), and 2 (▲) shown. Particles binned by initial seed particle diameter (bin width of 0.5 nm), with bins containing less than 3 particles omitted for clarity, and 90-95% of particles located within 4 bins.

In contrast with Pd clusters, $\Delta d$ values increased as the Pt seed clusters became larger (Fig. 5a), suggesting that Au atoms deposit on larger Pt seeds more frequently than predicted from their surface areas alone. Au and Pt, unlike Au and Pd, are immiscible within large bulk crystals ($\Delta H_{AuPt} = +2.3$ kJ mol$^{-1}$ vs. $\Delta H_{AuPd} = -6.7$ kJ mol$^{-1}$), thus exhibiting a greater tendency for intracluster segregation, which would preferentially place Au atoms, with their lower surface energies, at bimetallic surfaces. Au surface segregation becomes more evident for larger particles because their larger bulk reservoirs mitigate the depletion of Au from the bulk upon segregation, thus maintaining the thermodynamic driving force for Au surface enrichment.

As Au atoms diffuse to the cluster surface, Pt surface coverage decreases, thus increasing the probability that solvated Au cations will encounter surface Au$^0$ atoms instead of the Pt$^0$ atoms required for GDR. Consequently, the reduction of Au cations by Pt$^0$ via galvanic displacement is hindered, and autocatalytic reduction by ethylene glycol on Au$^0$ sites becomes the predominant reduction route (Scheme 4). Autocatalytic reduction processes are fast, as shown by the formation of large Au clusters in the absence of Pt seeds. Larger AuPt particles with higher Au$^0$ surface contents quickly scavenge Au cations via autocatalytic routes, leading such larger particles to acquire an amount of Au no longer in proportion to their respective surface areas, with $\Delta d$ values larger than for smaller clusters (Fig. 5a). Such phenomena become apparent for AuPt, but are not detectable for AuPd, because endothermic alloys exhibit a much greater preference for Au surface segregation than their exothermic counterparts.
The protocols developed for AuPd clusters (Section 2.2.1d; with EG instead of EtOH/H₂O as solvent) led to a bimodal distribution of AuPd cluster sizes ((Au/Pt)₀ = 1; Fig. S1 in Section 2.6.4 of SI), with one component identical in size and shape to that of the initial Pt seed clusters, and another consisting of much larger clusters (~5-20 nm). These larger clusters contain a disproportionate fraction of the Au atoms, thus compromising the size and compositional uniformity of the bimetallic materials. Next, we discuss the synthetic protocols that we have developed in order to synthesize more uniform AuPt clusters, and which were used to synthesize the bimetallic AuPt clusters discussed in detail in the preceding sections.

2.3.4 Synthetic Protocols to Enhance Compositional Uniformity of AuPt Bimetallic Clusters

The thermodynamic driving force for galvanic displacement of Pt⁰ by Au cations is lower than for the corresponding Pd⁰ reaction in the AuPd system (Scheme 1.2a; ΔE₀(redox,AuPd) = 0.50 V, ΔE₀(redox,AuPt) = 0.74 V; Table 1). In addition, a stronger reductant (EG instead of EtOH used for AuPd; E₀(EG) = -0.8 V, E₀(EtOH) = -0.197 V) was required to stabilize Pt seed clusters (as discussed in Section 2.2.1b). The less favorable GDR thermodynamics for AuPt lead to slower displacement processes at cluster surfaces, while the stronger reductant competes with Pt⁰ surface atoms in reducing solvated Au cations. These kinetic and thermodynamic hurdles conspire to increase non-uniformity and to favor the creation of pure Au nuclei in solution (homogeneous nucleation) or on the surfaces of pre-formed seed clusters (heterogeneous nucleation); these small Au structures then quickly grow into monometallic Au clusters or Au-rich clusters, respectively, without the intervention of Pt⁰ atoms as reductants.

UV-visible spectroscopy was used to examine Au atom deposition dynamics and the role of Pt seeds in scavenging Au cations in order to design synthetic protocols that would favor GDR processes over competing reduction routes. UV-visible spectra (Section 2.2.3) were used to monitor changes in the concentration of solvated Au³⁺ precursors (323 nm)¹⁷ and to detect the incipient formation of Au-rich surfaces on clusters (530 nm; LSPR band)²⁶ during the reduction of Au cations at 423 K in EG, with and without the presence of Pt seed clusters.

Au³⁺ cations were reduced to concentrations below detection limits in < 0.3 ks when Pt seed clusters were not present. The Au⁰ LSPR band, characteristic of the nucleation and growth of Au
clusters, emerged only after the Au$^{3+}$ spectral features disappeared (Fig. 6a). The reduction of Au$^{3+}$ cations without the concomitant formation of Au clusters indicates that Au$^{3+}$ reduced to Au$^{+}$, which absorbs at photon energies below 200 nm$^{[28]}$ (a spectral range inaccessible in these studies), or to Au$^{0}$. The background absorbance in spectral regions without Au$^{3+}$ bands or LSPR features (i.e. 410 nm) was negligible in the absence of nanoparticles, but became more intense after Au nucleation as a result of an increase in the particle mass present in the suspension, which became darker and redder after nucleation. The overall reaction appears to involve the sequential reduction of Au$^{3+}$ precursors (stage I) and the growth of Au clusters (stage II), mediated by the intervening formation of nuclei (Fig. 6a).

![Figure 6](image)

**Figure 6** UV-visible spectra of Au$^{3+}$ in EG heated to 423 K in a) the absence of Pt clusters and b) the presence of Pt clusters. The intensity of the Au$^{3+}$ precursor band at 323 nm (●) decreased to negligible values (stage I), at which point the Au species nucleated (*) and a LSPR band emerged at 530 nm (▲, stage II). Absorbance in the background region of the spectra at 410 nm (▲) in stage I was negligible and constant in the absence of Pt clusters (a), but increased steadily in the presence of Pt clusters (b).

Au$^{3+}$ cations added to a suspension of Pt clusters and treated similarly to the seed-free solution were reduced fully in < 0.3 ks (stage I) before the detection of the Au$^{0}$ LSPR band characteristic of the nucleation and growth of Au-rich clusters (stage II; Fig. 6b). The background absorbance was evident at the beginning of stage I because Pt seed clusters were present. This background absorbance subsequently increased monotonically with time—without the concomitant emergence of detectable LSPR bands—in contrast to the negligible and invariant background evident during Au$^{3+}$ reduction in the absence of Pt seeds (stage I, Fig. 6a). This increase in background absorbance is indicative of an increase in particle mass, which, taken together with the absence of LSPR features in stage I, suggests that seed clusters grow without evidence for the formation of monometallic Au surfaces. Transmission electron micrographs of the clusters formed indicate that the size distribution shifted uniformly to clusters larger than the Pt seeds (Fig. 7a), consistent with the uniform placement of Au atoms among all Pt clusters in stage I. Larger clusters (~5-10 nm), absent in the parent seed distribution, were also evident in these micrographs. These large clusters were Au-rich, and their formation reflects the inability of Pt$^{0}$...
surface atoms to reduce all the solvated Au cations before they can form nuclei that grow via fast autocatalytic reduction routes. The formation of bimetallic particles of uniform size and composition thus requires that we extend stage I for longer periods of time in order to allow the uniform dispersion of all Au atoms onto the Pt seeds, while preventing the nucleation and growth that leads to large Au-rich clusters (stage II). The discussion that follows aims to describe how various synthesis parameters can be adjusted to inhibit Au nucleation and instead promote GDR reduction by surface Pt$^0$ atoms.

**Figure 7** Particle size distributions of clusters with nominal (Au/Pt)$_a$ of unity, synthesized with a) EG or b) BD as the reductive solvent. The Au precursor solution was added all at once to a suspension of the pre-formed Pt seed particles heated to 423 K.

### 2.3.4a Effects of solvent reduction potential on the formation of bimetallic AuPt clusters

The nucleation of Au-rich clusters may be prevented by the exclusion of all reductants, other than the Pt seeds, from synthesis mixtures, which would ensure that Pt$^0$ surface atoms are the only reductant. The formation of the initial seed clusters and the reduction of Pt cations formed in galvanic displacement processes (Scheme 1.2b), however, require an additional reductant, which, in this case, also acts as the solvent; this reductant competes with Pt$^0$ atoms in the reduction of Au cations (Scheme 1). Here, we examine how the reduction potential of the solvent impacts the extent to which Au and Pt atoms combine to form bimetallic AuPt clusters.

The mean diameter of monometallic Pt clusters synthesized in butanediol (BD; 2.3 nm ± 0.02) is smaller and their size more narrowly distributed than Pt clusters prepared via similar protocols with EG (2.7 nm ± 0.03; Fig. 7), consistent with the faster reduction of Pt cations by BD than EG and with the subsequent formation of more Pt nuclei that then grow into smaller and more narrowly distributed clusters;[^29] thus, BD acts as a stronger reductant than EG. Next, we show that increasing the reductive strength of the solvent (from EG to BD) also decreases the growth of Pt seeds as bimetallic clusters uniform in composition, and promotes instead the formation of large Au-rich clusters.
AuPt suspensions \( ((\text{Au/Pt})_{\text{at.}} = 1) \) were prepared by adding a \( \text{Au}^{3+} \) solution all at once to a suspension of Pt seed clusters and treating the resulting mixture at 423 K for 0.33 h. Figure 8 shows the LSPR intensity of the AuPt suspensions formed from these protocols with either EG or BD as solvents (deconvolution methods in Section 2.2.3). Samples formed with BD gave more intense LSPR features than with EG, indicating that the stronger reductant favors the formation of monometallic Au surfaces. TEM-derived size distributions were bimodal for BD-derived samples, with one component identical in size and shape to that for the Pt seed clusters and another composed of much larger clusters (> 5.5 nm; Fig. 7b), apparently formed via nucleation and growth of Au-rich clusters. With EG as the solvent, a few large clusters also formed, but the predominant component consisted of clusters shifted in size from those of the Pt seeds (Fig. 7a), consistent with the predominant deposition of Au atoms onto seed clusters.

![Figure 8](image-url) LSPR intensity of bimetallic clusters \( ((\text{Au/Pt})_{\text{at.}} = 1) \) synthesized in EG (a, ——) and BD (b, ——) at 423 K. The Au precursor solution was added all at once to a suspension of pre-formed Pt seed particles heated to 423 K.

These data show that stronger reductants increase the rate of nucleation and growth of Au-rich clusters (Scheme 1.1), thus precluding the reduction of Au cations by Pt\(^0\) surface atoms via GDR processes (Scheme 1.2), a requirement for compositional uniformity. Weaker reductants favor GDR, but must still be capable of stabilizing clusters and of reducing the cations formed from seed clusters in GDR processes in order to return the less noble metal to the bimetallic clusters (Scheme 1.2b).

2.3.4b Effects of the \( \text{Au}^{3+} \) addition rate on the size and compositional uniformity of AuPt clusters

Nucleation rates can be decreased by decreasing the concentration of the solute that forms the nuclei.\[30\] We show here that adding the Au precursor solution in a slow and precise manner using a syringe pump is able to maintain a low concentration of Au species in solution and to extend the regime of uniform Pt seed cluster growth (stage I; Fig. 6) by delaying or even preventing nucleation of Au to form Au-rich clusters. The effects of the Au cation addition rate
on the size and compositional uniformity of the resulting bimetallic clusters ((Au/Pt)$_{at.} = 1$) was determined by adding EG solutions of Au precursors drop-wise at varying rates to the starting Pt seed cluster suspensions (in the EG solvent) at 423 K.

LSPR bands were not detected when Au precursor solutions were added slowly ($\leq 25$ nmol Au$^{3+}$ s$^{-1}$) to Pt cluster suspensions; large clusters ($> 5.5$ nm) were not detected by TEM in the clusters formed (Fig. 9). The surface-averaged mean diameter (Eq. 2) of AuPt clusters prepared using a Au$^{3+}$ addition rate of 16.7 nmol s$^{-1}$ is consistent with the homogeneous distribution of Au atoms among seed clusters (Eq. 5; Table 2) and with EDS analysis of $> 100$ clusters showing no Au-rich clusters (Fig. 3a). Higher rates of addition of Au precursors ($> 25$ nmol Au$^{3+}$ s$^{-1}$) led to AuPt samples with significant LSPR bands (Fig. 9a), consistent with the extensive formation of Au-rich clusters.

The slow addition of Au precursors minimizes the concentration of solvated Au species and precludes conditions that favor the abrupt creation of a large number of Au nuclei, typically denoted as a nucleation burst.$^{[31]}$ Au nuclei rapidly consume all solvated Au cations via deposition onto Au-rich clusters, thus preventing their incorporation into AuPt clusters. Slow Au$^{3+}$ addition rates therefore ensure that Pt$^0$ atoms present at bimetallic cluster surfaces—as confirmed by the Pt-like UV-visible spectra of AuPt clusters (Fig. 2)—are able to reduce Au cations via GDR processes, while coexisting with Au$^0$ surface atoms that reduce solvated Au cations via autocatalytic routes.$^{[32]}$ (as discussed in Section 2.3.3). The slow drop-wise addition of Au precursors is not required for AuPd systems, which are prepared with a weaker reductant as solvent and are less prone to segregate Au atoms to cluster surfaces because of their favorable mixing enthalpies. Autocatalytic reduction pathways are not observed in AuPd compositions (Section 2.3.3), for which the reduction of Au cations by Pt$^0$, required for galvanic displacement, is more thermodynamically favorable than in AuPt.

The intensity of LSPR bands decreased monotonically with increasing Au$^{3+}$ addition rate when Au precursor solutions were added quickly ($> 25$ nmol Au$^{3+}$ s$^{-1}$; Fig. 9b). Higher Au$^{3+}$ addition rates result in a larger fraction of Au atoms added to synthesis mixtures and in contact with Pt seeds during the critical period of bimetallic cluster growth (stage I), thus increasing the fraction of Au atoms incorporated as AuPt clusters before reaching conditions that result in a nucleation burst. Consequently, the fraction of Au species available for Au cluster growth (stage II) is smaller and lead to weaker LSPR bands in the UV-visible spectra of the resulting sample.
2.3.4c Effects of synthesis temperature on the size and compositional uniformity of bimetallic clusters

Nucleation rates increase with temperature, suggesting that lower synthesis temperatures may promote the formation of bimetallic particles via GDR (stage I) by delaying the nucleation of Au clusters. GDR rates are also affected by temperature, however, rendering the effects of synthesis temperature on the size and compositional uniformity of bimetallic clusters difficult to establish without direct experimental evidence. Such effects were determined by synthesizing bimetallic clusters ((Au/Pt)$_{at}$ = 1) at various temperatures (388-423 K; Au precursor solutions in EG added at 16.7 nmol Au$^{3+}$ s$^{-1}$ to Pt seed cluster suspensions in EG).

LSPR band intensities of AuPt suspensions prepared using these protocols decreased with increasing synthesis temperature (Fig. 10a), indicating that lower temperatures favor the formation of monometallic Au surfaces, in spite of the lower Au nucleation rates. Au-rich clusters that result from homogeneous or heterogeneous nucleation events are significantly larger in diameter (> 5.5 nm) than the Pt clusters that grow uniformly via addition of Au, resulting in a bimodal size distribution (Fig. 7a). Here, we isolate the uniform growth component of these distributions by calculating the mean cluster diameter while omitting clusters larger than 5.5 nm ($\langle d'_{\text{AuPt}} \rangle$). The $\langle d'_{\text{AuPt}} \rangle$ value of clusters prepared at 388 K remained the same as that of the parent Pt seeds (Fig. 10b), indicative of the absence of bimetallic growth. Higher synthesis temperatures led to larger $\langle d'_{\text{AuPt}} \rangle$ values. The surface-averaged mean diameter of AuPt clusters synthesized at 423 K agreed well with the expected diameter (Eq. 5), and no large Au-rich clusters were detected, consistent with the consumption of all Au species within AuPt clusters, and the effective prevention of Au$^0$ nucleation.
Figure 10  a) Plasmon resonance intensity and b) the surface-averaged mean particle diameter of clusters < 5.5 nm in diameter ($d_{\text{AuPt}}^\text{max} = 1$) prepared at various synthesis temperatures. Black horizontal dashed lines in b) denote the initial Pt seed diameter (bottom) and the expected AuPt diameter (using Eq. 5, top). Clusters prepared in EG by adding the Au precursor to a stirring, heated suspension of Pt seed clusters at a rate of 16.7 nmol s$^{-1}$.

These data indicate that elevated temperatures favor the bimetallic growth characteristic of GDR processes. The unfavorable mixing enthalpies of AuPt formation are compensated by entropies of mixing that influence Gibbs free energies more strongly at higher temperatures.$^{[11]}$ In contrast, exothermic alloys such as AuPd can be synthesized at ambient temperature with GDR as the predominant growth mechanism.$^{[8]}$

2.3.4d Synthesis of AuPt clusters with > 50 % at. Au content

The synthesis of uniform AuPt suspensions with > 50 % at. Au requires additional synthetic strategies to prevent the formation of large Au-rich clusters. AuPt samples composed of ≤ 50 % at. Au were prepared by adding Au precursor solutions drop-wise (16.7 nmol Au$^{3+}$ s$^{-1}$) to Pt seed cluster suspensions at 423 K and adjusting the volumetric ratio of the Au precursor solutions (5·10$^{-4}$ M in EG) and the Pt cluster suspensions (5·10$^{-4}$ M, Pt atom basis; in EG) used in order to reflect the desired atomic ratio; these materials exhibited no detectable LSPR features (Fig. 11a). Using the same protocols to form samples with higher Au contents (> 50 % at.), however, led to materials with significant LSPR features (Table S1 in SI Section 2.6.5) and broad cluster size distributions (Fig. S2 in SI Section 2.6.5); these data indicate the substantial presence of Au-rich clusters that form via homogeneous or heterogeneous nucleation of Au.

Previously, we showed that decreasing Au precursor addition rates (to ≤ 25 nmol Au$^{3+}$ s$^{-1}$) minimized the concentration of solvated Au species, thus preventing the nucleation of Au during the synthesis of AuPt clusters with 50 % at. Au (Section 2.3.4b). Next, we show that the synthesis of bimetallic samples with higher Au contents requires further decreases in the addition rate of Au precursors in order to accommodate the larger number of solvated Au cations required
for such compositions without causing a nucleation burst. AuPt suspensions with > 50 % at. Au content were prepared by first synthesizing bimetallic clusters with 50 % at. Au (as described above) and subsequently adding the balance Au precursor solution at a slower rate (4.17 nmol Au\(^{3+}\) s\(^{-1}\)). The LSPR intensities of the resulting cluster suspensions rose monotonically with increasing Au content up to 76 % at. Au, then increased markedly from 76 % at. to 85 % at. Au (Fig. 11a). Further reductions of Au\(^{3+}\) addition rate did not influence the LSPR intensities of the resulting clusters (Table S1 in Section 2.6.5 of SI).

![Figure 11](image.png)

**Figure 11** Changes in a) plasmon resonance intensity and b) dispersity index \((D_A, \text{Eq. 4})\) of AuPt clusters with increasing Au content. Clusters prepared (in EG) by adding the Au precursor drop-wise to a stirring, heated suspension of Pt seed clusters.

The stronger LSPR bands for suspensions with higher mean Au contents may be caused by either an increase in the atomic fraction of Au at bimetallic cluster surfaces or by the formation of large Au-rich clusters that compromise size and compositional uniformity. A measure of size uniformity, \(D_A\) (Eq. 3), was used to identify bimetallic cluster suspensions containing large Au-rich clusters; clusters with \(D_A\) values > 1.5 are considered non-uniform in size\(^{18,23}\) and are therefore non-uniform in composition as well due to their high Au contents. \(D_A\) values near unity for AuPt suspensions with \(\leq 76\) % at. mean Au content (Fig. 11b) indicate that such samples are uniform in size and therefore composition, and suggest that their monotonic rise in LSPR intensity with increasing Au composition reflects an increase in the number of Au atoms at their bimetallic surfaces. These conclusions are consistent with the elemental analysis of 67 % at. Au clusters using EDS, which detected no monometallic Au clusters, and with previous conclusions of cluster surfaces becoming enriched in Au during synthesis (Section 2.3.3). The large \(D_A\) value (14.8) of the suspension containing 85 % at. Au indicates the presence of large Au-rich clusters that account for the strong LSPR band in this sample (Fig. 11a). This suggests that the protocols employed here are ineffective at preventing the nucleation of Au\(^0\) in mixtures with very high Au contents (\(\geq 85\) % at. Au).
The slower rates of Au$^{3+}$ addition required for AuPt cluster suspensions composed of > 50 % at. Au reflect the increasing difficulty of synthesizing uniform AuPt clusters as the surface becomes Au-rich and favors autocatalytic reduction by Au$^0$ surface atoms instead of GDR processes that use Pt$^0$ surface atoms as reductants. The lower rates of Au precursor addition maintain a low concentration of Au species in the synthesis mixture, thus preventing the nucleation of Au$^0$ and the formation of large Au-rich particles. In contrast, the synthesis of uniform AuPd clusters with > 50 % at. nominal Au content does not require slow addition of the Au precursors,[8] reflecting the greater ease of synthesizing bimetallic particles of miscible metals, which do not exhibit intracluster segregation in the time scale of these synthesis protocols, thus maintaining higher surface coverages of the less noble metal that favor GDR processes.

2.3.5 Removal of Polyvinylpyrrolidone (PVP) Species from Cluster Surfaces

The preparation of heterogeneous catalysts from colloidal suspensions of polymer-protected particles requires that we disperse such clusters onto a support, separate the solvent, and subsequently remove the polymer from metal surfaces in order to expose the active sites required for catalysis.

High-temperature treatments in O$_2$ are typically used to such polymers, but often lead to crosslinking and densification that ultimately result in site-blocking amorphous carbon.[33] In contrast, treating supported clusters in H$_2$ at low temperatures displaces the surface-binding carbonyl of PVP, releasing it from the metal surface without causing polymer densification.[33b] Here, we disperse clusters onto SiO$_2$, remove the solvent via centrifugation (as described in Section 2.2.4) and use a low-temperature (≤ 423 K) treatment in a reducing environment (H$_2$ or 1:1 by volume EtOH:H$_2$O) to clean metal surfaces. Treated clusters are considered clean and chemically accessible when the surfaces of the clusters detected by TEM can be accurately titrated by chemisorbed oxygen, a condition that is met when the TEM-derived surface-averaged mean particle diameter becomes equal to the chemisorption-derived mean particle diameter. Pt surface atoms, but not Au surface atoms, can be accurately probed by chemisorbed oxygen;[19] hence, monometallic Pt clusters, not bimetallic AuPt clusters, were used in all deprotection studies. Au atoms that do not chemisorb oxygen effectively also bind adsorbates such as PVP more weakly than Pt atoms.[34] Monometallic Pt clusters therefore bind PVP more strongly than AuPt clusters, and are an appropriate material to probe polymer removal protocols for AuPt alloys.

2.3.5a Removal of PVP from Pt cluster surfaces with H$_2$

The chemisorption-derived diameter of SiO$_2$-supported Pt clusters treated in flowing H$_2$ at 523 K (1 h; 0.033 K s$^{-1}$ ramp rate)—a temperature much higher than that at which PVP incipiently crosslinks (423 K) to form dense and refractory polymer networks$^{[33c]}$—was larger than the surface-averaged diameter from TEM (Fig. 12a), an indication of surface blockage by polymeric residues. The surface-averaged mean cluster diameter increased after treatment in flowing H$_2$ at 523 K (from 2.7 ± 0.03 nm to 3.0 ± 0.03 nm; measured by TEM). In contrast, the chemisorption-derived mean diameter of clusters treated at a lower temperature (423 K for 1 h; 0.033 K s$^{-1}$) in flowing H$_2$ was similar to its TEM-derived mean diameter, suggesting that H$_2$ can remove PVP from Pt surfaces by treatment at temperatures below those leading to polymer densification.
Clusters treated at 423 K were slightly larger than untreated clusters, possibly as a consequence of local exotherms during polymer removal, which may have led to some coalescence among vicinal clusters.

The treatment of Pt clusters at a lower temperature (348 K for 1 h; 0.033 K s\(^{-1}\)) in flowing H\(_2\) before a subsequent treatment at 423 K (1 h; 0.033 K s\(^{-1}\)) led to clusters of similar size to untreated ones, but whose surfaces were still free of synthetic debris (Fig. 12a). The additional step at 348 K removes the polymer more slowly by prolonging treatment at lower temperatures and removes a larger fraction of surface-bound PVP before reaching higher temperatures, thus mitigating the generation of local exotherms from PVP removal reactions that lead to particle agglomeration. The chemisorption-derived mean diameter of clusters treated only at 348 K (1 h; 0.033 K s\(^{-1}\) ramp rate) was smaller than the mean diameter calculated from TEM, indicative of polymeric residues or partial Pt reduction.

![Figure 12 TEM-derived and chemisorption-derived mean particle diameters (Eqs. 2 and 4, respectively) of SiO\(_2\)-supported Pt clusters treated in a) flowing H\(_2\) at 523 K for 1 h (■), 423 K for 1 h (▲), 348 K for 1 h followed by 423 K for 1 h (●), and 348 K for 1 h (●), and of clusters treated in b) a stirring mixture of 1:1 by volume EtOH:H\(_2\)O (▲) or deionized H\(_2\)O (□) at 351 K for 20 h prior to treatment in flowing H\(_2\) at 423 K for 1 h. Points on the parity line indicate polymer-free surfaces. The dashed horizontal line at 2.7 nm denotes the diameter of untreated Pt clusters (determined by TEM).](image)

2.3.5b Removal of PVP from cluster surfaces with H\(_2\) and either EtOH/H\(_2\)O or H\(_2\)O

The versatility of these low-temperature reductive polymer removal methods was assessed by modifying the reductant. SiO\(_2\)-supported Pt clusters were treated in a reductive solvent (1:1 by volume EtOH:H\(_2\)O) maintained at 351 K for 20 h instead of the treatment in flowing H\(_2\) at 348 K. Clusters were subsequently separated from the liquid by centrifugation, dried in ambient air overnight at 356 K, and treated at 423 K (1 h; 0.033 K s\(^{-1}\) ramp rate) in flowing H\(_2\) before O\(_2\) uptake measurements. The chemisorption-derived and TEM-derived mean diameters of EtOH:H\(_2\)O/H\(_2\)-treated clusters were similar and equal to the mean particle size of untreated
clusters (determined by TEM; Fig. 12b), indicating that metal surfaces were clean and that treating clusters in EtOH:H₂O effectively replaces the H₂ treatment step at 348 K.

In contrast, identical protocols with deionized H₂O instead of EtOH:H₂O led to clusters similar to those treated only at 423 K in H₂. The particle diameters derived from TEM and chemisorption data lie along the parity line, indicative of clean surfaces, but both diameters were larger than the diameter of untreated clusters (Fig. 12b), a reflection of some particle agglomeration during treatment. Treating clusters in deionized H₂O failed to remove a significant amount of surface debris, thus leading to local exotherms that can cause particle growth during the subsequent treatment at 423 K in flowing H₂, as discussed in Section 2.3.5a. These results indicate that EtOH is required to remove the polymer from cluster surfaces, either as a reductant—helping to break the metal-PVP bond—or as a better solvent than H₂O for PVP.³⁵

2.4 Conclusions

AuPt clusters uniform in size and composition were synthesized by colloidal methods using reagents containing only C, H, O, and N. These clusters were dispersed onto SiO₂ and deprotected at low temperatures in a reducing environment without particle coalescence. In doing so, we provide not only catalysts of significant practical interest, but also ideal materials to study the rigorous mechanistic descriptions of the effects of metal mixing.

GDR synthesis protocols previously developed for an enthalpically favorable alloy (AuPd) were modified for an enthalpically unfavorable alloy (AuPt) to promote the uniform growth of Pt seeds via addition of Au and prevent the formation of large Au-rich clusters. Weaker reductants as solvents, slow addition of the Au precursors, high synthesis temperatures, and low Au surface compositions were found to promote a more uniform distribution of Au across the parent Pt clusters. We show that the segregation of immiscible metals leads to the enrichment of Au atoms at cluster surfaces, thus impeding reduction by surface Pt⁰ via GDR, and instead promoting fast autocatalytic reduction by surface Au⁰. The insights developed here can be applied to synthesize uniform bimetallic catalysts of other metal systems of interest, including those composed of immiscible metals.

2.5 Acknowledgements

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2.6 Supporting Information

2.6.1 Derivation of the Mathematical Expression for Seed Cluster Growth (Δd) via GDR Processes

The growth rate of a spherical particle, \( i \), that grows via GDR processes is proportional to its surface area (\( A_i \)), as expressed by:

\[
\frac{dN_i}{dt} = A_i k = \pi d_i^2 k
\]  

(S1)

where \( N_i \) is the moles of atoms in a growing cluster, \( k \) is the areal rate constant for the galvanic displacement reaction, and \( d_i \) is the cluster diameter. The particle volume (\( V_i \)) is given by

\[
V_i = N_i V'_i = \frac{1}{6} \pi d_i^3
\]  

(S2)

where \( V'_i \) is the atomic volume of the particle. Solving for \( N_i \) in Equation S2 and substituting into Equation S1 gives:

\[
\frac{d(d_i)}{dt} = 2V'_i k
\]  

(S3)

Equation S3 can be solved as:

\[
d_i(t) - d_{i,0} = \Delta d_i = 2V'_i k t
\]  

(S4)

where \( d_{i,0} \) is the size of the initial seed particle and \( d_i(t) \) is the particle diameter at time \( t \).

2.6.2 Calculation of Seed Cluster Growth (Δd) from EDS and HAADF Imaging Data

Here, we derive the expression for the thickness by which a seed cluster composed of \( M_A \) grows (\( \Delta d \)) as a result of the addition of Au via GDR processes. Using the atomic fraction of \( M_A \) and the diameter of a given bimetallic particle, obtained from EDS and HAADF imaging, respectively, the diameter of the initial seed cluster from which the bimetallic particle formed can be calculated. We assumed that the requirements of GDR synthesis hold true: surface \( M_A \) atoms reduce solvated Au cations via redox reactions (Scheme 1.2a), and are subsequently reduced back onto cluster surfaces by the reductive solvent (Scheme 1.2b) at a rate proportional to a cluster’s surface area, thus ensuring that the number of \( M_A \) atoms leaving a cluster surface is equal to the number that return, and that solvated Au cations always encounter an \( M_A \) surface atom (not a \( Au^0 \) atom).

The volume of a seed particle (\( V_{M_A,i} \)) as a function of the number of \( M_A \) atoms within the particle (\( N_{M_A,i} \)) and the atomic volume of \( M_A \) (\( V'_{M_A} \)) is:
\[ V_{M_A,i} = \frac{4}{3} \pi \left( \frac{d_{M_A,i}}{2} \right)^3 = \frac{N_{M_A,i} V'_{M_A}}{0.74} \] (S5)

where \( d_{M_A,i} \) is the diameter of particle, \( i \), and 0.74 is the atomic packing factor for FCC metals. Equation S5 then gives an equation for the diameter of the seed cluster:

\[ d_{M_A,i} = \left( \frac{6 N_{M_A,i} V'_{M_A}}{\pi 0.74} \right)^{\frac{1}{3}} \] (S6)

The number of M_A atoms in a seed particle is:

\[ N_{M_A,i} = N_{tot,i}(x_{M_A,i}) \] (S7)

where \( N_{tot,i} \) is the total number of atoms (Au and M_A) in a AuM_A particle and \( x_{M_A,i} \) is the atomic fraction of M_A. \( N_{tot,i} \) is obtained by expressing the volume of a AuM_A cluster (\( V_{AuM_A,i} \)) as:

\[ V_{AuM_A,i} = \hat{V}_{Au,i} + \hat{V}_{M_A,i} = \frac{4}{3} \pi \left( \frac{d_{AuM_A,i}}{2} \right)^3 \] (S8)

where \( \hat{V}_{Au,i} \) and \( \hat{V}_{M_A,i} \) are the volumes occupied by Au and M_A within a AuM_A cluster.

\[ \hat{V}_{Au,i} = \frac{(x_{Au,i}) N_{tot,i} V'_{Au}}{0.74} \quad \text{and} \quad \hat{V}_{M_A,i} = \frac{(x_{M_A,i}) N_{tot,i} V'_{M_A}}{0.74} \] (S9 and S10)

Here, \( V'_{Au} \) is the atomic volume of Au. Substituting Equations S9 and S10 into Equation S8 and rearranging yields:

\[ N_{tot,i} = 0.74 \left( \frac{\pi}{6} \right) \frac{\left( \frac{d_{AuM_A,i}}{x_{M_A,i} V'_{M_A} + x_{Au,i} V'_{Au}} \right)^3}{x_{M_A,i} V'_{M_A} + x_{Au,i} V'_{Au}} \] (S11)

Equation S11 is combined with Equations S6 and S7 to determine the diameter of a parent M_A seed particle from which a AuM_A particle formed:

\[ d_{M_A,i} = d_{AuM_A,i} \left( \frac{x_{M_A,i} V'_{M_A}}{x_{M_A,i} V'_{M_A} + x_{Au,i} V'_{Au}} \right)^{\frac{1}{3}} \] (S12)

These values are subtracted from \( d_{AuM_A,i} \) to calculate \( \Delta d_i \):

\[ \Delta d_i = d_{AuM_A,i} \left[ 1 - \left( \frac{x_{M_A,i} V'_{M_A}}{x_{M_A,i} V'_{M_A} + x_{Au,i} V'_{Au}} \right)^{\frac{1}{3}} \right] \] (S13)
2.6.3 Derivation of the Expected Seed Cluster Growth ($\Delta d$) using the TEM-Derived Particle Size Distribution of Pt Seed Clusters

Next, we derive the equations used to calculate $\Delta d$, the growth of $M_A$ seed clusters via GDR processes, using the TEM-derived particle size distribution of the initial $M_A$ seeds. The derivation is reproduced from previously reported work.$^{[8]}$ The cumulative volume of $M_A$ metal analyzed by TEM (with $N \geq 200$ clusters) of $M_A$ clusters ($V''_{M_A}$) is expressed as:

$$V''_{M_A} = \sum V_{M_A,i} = \sum \frac{1}{6} \pi d_{M_A,i}^3$$

(S14)

where $V_{M_A,i}$ is the volume of seed particle, $i$, with diameter $d_{M_A,i}$. The cumulative volume of bimetallic AuM$_A$ clusters ($V''_{AuM_A}$) that will form from the clusters represented by Equation S14 is then given by:

$$V''_{AuM_A} = V''_{M_A} + V''_{M_A} \left( \frac{V'_{M_A}}{V'_{M_A}} \right) \left( \frac{Au}{M_A} \right)_{at.}$$

(S15)

where $V'_{M}$ is the molar volume of metal $M$ and $N_{Au}/N_{M_A}$ is the nominal atomic ratio of the bimetallic clusters. $V''_{AuM_A}$ can also be expressed as:

$$V''_{AuM_A} = \sum \frac{1}{6} \pi (d_{M_A,i} + \Delta d)^3$$

(S16)

The growth of $M_A$ seed clusters via GDR processes is determined by setting Equation S16 equal to Equation S15 and solving iteratively for $\Delta d$. 
2.6.4 Attempted Synthesis of AuPt Particles using the Protocols Developed for AuPd Clusters

Figure S1 Transmission electron micrograph of clusters with mean (Au/Pt)_at. of unity using the protocols developed for AuPd clusters (298 K, Au precursor solution added all at once to a stirring suspension of Pt clusters) with EG as solvent.

2.6.5 Attempted Syntheses of AuPt Particles with 67 % at. Au Content

Table S1 Rate of Au^{3+} addition and the LSPR intensity of the resulting sample

<table>
<thead>
<tr>
<th>Rate of addition of Au^{2+} (nmol s^{-1})</th>
<th>First Au^{3+} dose</th>
<th>Second Au^{3+} dose</th>
<th>LSPR intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au^{3+} dose</td>
<td>LSPR intensity</td>
<td></td>
</tr>
<tr>
<td>16.7</td>
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<td>0.589</td>
<td></td>
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<tr>
<td>16.7</td>
<td>16.7</td>
<td>0.4</td>
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<td>16.7</td>
<td>8.3</td>
<td>0.334</td>
<td></td>
</tr>
<tr>
<td>16.7</td>
<td>4.2</td>
<td>0.142</td>
<td></td>
</tr>
<tr>
<td>16.7</td>
<td>1.7</td>
<td>0.198</td>
<td></td>
</tr>
</tbody>
</table>
Figure S2 Transmission electron micrograph of clusters in a AuPt sample with 67% at. Au, synthesized using the protocols developed for AuPt particles with 50% at. Au (423 K, EG solvent; Au$^{3+}$ added in a single dose at 16.7 nmol s$^{-1}$ to a stirring, heated suspension of Pt clusters).
2.7 References

Chapter 3

Displacement-Reduction Strategies for the Synthesis of Uniform PtPd Clusters with Clean Surfaces and Mechanistic Guidance for Other Bimetallic Systems

Abstract

Uniform bimetallic PtPd nanoparticles suitable as model catalysts to probe the structure-function relationship of alloying were synthesized using colloidal methods and reagents containing only C, H, O, and N. Galvanic displacement-reduction (GDR) protocols previously developed to synthesize AuPd and AuPt particles were extended to the PtPd system. GDR involves the reduction of solvated cations of the more noble metal (Pt) by the surface atoms of preformed seed particles composed of the metal with the lower reduction potential (Pd), thus taking advantage of their relative reduction potentials to promote metal mixing. PtPd clusters were characterized using transmission electron microscopy, UV-visible spectroscopy, energy dispersive X-ray spectroscopy and high-angle angular dark field spectroscopy, which show that all clusters are bimetallic, samples are uniform in size and composition, and that clusters grow at rates proportional to the seed cluster surface area, as predicted for GDR growth. These results, taken together with those reported previously for AuPd and AuPt systems, offer insights into the formation of bimetallic clusters via GDR processes that can be generalized and applied to other bimetallic systems of interest. Enthalpically favorable alloys such as PtPd and AuPd form exclusively from GDR pathways, in contrast to unfavorable alloys such as AuPt, for which alternative reaction pathways become significant. The compositional uniformity of bimetallic clusters that form via GDR processes is established by the uniformity of the initial seed particle diameters. Colloidal clusters were dispersed onto SiO₂ and the protecting polymer, polyvinylpyrrolidone (PVP), removed using a low temperature (≤ 423 K) treatment in a reducing environment (H₂ or EtOH/H₂O). Relative to Pt clusters, removing the protecting polymer from Pd cluster surfaces is more challenging because of the stronger Pd-PVP bond relative to the Pt-PVP bond. Increasing Pd cluster size and/or alloying Pd clusters with Pt facilitated polymer removal by decreasing the strength of the PVP bond to the cluster surface.

3.1 Introduction

Bimetallic catalysts have been shown to increase catalytic turnover rates, improve selectivity, or enhance stability.[1] The effects of alloying on the reactivity of small bimetallic clusters are often rendered ambiguous or imprecise, however, because of the size and/or compositional heterogeneity of materials prepared by prevalent synthesis techniques, such as incipient wetness impregnation.[2] Methods that provide greater control over size and composition, such as colloidal methods,[1b, 3] often invoke the use of reagents with heteroatoms that irreversibly titrate the catalyst surface (ex. S and B) and influence turnover rates. Here, we describe the colloidal synthesis of PtPd nanoparticles (2.1-2.9 nm) uniform in size and composition using reagents containing only C, H, O, and N, which we show can be removed from catalyst surfaces without significant particle agglomeration using a low temperature reductive treatment. Such materials are suitable for rigorous kinetic studies of the effects of alloying Pt and Pd.
PtPd clusters were synthesized using galvanic displacement-reduction (GDR) protocols previously shown to form AuPt\textsuperscript{[4]} and AuPd\textsuperscript{[5]} bimetallic nanoparticles. The synthesis of AuPt and AuPd clusters begins with a colloidal suspension of pre-formed nanoparticles composed of the metal (M\textsubscript{A} = Pt or Pd) with the lower standard reduction potential (E\textdegree\textsubscript{o}); these suspensions are then mixed with a solution of metal cations of the more noble element (M\textsubscript{B} = Au). The reduction of solvated M\textsubscript{B} cations by surface M\textsubscript{A} atoms is thermodynamically favorable (ΔE\textdegree\textsubscript{redox} = E\textdegree\textsubscript{B} - E\textdegree\textsubscript{A} > 0; Table 1), leading to the reduction and deposition of M\textsubscript{B} atoms onto cluster surfaces, and to the oxidation and dissolution of M\textsubscript{A} atoms into the solvent (Scheme 1.2a). Displaced M\textsubscript{A} cations are subsequently reduced by the solvent, which also acts as a reductant (ethanol or ethylene glycol), and deposited back onto cluster surfaces (Scheme 1.2b).\textsuperscript{[4-5]} In the current study, PtPd clusters were synthesized by adding a Pt precursor solution to a pre-formed suspension of Pd seed clusters, as prescribed by their relative reduction potentials (ΔE\textdegree\textsubscript{redox} = E\textdegree\textsubscript{Pt} - E\textdegree\textsubscript{Pd} > 0; Table 1).

PtPd particles were characterized using transmission electron microscopy, UV-visible spectroscopy, energy dispersive X-ray spectroscopy (EDS), and high-angle annular dark field (HAADF) imaging. Particle-by-particle EDS in tandem with HAADF imaging confirmed the exclusive formation of bimetallic clusters, and were used to verify the mechanistic features of GDR that are relevant to the compositional uniformity of a bimetallic sample. M\textsubscript{A} seed clusters that grow via GDR processes increase in size at rates proportional to their surface areas, and, thus, increase in diameter by an amount Δd that is independent of the initial seed particle size.\textsuperscript{[5]}
consequently, a distribution of $M_A$ seed cluster sizes that all grow by the same amount, $\Delta d$, leads to a distribution of bimetallic compositions such that $(M_B/M_A)_{\text{at.}}$ decreases with increasing parent seed cluster size. The compositional uniformity of a bimetallic sample prepared by GDR methods is therefore dictated by the breadth of the size distribution of the parent seeds.

We previously confirmed such mechanistic features of GDR for AuPd, an enthalpically favorable alloy ($\Delta H_{\text{AuPd}} = -6.7 \text{ kJ mol}^{-1}$),[7] but not AuPt, an unfavorable alloy ($\Delta H_{\text{AuPt}} = +2.3 \text{ kJ mol}^{-1}$),[8] for which additional Au cation reduction pathways—the autocatalytic reduction of Au cations by $Au^0$ surface atoms—competed with GDR processes as a result of the segregation of metal atoms within clusters.[4] The synthesis of uniform AuPt clusters therefore requires more precise synthesis protocols than AuPd synthesis in order to promote the reduction of Au cations by Pt$^0$ surface atoms via GDR. In the current study, EDS data confirmed that PtPd clusters, which are enthalpically favorable ($\Delta H_{\text{PtPd}} = -4.3 \text{ kJ mol}^{-1}$),[9] form via GDR processes. Consequently, the facile synthesis protocols used to prepare AuPd particles are appropriate for the synthesis of uniform PtPd clusters.

3.2 Methods

3.2.1 Catalyst Synthesis

![Scheme 2](image)

Scheme 2 Colloidal synthesis protocols for the preparation of bimetallic catalysts: (a) $M_A$ precursors (●), together with the protecting polymer ( ), were mixed in a reductive solvent (○) and heated to form a suspension of polymer-protected $M_A$ particles. (b) $M_B$ cations (●) were added to the seed cluster suspension and (c) were subsequently reduced and incorporated into the $M_A$ seed clusters to form bimetallic particles. (d) Clusters were dispersed onto the support (SiO$_2$) and (e) the protecting polymer was removed. Scheme adapted from previously reported work.[4]

3.2.1a Preparation of polyvinylpyrrolidone (PVP) protected Pd clusters (1.8 nm)

A mixture of 1:1 by volume ethanol (EtOH, Sigma Aldrich, >99.5 %) and deionized water (H$_2$O; resistivity ~0.06 $\mu$S cm$^{-1}$) containing PVP (0.02 M, monomeric unit basis; Sigma Aldrich, 40,000 amu) and Pd(NO$_3$)$_2$·2(H$_2$O) ($5\cdot10^{-4}$ M Pd, Sigma Aldrich, ~40 % wt. Pd basis) was heated to 368 K while stirring with a magnetic stir bar (310 rpm) in ambient air (one-neck flask, 0.1 L, reflux condenser) for 0.4 h.

3.2.1b Preparation of PVP protected Pd clusters (2.3 nm)

A solution of Pd(NO$_3$)$_2$·2(H$_2$O) ($5\cdot10^{-4}$ M Pd, Sigma Aldrich, ~40 % wt. Pd basis) in 1:1 by volume EtOH (Sigma Aldrich, >99.5 %) and deionized H$_2$O (resistivity ~0.06 $\mu$S cm$^{-1}$) was added to an equivalent volume of a monometallic 1.8 nm Pd cluster suspension ($5\cdot10^{-4}$ M Pd, prepared as described in Section 3.2.1a). The resulting mixture was stirred (310 rpm) in ambient air at 363 K for 0.33 h.
3.2.1c Preparation of PVP protected PtPd clusters

H₂PtCl₆ (5·10⁻⁴ M Pt, Sigma Aldrich, 8 % wt. in H₂O) in 1:1 by volume EtOH (Sigma Aldrich, >99.5 %) and deionized water (resistivity ~0.06 μS cm⁻¹) was added to an equivalent volume of the monometallic 1.8 nm Pd cluster suspension (5·10⁻⁴ M Pd, prepared as described in Section 3.2.1a) and allowed to stir (310 rpm) in ambient air at 363 K for 0.33 h to form clusters with a bulk (Pt/Pd)ₐt. of unity. Bimetallic PtPd clusters of different atomic ratios were synthesized by adjusting the volumetric ratio of the Pt precursor solution and Pd seed cluster suspension.

3.2.1d Preparation of PVP protected Pt and AuPt clusters

Pt and AuPt clusters were prepared by previously reported methods.[⁴]

3.2.1e Preparation of polyvinylalcohol (PVA) protected Pd and AuPd clusters

Pd and AuPd clusters were prepared by previously reported methods.[⁴]

3.2.1f Dispersion of PVP protected clusters onto SiO₂

A Pd cluster suspension (52 cm³), prepared as described in Section 3.2.1a) was added drop-wise (~0.2 cm³ s⁻¹) to a suspension of fumed SiO₂ (0.55 g, Sigma Aldrich, 7 nm particle size, 395 m² g⁻¹ surface) dispersed in deionized H₂O (52 cm³, resistivity ~ 0.06 μS cm⁻¹). After stirring the mixture for 1 h at ambient temperature, the solids were recovered by centrifugation (133 Hz, 0.6 ks). Absence of residual clusters in the supernatant solutions was confirmed by the absence of absorbance in their UV-visible spectra. Supported clusters were washed two times in deionized water (52 cm³, resistivity ~ 0.06 μS cm⁻¹, 1 h) before treating samples overnight at 356 K in ambient air. These procedures led to a metal loading of 0.5 % wt. Similar procedures were used to disperse bimetallic PtPd clusters on SiO₂, resulting in metal loadings of 0.5 % wt., 0.58 % wt., and 0.7 % wt. for PtPd samples with nominal (Pt/Pd)ₐt. ratios of 0.11, 0.33, and 1, respectively.

3.2.2 Nanoparticle Characterization

3.2.2a Transmission electron microscopy (TEM)

Bright-field transmission electron micrographs were obtained using a JEOL 1200 EX microscope operated at 80 kV. TEM samples of colloidal Pd, AuPd, and PtPd clusters synthesized in EtOH/H₂O mixtures were prepared by depositing a drop of the cluster suspension in its synthesis medium onto holey-carbon Cu grids (Ted Pella Inc.), and allowing the solvent to evaporate in air at ambient temperature. TEM samples of colloidal Pt and AuPt samples synthesized in ethylene glycol, a less volatile solvent, were re-dispersed in deionized water before TEM grid preparation (methods reported previously)[⁴] in order to prepare grids without thermal treatments that could affect cluster size and composition. Clusters supported on SiO₂ were first suspended in acetone before placing on Cu grids. A minimum of 200 clusters were analyzed per sample, and surface-averaged mean diameters were calculated from transmission electron micrographs using the equation:
\[ \langle d \rangle = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \]  

where \( n_i \) is the number of clusters with diameter \( d_i \). Particle size uniformity was quantified by calculating the dispersity index (\( D_A \)) of each sample using the equation:\[10^3\]

\[ D_A = \frac{\sum n_i (\pi d_i^2)^2}{(\sum \pi d_i^2 n_i)^2} \]  

3.2.2b Ultraviolet-visible spectroscopy

UV-visible spectra (200-800 nm) of cluster suspensions (3 cm\(^3\)) in quartz cuvettes (10 cm\(^3\), Agilent) were collected using a two-beam spectrophotometer (Varian Cary 400 Bio) with a 5 nm s\(^{-1}\) scan rate. Spectra collected during synthesis were obtained by withdrawing 3 cm\(^3\) samples at designated time intervals using a disposable glass pipette.

3.2.2c Elemental analysis of bimetallic clusters

Energy dispersive X-ray spectroscopy (EDS) data were obtained using an FEI Titan microscope fitted with an FEI Super X-Quad windowless detector based on silicon drift technology and operated at 200 kV. Atomic compositions were quantified using Cliff-Lorimer k-factors and Bruker Esprit software calibrated against mineral standards. High-angle annular dark field (HAADF) micrographs, collected concurrently to EDS X-rays, were acquired using a Fischione detector with a convergence semi-angle (\( \alpha \)) of 10 milliradians and an inner semi-angle (\( \beta \)) of 50 milliradians. Sample preparation of particles in colloidal suspensions was as described in Section 3.2.2a.

The diameters of bimetallic particles (\( d_{M\text{M}A} \)) were measured from HAADF micrographs using ImageJ software. The volume-averaged mean atomic fraction of a metal M (\( \langle x_M \rangle_{\text{at.}}; \ M = \text{Au, Pt, or Pd} \)) in a sample (\( N > 100 \) particles) was calculated using the equation:

\[ \langle x_M \rangle_{\text{at.}} = \frac{\sum x_{M,i} d_{MBM,A,i}^3}{\sum d_{MBM,A,i}^3} \]  

which accounts for the greater contribution of larger particles to the total metal content.

3.2.3 Removal of the Protecting Polymer and Assessment of Surface Cleanliness using \( O_2 \) Chemisorption

3.2.3a Removal of the protecting polymer via treatment in \( H_2 \) at low temperatures

SiO\(_2\)-supported Pd clusters (0.5 % wt.; prepared as described in Sections 3.2.1a and 3.2.1e) or PtPd clusters (0.5 % wt., 0.58 % wt., and 0.7 % wt. PtPd clusters with (Pt/Pd)\(_{\text{at.}}\) of 0.11, 0.33, and 1, respectively; prepared as described in Sections 3.2.1b and 3.2.1e) were treated in flowing \( H_2 \) (Praxair 99.999 %, 0.25 cm\(^3\) s\(^{-1}\) g\(^{-1}\)) at 348 K for 1 h followed by treatment at 423 K for 1 h
Chemisorbed O₂ uptake was determined as described in Section 3.2.3c immediately after treatment.

3.2.3b Removal of the protecting polymer via treatment in EtOH/H₂O and H₂ at low temperatures

SiO₂-supported Pd clusters (0.5 % wt.; prepared as described in Sections 3.2.1a and 3.2.1e) were stirred for 20 h in 50 cm³ g⁻¹ of 1:1 by volume EtOH (Sigma Aldrich, >99.5 %) and deionized H₂O (resistivity ~0.06 µS cm⁻¹) heated to 351 K in ambient air. The catalyst was recovered by centrifugation (133 Hz, 0.6 ks⁻¹) and maintained at 353 K in stagnant air overnight before treatment in flowing H₂ (Praxair 99.999 %, 0.25 cm³ s⁻¹ g⁻¹) at 423 K (0.033 K s⁻¹) for 1 h. Chemisorbed O₂ uptake was determined as described in Section 3.2.3c immediately after treatment.

3.2.3c O₂ chemisorption uptakes

The number of accessible surface metal atoms was measured from catalyst O₂ uptakes. TEM-derived surface-averaged particle diameters similar to chemisorption-derived particle diameters indicate that the surfaces visible by TEM are fully accessible to probe molecules, and that the metal surface is free of synthetic detritus. Chemisorption uptakes were measured using a volumetric adsorption apparatus equipped with a Baratron gauge and a turbomolecular pumping system (Pfeiffer Vacuum; <1 Pa dynamic vacuum). SiO₂-supported Pd clusters (0.5 % wt.) or PtPd clusters (0.5 % wt., 0.58 % wt., and 0.7 % wt. with (Pt/Pd)ₐt. = 0.11, 0.33, and 1, respectively) were treated as described in Section 3.2.3a or 3.2.3b, and then evacuated for 1 h at 423 K before cooling to 298 K. Isotherms were measured in a range between 0.013 kPa to 101.3 kPa O₂ (Praxair, 99.999 %), with an equilibration time of 0.07 h. O₂ uptakes were estimated by extrapolation to zero O₂ pressure, and dispersions were calculated assuming one O-atom per metal surface atom. The particle diameter was calculated from the chemisorption-derived dispersion (D) using:

\[ d = \frac{C}{D} \]  

where \( d \) is diameter in nm and \( C \) is a function of the metal identity (1.13 nm for Pt, 1.12 nm for Pd, and a weighted average, based on atomic composition, for PtPd bimetallic samples), calculated assuming a spherical geometry and using the density of the bulk metals.

3.3 Results and Discussion

3.3.1 Synthesis and Characterization

Particle diameter measurements obtained by TEM of Pd clusters and bimetallic PtPd clusters with (Pt/Pd)ₐt. of 0.5, 1, and 2 (Fig. 1) were used to calculate surface-averaged mean diameters (Eq. 1; Table 2). Mean PtPd cluster size increased monotonically with increasing mean Pt content of the sample, consistent with the reduction and deposition of solvated Pt cations onto the starting Pd seeds. Cluster uniformity was determined by calculating the dispersity index (\( D_A \)) of each sample using Equation 2. \( D_A \) values (1.13-1.20) were < 1.5 for all PtPd samples,
indicating that clusters were essentially monodisperse, as defined by IUPAC. Relative standard deviations (16-19 %), a more commonly reported—but less precise—measure of uniformity, are also included in Table 2, and similarly indicates that bimetallic clusters are narrowly distributed in size. Clusters with similar size distributions are typically obtained by colloidal methods using NaBH₄ as a reductant and/or protecting agents with thiol groups, which are difficult to remove from catalyst surfaces, and which we have successfully avoided in this study without loss of size uniformity.

![Figure 1](image)

**Figure 1** Particle size distributions and sample micrographs of clusters with nominal (Pt/Pd)$_{at}$ ratios of a) 0, b) 0.5, c) 1, and d) 2.
Table 2 Surface-averaged mean diameter, expected bimetallic diameter, dispersity indices, and relative standard deviations

<table>
<thead>
<tr>
<th>(Pt/Pd)$_{Ma}$</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM-derived surface-averaged diameter, $d_b$ (nm, Eq. 2)</td>
<td>1.8 ± 0.02</td>
<td>2.1 ± 0.03</td>
<td>2.5 ± 0.03</td>
<td>2.9 ± 0.03</td>
</tr>
<tr>
<td>Expected diameter, $d_{PtPd}$ (nm, Eq. 4)</td>
<td>--</td>
<td>2.2</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Dispersity index, $D_A$ (Eq. 3)</td>
<td>1.20</td>
<td>1.18</td>
<td>1.15</td>
<td>1.13</td>
</tr>
<tr>
<td>Relative standard deviation (%)</td>
<td>19.7</td>
<td>18.5</td>
<td>18.0</td>
<td>16.7</td>
</tr>
</tbody>
</table>

Expected mean bimetallic cluster diameters ($d_{M_B M_A}$) were calculated using the surface-averaged mean diameter of the seed clusters ($d_{M_A}$) and the equation (Table 2):

$$
\langle d_{M_B M_A} \rangle = \langle d_{M_A} \rangle \left(1 + \frac{V'_M N_{M_B}}{V'_{M_A} N_{M_A}}\right)^{1/3}
$$

where, $V'_M$ is the atomic volume of metal $M$ and $N_M$ is the number of atoms of metal $M$. Equation 5 assumes that solvated $M_B$ cations are reduced and deposited homogeneously across all $M_A$ seed clusters, thus precluding the homogeneous nucleation and growth of monometallic $M_B$ particles in solution—resulting in no cluster growth of the initial $M_A$ seeds—and/or the nucleation of $M_B$ species on the surface of a fraction of seed clusters, known as heterogeneous nucleation, that grow at the expense of the majority. The homogeneous or heterogeneous nucleation of $M_B$ would lead to bimodal distributions of particle size and the mean cluster diameter would not be accurately described by Equation 5. Figure 2 shows that measured $d_{PtPd}$ values agree well with those calculated from Equation 5, consistent with the absence of homogeneous or heterogeneous nucleation of Pt during synthesis. No monometallic particles were detected from elemental analysis using EDS (N > 100 clusters per sample), in further support of such conclusions. The mean atomic fraction of each metal component (Eq. 3) within each bimetallic PtPd sample was consistent with the synthesis reagents used (Fig. 3a), confirming that all metal precursors were recovered in the resulting solids.
Figure 2 Parity plot of the measured (Eq. 2) and expected (Eq. 4) mean PtPd diameter ($d_{\text{PtPd}}$) of clusters synthesized at 363 K (◊) with (Pt/Pd)$_{\text{at.}}$ ratios of 0.5, 1, and 2, and of clusters synthesized at ambient temperature (▲) and 323 K (■) with (Pt/Pd)$_{\text{at.}}$ of unity.

Figure 3 Parity plots of the mean $M_B$ to $M_A$ atomic ratio ($M_B/M_A$, calculated from EDS data) and the expected $M_B/M_A$, of a) PtPd, b) AuPd, and c) AuPt bimetallic samples. At least 100 particles analyzed for each sample. Figures b) and c) reproduced from previously reported work.[4]

UV-visible spectra were used to monitor the disappearance of the Pt precursor band (266 nm) during synthesis (298 K, 1:1 by volume EtOH/H$_2$O; Section 3.2.1c) in order to confirm the full reduction of solvated Pt cations by the Pd seeds (Fig. 4a). The intensity of the Pt precursor band decreased (Fig. 4a) and the particle size increased (from transmission electron micrographs; Fig. 4b) with reaction time, consistent with the reduction and deposition of Pt cations as Pt$^0$ onto the Pd seeds. Pt precursor features were no longer detected after 46.5 h, thus confirming the reduction of all solvated Pt cations. The UV-visible spectra of the clusters formed were similar to
those of the initial Pd seed clusters (Fig. 5), as expected for the similar spectral properties of Pt and Pd clusters in the UV-visible range.\textsuperscript{14} An increase in the synthesis temperature led to the faster reduction of solvated Pt cations (~3 h at 323 K, ~0.33 h at 363 K); UV-visible spectra (Fig. 5) and particle size distributions (Fig. 2) of the clusters formed at 298 K, 323 K, and 363 K were similar.

![Figure 4](image1.png)

**Figure 4** a) UV-visible spectra of Pd seed particles (---) and bimetallic PtPd particles (mean (Pt/Pd)$_{\text{at.}}$ = 1) during synthesis at ambient temperature after 2.7 h (--), 7.3 h (-----), 22 h (---), and 46.5 h (----). b) Surface-averaged particle diameters ($\langle d \rangle$; measured by TEM) with reaction time.

![Figure 5](image2.png)

**Figure 5** UV-visible spectra of Pd clusters (---) and bimetallic PtPd clusters (mean (Pt/Pd)$_{\text{at.}}$ = 1) synthesized at ambient temperature (-----), 323 K (---), and 363 K (----).
In contrast with solvated Pt cations, Au cations in contact with Pd seed clusters at ambient temperature reduced fully within 2 h (versus ~46.5 h for Pt).\textsuperscript{[5]} Pd surface atoms reduce Pt cations more slowly than Au cations and, thus, form bimetallic PtPd clusters at slower rates than AuPd clusters, a reflection of the lower thermodynamic driving force for the displacement step of GDR for PtPd systems (\(\Delta E^\text{redox, AuPd} = 0.74 \text{ V}\), \(\Delta E^\text{redox, PtPd} = 0.24 \text{ V}\); Scheme 1.2a). In spite of these different reduction rates, enthalpically favorable alloys such as AuPd and PtPd (\(\Delta H_{\text{AuPd}} = -6.7 \text{ kJ mol}^{-1}\) and \(\Delta H_{\text{PtPd}} = -4.3 \text{ kJ mol}^{-1}\))\textsuperscript{[7, 9]} can be synthesized at ambient temperature. In contrast, AuPt, an enthalpically unfavorable alloy (\(\Delta H_{\text{AuPt}} = +2.3 \text{ kJ mol}^{-1}\)),\textsuperscript{[8]} requires elevated synthesis temperatures (423 K) to compensate for unfavorable mixing enthalpies through mixing entropies that become more consequential for Gibbs free energies at higher temperatures.\textsuperscript{[4]}

### 3.3.2 Bimetallic Cluster Formation Mechanism

Particle-by-particle elemental analysis using EDS is used next to probe the mechanistic features of bimetallic cluster formation via GDR. GDR processes require that:\textsuperscript{[4-5]}

(a) solvated \(M_B\) cations be reduced exclusively by \(M_A\) surface atoms (Scheme 1.2a),
(b) \(M_A\) atoms brought into solution by galvanic displacement reactions in (a) be subsequently reduced by solvent molecules and deposited on cluster surfaces (Scheme 1.2b), and
(c) \(M_A\) atoms remain accessible at the growing bimetallic cluster surface to reduce solvated \(M_B\) cations, thus fulfilling requirement (a).

GDR growth therefore depends on the availability of \(M_A\) surface atoms to reduce solvated \(M_B\) cations. When conditions a-c are fulfilled, the growth rate of a particle, \(i\), is proportional to its surface area \((A_i)\):

\[
\frac{dN_i}{dt} = A_i k
\]

where \(N_i\) is the moles of atoms in a growing cluster and \(k\) is the areal rate constant for the galvanic displacement reaction. The amount by which each cluster grows (\(\Delta d_i\)) as a result of the addition of \(M_B\) atoms can be derived from Equation 6 by expressing \(A_i\) and \(N_i\) as functions of the cluster diameter \((d_i\); derivation in Section 3.6.1, SI).\textsuperscript{[5]}

\[
\Delta d_i = 2V_i/k't
\]

Here, \(V_i\) is the atomic volume and \(t\) is time. According to Equation 7, clusters that grow at a rate proportional to their respective surface areas (Eq. 6) would increase in size by a value \(\Delta d_i\) that is independent of the diameter of the parent cluster.\textsuperscript{[5, 15]} Consequently, a suspension of \(M_A\) seed particles of varying particle sizes all grow by the same thickness \((\Delta d)\) by the addition of a second metal \((M_B)\), thus forming bimetallic \(M_BM_A\) clusters with a distribution of compositions such that \((N_{M_B}/N_{M_A})\) decreases with increasing seed particle diameter (Scheme 3). This inverse relationship between \((N_{M_B}/N_{M_A})\) and seed particle diameter \((d_{M_A})\) is obtained by rearranging Equation 5 for each single particle, \(i\):

49
\[
\left( \frac{N_{MB}}{N_{MA}} \right)_i = \left[ \left( 1 + \frac{\Delta d}{d'_{MA,i}} \right)^3 - 1 \right] \frac{V'_{MA}}{V'_{MB}}
\]

(8)

where \( d_{M_BM_A} \) in Equation 5 is replaced by:

\[
d_{M_BM_A} = d_{MA} + \Delta d
\]

(9)

Scheme 3 M_A seed particles of varying size that grow via galvanic displacement-reduction processes grow at a rate proportional to their surface area, and therefore increase in size by an amount \( \Delta d \) that is independent of the original seed particle diameter.\(^5\) Thus, the \((M_B/M_A)_{at.}\) of the resulting bimetallic particles decreases with increasing particle size. Scheme reproduced from previously reported work.\(^4\)

The compositional uniformity of bimetallic clusters formed from GDR processes is therefore determined by the breadth of the parent seed cluster size distribution. Next, we establish the relationship between the uniformity of the seed particle diameters and the uniformity of the resulting bimetallic cluster compositions using numerical methods and the coefficient of variation (CV),

\[
CV = \frac{\sigma}{\mu}
\]

(10)

where \( \sigma \) is the sample standard deviation and \( \mu \) is the sample mean, to characterize uniformity. Probability density functions representing lognormally distributed seed particles,\(^{15a}\) each with a different CV value (0-0.4), were transformed into their corresponding probability density functions representing the compositions of the bimetallic nanoparticles formed through GDR processes, from which we could calculate CV values (derivation Section 3.6.2, SI). Figure 6a shows the resulting curve relating the CV of seed particle distributions to the CV of bimetallic composition distributions, which demonstrates how a sharpening of the size distribution of the seed clusters leads to bimetallic clusters that are more uniformly distributed in composition.
Figure 6 a) Expected relationship (---) between the coefficient of variation (CV) of parent seed cluster diameters (d_{MA}) and the CV of the resulting bimetallic cluster compositions (N_{MB}/N_{MA}). Measured CV values for 1-1 AuPt (●), PtPd (▲), and AuPd (■) clusters shown (determined from EDS data). b) Deviation between measured and expected CV values of 1-1 AuPt, PtPd, and AuPd samples.

Deviations from GDR pathways can be confirmed using the curve in Figure 6a, which was created assuming GDR growth. Data obtained from EDS elemental analysis of bimetallic AuPt, PtPd, and AuPd clusters and transmission electron micrographs of Pt and Pd seed particle size distributions are plotted in Figure 6a to identify bimetallic systems that deviate from the curve expected for particles formed from GDR processes. AuPt clusters (an endothermic alloy) show the largest deviation, while AuPd and PtPd clusters (exothermic alloys) lie closer to the curve (Fig. 6b), consistent with GDR reduction pathways prevailing for the latter two bimetallic systems. Such conclusions are consistent with PtPd and AuPd clusters exhibiting an inverse relation between (M_{B}/M_{A})_{at} and seed cluster size, as expected for clusters formed from GDR processes (Scheme 3), in contrast to AuPt clusters, which do not (Fig. 7). These data are consistent with the fulfillment of all GDR requirements (a-c) during AuPd and PtPd cluster synthesis, but not AuPt cluster synthesis, for which additional growth pathways exist.
Figure 4 Changes in mean $M_B$ to $M_A$ atomic ratio ($\langle \frac{M_B}{M_A} \rangle_{\text{at.}}$, calculated from EDS data) with increasing bimetallic particle diameter ($d_{\text{MB/MA}}$, measured from HAADF micrographs) for a) PtPd, b) AuPd, and c) AuPt particles. Data obtained for individual clusters and binned by particle size (bin width of 0.5 nm). Bimetallic samples with nominal $M_B/M_A$ ratios of 0.5 (▲), 1 (■), and 2 (▲) shown. At least 100 particles analyzed for each sample, with 74-98% of particles located in 4 bins. Bins containing less than 3 particles omitted for clarity. Figures b) and c) reproduced from previously reported work.[4]

The formation mechanism can also be probed for these three bimetallic systems using HAADF micrographs collected in tandem with particle-by-particle EDS analysis of individual bimetallic clusters to measure both their diameters ($d_{\text{MB/MA},i}$) and $M_A$ atomic fractions ($X_{M_A,i}$), respectively. These data can then be used to calculate the size of the seed cluster from which each bimetallic cluster, $i$, formed, and, in turn, the thickness by which each cluster grows ($\Delta d_i$) using:[4]

$$\Delta d_i = d_{\text{MB/MA},i} \left[ 1 - \left( \frac{x_{M_A,i}V'_{M_A}}{x_{M_A,i}V'_{M_A} + x_{M_B,i}V'_{M_B}} \right)^{1/3} \right]$$ (11)

where $V_M$ is the atomic volume (derivation in Section 3.6.3, SI). Figures 8a-b show that the seed clusters for AuPd and PtPd particles grow by a value $\Delta d$ that is constant and independent of seed particle size, as predicted for growth mechanisms involving GDR processes. The expected $\Delta d$ value for a bimetallic sample can be calculated from the TEM-derived size distribution of its starting seed clusters, onto which $M_B$ atoms are distributed based on the surface area of each cluster, as dictated for GDR processes (derivation in Section 3.6.4, SI).[4-5] The expected $\Delta d$ values for AuPd and PtPd samples agree well with experimental values calculated from EDS and HAADF data (Figs. 8a-b; dashed lines indicate expected $\Delta d$ values), consistent with the predominant involvement of GDR processes in their growth.
In contrast, the Pt seed clusters of AuPt particles grow by a value $\Delta d$ that increases monotonically with the diameter of the parent seed clusters (Fig. 8c), suggesting that bimetallic growth pathways other than GDR are involved in their synthesis. We have discussed these results for AuPt clusters elsewhere. Briefly, enthalpically unfavorable alloys such as AuPt (mixing enthalpy, $\Delta H_{\text{AuPt}} = +2.3$ kJ mol$^{-1}$)\cite{8} segregate within clusters to minimize the enthalpic penalties of mixing, consequently driving the metal with the lower surface energy (Au),\cite{16} to the surface (Scheme 4). The enrichment of Au at cluster surfaces is greater for larger clusters because their larger bulk reservoirs mitigate the depletion of Au atoms from the cluster bulk, thus maintaining the thermodynamic driving force for Au surface enrichment.\cite{17} Consequently, the Au$^0$ surface content of AuPt particles increases with particle size, displacing from the surface the Pt$^0$ atoms required to reduce solvated Au cations via GDR, and promoting instead autocatalytic reduction of Au cations by solvent molecules on Au$^0$ sites. Autocatalytic reduction by Au$^0$ is a fast reaction that scavenges solvated Au cations from smaller clusters,\cite{18} leading the larger Pt seed clusters to amass more Au than would be predicted from their surface areas alone. Fast, autocatalytic reduction on the surfaces of the larger clusters renders the homogeneous addition of Au cations to all Pt seeds challenging, as reflected in the more stringent synthesis protocols required to synthesize uniform AuPt clusters relative to the protocols appropriate for clusters of thermodynamically favorable metals (such as Au-Pd and Pt-Pd) that maintain M$\text{A}$ atoms at cluster surfaces.\cite{4}
Parent Pd seed clusters increase in diameter by a value $\Delta d$ that is independent of seed cluster size, confirming that solvated Au or Pt cations encounter Pt$^0$ atoms at the growing bimetallic surface, and that GDR processes predominate during bimetallic cluster synthesis. b) In contrast, the enthalpic unfavorability AuPt clusters leads to the segregation of Au atoms at the particle surface, thus hindering GDR while promoting the fast, autocatalytic reduction of Au. Parent Pt seed clusters increase in diameter by a value $\Delta d$ that increases with seed cluster size, consistent with higher Au$^0$ concentrations at the surface of the larger bimetallic clusters. Scheme modified from previously reported work.\textsuperscript{[4]}

3.3.3 Removal of the Protecting Polymer from Metal Cluster Surfaces using a Reductive Treatment at Low Temperatures

3.3.3a PVP removal from monometallic Pd cluster surfaces using $H_2$

Our previous studies using SiO$_2$-supported monometallic Pt clusters has shown that PVP, the polymer used during colloidal synthesis to prevent particle agglomeration in solution, can be removed from metal surfaces without particle growth by treating the catalyst in a reductive gas ($H_2$) or liquid (1:1 by volume EtOH/H$_2$O) at low temperatures (up to 423 K).\textsuperscript{[4]} PVP binds to metal surfaces via the carbonyl oxygen of the pyrrolidone group, which donates an electron pair into an empty orbital of the metal surface. Exposing clusters to a reducing environment at mild temperatures fully reduces the metal surface and releases the carbonyl groups of PVP without reaching temperatures that lead to polymer densification and amorphous carbon formation, thus averting the consequences of standard surface cleaning techniques at higher temperatures that result in the obstruction of catalytically active surface atoms.\textsuperscript{[19]} Here, we extend these protocols to SiO$_2$-supported Pd clusters coated in PVP. Surface cleanliness of treated clusters was probed by titration of chemically accessible metal surface atoms using O$_2$ to determine metal dispersions, which were used to calculate surface-averaged diameters (Eq. 4) that could be compared to particle size measurements obtained from TEM images. Particle diameters derived from chemisorption experiments that agreed with those measured by TEM indicated that surfaces were free of synthetic residues.

The chemisorption-derived mean diameter of Pd clusters treated in flowing $H_2$ using a two-step protocol previously shown to remove PVP from Pt cluster surfaces (348 K for 1 h, followed by 423 K for 1 h; 0.033 K s$^{-1}$ ramp rate; Section 3.2.3a) was larger than the surface-averaged cluster diameter estimated from transmission electron micrographs (Fig. 9), indicating that residual material remained on metal surfaces; treated Pd clusters were larger in size than untreated clusters (1.8 nm before treatment, 3.2 nm after treatment; determined by TEM). Failure to fully remove PVP from Pd cluster surfaces using protocols suitable for Pt clusters reflects the higher heat of oxygen adsorption for Pd relative to Pt.\textsuperscript{[20]} and/or the smaller initial cluster diameter of Pd.
clusters (1.8 nm Pd clusters, 2.6 nm Pt clusters) that results in a higher fraction of under-coordinated surface metal atoms that bind adsorbates more strongly. Consequently, the metal-PVP bond is stronger on 1.8 nm Pd clusters than 2.6 nm Pt clusters.

![Figure 6 Parity plot of TEM-derived and chemisorption-derived particle diameters of Pd/SiO$_2$ after treatment in flowing H$_2$ (triangle, 348 K for 1 h and 423 K for 1 h, 0.033 K s$^{-1}$) or in stirring 1:1 by volume EtOH:H$_2$O (square, 351 K for 20 h) followed by treatment in flowing H$_2$ (423 K for 1 h). Pd clusters with initial diameters of 1.8 nm (black) and 2.3 nm (grey) shown. Points on the parity line indicate clean surfaces, with the initial untreated Pd particle size indicated by the horizontal dashed lines.](image)

The metal-PVP bond of 1.8 nm Pd clusters may be weakened by 1) populating the surface with metal atoms that bind oxygen more weakly (discussed in Section 3.3.3c) or 2) increasing the cluster size to decrease the fraction of under-coordinated surface atoms. Larger Pd clusters (2.3 nm; prepared as described in section 3.2.1b) were treated using the protocols described in the preceding paragraph; the surface-averaged particle diameter estimated from TEM images of the treated clusters was similar to the diameter measured from chemisorption experiments (Fig. 9), consistent with clean and accessible metal surfaces. Larger particles with lower surface energies bind PVP more weakly, thus facilitating its removal. Despite these results, increasing the starting cluster diameter did not prevent particle growth during H$_2$ treatment (from 2.3 nm to 3.1 nm; determined by TEM). Pt clusters (2.6 nm) treated by identical protocols, however, did not increase in size, reflecting the greater susceptibility of Pd clusters to sinter in non-oxidizing atmospheres, such as He and H$_2$, relative to Pt.

3.3.3b PVP removal from monometallic Pd cluster surfaces using EtOH/H$_2$O and H$_2$

The protocols developed to remove PVP from Pt cluster surfaces using H$_2$ can be modified without compromising surface cleanliness or metal dispersion, provided that clusters are treated in a reducing environment at mild temperatures for a sufficient length of time. Pt clusters treated in H$_2$ at 423 K (1 h) have clean surfaces but increase slightly in size; a preceding step at 348 K (1 h) is required to fully remove the polymer slowly at lower temperatures and avoid the generation
of local exotherms resulting from higher polymer removal rates at higher temperatures that induce particle agglomeration.\textsuperscript{[4]} This additional treatment step in $\text{H}_2$ at 348 K can be replaced without compromising surface cleanliness or metal dispersion by instead treating Pt clusters in a reductive solvent (1:1 by volume EtOH:H$_2$O, 351 K, 20 h) before the step at 423 K in $\text{H}_2$, thus demonstrating the versatility of the reductive polymer removal approach.\textsuperscript{[4]} The diameters estimated from transmission electron micrographs of Pd clusters (1.8 nm) treated using the combined EtOH/H$_2$O and $\text{H}_2$ protocol agree well with those calculated from chemisorption experiments (Fig. 9), indicating that metal surfaces are free of chemisorbed material; clusters still increase in size (to 3.2 nm; determined by TEM) as a result of treatment. In contrast, the surfaces of 1.8 nm clusters treated using the protocols using $\text{H}_2$ alone were not chemically accessible (Fig. 9). Protocols using EtOH/H$_2$O are more effective for removing PVP because of the greater contact time between the reductant and the metal surface (20 h in EtOH/H$_2$O at 351 K; 1 h in flowing $\text{H}_2$ at 348 K) and/or the ability of the solvent to dissolve and disperse the polymer away from cluster surfaces.

3.3.3c PVP removal from bimetallic PtPd cluster surfaces using $\text{H}_2$

Pt clusters bind more weakly to oxygen than Pd,\textsuperscript{[20]} and are also more resistant to sintering in $\text{H}_2$.\textsuperscript{[22]} Next, we investigate whether adding Pt atoms to Pd clusters can facilitate polymer removal while preventing the agglomeration of particles during treatment. PtPd clusters with $(\text{Pt/Pd})_{\text{at.}}$ ratios of 0.11, 0.33, and 1 were treated in flowing $\text{H}_2$ (348 K for 1 h, followed by 423 K for 1 h; 0.033 K s$^{-1}$ ramp rate; Section 3.2.3a) and subsequently characterized by titration with chemisorbed of O$_2$ and TEM (Fig. 10). The chemisorption-derived mean particle diameter of treated PtPd clusters with $(\text{Pt/Pd})_{\text{at.}}$ of 0.11 was larger than its TEM-derived surface averaged mean diameter (Fig. 10a), indicating that, as with monometallic Pd particles, surface residues remained; treated clusters were larger in size than untreated clusters (2 nm to 2.3 nm; determined by TEM). In contrast, PtPd clusters with $(\text{Pt/Pd})_{\text{at.}}$ of unity (2.5 nm diameter; determined by TEM) that were treated using identical protocols did not increase in size (Fig. 10c); cluster diameters estimated from TEM images agreed well with those obtained from chemisorption experiments, indicating that 1-1 PtPd clusters were free of surface residues and were resistant to sintering during treatment. PtPd clusters of intermediate composition ($(\text{Pt/Pd})_{\text{at.}} = 0.33$) exhibited intermediate cluster growth and surface cleanliness: clusters were slighter larger in size after $\text{H}_2$ treatment (2.4 nm to 2.6 nm; determined by TEM) and had a chemisorption-derived diameter that was slightly larger than its TEM-derived diameter (Fig. 10b).
Figure 7 Parity plots of TEM-derived and chemisorption-derived particle diameters of PtPd clusters with bulk (Pt/Pd)_{at} ratios of a) 0.11, b) 0.33, and c) 1 treated in flowing H\textsubscript{2} (\(\Delta E\text{\textsubscript{redox}}\) for 1 h and 423 K for 1 h, 0.033 K s\(^{-1}\)). Points on the parity line indicate clean surfaces, with the untreated particle size indicated by the horizontal dashed lines.

Adding Pt to Pd clusters facilitates the removal of surface-bound PVP and renders clusters more resistant to sintering during treatment in H\textsubscript{2}. These data, however, cannot distinguish whether the consequences of alloying are attributed to an increase in mean particle diameter, population of the cluster surface with a metal that binds more weakly to PVP, electronic ligand effects of alloying Pt and Pd that decrease the binding energy of PVP to the cluster surface, or a combination of such factors.

3.4 Conclusions

Using reagents containing only C, H, O, and N, we have prepared colloidal PtPd clusters that are uniform in size and composition and expose clean and accessible metal surfaces. Clusters were formed via GDR processes—as confirmed by particle-by-particle elemental analysis using EDS—that lead to clusters with (Pt/Pd)\textsubscript{at} ratios that decrease with increasing particle diameter. Consequently, the compositional uniformity of a PtPd bimetallic sample is dictated by the breadth of the size distribution of the parent Pd seeds. PtPd cluster formation was slower than the formation of AuPd clusters under identical conditions because of a lower thermodynamic driving force (\(\Delta E\text{\textsubscript{redox}}\)) for the reduction of Pt cations—relative to Au cations—by Pd\(^0\) surface atoms (Table 1: Scheme 1.2a). PtPd and AuPd clusters can be synthesized at ambient temperatures because of the enthalpic favorability of such metal combinations. In contrast, the positive mixing enthalpies of AuPt clusters require elevated synthesis temperatures (423 K) to promote the entropic benefits of alloying that influence Gibbs free energies more strongly at higher temperatures.

Pd clusters were dispersed onto SiO\textsubscript{2} and treated at low temperatures (\(\leq 423\) K) in a reducing environment (EtOH/H\textsubscript{2}O and/or H\textsubscript{2}) to remove the protecting polymer, PVP. Removing PVP from metal surfaces without compromising cluster size was more challenging for Pd clusters relative to Pt clusters because of the stronger M-PVP bonds and the greater susceptibility of Pd clusters to sinter in H\textsubscript{2}. Pd clusters of larger diameter and bimetallic PtPd clusters had weaker M-
PVP bonds, which facilitated polymer removal. The protocols developed here can be used to synthesize clean and uniform bimetallic materials suitable for the rigorous assessment of the structure-function relationship of alloying Pt and Pd.

3.5 Acknowledgements

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3.6 Supporting Information

3.6.1 Derivation of the Mathematical Expression of the Increase in Seed Cluster Diameter (Δd) via GDR Processes

The growth of a particle, \( i \), via GDR processes depends on its surface area (\( A_i \)), with its growth rate expressed as:

\[
\frac{dN_i}{dt} = A_i k = \pi d_i^2 k
\]  

(S1)

where \( N_i \) is the moles of atoms in a growing cluster, \( k \) is the areal rate constant of the galvanic displacement reaction, and \( d_i \) is the cluster diameter. The particle volume (\( V_i \)) can be written as:

\[
V_i = N_i V_i' = \frac{1}{6} \pi d_i^3
\]  

(S2)

where \( V_i' \) is the atomic volume. Combining Equations S1 and S2 yields:

\[
\frac{d(d_i)}{dt} = 2V_i' k
\]  

(S3)

If \( d_{i,o} \) is the initial cluster diameter and \( d_i(t) \) is the diameter at time \( t \), Equation S3 can be solved as:

\[
d_i(t) - d_{i,o} = \Delta d_i = 2V_i' kt
\]  

(S4)

3.6.2 Derivation of the Curve Relating the Coefficient of Variation (CV) of Seed Particle Diameters to the CV of the Resulting Bimetallic Particle Compositions

Here, we outline the methods used to relate the uniformity of the parent seed particle diameters (\( d_{MA} \)) to the uniformity of the resulting bimetallic particle compositions (\( \chi = N_{MB}/N_{MA} \), where \( N_M \) is the number of M atoms). Uniformity was quantified using the coefficient of variation (CV), which is defined as:

\[
CV = \frac{\sigma}{\mu}
\]  

(S5)

where \( \sigma \) is the sample standard deviation and \( \mu \) is the sample mean. The probability density function (PDF; \( f_{dMA}(d_{MA}) \)) representing the lognormally distributed colloidal seed particles\(^{15a}\) has the form:\(^{23}\)

\[
f_{dMA}(d_{MA}) = \frac{1}{d_{MA} \beta \sqrt{2\pi}} e^{-[\ln(d_{MA}) - \alpha]^2 / 2\beta^2} ; 0 < d_{MA} < \infty
\]  

(S6)

where \( \alpha \) and \( \beta \) are the scale and shape parameters, respectively, and are given by:
\[ \alpha = \ln \left( \frac{\mu^2}{\mu^2 + \sigma^2} \right) \quad \text{and} \quad \beta = \sqrt{\ln \left( \frac{\mu^2 + \sigma^2}{\mu^2} \right)} \]  

(S7) and (S8)

The values of \( \mu \) and \( \sigma \) were varied to represent parent seed clusters with varying CV values. The PDFs representing the bimetallic compositions \( f_\chi(\chi) \) of the \( M_B M_A \) clusters formed via GDR processes from the seed clusters represented by Equation S6 were determined using the equation:[23]

\[ f_\chi(x) = f_{d_{M_A}}[\psi(\chi)]|\psi'(\chi)| \]  

(S9)

Here, \( \psi(\chi) \) is the inverse transformation that relates each \( d_{M_A} \) value to a \( \chi \) value, and \( |\psi'(\chi)| \) is the absolute value of the Jacobian of the inverse transformation, given by:

\[ \psi(\chi) = d_{M_A} = \frac{\Delta d}{\left[ \frac{V'_{M_B}}{V'_{M_A}} \chi + 1 \right]^{\frac{1}{3}} - 1} \]  

(S10)

\[ |\psi'(\chi)| = \frac{\frac{V'_{M_B}}{V'_{M_A}} \Delta d}{3 \left( \frac{V'_{M_B}}{V'_{M_A}} \chi + 1 \right)^{\frac{2}{3}} \left[ \left( \frac{V'_{M_B}}{V'_{M_A}} \chi + 1 \right)^{\frac{1}{3}} - 1 \right]^2} \]  

(S11)

where \( V'_{M_x} \) is the atomic volume of metal \( M_x \) and \( \Delta d \) is the amount by which parent seed clusters grow via GDR processes to yield bimetallic 1-1 \( M_B M_A \) clusters. The value of \( \Delta d \) for seed clusters of a given CV value was determined by generating \( 10^5 \) lognormally distributed values[15a]—using Equations S7 and S8 to calculate \( \alpha \) and \( \beta \)—that represented the parent seed particle diameters \( (d_{M_A}) \), and subsequently using the methods outlined in Section 3.6.4 of the SI.

Equation S9, together with Equations S11, S10, and S6, was used to calculate \( \mu \) and \( \sigma \) of the \( \chi \) values represented by the PDF \( f_\chi(\chi) \):

\[ \mu = \int_{0}^{\infty} \chi f(\chi) \, d\chi \quad \text{and} \quad \sigma = \int_{0}^{\infty} (\chi - \mu)^2 f(\chi) \, d\chi \]  

(S12) and (S13)

which were used in Equation S5 to determine the CV. This procedure was repeated for parent seed clusters of varying CV values to create a curve relating the CV of seed particle diameters to the CV of the bimetallic compositions of the resulting bimetallic clusters formed via GDR processes. Cluster size distributions with identical CV values but different \( \sigma \) and \( \mu \) values all collapsed onto the same curve. Differences in \( V'_{M} \) values of the metals used in this study (Au, Pt, Pd) do not significantly alter the CV of the bimetallic compositions.
3.6.3 Derivation of the Increase in Seed Cluster Diameter (Δd) Based on EDS and HAADF Data

Galvanic-displacement reduction processes result in MA seed clusters that grow via addition of a second metal (MB) and by a thickness Δd that is independent of the initial seed particle size. Here, we derive an expression for Δd of a given bimetallic particle, i, using its atomic fraction of MA (XMAn,i) and diameter (dMBMA,i); these data are obtained from particle-by-particle EDS in tandem with HAADF imaging, respectively. We assume that all MA seed cluster atoms that are galvanically displaced and oxidized into solution (Scheme 1.2a) return to seed cluster surfaces at a rate proportional to cluster surface area (Scheme 1.2b), resulting in zero net loss or gain of MA atoms for each cluster.

The volume of a seed cluster (VMAn,i) can be expressed as:

\[ V_{M_{An},i} = \frac{4}{3} \pi \left( \frac{d_{M_{An},i}}{2} \right)^3 = \frac{N_{M_{An},i} V'_{MA}}{0.74} \]  (S14)

where \( N_{M_{An},i} \) is the number of MA atoms within the seed, \( V'_{MA} \) is the atomic volume of MA, and the 0.74 is the atomic packing factor for FCC metals. Equation S14 can be rearranged to express the diameter of the seed cluster (dMA,i) as:

\[ d_{M_{An},i} = \left( \frac{6 N_{M_{An},i} V'_{MA}}{\pi 0.74} \right)^{\frac{1}{3}} \]  (S15)

The number of MA atoms in a seed particle (NMA,i) is:

\[ N_{M_{An},i} = N_{tot,i} (x_{M_{An},i}) \]  (S16)

where \( N_{tot,i} \) is the total number of atoms (MA and MB) in a MBMA particle. \( N_{tot,i} \) is obtained by first expressing the volume of a MBMA cluster (VMBMA,i) as:

\[ V_{M_{B}M_{A},i} = \hat{V}_{M_{B},i} + \hat{V}_{M_{A},i} = \frac{4}{3} \pi \left( \frac{d_{M_{B}M_{A},i}}{2} \right)^3 \]  (S17)

where \( \hat{V}_{M_{B},i} \) and \( \hat{V}_{M_{A},i} \) are the volumes occupied by MB and MA within a MBMA cluster, expressed as:

\[ \hat{V}_{M_{B},i} = \left( x_{M_{B},i} \right) N_{tot,i} V'_{MB} \] and \[ \hat{V}_{M_{A},i} = \left( x_{M_{A},i} \right) N_{tot,i} V'_{MA} \]  (S18) and (S19)

Here, \( V'_{MB} \) is the atomic volume of MB. Equations S18 and S19 can be inserted into Equation S17 to yield:
\[ N_{\text{tot},i} = 0.74 \left( \frac{\pi}{6} \right) \left( \frac{(d_{MBM_A,i})^3}{x_{M_A,i} V_{M_A} + x_{M_B,i} V_{M_B}} \right) \]  (S20)

The initial diameter of the \( M_A \) seed particle from which a given \( MBM_A \) particle originated can be obtained by combining Equation S20 with Equations S15 and S16:

\[ d_{M_A,i} = d_{MBM_A,i} \left( \frac{x_{M_A,i} V_{M_A}'}{x_{M_A,i} V_{M_A}' + x_{M_B,i} V_{M_B}'} \right)^{1/3} \]  (S21)

These values were subtracted from \( d_{MBMA} \) to calculate:

\[ \Delta d_i = d_{MBM_A,i} \left[ 1 - \left( \frac{x_{M_A,i} V_{M_A}'}{x_{M_A,i} V_{M_A}' + x_{M_B,i} V_{M_B}'} \right)^{1/3} \right] \]  (S22)

### 3.6.4 Derivation of the Expected Increase in Seed Cluster Diameter (\( \Delta d \)) Based on the TEM-Derived Seed Particle Size Distribution

The particle size distribution of \( M_A \) seeds can be used to calculate the expected amount of growth (\( \Delta d \)) via GDR by distributing the required number of \( M_B \) atoms based on seed particle surface area. Here, we derive the equations used to calculate \( \Delta d \), which are reproduced from previously reported work.\(^5\) The cumulative volume of \( M_A \) analyzed by TEM of \( M_A \) clusters (\( V''_{M_A} \)) can be expressed as:

\[ V''_{M_A} = \sum_i V_{M_A,i} = \sum_i \frac{1}{6} \pi d_{M_A,i}^3 \]  (S23)

where \( V_{M_A,i} \) is the volume of seed particle, \( i \), with diameter \( d_{M_A,i} \). The cumulative volume of bimetallic \( MBM_A \) clusters (\( V''_{MBMA} \)) that will form from the clusters represented by Equation S23 is then given by:

\[ V''_{MBMA} = V''_{M_A} + V''_{M_A} \left( \frac{N_{MB}}{V_{MBA}} \right) \left( \frac{N_{MA}}{N_{MA}} \right) \]  (S24)

where \( V''_{m} \) is the molar volume and \( N_{MB}/N_{MA} \) is the atomic ratio of the bimetallic clusters. \( V''_{MBMA} \) can also be expressed as:

\[ V''_{MBMA} = \sum_i \frac{1}{6} \pi (d_{M_A,i} + \Delta d)^3 \]  (S25)

By setting Equation S25 equal to Equation S24, we can solve for \( \Delta d \) iteratively.
3.7 References


Chapter 4

Consequences of Alloying Pt or Pd with Au on CO Oxidation and H₂ Oxidation Turnover Rates

Abstract

Turnover rates on Pd and Pt catalyst surfaces saturated in CO* and O* are limited by the dearth of vacancy sites needed for reactants to adsorb, and by the high kinetic barriers that must be overcome for strongly bound adsorbates to react. Here, we investigate the catalytic consequences of Au atoms at or near catalyst surfaces using SiO₂-supported AuPt nanoparticles for CO oxidation on surfaces saturated in CO* and using SiO₂-supported AuPt and AuPd nanoparticles for H₂ oxidation on surfaces saturated in O*. Infrared spectra collected during isotopic dilution studies were used to isolate the singleton CO* vibrational frequency in the absence of dipole-dipole coupling, and show that Pt-CO* binding energy decreases with increasing catalyst Au content, consistent lower apparent activation energies on AuPt catalysts. Despite these results, CO oxidation turnover rates (normalized per metal surface atom) decrease significantly with increasing Au content, presumably because highly mobile CO* adlayers mitigate the effects of changing CO* binding energy, leading Au to act primarily as an inert diluent of the active Pt ensembles required for catalysis. In contrast, H₂ oxidation rates (normalized per metal surface atom) on AuPd and AuPt catalysts are higher than on their monometallic counterparts (for AuPd catalysts consisting of up to 67 % at. Au and AuPt catalysts of up to 11 % at. Au). The observed increase in H₂ oxidation turnover rates are attributed to weaker O* binding on Au-containing alloys resulting from a ligand effect similar to the one shown for AuPt catalysts with CO*-saturated surfaces and/or from ensemble effects resulting from Au atoms participating in three-fold hollow O* binding sites and disrupting the densification of the O* adlayer. Our results are consistent with the reported structure sensitivity of reactions on O*-saturated catalyst surfaces and the structure insensitivity of reactions on CO*-saturated surfaces, thus confirming that O*-saturated surfaces are more sensitive to changes in adsorbate binding strength.

4.1 Introduction

The strong adsorption of chemisorbed CO and oxygen (CO* and O*) on the surfaces of supported metal clusters leads to near-saturation coverages that limit catalytic turnovers of surface-catalyzed reactions. For example, NO oxidation rates on Pt and Pd are limited by the adsorption of molecular O₂ on isolated vacancy sites within nearly saturated O* adlayers.[1] O₂ dissociation during CO oxidation at low temperatures (360–445 K) on Pt requires that O₂* react with vicinal CO* species—rather than a surface vacancy—due to the scarcity of vacancy sites and the high kinetic barriers of breaking O-O bonds on CO*-saturated surfaces.[2] The mechanism and rates of alkane oxidation on Pt and Pd vary significantly based on the surface coverage—and, thus, binding energy—of O*.[3]

Decreasing the binding energy of strongly-bound adsorbates can increase turnover rates on catalyst surfaces by rendering such surface species more reactive, and by creating the vacancy sites required for catalysis. Here, we use bimetallic AuPt and AuPd clusters of uniform size and composition that were synthesized by the colloidal methods discussed in Chapters 2 and 3 to
investigate whether combining Au atoms with active Pt and Pd atoms within small clusters (< 5 nm) can increase the turnover rates of CO oxidation on CO*-saturated Pt surfaces and of H$_2$ oxidation on O*-saturated Pt and Pd surfaces.

Alloying can decrease the binding energy of adsorbates by altering the electronic properties of catalytic surfaces (ligand effect),$^4$ or by impeding preferred configurations of reactants and/or transition states (geometric effect).$^5$ Here, the high electronegativity of Au relative to Pt or Pd$^6$ leads to a shift in electron density from vicinal Pt and Pd atoms to Au atoms,$^7$ potentially decreasing the binding energy of adsorbates to Pt and Pd sites through a ligand effect. Moreover, Au binds CO* and O* much more weakly than either Pt or Pd,$^8$ leaving its surfaces vacant under most reaction conditions; the presence of bare Au atoms amidst covered Pt and Pd atoms can therefore prevent the formation of the dense, stable, and unreactive CO* and O* adlayers that prevail on monometallic Pt and Pd clusters. Adsorbates that bind preferentially on an ensemble of atoms (three-fold hollow or bridge sites) may also bind more weakly to cluster surfaces if atoms within an ensemble are replaced by Au atoms.

Our studies show that CO oxidation rates (normalized per total surface metal atom) on AuPt clusters at 443 K decrease with increasing Au content, in spite of lower apparent activation energy barriers and weaker CO* binding energies (determined by infrared isotopic dilution studies) on AuPt catalysts. In contrast, H$_2$ oxidation rates (normalized per total surface metal atom) on AuPd and AuPt clusters at 309 K are higher than on monometallic Pd or Pt clusters for bimetallic clusters of up to 66.7 % at. Au and 25 % at. Au, respectively. The consequences of alloying Pt and Pd with Au on oxidation rates occurring on CO*- and O*-saturated surfaces are in stark contrast, and thus reflect the greater sensitivity of O*-saturated surfaces to changes in adsorbate binding energy relative to CO*-saturated surfaces. Such conclusions are consistent with the significant cluster size effects reported for O*-saturated surfaces (NO oxidation on Pt$^{1a}$ and Pd,$^{1b}$ dimethyl ether oxidation on Pt$^9$); turnover rates increase with increasing cluster size due to the increasing fraction of highly-coordinated terrace sites that bind surface species more weakly than under-coordinated corner and edge sites prevalent on smaller particles.$^{10}$ In contrast, turnover rates of reactions occurring on CO*-saturated surfaces (ex. CO oxidation rates on Pt,$^2$ CO hydrogenation rates on Co$^{11}$) are invariant with cluster size, and, hence, depend weakly on changes in CO* binding energy, as the current study demonstrates. Highly mobile CO* adlayers mitigate the effects of strong CO* binding by accessing configurations that facilitate turnovers, whereas O* adlayers—which bind more strongly to metal surfaces, have fewer accessible binding configurations, and have less facile desorption pathways than CO*—are less capable of rearranging. Consequently, Au atoms act primarily as inert diluents of active Pt ensembles during CO oxidation—thus decreasing CO oxidation turnover rates—but facilitates the mobility and reactivity of O* and OH* during H$_2$ oxidation, thus increasing H$_2$ oxidation turnover rates.
4.2 Methods

4.2.1 Catalyst Preparation and Characterization

Scheme 1 Colloidal synthesis protocol for bimetallic nanoparticles: (a) a mixture of the precursor to \([M]_a\) \((\bullet = \text{Pd, Pt or Au})\) with the protecting polymer \((\bigcirc = \text{PVP})\) in a reducing solvent \((\bullet = \text{ethanol or ethylene glycol})\) is heated to form a suspension of polymer-protected seed clusters to which (b) the precursor to \([M]_b\) \((\bullet = \text{Au})\) is added and (c) subsequently reduced and incorporated into the \([M]_a\) seed clusters to form bimetallic particles. Clusters are (d) dispersed onto a support and (e) the protecting polymer is removed prior to catalysis. Scheme reproduced from previously reported work.\(^{[12]}\)

Monometallic Pd, Pt, and Au clusters, and bimetallic AuPd and AuPt clusters were prepared via colloidal methods using methods previously reported in detail in Chapters 2 and 3.\(^{[12-15]}\) Briefly, monometallic Pd clusters were prepared by treating \(\text{Pd(NO}_3\text{)}_2 \cdot 2\text{H}_2\text{O}\) \((5 \times 10^{-4} \text{M, Sigma Aldrich,} \sim 40\% \text{ Pd basis})\) and polyvinylpyrrolidone \((\text{PVP}; 0.02 \text{ M, monomeric unit basis; 40,000 amu, Sigma Aldrich})\) dissolved in a 1:1 by volume solution of ethanol \((\text{EtOH, Sigma Aldrich,} \sim 99.5\% )\) and deionized water \((\text{resistivity } \sim 0.06 \mu\text{S cm}^{-1})\) in ambient air at 368 K (Scheme 1a) for 0.5 h. Monometallic Pt clusters were prepared by treating \(\text{H}_2\text{PtCl}_6\) \((\text{Sigma Aldrich, 8 wt. %, in H}_2\text{O})\) and PVP \((0.02 \text{ M, monomeric unit basis; 40,000 amu, Sigma Aldrich})\) dissolved in ethylene glycol \((\text{EG, Fischer Scientific})\) in ambient air at 423 K (Scheme 1a) for 0.5 h. Monometallic Au clusters were prepared by treating \(\text{HAuCl}_4 \cdot (\text{H}_2\text{O})_3\) \((5 \times 10^{-4} \text{M, Sigma Aldrich})\) and PVP \((0.02 \text{ M, monomeric unit basis; 40,000 amu, Sigma Aldrich})\) dissolved in EG \((\text{Fischer Scientific})\) in ambient air at 423 K (Scheme 1a) for 0.5 h.

Bimetallic AuPd clusters were prepared by combining a solution of \(\text{HAuCl}_4 \cdot (\text{H}_2\text{O})_3\) \((5 \times 10^{-4} \text{M, Sigma Aldrich})\) in 1:1 by volume \(\text{EtOH (Sigma Aldrich, } \sim 99.5\% )\) and deionized water \((\text{resistivity } \sim 0.06 \mu\text{S cm}^{-1})\) with a suspension of monometallic Pd clusters \((5 \times 10^{-4} \text{M, Pd atom basis})\) and stirring \((310 \text{ rpm})\) the mixture for 2 h at ambient temperature in air (Scheme 1b). Bimetallic AuPt clusters were prepared by preparing a solution of \(\text{HAuCl}_4 \cdot (\text{H}_2\text{O})_3\) \((5 \times 10^{-4} \text{M, Sigma Aldrich})\) in \(\text{EG (Fischer Scientific)}\) drop-wise at 16.7 nmol s\(^{-1}\) using a syringe pump \((\text{KD Scientific KDS 100})\) to a pre-heated suspension of monometallic Pt clusters \((5 \times 10^{-4} \text{M, Pd atom basis})\) at 423 K. The mixture was stirred \((310 \text{ rpm})\) and maintained for 0.33 h (Scheme 1b). The composition of a bimetallic sample was adjusted by changing the volumetric ratio of the metal precursor solution and the Pd or Pt seed cluster suspension used. AuPt clusters of greater than 50% at. Au content were synthesized by first preparing a suspension of 50% at. Au clusters and subsequently adding the remaining required Au precursor solution at a rate of 4.17 nmol s\(^{-1}\).

Clusters were adsorbed onto fumed \(\text{SiO}_2\) \((\text{Sigma Aldrich, 7 nm particle size, 395 m}^2\text{ g}^{-1}\text{ surface})\) by first dispersing \(\text{SiO}_2\) in deionized water \((20 \text{ g/L, resistivity } \sim 0.06 \mu\text{S cm}^{-1})\) and subsequently adding the required volume of the colloidal suspension dropwise \((\sim 0.2 \text{ cm}^{-2} \text{s}^{-1})\) to yield the desired weight loadings (Table 1). The slurry was stirred \((310 \text{ rpm})\) for 2 h (Scheme 1d), at which point the catalyst was recovered by centrifugation \((133 \text{ Hz, 0.6 ks})\). Monometallic Pd catalysts were stirred \((310 \text{ rpm})\) in 1:1 by volume \(\text{EtOH (Sigma Aldrich, } \sim 99.5\% )\) and deionized...
water (resistivity ~0.06 µS cm\(^{-1}\)) maintained at 353 K for 20 h to facilitate polymer removal.\(^{[13b]}\) All other catalysts were washed twice with deionized (0.05 L) at ambient temperature. All catalysts were dried overnight in ambient air at 356 K.

Catalysts were characterized by bright-field transmission electron microscopy (TEM) using a JEOL 1200 EX microscope at an accelerating voltage of 80 kV to measure the surface-averaged mean cluster diameters (\(\langle d \rangle\)) of each sample using a minimum of 200 clusters and the equation:

\[
\langle d \rangle = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}
\]

where \(n_i\) is the number of clusters with diameter \(d_i\). Samples were prepared for microscopy by suspending the finely-ground catalyst in acetone, placing 2-3 drops onto holey-carbon Cu grids, and allowing the solvent to evaporate at ambient temperature.

### 4.2.2 CO Oxidation Rate Measurements

Catalytic CO oxidation rates were measured at 443 K using a tubular packed-bed quartz reactor with a K-type thermocouple (Omega) at its exterior wall. Catalysts (Table 1) were diluted with fumed SiO\(_2\) (Sigma Aldrich, 7 nm particle size, 395 \(\text{m}^2\ \text{g}^{-1}\) surface) to give an intrapellet mass ratio of 1:10 (catalyst:SiO\(_2\)), and then pelletized, crushed, and sieved to retain 100-250 µm aggregates. Samples were treated in flowing \(\text{H}_2\) (0.83 cm\(^3\) s\(^{-1}\), 99.999%, Praxair) and \(\text{He}\) (0.83 cm\(^3\) s\(^{-1}\), 99.999%, Praxair UHP grade) at three successive temperatures, each for 1 h.\(^{[12, 13b]}\) 348 K, 423 K, and 523 K (heating rate of 0.033 K s\(^{-1}\)). The treated catalyst was brought to reaction temperature in the \(\text{H}_2/\text{He}\) mixture, and all lines were purged in He before introducing the reactants (1% CO/He, Praxair certified standard; 25% O\(_2\)/He, Praxair UHP grade; balance He, Praxair UHP grade). All gases were metered using electronic mass flow controllers (Porter, type 201), and the reactant and product concentrations were measured by online gas chromatography (Shimazdu GC-2014) using a Porapak Q packed column (80/100 mesh, stainless steel, 0.32 cm OD, 0.02 cm ID) connected to a thermal conductivity detector. CO conversions in all experiments were kept below 10% to ensure differential reactor conditions. No reaction products were detected when the SiO\(_2\) diluent alone was tested at the conditions of the catalytic measurements.

### 4.2.3 Infrared Spectroscopy Measurements during CO Oxidation

The infrared spectra of chemisorbed CO species (CO\(^*\)) during CO oxidation at 348 K were collected using a Thermo Nicolet 8700 infrared spectrophotometer (40 scan averages) equipped with a Hg-Cd-Te (MCT) detector. Catalyst samples (Table 1) were pressed into self-supported wafers (40 mg cm\(^{-2}\)) and placed between CaF\(_2\) windows within a custom flow cell.\(^{[14]}\) Samples were treated in flowing \(\text{H}_2\) (0.83 cm\(^3\) s\(^{-1}\), 99.999%, Praxair) and \(\text{He}\) (0.83 cm\(^3\) s\(^{-1}\), 99.999%, Praxair UHP grade) at 348 K (heating rate of 0.033 K s\(^{-1}\)) for 1 h followed by treatment at 423 K (heating rate of 0.033 K s\(^{-1}\)) for 1 h.\(^{[12, 13b]}\) The treated catalyst was brought to reaction temperature (348 K) in the \(\text{H}_2/\text{He}\) mixture, and all lines were purged with He before introducing the reactants. Infrared spectra were taken under a constant flow of the reactant stream: 0.1 kPa CO, 10 kPa O\(_2\), and balance He (0.16 cm\(^3\) s\(^{-1}\) of 1% CO/He, Praxair certified standard; 0.66 cm\(^3\)
s\(^{-1}\) of 25\% O\(_2\)/He, Praxair UHP grade; 0.85 cm\(^3\) s\(^{-1}\) of He, Praxair UHP grade). All gases were metered using electronic mass flow controllers (Porter, type 201), and the reactant and product concentrations at the outlet of the infrared cell were measured by gas chromatography (Agilent 3000A Micro GC) using PoraPLOT Q and Mol Sieve 5A columns connected to a thermal conductivity detector. CO conversions were kept below 5\% to ensure differential reactor conditions.

### 4.2.4 Isotopic Dilution Studies and Infrared Spectra of Adsorbed CO

The singleton CO* vibrational frequency in the absence of dipole-dipole coupling was measured by monitoring changes in the band frequency of unlabeled CO* as its surface coverage increased via exchange with pre-adsorbed \(^{13}\text{C}^{18}\text{O*}.\) Spectra were obtained using the equipment and protocols described in Section 4.2.3. Catalyst samples (Table 1) were pressed into self-supporting wafers (40-50 mg cm\(^{-2}\)) and treated as described in Section 4.2.3. The treated catalyst was cooled to 303 K in the pretreatment gas, and all lines were purged with He before introducing \(^{13}\text{C}^{18}\text{O(g)}\) (0.083 cm\(^3\) s\(^{-1}\), Isotec, 99\% chemical purity); the catalyst surface was considered saturated with \(^{13}\text{C}^{18}\text{O*}\) once the intensity of the \(^{13}\text{C}^{18}\text{O}\) band no longer changed with time (~ 1.2 ks). Residual \(^{13}\text{C}^{18}\text{O(g)}\) was removed by flowing He (1.5 cm\(^3\) s\(^{-1}\)) over the catalyst for 3.6 ks prior to introducing a stream of 0.1 kPa unlabeled CO in He (0.33 cm\(^3\) s\(^{-1}\)). Using Origin software, surface coverage of \(^{13}\text{C}^{18}\text{O*}\) and unlabeled CO* was determined by deconvoluting the infrared signal into two bands with Lorentzian distributions, and calculating the area under each band.

### 4.2.5 H\(_2\) Oxidation Rate Measurements

Catalytic H\(_2\) oxidation rates were measured at 309 K using a tubular packed-bed quartz reactor with a K-type thermocouple (Omega) at its exterior wall. Catalysts (Table 1) were diluted with fumed SiO\(_2\) (Sigma Aldrich, 7 nm particle size, 395 m\(^2\) g\(^{-1}\) surface) to give an intrapellet mass ratio of 1:20 (catalyst:SiO\(_2\)), and then pelletized, crushed, and sieved to retain 100-250 \(\mu\)m aggregates. Samples were treated in flowing H\(_2\) (0.83 cm\(^3\) s\(^{-1}\), 99.999\%, Praxair) and He (0.83 cm\(^3\) s\(^{-1}\), 99.999\%, Praxair UHP grade) at 348 K (heating rate of 0.033 K s\(^{-1}\)) for 1 h followed by treatment at 423 K (heating rate of 0.033 K s\(^{-1}\)) for 1 h.\(^{[12,13b]}\) The treated catalyst was brought to reaction temperature in the H\(_2\)/He mixture, and all lines were purged in He before introducing the reactants (1\% CO/He, Praxair certified standard; 25\% O\(_2\)/He, Praxair UHP grade; balance He, Praxair UHP grade). All gases were metered using electronic mass flow controllers (Porter, type 201), and the reactant and product concentrations were measured by gas chromatography (Shimadzu GC-2014) using a Porapaq Q packed column (80/100 mesh, stainless steel, 0.32 cm OD, 0.02 cm ID) connected to a thermal conductivity detector. CO conversions were kept below 10\% to ensure differential reactor conditions. No reaction products were detected when the SiO\(_2\) diluent alone was tested at the conditions of catalytic measurements.
Table 1 Crystallite Diameters Using Equation 1, Catalyst Weight Loadings, Intrapellet Dilution Ratios, and Reaction Temperatures

<table>
<thead>
<tr>
<th>sample</th>
<th>mean diameter (nm, TEM)</th>
<th>% wt.</th>
<th>intrapellet dilution ratio (SiO₂/catalyst)</th>
<th>reaction temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>2.6 ± 0.03</td>
<td>0.1⁺⁵, 0.5ᵇ</td>
<td>1⁰, 0ᵇ, 2⁰</td>
<td>42³ᵃ, 34⁸ᵇ, 3⁰⁸ᶜ</td>
</tr>
<tr>
<td>Au₁₁Pt₈⁹</td>
<td>2.7 ± 0.03</td>
<td>0.1ᵃ⁺⁵, 0.5ᵇ</td>
<td>1⁰, 0ᵇ, 2⁰</td>
<td>42³ᵃ, 34⁸ᵇ, 3⁰⁸ᶜ</td>
</tr>
<tr>
<td>Au₂₅Pt₇₅</td>
<td>2.8 ± 0.03</td>
<td>0.1ᵃ⁺⁵, 0.5ᵇ</td>
<td>1⁰, 0ᵇ, 2⁰</td>
<td>42³ᵃ, 34⁸ᵇ, 3⁰⁸ᶜ</td>
</tr>
<tr>
<td>Au₃₃Pt₆⁷</td>
<td>3.3 ± 0.04</td>
<td>0.7₅ᵇ</td>
<td>0ᵇ</td>
<td>3⁰⁸ᵇ</td>
</tr>
<tr>
<td>Au₅₀Pt₅₀</td>
<td>3.6 ± 0.05</td>
<td>0.1ᵃ⁺⁵, 1.0ᵇ</td>
<td>1⁰, 0ᵇ, 2⁰</td>
<td>42³ᵃ, 3⁰⁴ᵇ, 3⁰⁸ᶜ</td>
</tr>
<tr>
<td>Au</td>
<td>12.2 ± 2.4</td>
<td>0.1ᶜ</td>
<td>1ᶜ</td>
<td>3⁰⁸ᶜ</td>
</tr>
<tr>
<td>Pd</td>
<td>2.2 ± 0.5</td>
<td>0.⁰₅ᶜ</td>
<td>2⁰ᶜ</td>
<td>3⁰⁸ᶜ</td>
</tr>
<tr>
<td>Au₂₃Pd₇₅</td>
<td>2.5 ± 0.7</td>
<td>0.⁰₇₅ᶜ</td>
<td>2⁰ᶜ</td>
<td>3⁰⁸ᶜ</td>
</tr>
<tr>
<td>Au₅₀Pd₃₀</td>
<td>3.3 ± 1.1</td>
<td>0.⁰₇₅ᶜ</td>
<td>2⁰ᶜ</td>
<td>3⁰⁸ᶜ</td>
</tr>
<tr>
<td>Au₄₇Pd₃₃</td>
<td>3.6 ± 1.0</td>
<td>0.⁰₈₄ᶜ</td>
<td>2⁰ᶜ</td>
<td>3⁰⁸ᶜ</td>
</tr>
</tbody>
</table>

ᵃ CO oxidation, plug flow reactor  
ᵇ CO oxidation, FTIR  
ᶜ H₂ oxidation

4.3 Results and Discussion

4.3.1 Cluster Size Measurements and Dispersion

Surface-averaged mean cluster diameters (〈d〉, nm, Eq. 1) were determined from TEM micrographs of catalyst samples exposed to the pretreatment conditions described in Sections 4.2.2 and 4.2.3 (Table 1). Metal dispersions (D) were calculated using the equation:

\[ D = \frac{C}{〈d〉} \]  

(2)

where C is a function of the metal identity (1.13 nm, 1.12 nm, and 1.16 nm for Pt, Pd, and Au, respectively, and a weighted average (by composition) of these values for bimetallic samples), calculated assuming a spherical geometry and using the density of the bulk metal.[¹⁵] TEM-derived dispersions were used in place of chemisorption-derived dispersions to normalize oxidation turnover rates because Au atoms present at the surface of Au-containing alloys do not chemisorb molecular titrants effectively (O₂, H₂, and CO),[⁸ᵃ] and therefore cannot be probed accurately by chemisorption methods. Previous work, however, has shown that TEM- and chemisorption-derived dispersion values are equal for Pt (Chapter 2) and Pd (Chapter 3) clusters pretreated using the methods described in Sections 4.2.2 and 4.2.3. Thus, dispersion values obtained from TEM micrographs accurately represent the total accessible metal surface. TEM derived dispersion values equal to chemisorption derived dispersion values also indicate that the pretreatment methods used here result in clean and accessible Pt and Pd metal surfaces free of residual surface detritus.[¹²]
4.3.2 Elimination of Heat and Mass Transfer Effects

Measured CO oxidation turnover rates (to CO$_2$) on 0.1 % wt. Pt/SiO$_2$ with different intrapellet dilution ratios (SiO$_2$/catalyst = 10 and 20) and H$_2$ oxidation turnover rates (to H$_2$O) on 0.05 % wt. Pd/SiO$_2$ with different intrapellet dilution ratios (SiO$_2$/catalyst = 10 – 40) were independent of dilution ratio. These data indicate that intrapellet temperatures and concentrations are equal to those in the extrapellet fluid phase, and that the rates reported herein are devoid of heat artifacts and reactant concentration gradients.

![Figure 1](image)

**Figure 1** CO oxidation turnover rates (normalized per total surface metal atom; black) for 0.1 % wt. Pt/SiO$_2$ at 443 K (0.1 kPa CO, 10 kPa O$_2$, balance He) and H$_2$ oxidation turnover rates (normalized per total surface metal atom; grey) for 0.05 % wt. Pd/SiO$_2$ at 309 K (0.5 kPa H$_2$, 10 kPa O$_2$, balance He) measured at 10, 20, and 40 intrapellet dilution ratios (SiO$_2$/catalyst).

4.3.3 Adlayer Densification with Time on Stream

CO oxidation turnover rates on Pt/SiO$_2$ and H$_2$ oxidation turnover rates on Pt/SiO$_2$ and Pd/SiO$_2$ decreased sharply during 0-5 ks on stream, and continued to decrease more gradually with time on stream after ~5 ks (Fig. 2). Initial rates were recovered by re-treating catalysts (443 K; 50 kPa H$_2$, balance He), indicating the absence of irreversible surface titrants or particle sintering. Similar trends were observed on all AuPt and AuPd bimetallic catalysts. These results are consistent with the densification of CO* and O* monolayers that become increasingly more compact, stable, and unreactive with exposure to the reactant stream.$^{[16]}$ All rates reported in subsequent sections were obtained by fitting time on stream data (after the initial rapid decrease in rates) to the equation:

$$r_t = r_0 e^{-k_d t} \quad (3)$$

and extrapolating rates back to zero time on stream. Here, $k_d$ is the densification rate constant, $r_0$ is the rate at zero time on stream, and $r_t$ is the rate at time $t$. Equation 3 assumes that CO* and O*
densify at a rate that depends on the length of time spent under reaction conditions and the number of remaining accessible surface sites.\[17\]

In contrast to H\(_2\) oxidation rates on monometallic Pt/SiO\(_2\) and Pd/SiO\(_2\), H\(_2\) oxidation rates on Au/SiO\(_2\) were negligible initially and then increased (up to 0.34 s\(^{-1}\) after ~ 5 ks), after which rates remained stable with time on stream (Fig. 2b). Low initial rates reflect the difficulty for bare Au surfaces to activate O\(_2\).\[8b\] Rates increase as surface species (O\(_2^*\), O\(^*\), *OH, *OOH, etc.) generated by occasional catalytic turnovers begin to populate the catalyst surface, increasing the concentration of surface species required to form H\(_2\)O. Such adsorbates assist in cleaving O-O bonds, thus decreasing the energy barriers for O\(_2\) dissociation and increasing oxidation rates.\[18\]

H\(_2\) oxidations rates on Au/SiO\(_2\) catalysts do not decrease with time on stream after ~ 5 ks because, unlike catalysts containing less noble metals like Pt and Pd, Au surfaces do not become saturated with O\(^*\) at the conditions used in this study.\[19\] Au/SiO\(_2\) is expected to be inactive relative to Pt for CO oxidation at the conditions presented in this study.\[19\]

![Figure 2](image)

**Figure 2** a) CO oxidation turnover rates (normalized per total surface metal atom) with time on stream on (●) 0.1 % wt. Pt/SiO\(_2\) (10 kPa O\(_2\), 0.1 kPa CO, balance He; 443 K) and b) H\(_2\) oxidation turnover rates (normalized per total surface metal atom) with time on stream on (●) 0.1 % wt. Pt/SiO\(_2\), (■) 0.05 % wt. Pd/SiO\(_2\), and (▲) 0.1 % wt. Au/SiO\(_2\) (20 kPa O\(_2\), 0.5 kPa H\(_2\), balance He; 309 K).

**4.3.4 Effects of CO and O\(_2\) Pressures on CO Oxidation Rates on Pt/SiO\(_2\) and Au\(_{25}\)Pt\(_{75}\)/SiO\(_2\)**

CO oxidation turnover rates (normalized per total surface metal atom) on Pt/SiO\(_2\) and Au\(_{25}\)Pt\(_{75}\)/SiO\(_2\) catalysts were first-order in O\(_2\) pressure (443 K, 5-19 kPa O\(_2\), 0.1 kPa CO; Fig. 3a) and inversely proportional to CO pressure (443 K, 0.05-0.2 kPa CO, 10 kPa O\(_2\); Fig. 3b), consistent with Equation 4:

\[
r = k_{\text{eff}} \frac{[O_2]}{[CO]} \tag{4}
\]
where $[X]$ indicates a pressure, $r$ is the turnover rate normalized by the number of surface metal atoms, and $k_{\text{eff}}$ is the effective rate constant, with a value of $0.0047 \pm 0.0002 \text{ s}^{-1}$ for Pt/SiO$_2$ and $3.3 \times 10^{-4} \pm 2 \times 10^{-5} \text{ s}^{-1}$ for Au$_{25}$Pt$_{75}$/SiO$_2$. The observed rate dependencies are consistent with the proposed mechanism for CO oxidation on Pt/SiO$_2$ (360-445 K, 4-18 kPa O$_2$, 0.08-0.2 kPa CO), which involves first the quasi-equilibrated adsorption of CO and O$_2$ (with equilibrium constants $K_{\text{CO}}$ and $K_{\text{O}_2}$), followed by a kinetically relevant O$_2^*$-assisted dissociation step to form CO$_2^*$ and O* (with rate constant $k'$). Subsequently, O* and CO* react in a kinetically-relevant step to form CO$_2^*$, which desorbs from the surface.$^{[2]}$ These steps lead to the following rate equation at the near-saturation CO* coverages ($K_{\text{CO}[\text{CO}] >> 1}$) expected for these conditions:

$$r = \frac{k'K_{\text{O}_2}[O_2]}{K_{\text{CO}[\text{CO}]}} = k_{\text{eff}} \frac{[O_2]}{[\text{CO}]} \quad (5)$$

$k_{\text{eff}}$ reflects the energy difference between the CO*-saturated surface and the kinetically relevant transition state—the CO*-assisted dissociation of O$_2$ (Scheme 2).$^{[2]}$ Additional kinetic analyses on a wider range of bimetallic compositions, reactant pressures, and temperatures, as well as additional characterization under reaction conditions, are required to further support that the elementary steps previously proposed on Pt catalysts are valid for AuPt catalysts; the data in Figure 3, however, suggest that at the conditions presented here, adding Au to Pt clusters does not alter the kinetic behavior of the resulting alloy. These conclusions are consistent with Au acting as an inert diluent of surface Pt ensembles, without influencing their catalytic properties.

Figure 3 Effects of a) O$_2$ pressure and b) CO pressure on CO oxidation rates and inverse rates (normalized per total surface metal atom), respectively, for (●) 0.1 % wt. Pt/SiO$_2$ and (●) 0.1 % wt. Au$_{25}$Pt$_{75}$/SiO$_2$ at 443 K.
4.3.5 Effects of Catalyst Au Content on CO Oxidation Rates and Apparent Activation Energies

Figure 4 shows CO oxidation turnover rates (normalized per total surface metal atom; 10 kPa O$_2$, 0.1 kPa CO) at 348 K and 443 K on Pt/SiO$_2$ and AuPt/SiO$_2$ catalysts of varying compositions; turnover rates decrease significantly with increasing Au content at both temperatures studied. These data suggest that any electronic ligand effects proffered by Au atoms that weaken CO* binding—and thus increase the number of turnovers by rendering CO* more reactive and promoting the formation of surface vacancies—are negligible relative to the pronounced geometric effects of Au serving as an inert diluent of the active Pt ensembles required for CO oxidation catalysis.

Figure 4 Effects of catalyst Au content on CO oxidation turnover rates (normalized per total surface metal atom; 10 kPa O$_2$, 0.1 kPa H$_2$, balance He) at 443 K (■) and 348 K (●).
CO oxidation effective rate constants were measured for Pt/SiO\textsubscript{2} between 323 K and 454 K, and for AuPt/SiO\textsubscript{2} catalysts of varying Au content at 443 K and 348 K to determine apparent activation energies ($E_{\text{app}}$; Fig. 5), which reflect the energy difference between the CO*-saturated surface and the kinetically relevant transition state—the CO*-assisted dissociation of O\textsubscript{2} (Scheme 2).\textsuperscript{[2]} Activation energies decrease with increasing catalyst Au content (Fig. 5b). CO oxidation rates (normalized per total surface metal atom) are lower on AuPt catalysts (Fig. 4), however, indicating that the lower activation energy barriers proffered by the addition of Au do not compensate for the replacement of active Pt atoms by inert Au atoms at the catalyst surface.

Lower $E_{\text{app}}$ values are consistent with Au destabilizing the ground state by weakening the Pt-CO* bond and/or stabilizing the transition state (Scheme 2). In the following section, we use isotopic dilution studies to probe whether Au influences Pt-CO* binding energies to further elucidate the effects of Au on CO oxidation rates at AuPt catalyst surfaces.

**Figure 5** a) Effective rate constants for CO oxidation (10 kPa O\textsubscript{2}, 0.1 kPa CO) on (○) Pt/SiO\textsubscript{2}, (■) Au\textsubscript{11}Pt\textsubscript{89}/SiO\textsubscript{2}, (▲) Au\textsubscript{15}Pt\textsubscript{75}/SiO\textsubscript{2}, and (●) Au\textsubscript{50}Pt\textsubscript{50}/SiO\textsubscript{2} as a function of temperature and b) the effects of catalyst Au content on the apparent activation energy for CO oxidation (10 kPa O\textsubscript{2}, 0.1 kPa CO).

### 4.3.6 Assessment of Pt-CO* Binding Energies on AuPt Catalysts

The infrared spectra of Pt and AuPt catalysts exposed to CO\textsubscript{(g)} decrease in intensity with increasing Au content, consistent with the replacement of Pt surface atoms by Au atoms, and feature a band at ~2060 cm\textsuperscript{-1} that is assigned to CO* bound in the linear atop configuration on Pt sites (Fig. 6a).\textsuperscript{[2]} The C-O bond vibrational frequency of CO* on Pt is sensitive to the Pt-CO* binding energy,\textsuperscript{[20]} and can provide information of the electronic effects of alloying with Au. Au is more electronegative than Pt,\textsuperscript{[6]} and can therefore withdraw electron density from vicinal Pt atoms.\textsuperscript{[7]} Reduced electron density on Pt would reduce the back donation of electron density from the d-orbital on Pt to the π* antibonding orbital on CO*, thus weakening the Pt-CO* bond while increasing the bond order in the CO* molecule and strengthening the C-O bond; this leads to a shift of the Pt-CO* band to higher wavenumbers.\textsuperscript{[20]} The C-O vibrational frequency of CO*
on Pt is also sensitive, however, to CO* coverage and CO*-CO* dipole coupling. Au atoms that dilute Pt surface atoms weaken dipole coupling by impeding the alignment of vicinal CO* dipoles, thus shifting Pt-CO* bands to lower wavenumbers.\[21\] The electronic and geometric effects of Au atoms at AuPt surfaces on the vibrational frequency of the C-O bond are therefore in stark contrast: electronic effects that weaken Pt-CO* binding would increase the vibrational frequency, while geometric effects that dilute surface Pt atoms decrease the vibrational frequency. Infrared spectra of Pt and AuPt catalysts exposed to CO oxidation conditions (10 kPa O₂, 0.1 kPa CO, 348 K) show that CO* bands broadened and shifted to lower frequencies with increasing Au content (Fig. 6), indicating that Au acts primarily as a diluent of CO*—thus decreasing the coupling of CO* dipoles—and that the electronic effects of Au, if any, are minimal relative to such geometric effects. These results are consistent with CO oxidation turnover rates (normalized per total surface metal atom) that decrease with increasing Au content (Fig. 4), in spite of lower apparent activation energy barriers (Fig. 5b).

\[21\]

The electronic effects of vicinal Au atoms on the strength of Pt-CO* bonds are coupled with the consequences of reduced dipole-dipole coupling in Figure 6; isotopic dilution studies (with \(^{13}\)C\(^{18}\)O* and unlabeled CO*), however, can be used to extract intrinsic vibrational frequencies in the absence of dipole-dipole coupling.\[2\] \(^{13}\)C\(^{18}\)O* and CO* do not couple due to a 50 cm\(^{-1}\) difference in vibrational frequency.\[2\] Isotopic dilution protocols involve first saturating the catalyst surface with \(^{13}\)C\(^{18}\)O*, and subsequently flowing unlabeled CO\(_{(g)}\) over the catalyst to gradually replace its isotopologue.\[2\] Such studies were performed at 303 K in order to capture the transient exchange of isotopologues on the catalyst surface. Figure 7 shows infrared spectra of the exchange of CO* with pre-adsorbed \(^{13}\)C\(^{18}\)O*. The CO* band shifted to higher wavenumbers as its surface coverage increased, consistent with stronger dipole-dipole coupling; consequently, the \(^{13}\)C\(^{18}\)O* band shifted to lower wavenumbers as its surface coverage decreased. The singleton vibrational frequency (in the absence of dipole-dipole coupling) of CO* within a
monolayer of $^{13}$C$^{18}$O$^*$ was measured by extrapolating the CO$^*$ vibrational frequency to zero CO$^*$ coverage.

![Infrared spectra](image)

**Figure 7** Infrared spectra during exchange of chemisorbed $^{13}$C$^{18}$O$^*$ with unlabeled CO$\text{g}l$ at 303 K.

Singleton CO$^*$ frequencies increased with increasing bulk Au content of the catalyst (Fig. 8), consistent with stronger C-O bonds and, thus, weaker Pt-CO$^*$ bonds. These results indicate that Pt atoms in proximity to Au atoms bind more weakly to CO$^*$ as a result of the electron withdrawing properties of Au that decrease the amount of back donation of Pt d-orbitals into $\pi^*$ antibonding orbitals of CO$^*$. Au therefore destabilizes the CO$^*$-saturated surface (Scheme 2), consistent with lower apparent activation energies on AuPt catalysts (Fig. 5b).
Figure 8 Effects of catalyst Au content on the singleton C-O vibrational frequency of unlabeled CO* in the absence of dipole coupling on surface Pt atoms, as determined by infrared spectra of the exchange of $^{13}$C$^{18}$O* with CO*.

Such electronic effects, however, do not compensate for the replacement of reactive Pt atoms with inert Au atoms, and the dilution of the Pt ensembles required for catalysis, resulting in lower CO oxidation rates (normalized per total surface metal atom) as Au content increases (Fig. 4). CO oxidation rates on Pt surfaces have been shown to be structure insensitive,[2] turnover rates do not depend on cluster size, despite larger clusters having a higher fraction of highly coordinated surface metal atoms at terraces that bind more weakly to CO*.[10] Density functional theory (DFT) studies show that the consequences of increasing metal atom coordination number (from corners to edges to terraces) on CO oxidation turnover rates are two-fold: although CO* adsorption energy decreases, thus destabilizing the ground state, the energy required to form the kinetically-relevant transition state (CO*-assisted O$_2$ dissociation) increases (Scheme 2). These two effects compensate for one another and result in a weak dependence of the apparent activation energy—and thus CO oxidation turnover rates—on cluster size.[2]

In the current study, the negligible effects of changes in CO* binding energy (by alloying with Au) on CO oxidation rates are consistent with the structure insensitivity of this reaction. Isotopic dilution experiments confirm that CO* adsorption energies decrease with increasing Au content in bimetallic clusters (Fig. 8), however we expect that, similar to increasing Pt cluster size, the presence of Au at cluster surfaces also increases the activation barrier of the kinetically relevant transition state.[2] Apparent activation energies, however, decrease with increasing Au content (Fig. 5b), suggesting that an increase in activation barrier for the CO*-assisted O$_2$ dissociation step does not completely offset the decrease in CO* adsorption, in contrast to the effects of increasing particle size.

The rates reported in the preceding sections are not normalized by the active surface metal (Pt), and thus include the inactive Au surface sites that do not contribute significantly to turnover rates at these conditions.[19] Consequently, these rates do not isolate the intrinsic catalytic reactivity of
the Pt atoms within an alloyed surface, and instead represent the average reactivity of the AuPt surface. Next, we use the intensity of the Pt-CO* infrared band to account for the amount of Pt surface sites at AuPt cluster surfaces under reaction conditions to normalize CO oxidation rates by the active surface metal, and thus determine how the intrinsic reactivity of Pt atoms in contact with or in the vicinity of Au atoms differ from pure Pt surfaces.

4.3.7 Determination of Pt Surface Content of AuPt/SiO₂ Catalysts using Infrared Spectroscopy

The area of the Pt-CO* band is determined by the number of Pt-bound CO* molecules within the beam path,[22] and is therefore proportional to the number of Pt surface atoms within a sample. Here, we measure the intensity of the linear atop Pt-CO* band of Pt/SiO₂ and AuPt/SiO₂ samples of varying Au content under CO oxidation conditions (10 kPa O₂, 0.1 kPa CO, 348 K) to determine the fraction of AuPt surface atoms that are composed of Pt. Self-supporting catalyst wafers of similar mass (40 mg) and diameter (2 cm) were prepared for infrared studies in order to ensure that wafer thickness—and thus the amount of catalyst sampled by the infrared beam—did not vary significantly from sample to sample.

Pt-CO* band areas (A_{AuPt} and A_{Pt} for AuPt and Pt catalysts, respectively) normalized by the number of total surface metal atoms (M_{s,Au+Pt} and M_{s,Pt} for AuPt and Pt catalysts, respectively; calculated using TEM micrographs) were used to determine the fraction of surface atoms composed of Pt (X_{s,Pt}) at AuPt catalyst surfaces:

\[ X_{s,Pt} = \left( \frac{A_{AuPt}}{m_{s,Au+Pt}} \right) \left( \frac{m_{s,Pt}}{A_{Pt}} \right) \]  

Pt surface content decreased with increasing bulk Au content (Fig. 9a), confirming that Au atoms replace Pt sites at AuPt catalyst surfaces. Product concentrations (CO₂) were measured concurrently with the collection of infrared spectra, and used together with X_{s,Pt} values to calculate CO oxidation turnover rates normalized per surface Pt atom (348 K, 10 kPa O₂, 0.1 kPa CO). Rates increased monotonically with increasing Au content (Fig. 9b), consistent with weaker CO* binding (Section 4.3.6) and lower apparent activation energies (Section 4.3.5) that render Pt sites in proximity to Au atoms more reactive than Pt sites on monometallic Pt clusters. These data, however, do not exclude the possibility that Au sites in proximity to Pt atoms have lower O₂ dissociation barriers, thus leading to additional turnovers that are not accurately accounted for when rates are normalized per surface Pt atom.
Figure 9 Effects of catalyst Au content on a) Pt content at the catalyst surface (Eq. 6) and b) CO oxidation turnover rates (normalized per Pt surface atom; 10 kPa O₂, 0.1 kPa CO, balance He; 348 K).

In addition to the ligand effects reported in the preceding sections, higher rates with increasing Au content may also result from geometric effects. Bare Au atoms amidst CO* adlayers on Pt obstruct the formation of dense, stable, and unreactive CO* monolayers that prevail on monometallic Pt clusters, similar to the role of chemisorbed C* on Pt clusters saturated in CO*; C* blocks active surface atoms but obstructs the formation of saturated CO* adlayers, thus increasing CO oxidation rates in H₂-CO mixtures. A combination of ligand and ensemble effects together may influence CO oxidation rates on AuPt/SiO₂.

4.3.8 Effects of H₂ and O₂ Pressures on H₂ Oxidation Rates on Pd/SiO₂ and Au₅₀Pd₅₀/SiO₂

Studies of H₂ oxidation on Pd and Pt have primarily been limited to electrocatalytic reactions in an alkaline or acidic solvent, and the proposed sequence of elementary steps varies depending on reaction conditions (solvent pH, addition of mineral acids, identity of the catalyst, etc.). High oxygen binding energies on Pd and Pt (-382 kJ mol⁻¹ and -354 kJ mol⁻¹ for isolated O* chemisorbed on Pd(111) and Pt(111) surfaces, respectively; DFT-calculated values) lead to surfaces saturated in stable and unreactive O* and OH* species and sparse surface vacancies. The proposed kinetically relevant step is either H*-assisted O₂* dissociation or the removal of O* and OH* as H₂O to clear the surface. Here, the oxidation of H₂ was studied using gas-phase reactants (H₂ and O₂) in the absence of an aqueous solvent to isolate the catalytic consequences of alloying Pt and Pd with Au and remove the complicating influences of the solvent. Pd binds more strongly to oxygen than Pt, and is therefore less reactive than Pt for this chemistry (Fig. 2b); thus, the effects of alloying with Au should be most observable on the AuPd system, and will be explored in depth here. H₂ oxidation on AuPt catalysts will be discussed briefly in Section 4.3.9.

H₂ oxidation turnover rates (normalized per total surface metal atom) at 309 K on Pd/SiO₂ and Au₅₀Pd₅₀/SiO₂ are shown in Figure 9. Rates on both Pd and Au₅₀Pd₅₀ increase with increasing H₂
pressure (0.045-1 kPa H₂, 1-15 kPa O₂; Fig. 9a and b). Rates decrease with increasing O₂ pressure on Pd, in contrast to rates on Au₅₀Pd₅₀, which increase and then become independent of O₂ pressure (0.5-20 kPa O₂, 0.2-0.8 kPa H₂; Fig. 9c and d). The distinct kinetic behavior of these two catalysts indicates a change in the rate expression— and thus in the kinetically relevant step and/or surface coverage—upon alloying Pd with Au. These results are in contrast to CO oxidation rates on Pt and AuPt catalysts (Section 4.3.4), which did not differ in kinetic behavior. Moreover, Au is active for H₂ oxidation at these conditions, albeit with much lower turnover rates (Fig. 2b), but was not active for CO oxidation at the conditions of this study.[19] Thus, we expect Au atoms to have greater mechanistic implications for H₂ oxidation catalysis on Pd than they did for CO oxidation catalysis on Pt, in which they acted primarily as inert diluents of the active metal.

**Figure 6** Effects of H₂ pressure on H₂ oxidation turnover rates (normalized per total surface metal atom) on a) 0.05 % wt. Pd/SiO₂ and b) 0.075 % wt. Au₅₀Pd₅₀/SiO₂, and the effects of O₂ pressure on H₂ oxidation turnover rates.
H₂ oxidation turnover rates that decrease on Pd/SiO₂ but increase on Au₅₀Pd₅₀/SiO₂ with increasing O₂ pressure (Fig. 10) suggest that within the conditions presented here, adding Au to Pd clusters minimizes the inhibitory consequences of O₂. The effects of changing space velocity—and thus conversion—on H₂ oxidation turnover rates can also provide information on how surface species influence turnover rates. Decreasing space velocity (thus increasing conversion) led to lower rates on Pd/SiO₂, but did not affect rates on Au₅₀Pd₅₀/SiO₂ (Fig. 11). These results are consistent with a product of the reaction (H₂O)—present at greater concentrations at higher conversions—inhibiting rates on Pd clusters but not affecting rates on Au₅₀Pd₅₀ clusters.

The adsorption energy of H₂O* on Pd is lower than O* and OH*,⁴ and the Gibbs free energy for H₂O displacement by O₂ is favorable,⁵ thus indicating that H₂O* is unable to compete with O* and OH* for surface sites. H₂O, however, can dissociate on Pd into H* and OH* or, when assisted by O*, into two OH* molecules; these surface hydroxyl species bind strongly to Pd active sites and inhibit rates.⁶ The dissociative adsorption of H₂O and resulting inhibition of rates has been reported previously for CH₄ oxidation on Pd.⁷ The absence of a space velocity effect for Au₅₀Pd₅₀ indicates that H₂O does not return to the surface and dissociate on AuPd alloy surfaces, possibly because the stability of the resulting dissociated product (OH*) on the surface is lower. These findings, together with the weakened inhibitory effects of O₂ pressure on Au₅₀Pd₅₀ clusters relative to Pd clusters (Fig. 9d), suggest that Au₅₀Pd₅₀ binds more weakly to O*-containing surface species than Pd, as previously proposed by Boudart.⁴ Next, we examine how the Au content, and thus the binding strength of the catalyst surface, influences H₂ oxidation turnover rates.

![Figure 7](image_url)

**Figure 7** Effects of changing space velocity on H₂ oxidation turnover rates (normalized per total surface metal atom) for a) 0.05 % wt. Pd/SiO₂ and b) 0.075 % wt. Au₅₀Pd₅₀/SiO₂ (10 kPa O₂, 0.5 kPa H₂, balance He; 309 K).
4.3.9 Effects of Catalyst Au Content on H₂ Oxidation Rates

H₂ oxidation turnover rates (normalized per total surface metal atom; 10 kPa O₂, 0.5 kPa H₂, 309 K) on Pd/SiO₂ and AuPd/SiO₂ catalysts of varying compositions are shown in Figure 11. Turnover rates increase with increasing Au content up to 50 % at. Au, then decrease with increasing Au content. Turnover rates on all AuPd samples (25-67 % at. Au) were greater than on the monometallic Pd catalyst, a result of weaker O* binding on bimetallic AuPd surfaces (Section 4.3.8).

The combination of Au and Pd atoms within a cluster can decrease the binding energy of O* in three distinct ways. First, a shift in electron density from Pd to Au, as dictated by their relative electronegativities,[6] would decrease the O* binding energy on Pd, but increase it on Au, thus increasing H₂ oxidation rates on both metals via a ligand effect. Such a weakening of adsorbate binding strength to a Group VIIB metal was observed on CO*-saturated AuPt catalysts (Section 4.3.6). Ensemble effects may also lead to a decrease in O* binding energy. O* strongly favors binding in the three-fold hollow site on Pd surfaces,[26] thus requiring an ensemble of three Pd atoms to bind. Ensembles containing one or two Au atoms, however, would bind O* more weakly than monometallic Pd ensembles, and thus exhibit higher turnover rates. Finally, bare Au atoms amidst O* adlayers on Pd may also increase rates by preventing the formation of the dense, stable, and unreactive O* monolayers that prevail on monometallic Pd clusters, similar to the role of chemisorbed C* on Pt clusters saturated in CO* that block active surface atoms but obstruct the formation of saturated CO* adlayers, thus increasing CO oxidation rates in H₂-CO mixtures.[16] We expect that a combination of ligand and ensemble effects together influence the binding energy of O* on AuPd/SiO₂.

![Figure 8](image_url) Effects of catalyst Au content on H₂ oxidation turnover rates (normalized per total surface metal atom) on (■) AuPd/SiO₂ and (◆) AuPt/SiO₂ bimetallic systems (10 kPa O₂, 0.5 kPa H₂, balance He; 309 K).

Next, we discuss the effects of Au content on H₂ oxidation turnover rates on AuPt clusters in order to extend our findings to a different bimetallic system. Turnover rates on AuPt/SiO₂...
catalysts first increase with increasing Au content (up to 11 % at. Au), then decrease below the rates observed on monometallic Pt clusters (Fig. 11), in contrast to turnover rates on AuPd/SiO₂ catalysts, which were higher than rates on Pd/SiO₂ at all bimetallic compositions studied (up to 67 % at. Au). The electronegativities of Pt and Pd are similar,⁶ thus a ligand effect analogous to the one for AuPd catalysts is expected for AuPt catalysts. In addition, O* binds in three-fold hollow sites on Pt as it does on Pd,¹² suggesting similar ensemble effects for both AuPd and AuPt systems. Pd and Pt differ, however, in that the binding strength of O* is weaker on Pt than Pd,²⁵ thus decreasing the inhibiting effects of O* and leading to higher H₂ oxidation rates on monometallic Pt clusters relative to Pd clusters (Fig. 2).

The relationship between M-O* binding energy and H₂ oxidation rates leads to a volcano-shaped dependence. Metals that bind too strongly (Pd) or weakly (Au) to O* exhibit low rates due to the high energy barriers of removing O* and OH* from the metal surface, or of dissociating O₂*, respectively. Metals with intermediate O* binding energy (Pt) have the lowest kinetic barriers and exhibit the highest rates.²⁵ Pt catalysts are located closer to the apex of the volcano curve than either Au or Pd, and are therefore less sensitive to changes in O* binding strength than metals located on the steeper upward and downward sloping regions of the curve. Consequently, the ligand and ensemble effects of Au alloys, which are expected to decrease O* adsorption strength on Pt and Pd surfaces in similar manners, are less effective for increasing H₂ oxidation rates on Pt-based catalysts relative to Pd-based catalysts (Fig. 12). AuPt catalysts with greater than 11 % at. Au may begin to be limited by higher O₂* dissociation barriers that counteract the effects of decreasing O* binding energy, or may be affected more strongly than AuPd catalysts by the displacement of active Pt atoms with less active Au atoms due to the weaker effects of changing O* binding energy on rates.

4.3.10 Consequences of Alloying with Au on CO*- versus O*-Saturated Surfaces

CO oxidation rates (normalized per total surface metal atom) on CO*-saturated surfaces decreased with increasing Au content (Fig. 4), in contrast to H₂ oxidation rates (normalized per total surface metal atom) on O*-saturated surfaces that increased with the addition of Au (Fig. 12). The opposing consequences of alloying with Au, and thus of decreasing CO* and O* binding energies, are consistent with the opposing particle size effects for reactions on CO*- and O*-saturated surfaces. Decreasing adsorbate binding strength by increasing particle size leads to higher oxidation turnover rates on O*-saturated surfaces,¹³ but does not affect CO oxidation rates.²

Such differences, as well as the opposing effects of alloying with Au reported here, reflect the differences in adsorbate binding strength, site preference, and desorption paths between CO* and O*. O* binds preferentially at three-fold hollow sites,¹² and binds more strongly to metal surfaces than CO* (CO* adsorption energies range from -171 to -120 kJ mol⁻¹ while O* adsorption energies range from -426 to -271 kJ mol⁻¹ on Pt).² In contrast, CO* binds primarily at atop sites, but can access other binding configurations with minor differences in energy (<10 kJ mol⁻¹).² Moreover, the molecular desorption of CO* makes it easier for CO* (relative to O*) to adsorb and desorb quickly. Consequently, CO* adlayers are able to rearrange and access configurations that facilitate turnovers, thus helping mitigate the effects of strong CO* binding. Less mobile O* adlayers, meanwhile, lead to surfaces in which the formation of vacancy sites is
more energetically unfavorable, and thus show greater sensitivity to changes in O* binding energy.

4.4 Conclusions

Adding Au to Pt and Pd catalysts decreases the binding energy of strongly bound adsorbates such as CO* and O* relative to monometallic Pt and Pd clusters, however the consequences on turnover rates depends on the sensitivity of the reaction to changes in binding energy. CO oxidation rates depend weakly on CO* binding energy because changes to CO* adlayer stability similarly affect the stability of the transition state, thus offsetting each other and resulting in activation energy barriers that depend weakly on CO* binding energy. Furthermore, facile reconstruction of CO* adlayers allows CO*-saturated surfaces to access configurations that facilitate turnovers, thus mitigating the effects of strong CO* binding. As a result, AuPt catalysts have lower CO oxidation rates (normalized per total surface metal atom) than monometallic Pt catalysts because Au atoms displace and dilutes the more active Pt metal ensembles. O* adlayers, meanwhile, are more strongly bound to Pt and Pd metal surfaces and less mobile than CO* adlayers, and are therefore less able to reconstruct and form the vacancies required for turnovers. H2 oxidation rates depend more strongly on adsorbate binding energy than CO oxidation, and rates on Pt and Pd increase upon alloying with Au. The positive effect on rates is most evident for AuPd than AuPt due to the higher O* binding energies on Pd.

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4.6 References