Displacement-reduction routes to PtPd clusters and mechanistic inferences for the synthesis of other bimetallic compositions

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Abstract

Bimetallic PtPd clusters (2.1–2.9 nm) dispersed on SiO₂ and uniform in composition and size were prepared using colloidal methods with reagents containing only C, O, H, and N atoms. These synthetic protocols extend galvanic displacement-reduction (GDR) processes previously used to prepare AuPd and AuPt clusters. Such processes exploit the different redox potentials of two elements to encourage their deposition within the same cluster. The size, composition, and formation mechanism of PtPd clusters were probed using transmission electron microscopy, UV–visible spectroscopy, energy-dispersive X-ray spectroscopy, and high-angle annular dark-field imaging. Taken together with previous data for AuPd and AuPt systems, these findings highlight key general features, properties, and protocols required to form uniform bimetallic clusters. Exothermic alloys, such as PtPd and AuPd, form predominantly via selective GDR routes; in contrast, alternate routes become significant for endothermic alloys, such as AuPt. Bimetallic clusters grow via GDR processes (PtPd, AuPd) at rates proportional to the surface area of each cluster; therefore, compositional uniformity is dictated by the size distribution of the seed clusters. The rate of GDR processes reflects the difference in reduction potentials of the two components, as shown by more facile formation of AuPd than PtPd clusters. These considerations and experimental evidence provide useful guidance for conditions and protocols likely to succeed for other bimetallic pairs.

Low-temperature (≤423 K) reductive treatments (in H₂ or EtOH) successfully removed all synthetic detritus from Pd and PtPd clusters dispersed on SiO₂, without significant coalescence. Such removal strategies are more challenging for Pd than for Pt clusters because of stronger Pd-polymer bonds and the greater sintering tendency of Pd clusters.

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1. Introduction

Bimetallic catalysts have been shown to increase catalytic turnover rates, improve selectivity, and enhance stability [1,2]. The reported interpretations of the effects of alloying on the reactivity of small bimetallic clusters are often equivocal or inaccurate, however, because of the complexity introduced by the size and compositional heterogeneity of bimetallic materials prepared by typical synthesis techniques, such as incipient wetness impregnation [3–6]. Alternatively, electroless deposition (ED) [7–10] and galvanic displacement (GD) [11,12] techniques selectively reduce solvated metal cations onto the surfaces of supported metal clusters by activating the metal surface with a reducing agent or using the metal surface itself as the reducing agent, respectively; such methods can exclusively form bimetallic particles. The selective placement of the second metal, however, is impeded upon obstruction of the seed cluster surface with the deposited metal, thus limiting the bimetallic compositions that can be prepared. Metal cation-support interactions must also be carefully avoided in order to prevent the formation of monometallic particles on the support, and the broad particle size distributions of the initial supported metal clusters prepared by incipient wetness impregnation lead to broad bimetallic particle size distributions. Colloidal methods, however, avoid all metal-support interactions during cluster formation, while also providing better control over particle composition and size [2,13]; in spite of this, they frequently require the use of reagents that poison the catalyst surface (e.g., protecting agents with thiol groups) and thus influence turnover rates. Here, we describe the colloidal synthesis of PtPd nanoparticles (2.1–2.9 nm) uniform in composition and size via galvanic displacement-reduction (GDR) methods using reagents comprised of only C, O, H, and N atoms; we show that such materials can be
removed from SiO$_2$-supported Pd and PtPd cluster surfaces without significant particle agglomeration using low-temperature reductive treatments, thus yielding chemically accessible metal catalyst surfaces. We discuss our results within the broader context of developing bimetallic procedures for other metal combinations based on comparisons of PtPd with AuPt [14] and AuPd [15] bimetallic systems prepared using similar methods.

PtPd clusters were synthesized in this study using GDR protocols previously shown to form AuPd [14] and AuPd [15] bimetallic nanoparticles. The synthesis of AuPt and AuPd clusters begins with a colloidal suspension of nanoparticles composed of the less noble metal ($M_A = $ Pt or Pd), which is subsequently combined with metal cations of the more noble species ($M_B = $ Au). The reduction of solvated $M_B$ cations by surface $M_A$ atoms is thermodynamically favorable, as indicated by their relative standard reduction potentials ($E^0$, $\Delta^\text{redox}$ = $E_B^0$ - $E_A^0$ > 0; Table 1), thus leading to the reduction and deposition of $M_B$ atoms onto cluster surfaces and to the oxidation and dissolution of $M_A$ atoms into the solvent (Scheme 1(1a)). The solvent, also acting as the reductant (ethanol or ethylene glycol for AuPd or AuPt clusters, respectively), is at a much higher concentration than the counterions of the metal precursors (e.g. NO$_3^-$ or Cl$^-$); hence the solvent coordinates to the $M_A$ cations, subsequently reducing and depositing them back onto particle surfaces (Scheme 1(1b)) at greater rates than the reduction of the $M_B$ metal precursors (e.g. HAuCl$_4$) [16]. Consequently, the kinetically relevant step of the GDR sequence is the galvanic displacement step (Scheme 1(1a)) [14,15]. Re-reduction of $M_A$ atoms by the solvent ensures that $M_B$ atoms are continuously accessible at the particle surface to reduce $M_A$ cations; the presence of $M_A$ atoms (Pt or Pd) at the AuPd or AuPt bimetallic particle surface was confirmed by UV–visible spectroscopy.

These mechanistic details led us to conclude that the GDR approach would also lead to successful syntheses of other metal combinations, provided that cations of the nobler metal are added to suspensions of clusters composed of the less noble metal in the presence of a reducing agent. We show here that this is indeed the case for PtPd clusters, which were synthesized by adding a Pt precursor solution to a pre-formed suspension of Pd seed clusters in an ethanol-water mixture, a sequence prescribed by guidance from the standard reduction potentials (Table 1) of Pd$^0$ seed surface atoms by Pt cations relative to Au atoms ($\Delta^\text{redox,AuPd} > \Delta^\text{redox,PtPd}$; Table 1) leads to lower rates of bimetallic PtPd cluster formation compared with those of AuPd formation. The endothermic nature of AuPt mixing ($\Delta H_{\text{mix}} = +2.3$ kJ mol$^{-1}$ [20]) results in intraparticle segregation and to Au enrichment at cluster surfaces, thus inhibiting GDR by Pt$_{\text{av}}$ sites and introducing additional growth pathways that lead to non-uniform distributions of Au atoms among the Pt seeds [14]. Solvents with high reduction potentials (e.g. butanediol), which compete with $M_A$ surface atoms as reductants of $M_B$ cations, have also been shown to lead to bimodal distributions of bimetallic clusters by promoting the homogeneous or heterogeneous nucleation of $M_B$-rich clusters. Employing GDR protocols to prepare bimetallic clusters of immiscible metals or to prepare clusters within solvents of high reduction potentials therefore requires more rigid synthesis protocols to promote the formation of uniform bimetallic clusters [14].

These systematic studies of PtPd, AuPd, and AuPt systems have demonstrated the general applicability of synthetic protocols that exploit GDR processes in preparing bimetallic clusters of diverse metal combinations using innocuous reagents that can be removed by low-temperature treatments; these studies have also shown how differences in $\Delta^\text{redox}$ metal miscibility, and solvent reduction potential require, in turn, that such synthesis protocols be adapted to prevent the formation of bimodal particle distributions [14,15]. In addition to the three bimetallic systems discussed herein, we propose that other catalyst compositions—such as PdRh starting from Rh seed clusters or PtAg starting from Ag seed clusters (Table 1)—can also be synthesized using the GDR approach.

### Table 1

<table>
<thead>
<tr>
<th>Metal</th>
<th>Standard reduction potential ($E^0$, V)</th>
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<tbody>
<tr>
<td>Au$^{+}$</td>
<td>1.52</td>
</tr>
<tr>
<td>Pt$^{2+}$</td>
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<tr>
<td>Pd$^{2+}$</td>
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<tr>
<td>$\text{AuPd}^*$</td>
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<tr>
<td>Ag$^{+}$</td>
<td>0.80</td>
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<td>Rh$^{3+}$</td>
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<td>Ru$^{3+}$</td>
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<tr>
<td>Ni$^{2+}$</td>
<td>0.26</td>
</tr>
<tr>
<td>$\text{Co}^{2+}$</td>
<td>-0.28</td>
</tr>
</tbody>
</table>

2. Materials and methods

2.1. Catalyst synthesis

2.1.1. 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; conductivity ~0.06 $\mu$S cm$^{-1}$) with solvated PVP (0.02 M, monomeric unit basis; Sigma Aldrich, 40,000 amu) and Pd(NO$_3$)$_2$:2(H$_2$O) ($5 \times 10^{-4}$ M Pd atoms; 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. Spectral features of the Pd precursors.
were not detected via UV–visible spectroscopy of the colloidal suspension, thus indicating their complete reduction.

2.1.2. Preparation of PVP protected Pd clusters (2.3 nm)

A solution of Pd(NO\textsubscript{3})\textsubscript{2}-2(H\textsubscript{2}O) (5 \times 10^{-4} M Pd atoms; Sigma Aldrich, ~40 wt.\% Pd basis) in 1:1 by volume EtOH (Sigma Aldrich, >99.5\%) and deionized H\textsubscript{2}O (conductivity ~0.06 \mu S cm\textsuperscript{-1}) was added to an equivalent volume of a monometallic 1.8 nm Pd cluster suspension (5 \times 10^{-4} M Pd atoms, prepared as described in Section 2.1.1). The resulting mixture was stirred (310 rpm) in ambient air (one-neck flask, 4 L, reflux condenser) at 368 K for 0.33 h. Spectral features of the Pd precursors were not detected via UV–visible spectroscopy of the colloidal suspension, thus indicating their complete reduction.

2.1.3. Preparation of PVP protected PtPd clusters

H\textsubscript{2}PtCl\textsubscript{6} (5 \times 10^{-4} M Pt atoms; Sigma Aldrich, 8 wt.\% in H\textsubscript{2}O) in a mixture of 1:1 by volume EtOH (Sigma Aldrich, >99.5\%) and deionized H\textsubscript{2}O (conductivity ~0.06 \mu S cm\textsuperscript{-1}) was added to an equivalent volume of the monometallic 1.8 nm Pd cluster suspension (5 \times 10^{-4} M Pd atoms, prepared as described in Section 2.1.1) and stirred (310 rpm) in ambient air (one-neck flask, 0.1 L, reflux condenser) at 363 K for 0.33 h. Spectral features of the Pd precursors were not detected via UV–visible spectroscopy of the colloidal suspension, thus indicating their complete reduction.

2.1.4. Preparation of PVP protected Pt and AuPt clusters

Pt and AuPt clusters were prepared by previously reported methods [14]. Briefly, Pt clusters were synthesized by heating a stirred solution of H\textsubscript{2}PtCl\textsubscript{6} (5 \times 10^{-4} M Pt atoms) and PVP (0.02 M, monomeric unit basis) in ethylene glycol (EG) at 423 K in ambient air (one-neck flask, 0.1 L, reflux condenser) for 0.33 h. AuPt clusters were prepared by adding a solution of HAuCl\textsubscript{4}-3(H\textsubscript{2}O) (5 \times 10^{-4} M Au atoms, in EG) at a rate of 16.7 nmol Au s\textsuperscript{-1} to a suspension of Pt\textsubscript{50}Pd\textsubscript{50} clusters at 368 K for 0.5 h. AuPt clusters of different atomic compositions were synthesized by modifying the volumetric ratio of the Pd seed particle suspension and the Pt precursor solution. Spectral features of the Pt precursors were not detected via UV–visible spectroscopy of the colloidal suspension, thus indicating their complete reduction.

2.1.5. Preparation of polyvinylalcohol (PVA) protected Pd and AuPd clusters

Pd and AuPd clusters were prepared by previously reported methods [15]. Briefly, Pd clusters were synthesized by heating a stirred solution of Pd(NO\textsubscript{3})\textsubscript{2}-2(H\textsubscript{2}O) (5 \times 10^{-4} M Pd atoms) and PVA (0.02 M, monomeric unit basis) in 1:1 by volume EtOH and deionized H\textsubscript{2}O to 368 K in ambient air (one-neck flask, 0.1 L, reflux condenser) for 0.5 h. AuPd clusters were prepared by adding a solution of HAuCl\textsubscript{4}-3(H\textsubscript{2}O) (5 \times 10^{-4} M Au atoms, in 1:1 EtOH: H\textsubscript{2}O) to a suspension of Pd clusters (5 \times 10^{-4} M Pd atoms) and stirring the resulting mixture for 2 h in air at ambient temperature (one-neck flask, 0.1 L). PVA was used as the protecting polymer in our initial bimetallic nanoparticle synthesis studies of AuPd clusters; however, our more recent studies (i.e. AuPt and PtPd) use PVP because it typically offers greater colloidal stability over time and was more soluble in the solvents used.

2.1.6. Dispersion of PVP protected clusters onto SiO\textsubscript{2}

A Pd cluster suspension (52 cm\textsuperscript{3}, prepared as described in Section 2.1.1) was added dropwise (~0.2 cm\textsuperscript{3} s\textsuperscript{-1}) to a suspension of fumed SiO\textsubscript{2} (0.55 g, Sigma Aldrich, 7 nm particle size, 395 m\textsuperscript{2} g\textsuperscript{-1} surface area) in deionized H\textsubscript{2}O (52 cm\textsuperscript{3}, conductivity ~0.06 \mu S cm\textsuperscript{-1}; Scheme 1(1c)). The solids were collected by centrifugation (133 Hz, 0.6 ks) after stirring the mixture for 1 h at ambient temperature. Complete deposition of clusters onto SiO\textsubscript{2} was confirmed by the absence of absorbance in the UV–visible spectra of the supernatant solutions. Supported clusters were washed two times in deionized H\textsubscript{2}O (52 cm\textsuperscript{3}, conductivity ~0.06 \mu S cm\textsuperscript{-1}, 1 h) and subsequently treated overnight in ambient air at 356 K. These procedures resulted in catalysts with 0.50 wt.\% metal loadings. Similar procedures were used to disperse bimetallic PtPd clusters onto SiO\textsubscript{2}, resulting in metal loadings of 0.50 wt.\%, 0.58 wt.\% and 0.70 wt.\% for Pt\textsubscript{10}Pd\textsubscript{90}, Pt\textsubscript{25}Pd\textsubscript{75}, and Pt\textsubscript{50}Pd\textsubscript{50} samples, respectively.

2.2. Nanoparticle characterization

2.2.1. Transmission electron microscopy (TEM)

A JEOL 1200 EX microscope operated at 80 kV was used to obtain bright-field transmission electron micrographs. TEM samples of colloidal Pd, AuPd, and PtPd clusters—synthesized in EtOH/H\textsubscript{2}O 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 AuPd samples synthesized in ethylene glycol, a less volatile solvent, were first re-dispersed in EtOH (methods reported previously [14]) in order to prepare grids without thermal treatments that could affect cluster composition and size. Clusters supported on SiO\textsubscript{2} 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 following equation:

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

where \(n_i\) is the number of particles with diameter \(d_i\). The dispersity index (\(D_s\)) was used to quantify particle size uniformity [21]:

\[ D_s = \frac{\text{maximum diameter}}{\text{minimum diameter}} \]
2.3.2. Low-temperature treatment in H2 to remove the protective polymer

SiO2-supported Pd particles (0.50 wt.%; prepared as described in Sections 2.1.1 and 2.1.6) and SiO2-supported bimetallic Pt50Pd50, Pt50Pd75, and Pt50Pd50 clusters (0.50 wt.%), 0.58 wt.%, and 0.70 wt. %, respectively; prepared as described in Sections 2.1.3 and 2.1.6) were treated at 348 K (0.033 K s\(^{-1}\)) for 1 h and subsequently cooled to 298 K. Isotherms were collected in a range from 0.013 to 101.3 kPa O\(_2\) (Praxair, 99.999%), with 0.07 h allotted for equilibration with the gas phase at each pressure. Extrapolating to zero O\(_2\) pressure led to estimates of O\(_2\) uptakes. Cluster dispersions were calculated assuming one oxygen atom per metal surface atom [22]. The particle diameter was calculated from the chemisorption-derived dispersion (\(D\)) using the following equation:

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

where C depends on the metal identity (determined by using the bulk density of the metals and assuming spherical clusters; 1.13 nm for Pt, 1.12 nm for Pd, and a weighted average, based on atomic composition, for bimetallic PtPd samples [23,24]) and \(d\) is diameter in nm. 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 free of synthetic detritus.

3. Results and discussion

3.1. Synthesis and characterization

Surface-averaged mean diameters (Eq. (1)) of Pd clusters and bimetallic Pt50Pd50, Pt50Pd75, and Pt50Pd50 clusters were calculated from particle diameter measurements obtained by TEM (Fig. 1; Table 2). Mean PtPd cluster size increased monotonically with increasing Pt content, consistent with the reduction and deposition of solvated Pt cations onto the parent Pd seeds. Cluster uniformity was determined by calculating the dispersity index (\(D_{32}\)) of PtPd samples using Eq. (2) [21]. These \(D_{32}\) values (1.13–1.20) were less than the value of 1.5 that IUPAC recommends to define monodispersity [21,25]. Relative standard deviations (16–19%), a more commonly reported but less rigorous measure of uniformity, are also included in Table 2, and similarly indicate that bimetallic PtPd clusters were narrowly distributed in size. Clusters with similar size distributions are typically obtained by colloidal methods using NaBH\(_4\) as a reductant and/or protecting agents with thiol groups [26,27], which are difficult to remove from catalyst surfaces. The synthetic protocols reported here successfully avoid such heteroatoms without loss of size uniformity.

Mean bimetallic cluster diameters (\(\langle d_{M,M}\rangle\); Table 2) predicted from Eq. (5) were calculated for each composition using the measured surface-averaged mean diameter of the Pd seed clusters (\(d_{M}\)):

\[
\langle d_{M,M}\rangle = \langle d_{M}\rangle \left(1 - \frac{V_{M}N_{M}}{V_{M,N_{M}}}\right)^{1/3}
\]

where \(V_{M}\) is the atomic volume of metal \(M\), and \(N_{M}\) is the number of atoms of metal \(M\). Eq. (5) assumes that solvated Pt (\(M_{p}\)) cations are reduced and deposited homogeneously across all Pd (\(M_{s}\)) seed clusters, thus precluding bimodal distributions of particle size. Such non-uniform size distributions would arise from the homogeneous nucleation and growth of monometallic Pt particles in solution or the nucleation of Pt on the surface of a fraction of seed clusters, known as heterogeneous nucleation; the former results in no clus-
ter growth of the initial Pd seeds while the latter results in the growth of a fraction of seed particles that become larger at the expense of the remaining clusters. Fig. 2 shows that measured \( d_{\text{PtPd}} \) values agreed well with those calculated from Eq. (5), consistent with the absence of homogenous or heterogeneous nucleation of Pt during synthesis. No monometallic particles were detected from particle-by-particle elemental analysis using EDS (\( N > 100 \) clusters per sample), thus confirming such conclusions. The mean atomic fractions of Pt and Pd (Eq. (3)) within each bimetallic PtPd sample were in agreement with the composition of the synthesis reagents used (Fig. 3a), consistent with the full recovery of all metal precursors in the solids.

The disappearance of the Pt precursor band (266 nm \([28]\)) during synthesis (ambient temperature, 1:1 by volume EtOH/H\(_2\)O solvent; Section 2.1.3) was monitored using UV–visible spectroscopy 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 (determined by TEM; 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 in the synthesis mixture 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 from the similar spectral prop-

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**Table 2**

<table>
<thead>
<tr>
<th>Pt content (% at.)</th>
<th>0</th>
<th>33</th>
<th>50</th>
<th>67</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM-derived surface-averaged diameter, ( d ) ( \pm ) STD N(^{-0.5}) (nm, Eq. (1))</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_{\text{PtPd}} ) (nm, Eq. (5))</td>
<td>2.2</td>
<td>2.5</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Dispersity index, ( D_d ) (Eq. (2))</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>

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Fig. 2. Parity plot of the measured (Eq. (2)) and expected (Eq. (4)) mean PtPd diameter \( (d_{\text{PtPd}}) \) of Pt\(_{33}\)Pd\(_{67}\), Pt\(_{50}\)Pd\(_{50}\), and Pt\(_{67}\)Pd\(_{33}\) clusters synthesized at 363 K (\( \circ \)), and of Pt\(_{50}\)Pd\(_{50}\) clusters synthesized at ambient temperature (\( \bullet \)) and 323 K (\( \blacksquare \)).
Higher synthesis temperatures led to the faster reduction of solvated Pt cations (1/C243 h at 323 K, 1/C240.33 h at 363 K); the UV–visible spectra (Fig. 5) and the particle size distributions (Fig. 2) of the clusters formed at ambient temperature, 323 K, and 363 K were similar. In contrast to solvated Pt cations, Au cations in contact with Pd seed clusters at ambient temperature reduced fully within 2 h (vs. 1/C2446.5 h for Pt; EtOH/H2O mixtures used as solvent for both AuPd and PtPd synthesis [15]). Pd surface atoms reduce Pt cations more slowly than Au cations and thus form bimetallic PtPd clusters at lower rates than AuPd clusters. The relative kinetics of PtPd and AuPd formation reflects their different thermodynamic driving forces (ΔE°(redox)) for the kinetically relevant step of the GDR sequence, galvanic displacement (Scheme 1(1a)), with the driving force for AuPd being greater than for PtPd systems (ΔE°(redox,AuPd) = 0.74 V, ΔE°(redox,PtPd) = 0.24 V; Table 1).

Unlike the Au-containing bimetallic systems reported previously (AuPt and AuPd) [14,15], the alloyed metals discussed here (Pt and Pd) have similar UV–visible spectra (Fig. 5). We were thus unable to determine the predominant surface metal of the PtPd alloys, and could not exclude the possibility that Pt cations deposit...
on activated Pd sites via electroless deposition (ED). Our previous studies lead us to suggest, however, that the thermodynamic driving force for galvanic displacement of Pd by Pt cations and the presence of a reducing agent to re-reduce oxidized Pd atoms would enhance the contributions from GDR pathways.

In addition to the magnitude of their $\Delta E_{\text{redox}}$ values, the thermodynamic miscibility of the alloyed metals and the reduction potential of the solvent influence the need for specific protocols to prepare bimetallic clusters of uniform composition and size [14]. Enthalpically favored mixtures, such as AuPd and PtPd ($\Delta H_{\text{AuPd}} = -6.7 \text{ kJ mol}^{-1}$ [18,30] and $\Delta H_{\text{PtPd}} = -4.3 \text{ kJ mol}^{-1}$ [18,30]), can be synthesized at ambient temperatures [15]. In contrast, the formation of AuPt alloys ($\Delta H_{\text{AuPt}} = +2.3 \text{ kJ mol}^{-1}$ [20]) is enthalpically unfavorable and requires elevated synthesis temperatures (423 K) because the positive entropies of mixing become more influential in determining Gibbs free energies at higher temperatures [14]. Additionally, AuPt clusters were synthesized in a different solvent (ethylene glycol, EG) than that used for AuPd and PtPd synthesis (1:1 by volume EtOH:H$_2$O) because the Pt seed suspensions could not be stabilized in EtOH/H$_2$O mixtures. EG, however, has a higher reduction potential than EtOH ($E^\circ_{\text{EG}} = -0.8 \text{ V vs. } E^\circ_{\text{EtOH}} = -0.197 \text{ V [17]}$), stronger reductants compete with M$_b$ surface atoms as reductants of M$_b$ cations, thus promoting the homogeneous or heterogeneous nucleation of clusters enriched in M$_b$ (Scheme 1(2)) that compromise sample uniformity [14]. The synthesis of clusters in solvents with high reduction potentials, such as EG in the case of AuPt, therefore requires the slow drop-wise addition of the M$_b$ precursor solution in order to maintain low concentrations of solvated M$_b$ cations in solution, thereby inhibiting processes that lead to the nucleation of M$_b$-rich clusters.

3.2. Steps and processes involved in the formation of bimetallic clusters

Particle-by-particle elemental analysis using EDS is used next to probe the mechanistic features of bimetallic particle formation via GDR processes. For parent clusters of element M$_a$, these processes require that [14,15]:

(a) solvated M$_a$ cations be reduced exclusively by M$_a$ surface atoms (Scheme 1(1a)),
(b) M$_b$ atoms brought into solution by galvanic displacement reactions in (a) be reduced by solvent molecules and deposited back onto particle surfaces (Scheme 1(1b)), and
(c) M$_a$ atoms remain accessible at the growing cluster surface to (galvanically) 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 as they reach cluster surfaces. When conditions (a)–(c) are met, the growth rate of a given particle, $i$, is proportional to the cluster surface area ($A_i$):

$$\frac{dN_i}{dt} = A_i k$$

(6)

where $k$ is the rate constant for galvanic displacement and $N_i$ is the number of atoms within the particle. The amount by which each cluster increases in diameter ($\Delta d_i$) via addition of M$_b$ atoms can be derived from Eq. (6) by expressing $A_i$ and $N_i$ as functions of the particle diameter ($d_i$; derivation in Section S1, SI):

$$\Delta d_i = 2V_i k t$$

(7)

Here, $t$ is time and $V_i$ is the atomic volume of the elements in the particle. According to Eq. (7), clusters that increase in diameter at a rate proportional to $A_i$ (Eq. (6)) would increase in size by a value $\Delta d$, that does not depend on the diameter of the parent M$_a$ cluster [15,31,32]. Consequently, a suspension of M$_a$ seed particles of varying particle sizes in which each particle grows by the same thickness ($\Delta d$) via addition of a second metal (M$_b$) leads to bimetallic M$_a$M$_b$ clusters with a distribution of compositions for which the atomic fraction of M$_b$ decreases with increasing seed particle size (Scheme 2). This inverse relationship between the atomic fraction of M$_b$ and the seed particle diameter ($d_{\text{M}_a}$) is evident from a rearrangement of Eq. (5) for a given particle, $i$:

$$\frac{N_{M_b}}{N_{M_a}}_i = \left(1 + \frac{\Delta d_i}{d_{M_a,i}}\right)^{-\frac{3}{2}} - 1 \frac{V_{M_b}}{V_{M_a}}$$

(8)

where $d_{M_a,i}$ in Eq. (5) has been replaced using Eq. (9).

$$d_{M_a,i} = d_{M_a} + \Delta d$$

(9)

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 derive a relationship between the uniformity of the seed particle diameters and the compositional uniformity of GDR-derived bimetallic clusters using the coefficient of variation (CV).

$$CV = \frac{\sigma}{\mu}$$

(10)

where $\sigma$ is the sample standard deviation and $\mu$ is the sample mean (of either seed diameters or bimetallic clusters compositions), as a measure of uniformity. Probability density functions (PDFs) of varying CV value (0–0.4) were generated to represent seed particle diameters with log-normal size distributions [31] of varying uniformity, and were subsequently transformed into PDFs representing the compositions of the bimetallic particles formed via GDR processes; compositional uniformity was then quantified by calculating the CV values of the PDFs of the bimetallic compositions (derivation in Section S2, SI). Fig. 6a shows how the CV of the bimetallic composition distributions decreases with decreasing CV of the seed particle diameters, thus demonstrating that sharper seed particle size distributions lead to concomitantly sharper compositional distributions.

Any deviations from GDR pathways can be assessed from the curve in Fig. 6a, which was derived for exclusive growth via GDR. Data obtained from EDS elemental analysis of bimetallic PtPd, AuPt, and AuPd clusters [14], together with transmission electron micrographs of Pt and Pd seed particle size distributions, are plotted in Fig. 6a to assess whether measured compositional uniformity (CV$_{\text{EDS}}$) deviates from that expected from GDR growth (CV$_{\text{GDR}}$). Deviations from the curve in Fig. 6a ($\chi_{\text{CV}}$) are defined as follows:

$$\chi_{\text{CV}} = \frac{\text{CV}_{\text{EDS}} - \text{CV}_{\text{GDR}}}{\text{CV}_{\text{GDR}}}$$

(11)

Scheme 2. M$_a$ seed particles of varying size that grow via galvanic displacement-reduction processes grow at a rate that is proportional to cluster surface area, and therefore increase in size by a thickness ($\Delta d$) that is independent of the original seed particle diameter. Thus, the M$_b$ content (at.%) of the resulting bimetallic particles is smaller for larger particles.
AuPt clusters (an endothermic alloy) show the largest deviation from GDR behavior, while AuPd and PtPd clusters (exothermic alloys) show the smallest deviations (Fig. 6b), suggesting that GDR reduction pathways are more prevalent during the synthesis of the latter two bimetallic systems. Such conclusions are consistent with PtPd and AuPd clusters that exhibit an inverse relationship between % at. MB and seed cluster size (Fig. 7), as expected for GDR-derived clusters (Scheme 2); in contrast, the atomic fraction of AuPt clusters increases with increasing particle size. These data indicate that GDR requirements (a)–(c) prevail during AuPd and PtPd cluster synthesis but not during AuPt cluster synthesis, for which additional growth pathways must contribute significantly to particle growth.

The formation mechanism can also be probed for these three bimetallic systems using HAADF images collected in tandem with particle-by-particle EDS analysis to measure both the diameters \(d_{MBMA,i}\) and \(X_{MA,i}\) of bimetallic clusters. These data are then used to calculate the size of the seed cluster from which each bimetallic cluster, \(i\), formed and, in turn, the amount by which each seed particle increased in diameter (\(\Delta d_i\)) using

\[
\Delta d_i = d_{MBMA,i} \left[ 1 - \left( \frac{V_{MA,i} \cdot V_{MB,i}}{V_{MA,i} + V_{MB,i}} \right)^{1/3} \right]
\]

Here, \(V_{MA,i}\) is the atomic volume of metal \(M_x\) (derivation in Section S3, SI). Figs. 8a and b show that the seed clusters of AuPd and PtPd particles grow by a value \(\Delta d\) that is independent of seed particle size, as predicted for GDR growth. The expected \(\Delta d\) value for each sample can be calculated from the TEM-derived size distribution of the parent seeds, onto which \(MB\) atoms are then distributed based on the surface area of each cluster, as dictated by GDR growth processes (derivation in Section S4, SI [14,15]). The expected \(\Delta d\) values for AuPd and PtPd samples agree well with experimental values calculated from EDS and HAADF data (Figs. 8a and 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 in the AuPt system grow by \(\Delta d\) values that increase monotonically with the seed cluster diameter (Fig. 8c), consistent with bimetallic growth pathways other than GDR involved in their synthesis, discussed elsewhere [14]. Metal
atoms within clusters of endothermic alloys, such as Au and Pt (mixing enthalpy, $\Delta H_{\text{AuPt}} = +2.3 \text{ kJ mol}^{-1}$ [20]), segregate in order to minimize the enthalpic penalties of mixing, driving the metal with the lowest surface energy, Au [33], to the surface (Scheme 3). The surface concentration of Au increases with cluster size because Au atom depletion from the cluster bulk is mitigated in larger clusters by their larger bulk reservoirs [34]. As the Au$^0$ surface content of AuPt particles increases with particle size, they displace from the surface the Pt$^0$ atoms required to reduce solvated Au cations via GDR, and instead promote the autocatalytic reduction of solvated Au cations by solvent molecules on Au$^0$ sites, a fast reaction [35,36]; this leads, in turn, to the preferential consumption of Au atoms by the surfaces of the larger clusters. Fast autocatalytic reduction on the larger clusters renders the uniform distribution of Au cations across all Pt seeds more challenging than for exothermic alloys (e.g., AuPd and PtPd), as reflected in the more stringent synthesis protocols required for the synthesis of AuPt clusters [14] than those for exothermic alloys that maintain $M_A$ atoms at cluster surfaces.

Our systematic study of the synthesis of AuPd, AuPt, and PtPd bimetallic systems has identified several key variables that influence the extent of metal mixing and the uniformity of the bimetallic clusters. Such features include the mixing enthalpy and relative reduction potentials of the alloyed metals, the solvent reduction potential, and the size uniformity of the parent seed clusters. Additionally, we have proposed several synthesis strategies to cope with those features that present challenges for the formation of bimetallic clusters uniform in composition and size. These synthesis protocols avoid the use of heteroatoms that ultimately compromise such uniformity because of the severe thermal and chemical treatments that become essential to remove synthetic debris from surfaces, a requirement of their ultimate use as catalysts.

3.3. Achieving clean metal cluster surfaces using reductive treatments at mild conditions

3.3.1. PVP removal from monometallic Pd cluster surfaces using $H_2$

Our previous studies of SiO$_2$-supported monometallic Pt clusters showed that PVP, the protective polymer used to prevent the agglomeration of Pt colloids, can be removed from supported cluster surfaces without causing particle growth by treating the catalyst in a gaseous ($H_2$) or liquid (1:1 by volume EtOH:H$_2$O) reductant at low temperatures (~423 K) [14]. PVP binds to metal surfaces via the carbonyl oxygen of the pyrrolidone group [37]. The reductant detaches such species before reaching temperatures that lead to PVP densification and the formation of amorphous carbon. Low temperature treatments in $H_2$ avoid the consequences of $O_2$ treatments requiring higher temperatures that often lead to the blockage of active surfaces by carbonaceous residues [37–40]. Here, we extend our protocols in $H_2$ first to SiO$_2$-supported Pd clusters protected by the presence of PVP in order to compare the monometallic systems, and then to bimetallic SiO$_2$-supported PtPd clusters. The extent of polymer removal from treated cluster surfaces was probed by the titration of chemically accessible metal surface atoms with $O_2$ to determine metal dispersions, which were then used to calculate surface-averaged particle diameters (Eq. (4)) that can be compared with those measured from TEM micrographs. Particle diameters derived from chemisorption experiments that agree with those measured by TEM indicate that polymer residues can be achieved by treatments at high temperatures (~423 K) in oxidative environments [41].
The chemisorption-derived mean diameter of Pd clusters treated in flowing H_2 using a two-step protocol previously shown to fully remove PVP from Pt cluster surfaces (348 K for 1 h, followed by 423 K for 1 h; at a ramp rate of 0.033 K s^{-1}; Section 2.3.1) was larger than the surface-averaged cluster diameter estimated from transmission electron micrographs (Fig. 9), indicating that residual polymeric material remained on metal surfaces after such treatments. Treated Pd clusters were also larger in size than untreated clusters (1.8 nm before treatment, 3.2 nm after treatment; determined by TEM). Since PVP binds to metal surfaces via carbonyl oxygen atoms [37–40] and the heat of oxygen adsorption is higher for Pd than Pt [42], the failure to fully remove PVP from Pd cluster surfaces using protocols suitable for Pt clusters appears to reflect the stronger binding energy of the polymer to Pd clusters. Incomplete polymer removal may also result from the smaller initial cluster size of the Pd clusters used here relative to the Pt clusters used previously (1.8 nm Pd clusters vs. 2.6 nm Pt clusters), which leads to a higher fraction of corner and edge surface atoms that bind adsorbates more strongly [43].

The metal-PVP bond on 1.8 nm Pd clusters may be weakened by populating the surface with metal atoms that bind oxygen more weakly, such as Pt (discussed later in Section 3.3.3), or by increasing the cluster size so as to reduce the fraction of under-coordinated surface atoms. Larger Pd clusters (2.3 nm; prepared as described in Section 2.1.2) were treated using the protocols described in the preceding paragraph. In contrast to 1.8 nm Pd clusters, the surface-averaged particle diameter estimated from TEM images of the treated 2.3 nm 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 polymer removal and leading to clean metal surfaces. 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 [14], apparently because Pd clusters are more susceptible to sintering in H_2 than Pt clusters [44].

3.3.2. PVP removal from monometallic Pd cluster surfaces using EtOH/H_2O 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 period 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 in H_2) is required to fully remove the polymer slowly at lower temperatures and avoid local exotherms that lead to particle agglomeration resulting from fast exothermic polymer removal at such higher temperatures [14]. This additional treatment step in flowing H_2 at 348 K can be substituted without compromising surface cleanliness or metal dispersion by instead treating Pt clusters in a reductive solvent (1:1 by volume EtOH/H_2O, 351 K, 20 h) before treatment at 423 K in H_2, thus demonstrating the versatility of the reductive polymer removal approach [14].

The diameters measured from transmission electron micrographs of Pd clusters (1.8 nm) treated using the combined EtOH/H_2O and H_2 protocol agreed well with those calculated from chemisorption experiments (Fig. 9), indicating that metal surfaces were free of chemisorbed material; clusters still increased in size (to 3.2 nm; determined by TEM) as a result of this treatment. In contrast, the surfaces of 1.8 nm clusters treated using the protocols using H_2 alone were not chemically accessible (Fig. 9). We therefore show here that protocols using EtOH/H_2O are more effective for removing PVP because of the greater contact time between the reductant and the metal surface (20 h in EtOH/H_2O at 351 K vs. 1 h in flowing H_2 at 348 K) and/or the ability of the solvent to dissolve and disperse the polymer away from cluster surfaces.

3.3.3. PVP removal from bimetallic PtPd cluster surfaces using H_2

Pt clusters bind more weakly to oxygen-containing species, such as PVP, than Pd clusters [42], and are also more resistant to sintering in H_2 [44]. Next, we investigate whether the presence of Pt atoms in Pd clusters will allow polymer removal without agglomeration. Pt_{10}Pd_{90}, Pt_{25}Pd_{75}, and Pt_{50}Pd_{50} clusters were treated in flowing H_2 (348 K for 1 h, followed by 423 K for 1 h; at a ramp rate of 0.033 K s^{-1}; Section 2.3.1) and subsequently examined by TEM and titration with chemisorbed O_2. The chemisorption-derived mean particle diameter of treated Pt_{10}Pd_{90} clusters was larger than its TEM-derived surface-averaged mean diameter (Table 3), indicating that, as with monometallic Pd particles, surface residues remained; treated clusters were larger in size than untreated clusters (2–2.3 nm; determined by TEM). In contrast, Pt_{50}Pd_{50} clusters (2.5 nm diameter; determined by TEM) treated using identical protocols did not increase in size (Table 3); cluster diameters estimated from TEM images agreed well with those obtained from chemisorption experiments, indicating that clusters composed of 50 % at. Pt were free of surface residues and resistant to coalescence during treatment. PtPd clusters with intermediate composition (Pt_{35}Pd_{65}) exhibited intermediate cluster diameters of 1.8 nm (black) and 2.3 nm (gray) are shown. Points on the parity line denote clean surfaces, with the initial untreated Pd particle size indicated by the horizontal dashed lines.

**Table 3**

<table>
<thead>
<tr>
<th>Pt content (% at.)</th>
<th>d_{TEM} (untreated)</th>
<th>d_{TEM} (treated in H_2)</th>
<th>d_{chemisorption} (treated in H_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.8</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>25</td>
<td>2.4</td>
<td>2.6</td>
<td>2.7</td>
</tr>
<tr>
<td>50</td>
<td>2.5</td>
<td>2.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>
growth and surface cleanliness: clusters were slightly larger in size after H₂ treatment (2.4–2.6 nm; determined by TEM) and had a chemisorption-derived diameter that was slightly larger than its TEM-derived diameter (Table 3).

The presence of Pt in PtPd clusters facilitates the removal of surface-bound PVP and renders clusters more resistant to sintering during treatment in H₂. These data, however, cannot conclude whether the consequences of alloying reflect the increase in mean particle diameter, the increase in the amount of metal atoms that bind more weakly to PVP, or synergistic electronic effects of alloying Pt and Pd that decrease the binding energy of PVP to bimetallic surfaces. We expect that weaker metal-PVP bonds result from both the increase in particle size (as discussed in Section 3.3.1) and the presence of Pt at cluster surfaces. PtPd alloys are more resistant to poisoning by oxygen-binding surface species [45–47], however, suggesting that perhaps all three factors may influence PVP adsorption strength.

4. Conclusions
Using reagents composed of only C, O, H, and N, we have prepared colloidal PtPd clusters that are uniform in composition and size with chemically accessible metal surfaces. Clusters were formed via GDR processes—as confirmed by particle-by-particle elemental analysis using EDS and HAADF imaging—which lead to cluster growth (Δd) that is independent of parent seed diameter. PtPd cluster formation was slower than the formation of AuPd clusters under identical conditions because of a lower thermodynamic driving force (ΔG°,redox) for the reduction of Pt cations—relative to Au cations—by Pd⁰ surface atoms. PtPd and AuPd clusters can be synthesized at ambient temperature 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 favorable entropic consequences of mixing that contribute more significantly to Gibbs free energies at higher temperatures.

Pt clusters were deposited onto SiO₂ and subjected to reducing environments (EtOH/H₂O or H₂) at low temperatures (up to 423 K) to remove the protecting polymer (PVP). Removing PVP from metal surfaces without compromising cluster dispersion was more challenging for Pt clusters relative to Pt clusters because of stronger metal-PVP bonds and the greater susceptibility of Pt clusters to sinter in H₂. Increasing Pt cluster size and alloying with Pt were shown to facilitate polymer removal by weakening the metal-PVP bond.

Our work here, together with the conclusions drawn from the study of AuPd [15] and AuPt [14] bimetallic systems, illustrates the consequences of relative redox potentials, mixing enthalpies, solvent reduction potential, and parent seed size uniformity on the size and compositional uniformity of bimetallic clusters. We further demonstrate the versatility of GDR synthesis methods in adapting to unfavorable conditions that encourage bimodal particle distributions. The methods and predictive design principles developed for AuPd, AuPt, and PtPd systems can be generalized and applied to other bimetallic systems to synthesize the clean and uniform bimetallic catalysts that are essential for catalytic studies seeking to develop rigorous structure-function relationships of bimetallic surfaces.

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Appendix A. Supplementary material
Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.10.007.

References


