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Introduction
Bimetallic nanoparticles can lead to catalysts with improved turnover rates and selectivities [1], but many synthetic protocols, such as impregnation or precipitation, typically form particles that are non-uniform in composition and size. Colloidal methods may be able to improve their uniformity [2], but often require reagents that poison catalytic surfaces. These compositional non-uniformity and ubiquitous impurities have prevented rigorous conclusions about the effects of alloying on reactivity and selectivity [3]. We describe here a sequential displacement-reduction colloidal synthesis method that leads to bimetallic Au(Pd), Au(Pt) and Pt(Pd) nanoparticles narrowly distributed in size. Particles were prepared using precursors containing only C, H, O and N, which we show can be removed from particle surfaces by post-synthetic treatments. Using CO oxidation as a probe reaction, we have examined the effects of bimetallic formation on the catalytic reactivity of cluster surfaces.

Materials and Methods
Au(Pd) and Pt(Pd) clusters were prepared at ambient temperature in 1:1 EtOH/H2O mixtures and protected by polyvinylalcohol (PVA). Au(Pt) clusters were prepared at 423K in ethylene glycol (EG) and protected by polyvinylpyrrolidone (PVP). Clusters were characterized by transmission electron microscopy (TEM), UV-visible spectroscopy, and energy dispersive X-ray spectroscopy (EDS). Clusters were deposited onto SiO2 supports. Polymer removal was achieved at 423 K under 1 bar H2, CO2 formed in catalytic CO oxidation on these samples was measured by gas chromatography.

Results and Discussion
Au(Pd), Au(Pt) and Pt(Pd) nanoparticles were synthesized by sequential colloidal reduction in which Au0 or Pt0 precursors were added to monometallic (Pd) or (Pt) clusters. TEM micrographs confirmed that initial seed cluster size increased uniformly with increasing Au0 or Pt0 content, with final bimetallic cluster dispersity values near unity indicating a narrow size distribution. Elemental analysis by EDS confirmed the formation of strictly bimetallic particles with the mean composition of the synthesis mixture (Figure 1-a).

The synthesis of Au(Pd) was monitored by in-situ UV-visible spectroscopy. A weak plasmon resonance (PR) peak appeared during the initial stages and then disappeared, consistent with the momentary formation of Au-covered clusters. These processes appear to involve Au0 deposition onto (Pd) clusters via galvanic displacement, with surface Pd0 atoms oxidized and Au0 ions reduced, as predicted from their relative reduction potentials (1.52 eV for Au0 vs. 0.99 eV for Pd0). The Pd0 ions that leached into the solution are then reduced by ethanol at cluster surfaces. The synthesis of other alloys, such as Au(Pt) and Pt(Pd), is expected to involve galvanic displacement-reduction if the standard reduction potential of the precursor is higher relative to the metal seed cluster. Endothermic alloys, such as Au(Pt), require higher synthesis temperatures to overcome enthalpic barriers for alloy formation and also the slow introduction of the precursor solution to maintain low precursor concentrations and thus inhibit homogeneous nucleation of pure Au clusters.

The sequential galvanic displacement-reduction 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 synthesis at ambient temperatures, but not for synthesis at elevated temperatures (Figure 1-b). These differences appear to reflect size-dependent intra-cluster diffusion during synthesis, which determines the composition of cluster surfaces and the availability of metal surface atoms for reducing solvated precursor cations.

Polymers bind to metal surfaces after synthesis via charge-transfer interactions [4]. After clusters were deposited on SiO2, adsorbed polymers were removed by low temperature treatment in H2 or EtOH. Reductants compete with the polymer at the metal surface, breaking the polymer-metal bond. The absence of surface residues or sintering was confirmed by the similar cluster sizes derived from O2 chemisorption and TEM measurements. CO oxidation turnover rates indicate that surface segregation under reaction conditions significantly alters surface composition, thereby changing catalyst activity. Possible electronic effects are at play.

Significance
Developing rigorous mechanistic conclusions about the size and composition effects of bimetallic clusters on reactivity and selectivity is key to understanding and designing valued catalysts. Knowledge of how to produce clusters that are uniform in structure and composition, such as those made in this study, is crucial to make such conclusions. We acknowledge support by the US Department of Energy and the National Science Foundation.

References