Improving Gold Catalysis of Nitroarene Reduction with Surface Pd

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Nitroarene reduction reactions are commercialized catalytic processes that play a key role in the synthesis of many products including medicines, rubbers, dyes, and herbicides. Whereas bimetallic compositions have been studied, a better understanding of the bimetallic structure effects may lead to improved industrial catalysts. In this work, the influence of surface palladium atoms supported on 3-nm Au nanoparticles (Pd-on-Au NPs) on catalytic activity for 4-nitrophenol reduction is explored. Batch reactor studies indicate Pd-on-Au NPs exhibit maximum catalytic activity at a Pd surface coverage of 150 sc%, with an initial turnover frequency of ~ 3.7 mol-nitrophenol/mol-metal_{surface}/s, which was $\sim 5.5\times$ and $\sim 13\times$ more active than pure Au NPs and Pd NPs, respectively. Pd NPs, Au NPs, and Pd-on-Au NPs below 175 sc% show compensation behavior. Three-dimensional Pd surface ensembles (with ~ 4 -5 atoms) previously identified through x-ray adsorption spectroscopy provide the active sites responsible for the catalytic maximum. These results demonstrate the ability to adjust systematically a structural feature (*i.e.*, Pd surface coverage) to yield a more active material.

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1.0 Introduction.

Pd-on-Au nanoparticles (Pd-on-Au NPs) are a model catalyst consisting of Au NPs with controllable amounts of Pd atoms deposited on the NP surface[1, 2]. The amount of deposited Pd, calculated as the Pd surface coverage ("sc", dictates the size of the Pd surface ensembles and extent of Pd oxidation [3, 4]. They have been studied extensively for a number of aqueous-phase reactions, i.e., the hydrodechlorination (HDC) of trichloroethene [1-5] and perchloroethene [6]), the reduction of nitrite anions [7], and, most recently, the partial oxidation of glycerol [8, 9]. For all these reactions, catalytic activity followed a volcano-shape dependence on Pd surface coverage, with maximum activities occurring when Pd surface coverage was less than 100% (equivalent to 1 calculated Pd monolayer). Enhanced activity for chloroform HDC was also observed when Pd atoms were deposited on Au/Al₂O₃ catalysts [10].

This work seeks to strengthen the understanding of Pd-on-Au catalysis by studying the NPs for 4-nitrophenol ("4-NL") reduction. This model reaction generates 4-aminophenol ("4-AP") selectively [11-13] in the presence of a metal catalyst using sodium borohydride as a reductant (scheme 1).[11, 14, 15] It can be carried out at room temperature and atmospheric pressure, and it is usually monitored through ultraviolet-visible spectroscopy, making it an ideal model reaction and the subject of review articles by Ballauff and coworkers[16] and Pal and coworkers.[17]

Scheme 1. Chemical equation for the catalytic reduction of 4-nitrophenol (4-NL) using sodium borohydride.

There is industrial interest in aromatic amines like 4-NL because they have widespread industrial uses for medicines, dyes and stains, pesticides, and explosives [18-20]. They are commercially produced through the Bechamp process (which involves using an acidic slurry of zerovalent iron reagent at ~75-100 °C [21]) and metal catalysis (which involves Pt, Pd, or Rh, and hydrogen at ~100-110 °C and ~20-60 atm [22]).

Several studies on PdAu composition effects on 4-NL reduction have been reported. Kaiser *et al.* synthesized a series of PdAu alloy NPs by co-reducing Pd and Au precursor salts. The activity of all the bimetallic catalysts was found to be higher than monometallic Au or Pd NPs, and was maximum at a Au mole fraction of 75 mol% (exhibiting ~10× higher activity than the monometallic NPs).[15] These results qualitatively agree with a study by Tang *et al.*, who studied PdAu alloy NPs formed via sequential reduction of Au precursor salt onto a Pd catalyst. This group found that increasing mole fraction Au also led to increased activity, with a molar ratio of Au:Pd of 2.1:1 (or equivalent Au mole fraction of 67 mol%) being most active. The maximum activity was ~3× higher compared to their monometallic Pd catalyst [23]. A study by Zhao *et al.* on a series of PdAu catalysts synthesized via coreduction showed the same higher activity of the bimetallic catalysts, though maximum activity occurred for the composition of Au:Pd molar ratio of 3:7 (30 mol% Au) [24]. While bulk metal composition can be controlled, the differences in catalysis indicate differences in the bimetal structure.

Pd-on-Au NPs with well-characterized Pd surface structures and a single Au particle size can offer additional insights into 4-NL reduction. In this work, batch reaction studies of a series of colloidal ~3nm NPs with different Pd surface coverages were carried for 4-NL reduction with sodium borohydride. Reaction rate constants and initial turnover frequencies were determined at room temperature (from 0 to 200 sc%, surface coverage), and compared with the Pd surface

structures previously determined from x-ray adsorption spectroscopy (XAS). New XAS analysis was carried out on Pd-on-Au NPs with a higher Pd surface coverage than previously studied (*i.e.*, 200 sc%). The activation energy and preexponential factor values were determined in the temperature range of 30-60 °C, and discussed in the context of a compensation effect.

2.0 Materials and Methods.

2.1 Materials

Palladium(II) chloride (PdCl_2 ; >99.99%), gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99%), tannic acid (>99.5%), potassium carbonate (>99.5%), and 4-nitrophenol (4-NL, >99%), were purchased from Sigma-Aldrich. Sodium citrate dihydrate (>99.5%) was obtained from Fischer Scientific. Sodium borohydride (>98%) was purchased from Acros (Lot number: B0116503). Sodium hydroxide (1.0M) was obtained from EMD Chemicals. Amorphous carbon powder (Vulcan XC-72 and Monarch 700) was purchased from Cabot. Ultra-high purity argon gas, nitrogen gas, and hydrogen gas were obtained from Matheson Tri-gas. Deionized (DI) water from a Barnstead NANOpure Diamond purifier (resistivity > 18 M Ω /cm) was used for all experiments. All chemicals were used as received unless otherwise noted.

2.2 Au NP synthesis

3-nm Au NPs were synthesized as previously reported.[4, 25] A 0.32 mM chloroauric acid (HAuCl_4) solution was added to a reductant solution (1.5 mM tannic acid, 7.0 mM trisodium citrate dihydrate, and 6.3 mM potassium carbonate), with both pre-heated to a temperature of 60 °C prior to mixing. The resulting brown sol was vigorously stirred and heated to a boil. After boiling for two min, the sol was cooled to room temperature and the total sol volume was

adjusted to 100 mL with additional DI water. The NP size was verified using transmission electron microscopy.[4] Au NPs were stored at 4 °C for no longer than 1 week before use.

2.3 Pd-on-Au NP synthesis

Pd-on-Au NPs with Pd surface coverages between 10 and 200% were synthesized by reducing aliquots (13-265 μ L) of a 2.47 mM chloropalladic (II) acid (H_2PdCl_4) solution with hydrogen gas onto the Au NP sols under ambient conditions as previously described (table S1).[4] The volume of 2.47 mM H_2PdCl_4 needed for a specific Pd surface coverage was calculated using the magic cluster model, in which each Au NP is viewed as a central Au atom surrounded by consecutive shells of Au atoms.[2, 26, 27] A 3-nm Au NP would consist of 5 consecutive Au shells, 561 total Au atoms, and 252 surface Au atoms (table S2). A surface coverage of 100% is then modeled as a 6th consecutive shell on the NP since Pd and Au atoms are nearly the same size. Surface coverages exceeding 100% refer to additional Pd layers, *e.g.*, "200 sc%" means that a 3-nm Pd-on-Au NP is modeled as a magic cluster of 5 Au shells and 2 Pd shells.[4] The concentration of NPs in the 3 nm Au NP sol was calculated to be 2.7×10^{14} NPs/mL. Elemental analysis indicated complete HAuCl_4 reduction and showed good agreement between calculated and actual Pd metal content.[4] The Au NP size has previously been found to be 3.0 ± 0.7 nm, and TEM confirmed no significant change in particle size (*i.e.*, beyond the initial Au particle size distribution) or size distribution when Pd was deposited on the Au NP surface.[4]

2.4 Pd NP Synthesis

The activity of Pd-on-Au NPs was compared to those of pure 3 nm and 4-nm Pd NPs. The synthesis of pure Pd NPs (~4 nm) has been reported in detail.[2] Briefly, Pd NPs were synthesized using an experimental protocol similar to the Au NPs except that a 0.32 mM PdCl_4^{2-}

solution (12 mL of 2.39 mM PdCl_4^{2-} diluted with 68 mL H_2O) was used. Pd sols were heated to boiling for ~25 min prior to cooling to room temperature under ambient conditions.[4]

2.4 X-ray absorption spectroscopy

X-ray absorption spectroscopy of carbon-supported 200% Pd NPs was conducted at the Advanced Photon Source at Argonne National Laboratory. Details concerning the XAS experiment protocol can be found in previous work.[3, 4]

2.5 Catalytic testing

A 10 mM 4-nitrophenol stock solution was made by adding 41.7 mg of 4-NL to 30 mL of water and sonicating for 20 min. An alkaline 0.1 M NaBH₄ stock solution was made by dissolving 0.038 g of NaBH₄ in 10 mL of an ice-cold 0.1 M NaOH solution (100 μ L of 0.01 M NaOH diluted with 9.9 mL water). A fresh NaBH₄ stock solution was made every 3 h. Catalytic testing was conducted in a closed batch reactor, in which a screw-cap quartz cuvette (1-cm path length) is filled with 2.7 mL water, 30 μ L of 10 mM 4-NL stock solution, and 200 μ L of 0.1 M NaBH₄ stock solution and sealed with a PTFE-silicone septum. The sealed cuvette was purged with an inert gas (either Ar or N₂) for 1 min to displace dissolved oxygen and fill the headspace (~1 atm).

An aliquot (51 μ L) of as-prepared 3-nm Pd-on-Au NP sols was diluted with 9.94 mL of water to prepare a diluted NP sol (total Au M concentration = 1.3×10^{-6} M; 260 ppb). The total Pd concentration ranged from 8.4×10^{-8} M (8.9 ppb) to 1.7×10^{-6} M (180 ppb), depending on the Pd surface coverage. The diluted NP sol (100 μ L) was then injected into the quartz cuvette at $t = 0$ min after the cuvette was purged with inert gas. The final concentration of Pd-on-Au NPs in the reactor was 4.5×10^{10} NP/mL. No UV-vis absorbance from the NPs was observed at this concentration. The final concentration of total Au in the reactor was 4.2×10^{-8} M while the total final Pd concentration ranged from 2.7×10^{-9} M to 5.5×10^{-8} M.

Monitoring of the 4-NL reduction reaction was started 30 s after NP injection using UV-vis spectroscopy, in which the absorbance of the 4-NL nitro group at $\lambda = 400$ nm (red-shifted from

~313 nm due to basic reaction conditions) was measured.[28] Initial concentrations of 4-NL and NaBH₄ were 9.7×10⁻² mM (~13.5 ppm) and 6.5 mM (~246 ppm), respectively. These initial reactant concentrations were within range of other published studies.[11, 12, 14, 15] All reactions were monitored for total t = 26.5 min using a Shimadzu 2450 UV-Vis spectrophotometer. Reaction spectra were acquired every 2 min. Between UV-vis scans, the quartz cuvette was mixed using a Fisher Scientific mini vortexer set at ~7. The reaction was determined to not be diffusion-limited under these experimental conditions based on calculated Damköhler number (D_a) values [16, 29]; D_a < 0.0015 for all the NP compositions tested, in good agreement with similar calculations by Ballauff and co-workers (see Supporting Information).

The catalytic reduction reaction can be modeled as a Langmuir-Hinshelwood mechanism in which adsorbed 4-NL and borohydride species react to form 4-AP, metaborate (BO₂⁻), and hydrogen.[12, 15, 16, 30]. Since the NaBH₄ concentration greatly exceeds (~65×) that of 4-NL, the reaction rate constants were calculated from a pseudo-first order rate law with respect to 4-NL [11, 12, 14, 31, 32]:

$$-dC_{4\text{-NL}}/dt = k_{\text{meas}}C_{4\text{-NL}} \quad (1)$$

where C_{4-NL} is the 4-NL concentration and k_{meas} is the measured pseudo-first-order rate constant. Each experiment was carried out at least three times.

Initial turnover frequency (TOF) values were calculated by normalizing the measured rate constant to the total concentrations of surface Au atoms (C_{Au surface atoms}) and surface Pd atoms (C_{Pd surface atoms}):

$$\text{TOF} = (k_{\text{meas}} C_{4\text{-NL}} / [(C_{\text{Pd surface atoms}}) + (C_{\text{Au surface atoms}})]) \quad (2)$$

For NPs with <100 sc%, the C_{Pd surface atoms} comes from the number of Pd atoms in the 6th shell of the magic cluster model and the C_{Au surface atoms} comes from the number of exposed Au atoms in

the 5th shell. For NPs with >100 sc%, $C_{\text{Pd surface atoms}}$ comes from the number of Pd atoms in the 7th shell and the exposed Pd atoms in the 6th shell. The concentration of Pd and Au surface atoms used for reported TOFs is provided in Table S3. The concentration of Pd and Au metal used in all batch reactor experiments were such that the observed reaction rates varied linearly with catalyst charge, as shown in figures S1-S4. The pH of the reaction solution (~10.4) did not change during the reaction. No reaction was observed in the absence of catalyst NPs.

Control experiments with monometallic Pd and Au NPs were performed as follows. Approximately 100 μL of a diluted~4 nm Pd NP sol (446 μL as prepared Pd NP sol diluted with 9.54 mL H_2O) was injected into the sealed quartz reactor (final Pd concentration in reactor = 4.4×10^{-7} M ; 47 ppb). A diluted 3-nm Au NP sol (206 μL as prepared Au NP sol diluted with 9.78 mL H_2O) was prepared and 100 μL of the diluted sol was injected into the quartz reactor (final Au concentration in reactor = 1.7×10^{-7} M ; 34 ppb). UV-vis absorbance by the NPs at these concentrations was negligible.

Activation energy values were determined for 3 nm Au NPs, 4 nm Pd NPs, and selected Pd-on-Au NPs by determining k_{meas} in the temperature range of 30-60 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}$ increments for each catalyst. The reactor temperature was controlled using a water-jacketed sample chamber located in the UV-Vis spectrometer, with the maximum temperature variation in the batch reactor observed to be ± 1 $^{\circ}\text{C}$ during a typical catalytic experiment. Thermal equilibration between the batch reactor and sample chamber occurred within ~30 sec, and no significant change in batch reactor temperature (< 1 $^{\circ}\text{C}$) was observed due to vortexing between UV-vis measurements. The activation energy and frequency factor of each catalyst was determined using the Arrhenius equation.

3.0 Results and Discussion.

3.1 Nanostructure of Pd-on-Au NPs

In an earlier report, the metal structure of Pd-on-Au NPs of different calculated Pd surface coverages up to 150% and at Au NP sizes of 3, 7, and 10 nm was studied via XAS analysis reported in our previous work.[4] The Pd metal of the 3-nm Pd-on-Au NPs was mostly isolated Pd atoms at surface coverages $\leq 30\%$. The Pd was in the form of 2D ensembles at ~ 50 sc%, and in the form of 3D ensembles at > 50 sc%. These 3D ensembles also included oxidized Pd, which was inferred to be the Pd atoms located on top of other Pd atoms. With surface coverages increasing from 70% to 150%, the Pd-Pd coordination numbers increased and the percentage of Pd in the oxidized state increased, suggestive of larger, more aggregated 3D Pd ensembles.[4]

Analogous XAS analysis was extended to 200 sc% Pd-on-Au NPs (Figure 1). The structure of the Pd-on-Au NPs is based on the XAS-measured Pd and Au coordination numbers (CNs), which are presented in a Punnett square. The details (CNs, bond distances, threshold absorption energies, and Debye-Waller factors, DWF's) for 3 nm Pd-on-Au NPs with 200% Pd sc are provided in tables S6-S7. The NPs with 200 sc% Pd did not have any XAS-detectible Pd²⁺;

a) <u>XAS Measured CNs</u>				b) <u>Calculated Alloy CNs</u>			
Absorbing atom		Scattering atom		Absorbing atom		Scattering atom	
		Au	Pd			Au	Pd
	Au	9.1	2.1		Au	4.9	6.3
	Pd	7.8	3.6		Pd	5.0	6.4

Figure 1. (a) XAS-measured CN's for 3 nm Pd-on-Au NPs with 200 sc% and (b) calculated CN's for theoretically alloyed Pd-Au NPs (see Eqn. S4-S7) with the same metal content (56.3 mol% Pd), total Au CN (Au-Au CN + Au-Pd CN = 11.2), and total Pd CN (Pd-Pd CN + Pd-Au CN = 11.4). Experimental CN's are those of as-prepared nanoparticles.

The Pd-Au, Pd-Pd, Au-Pd, and Au-Au CN (first atom is the absorber, second atom is the scatterer) of theoretical alloy particles were calculated based on the total Pd and total Au CN and the mol% of Pd and mol% of Au in the particle (see equations S4-S7).[4] A relative comparison of the measured and calculated alloy coordination numbers provides insight into the average structure of the NPs.[3, 4] The measured Au-Au CN (~9.1) was higher than the calculated alloy Au-Au CN (~4.9) and the measured Au-Pd CN was lower (~ 2.1) than the calculated alloy Au-Pd CN (~6.3), consistent with the NPs being Au-rich in the core and, by inference, Pd-rich at the surface. The measured Pd-Pd CN (~3.6) was lower than the calculated alloy Pd-Pd CN (~6.4) and the measured Pd-Au CN was ~7.8 which was higher than the calculated alloy Pd-Au CN (~5.0).

The lack of Pd²⁺ is indicative that no 3D ensembles were present, as oxidized Pd normally is found with 3D Pd ensembles in Pd-on-Au NPs [4]; indeed, direct contact between Pd and Au atoms prevents oxidation of surface Pd due to electronic effects of Au [33-36]. This implies that, on the surface, the Pd is only present in 2D ensembles (or as isolated atoms). Based on CN similarities, the surface of the 200 sc% Pd-on-Au NPs resembles that of 30 sc% Pd-on-Au NPs more than those with a similar loading, such as the 150 sc% Pd-on-Au NPs which has 3D Pd ensembles [4]. The unexpectedly high Pd-Au CN implies that much of the Pd has likely diffused into the Au NP, which is consistent with the many studies which have observed such Pd interdiffusion into Au surfaces [33, 35, 36].

3.2 Activity of Pd-on-Au NPs for 4-nitrophenol reduction

UV-vis absorbance spectra of the reaction medium were collected every 2 min for 26.5 min for all catalyst compositions, with figure 2 showing the results for 3 compositions: monometallic Au

NPs, monometallic Pd NPs, and Au NPs with a Pd surface coverage of 150%. No change in 4-NL absorbance was observed in the absence of metal NPs.

Figure 2. UV-Vis absorbance spectra of a) pure 3 nm Au NPs, b) pure 4 nm Pd NPs, and c) 3 nm Pd-on-Au NPs with 150% Pd sc. The downward (red) and upward (blue) arrows show the decreasing absorbance of 4-NP and increasing absorbance of 4-AP, respectively, as the reaction progresses. Reaction conditions: reaction time = 26.5 min, room temperature ($\sim 23^{\circ}\text{C}$), pH = 10.4, initial 4-NL concentration = 9.7×10^{-2} mM, initial NaBH_4 concentration = 6.5 mM, concentration of a) Au surface atoms = 7.6×10^{-8} M, b) Pd surface atoms = 14.8×10^{-8} M, and c) total Pd and Au surface atoms = 2.9×10^{-8} M.

The spectra exhibited isobestic points at $\sim 280\text{nm}$, $\sim 240\text{ nm}$, and $\sim 220\text{ nm}$. The presence of these isobestic points in the UV-vis spectra indicated that 4-aminophenol (4-AP) is the only aromatic byproduct formed, as concluded by several studies [11-13, 37]. The principal absorbance wavelengths of 4-NL and 4-AP are 400 nm and 293 nm, respectively. At the same concentration, 4-AP absorbance is less than 4-NL absorbance because the extinction coefficient of 4-AP is significantly lower than 4-NL at the measured wavelengths. A few research groups observed an induction period attributed to structural rearrangement of the catalyst [12, 29], but this was not observed in our study.

The 4-NL reduction catalytic activity of Au NPs, Pd-on-Au NPs, and Pd NPs is shown in Figure 3. The TOF values of the Au NPs and pure Pd NPs were determined to be $0.67\text{ mol } 4\text{-NL mol-Au}_{\text{surface atoms}}^{-1}\text{s}^{-1}$ ($= 40.3\text{ mol } 4\text{-NL mol-Au}_{\text{surface atoms}}^{-1}\text{min}^{-1}$) and $0.28\text{ mol } 4\text{-NL mol-Pd}_{\text{surface atoms}}^{-1}\text{s}^{-1}$ ($= 16.7\text{ mol } 4\text{-NL mol-Pd}_{\text{surface atoms}}^{-1}\text{min}^{-1}$), respectively. These values were found to be

in reasonable agreement with other studies of Pd and Au catalyzed 4-NL reduction, after calculating TOF values from published data with the magic cluster model and equation 2 (tables S4 and S5). There was wide range of these literature TOF values (from ~ 0.2 to >200 mol 4-NL/mol_{surface atom}/min for both Au and Pd catalysts), due to differences in catalyst support material, particle size, and reaction conditions.

Figure 3. TOF's (shown as bars) and proposed structures of Pd-on-Au NPs with different Pd surface coverages. The complete set of TOF values for Pd surface coverages in the 0-200% range is shown as the line curve. Cartoons of NP structures representing the XAS results are shown. NPs with 0 sc% are 3-nm Au NPs. The TOF of 4-nm Pd NPs is included for comparison. Error bars represent the standard deviation of at least three replicate experiments.

Catalytic activity of the Pd-on-Au NPs clearly varied with a volcano-shape dependence on Pd surface coverage. The 30 sc% sample essentially had the same activity as the pure Au NPs, and the 50 and 70 sc% samples were $\sim 20\%$ more active. At a Pd surface coverage of 90% and higher, the TOF values were several times larger than that of Au NPs. The highest activity

(TOF~3.7 s⁻¹) was exhibited by Pd-on-Au NPs with 150 sc%, at which Pd forms 3D ensembles. At this surface coverage, these ensembles consist of 4 to 5 Pd atoms on average.[4] At higher surface coverages, the NPs were less active (~3.0 s⁻¹ at 175 sc% and ~2.0 s⁻¹ at 200 sc%). Through XAFS analysis, at Pd surface coverages greater than 150% the 3D Pd surface ensembles grow such that extensive Pd-Au surface alloying occurs, with Pd atoms migrating into the Au NP. As a result of such alloying, no Pd oxide is present, and the activity of the NPs with Pd coverages greater than 150% decreases as geometrically the surface becomes more like the 30-70 sc% Pd-on-Au NPs, whose surfaces consist primarily of 2D Pd islands.

The enhanced activity of 150 sc% NPs (with partially oxidized 3D Pd ensembles) is likely due more to the spatial arrangement of the surface Pd atoms (and electronic effect of Au on Pd affecting adsorption enthalpies of reactants) than the presence of oxidized Pd. The majority (>90%) of the surface Pd atoms of the pure 4 nm Pd NPs are oxidized[3, 4]; hence, if simply the presence of Pd oxide resulted in significantly higher activity, one would expect the monometallic 4 nm Pd NPs to exhibit maximum activity. While it is thermodynamically possible for Pd oxide to be reduced by borohydride under our experimental conditions (see equations S1-S3),[38] significant particle structure change is unlikely since no induction time is observed.

3.3 Arrhenius equation analysis.

The activation energy and pre-exponential factors for catalytic 4-nitrophenol reduction by pure 3 nm Au NPs, pure 4 nm Pd NPs, and 3 nm Pd-on-Au NPs with Pd sc of 70%, 150%, 175%, and 200% were determined using the logarithmic form of the Arrhenius equation (equation 4):

$$\ln k_{\text{meas}} = \ln A - (E_a/RT) \quad (4)$$

where A is the pre-exponential factor, E_a the measured activation energy, R the gas constant (8.31 Jmol⁻¹K⁻¹), and T is the temperature (K). The pseudo-first order rate constant (k_{meas}) of

each of the aforementioned NP samples was measured at 30°C, 40°C, 50°C, and 60°C (see figure S10). Arrhenius plots ($\ln k_{\text{meas}}$ vs. $1/T$) were prepared to determine A and E_a for each catalyst (see figure S5 and S6).

Figure 4 plots the activation energy results as well as the TOF of the catalysts. As can be seen, the activation energy results for the catalysts are within the range previously reported for metallic catalysts (7.5 kJ/mol – 110 kJ/mol) [11, 14, 39-42]. The monometallic Au NPs had an activation energy of 12.7 kJ/mol. A range of activation energies are reported for Au nanoparticles and are thought to vary with particle shape (38 kJ/mol, Au nanorods) [12], stabilizing agent (21 kJ/mol for citrate stabilized vs. 31 kJ/mol for calcium alginate stabilized) [12], and/or support (31 kJ/mol for Au NPs on ~560- μm resin beads) [41]. Similarly, the reported activation energies of monometallic Pd NPs range from 7.5 kJ/mol (peptide-templated ~3 nm Pd NPs) [40] to 44 kJ/mol (~2.4 nm Pd NPs in spherical polyelectrolyte brush)[11]. The activation energy of the 4 nm Pd NPs (~16.3 kJ/mol) in this work is within this range. The activation energy of ~33-40 kJ/mol for the Pd-on-Au NPs (70-200 Pd sc%) is comparable to activation energies reported for other bimetallic Pd NPs (PtNi NPs=31 kJ/mol, PtPd nanocages=87-110 kJ/mol) [37, 43]. The variation in these activation energies has been ascribed to changes in bimetallic composition and its effect on active site structure.

Figure 4. Measured activation energy and TOF of Au NPs, Pd NPs, and selected Pd-on-Au NPs. Error bars represent standard deviations of at least three replicate experiments.

Compensation behavior, in which $\ln A$ and E_a follow a linear relationship according to equation 5

$$\ln A = aE_a + b \quad (5)$$

where a and b are constants [44], has previously been observed for the reduction of 4-NL over metal catalysts [16, 29]. For the same catalytic mechanism occurring on different catalytic materials, compensation behavior implies that any decrease in the energy barrier for reaction (decrease in E_a) will be counteracted by a decrease in the frequency factor (decrease in $\ln A$). That is, the stronger nitrophenol binds to an active site (lower $\ln A$), the more activated it is for reaction (lower E_a). [44] Figure 5 shows a Constable plot for the monometallic Pd NPs, monometallic Au NPs, and the Pd-on-Au NPs of various surface coverages. As can be seen, there is a linear relationship among the catalysts except for the 200 sc% Pd-on-Au NPs, which do not show a decrease in $\ln A$ with E_a . The cause of this deviation is unclear, but could be due to a change in the electronic structure of the active site [45]. This observed compensation behavior arises due to changes in adsorption enthalpies, surface coverage of reactants, and stability of the

transition state that allow the most active catalyst for this reaction (150 sc% Pd-on-Au NPs) to have the highest activation energy, which is compensated by its large pre-exponential factor [44]. The Pd-on-Au surface structure leads to higher activation energies and even higher pre-exponential factors, such that the bimetallic NPs have higher TOF's than the monometallic NPs. The slope of the $\ln A$ - E_a curve ($\sim 0.40 \ln(\text{min}^{-1}) \text{ mol kJ}^{-1}$) is similar to that reported by Herves *et al.* for several different metal catalysts (slope ~ 0.36) [16], indicating that the surface reaction on the NPs in this study (Au, Pd, and Pd-on-Au) follows similar kinetics.[16, 29]

Figure 5. Constable plot of 3 nm Au NPs, 4 nm Pd NPs, and representative Pd-on-Au NPs. The particle's activation energy and frequency factors were experimentally determined using the Arrhenius equation. Horizontal and vertical error bars represent the standard deviation of at least three replicate experiments.

4.0 Conclusions.

The catalytic reduction of 4-nitrophenol by NaBH_4 was studied using a series of model Pd-on-Au NPs with well controlled size and known surface structure. The NP catalysts followed a volcano-shaped dependence on Pd surface coverage and show compensation behavior. Maximum activity on surface atom basis (TOF of 3.7 s^{-1}), exhibited by the 150 sc% Pd-on-Au NP catalyst,

correlated to the presence of 3D Pd ensembles (consisting of 4-5 Pd atoms) on the Au NP surface. It was $\sim 5.5\times$ and $\sim 13\times$ higher than that of pure Au NPs ($\sim 0.7\text{ s}^{-1}$) and Pd NPs ($\sim 0.3\text{ s}^{-1}$), respectively. NPs with 200 sc% were less catalytically active. At this composition, extensive subsurface interdiffusion of Pd was observed, such that the surface sites more closely resemble the less active 2D Pd surface ensembles rather than 3D ensembles. These results show Au NPs can support Pd as surface ensembles up to a certain limit, beyond which Pd cannot be assumed to reside only on the nanoparticle surface.

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6.0 Supporting Information Available.

Details behind calculation of mass transfer resistances, detailed synthesis methods of Pd-on-Au NPs (Table S1), magic cluster calculations of Au NPs (Table S2), surface atom concentrations of NPs (Table S3), TOFs of Pd, Au, and Pd-Au catalysts studied by others (Tables S4-S5), details of XAS fitting and results for 3 nm NPs with 200% Pd sc (Tables S6-S7), Au, Pd, and Pd-on-Au NP concentration studies (Figure S1-S4), Arrhenius plots of Pd-on-Au NPs (Figures S5-S6), chemical equations for reduction of PdO(s) by $\text{BH}_4^-(\text{aq})$ (equations S1-S3), and equations used to

calculate the alloy coordination numbers of 3 nm Pd-on-Au NPs with 200% Pd sc (equations S4-S7).

7.0 References.

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