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Gold-doping of carbon-supported palladium improves reduction catalysis

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ABSTRACT

Bimetallic palladium-gold (PdAu) catalysts have better catalytic performance than monometallic catalysts for many applications. PdAu catalysts with controlled nanostructures and enhanced activities have been extensively studied but their syntheses require multiple and occasionally complicated steps. In this work, we demonstrated that supported PdAu catalysts could be simply prepared by doping a supported Pd catalyst with gold through wet impregnation and calcination. Resulting PdAu-on-carbon (PdAu/C) catalysts were tested for the room-temperature, aqueous-phase hydrodechlorination of trichloroethene. The most active PdAu/C catalyst (Pd 1.0 wt%, Au 1.1 wt%, dried/air/H₂ process) had an initial turnover frequency (TOF) of $34.0 \times 10^{-2} \text{ mol}_{Pd}^{-1} \text{ s}^{-1}$, which was >15 times higher than monometallic Pd/C (Pd 1.0 wt%, initial TOF of $2.2 \times 10^{-2} \text{ mol}_{Pd}^{-1} \text{ s}^{-1}$). Through X-ray absorption spectroscopy, the gold kept Pd from oxidizing under calcination at 400 °C. Probable nanostructure evolution pathways are proposed to explain the observed catalysis.

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1. Introduction

Palladium-gold (PdAu) catalysts have been investigated for several decades; like other bimetallic catalysts, the PdAu system attracts researchers' interest due to better catalytic activity, selectivity, and stability than monometallic catalysts in various reactions [1–4]. The explanation of bimetallic enhancement for PdAu catalysts has been attributed to two major effects: (1) the geometric effect, in which specific atomic ensembles are the most active sites [2,3,5–10], and (2) the electronic effect, in which interaction among surrounding atoms gives rise to electron density dislocation [11–15]. Nanoscale local atomic structures of bimetallic PdAu catalysts are crucial to catalytic activity [1,4]. Benefiting from the advances of nanoscale science, researchers now have the ability to understand and control the relationships between nanostructures and catalytic performance of catalysts. For PdAu catalysts, two major types of nanostructures have been extensively investigated: (1) the

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core-shell structure, in which one metal forms an inner core surrounded by the other metal as an outer shell [16–22], and (2) the alloy structure, in which the metal atoms are randomly distributed [17,19,22].

As a model catalyst, Pd-decorated Au nanoparticles (Pd-on-Au NPs) have been studied by our group for a variety of aqueous phase reactions, including hydrodechlorination reactions [4,23–29], glycerol oxidation [30–32], nitrophenol reduction [28], and nitrite reduction [33]. These catalysts often have orders-of-magnitude better activity then monometallic Pd catalysts, and also show resistance to deactivation from common catalyst poisons [25]. Supported PdAu catalysts also show promise for treating chloroform-contaminated groundwater [34,35].

While PdAu systems have been widely researched at the lab scale, there remains a gap between fundamental research and real-world applications for PdAu catalysts. Colloidal PdAu NP catalysts with uniform nanostructures have been synthesized by using reducing agents in the presence of stabilizers such as ligands [36,37], polymers [16,38,39], or dendrimers [19,21]. For potential real-world applications, they have been immobilized directly onto solid supports [40-42], or entrapped into support matrices via sol-gel chemistry [20,43,44]. However, such colloidal syntheses may be only practical on a laboratory scale because of scale-up difficulties, and the additional removal of surface stabilizers and solvents. To avoid these problems, researchers have investigated direct synthesis of PdAu NPs on supports. Monnier and coworkers [45,46] prepared supported Au-shell/Pd-core catalysts by electroless deposition (ED) to obtain core-shell bimetallic nanostructures at room temperature without stabilizers, but a special setup of ED bath (including choice of metal salts, reducing agents, and pH values) is necessary. A synthetic route using processes commonly used in industrial catalyst manufacture is more desirable [47,48]. Hutchings and coworkers [49,50] have shown that supported PdAu catalysts containing Pd-shell/Au-core domains of varying sizes are formed from conventional preparation steps (impregnation, drying, calcination, and reduction).

In this work, we investigated the effect of adding gold to commercially available supported Pd catalysts. We impregnated Au salt on a carbon-supported Pd catalyst, then treated it with a series of common industrial processes such as drying, calcination, and reduction. Catalysts were characterized with inductively coupled plasma spectrometry (ICP), transmission electron microscopy (TEM), and X-ray absorption spectroscopy (XAS). We tested the activity of the catalysts for the room-temperature, aqueous-phase hydrodechlorination (HDC) of trichloroethene (TCE), which converts TCE to ethane using hydrogen as a reductant. Results showed that activity could be improved by adding Au to commercially available supported Pd catalysts through commonly used catalyst preparation techniques.

2. Experimental

2.1. Catalyst preparation and treatments

All types of carbon-supported PdAu catalysts (PdAu/C) were prepared by adding Au salt to commercial Pd-on-carbon (Pd/C, 1 wt% Pd, Alfa Aesar) catalysts, then subjecting them to different treatments, as illustrated in Scheme 1. Pd/C powder was first pretreated by calcination in 100 ml/min air (breathing quality, Matheson) at 400 °C for 3 h. The sample was then cooled to room temperature in flowing air, followed by reduction in flowing hydrogen gas (100 ml/min, 99.99%, Matheson) at 400 °C for 3 h, then cooled to room temperature in flowing hydrogen gas. For each batch, 2 g Pd/C powder was dispersed in a mixture of 4–5 mL Nanopure water (>18.0 MΩ-cm, Barnstead NANOpure Diamond) and 0.2 mL isopropanol (>95%, ACS reagent, Fisher, added to aid in dispersing the Pd/C powder) at room temperature (22 ± 2 °C), followed by ultrasonication for 1 min. A solution of HAuCl₄ (0.236 mol/L; HAuCl₄·3H₂O, 99.9+%, Sigma-Aldrich; dissolved in water at room temperature) was then added into the mixture with stirring. The volume was adjusted with Nanopure water to make 5 mL total. The final powder suspension was kept stirring in the dark at room temperature for 6 h before drying in a 90 °C oven for 16 h.

The dried catalyst powder was divided into four samples, and each sample was treated with one of the procedures shown in Scheme 1; that is: (1) calcination in flowing air at 400 °C for 3 h and cooling to room temperature in flowing air (Dried/Air),



Scheme 1. Preparation routes of PdAu/C samples.

(2) calcination in flowing air at 400 °C for 3 h and cooling to room temperature in flowing air, then reduction in flowing hydrogen gas at 400 °C for 3 h and cooling to room temperature in flowing hydrogen gas (Dried/Air/H₂), (3) reduction in flowing hydrogen gas at 400 °C for 3 h and cooling to room temperature in flowing hydrogen gas (Dried/H₂), and (4) reduction in flowing hydrogen gas at 400 °C for 3 h and cooling to room temperature in flowing hydrogen gas, then calcination in flowing air at 400 °C for 3 h and cooling to room temperature in flowing hydrogen gas, then calcination in flowing air at 400 °C for 3 h and cooling to room temperature in flowing air core temperature in flowing as at 400 °C for 3 h and cooling to room temperature in flowing air (Dried/H₂/Air). These samples are designated as D-*x*, DA-*x*, DAH-*x*, DH-*x*, and DHA-*x*, respectively, where *x* reflects the weight percent of Au. Prepared samples were stored in air, in the dark at room temperature.

2.2. Catalyst characterization

2.2.1. ICP

Elemental analysis of catalysts was conducted with a PerkinElmer inductively coupled plasma optical emission spectrometer (ICP-OES) Optima 4300 DV. Catalyst powder was mixed with aqua regia containing 10 mL $HCl_{(aq)}$ (1 mol/L, Fisher), and 0.3 mL $HNO_{3(aq)}$ (70 wt%, Fisher); then heated at 90 °C for 30 min. After cooling down to room temperature, the solution was treated with a 0.45-µm filter before ICP analysis of Pd and Au loadings.

2.2.2. TEM

Particle size and morphology of catalysts were characterized with a JEOL 2100 TEM. Catalyst powder was dispersed in isopropanol with ultrasonication, then deposited on a 200-mesh carbon/formvar TEM grid, and air-dried at room temperature.

2.2.3. XAS

XAS measurements were performed on the insertion-device beamline 10-ID-B of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source at Argonne National Laboratory. The presence of harmonics was minimized with a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.07 s per data point. Measurements were made in transmission mode with the ionization chambers optimized for the maximum current with linear response (~1010 photons detected per sec) using a mixture of nitrogen and helium in the incident X-ray detector and a mixture of \sim 20% argon in nitrogen in the transmission X-ray detector. Absorption was measured at both Pd and Au edges; a Pd or Au foil spectrum was acquired simultaneously with each measurement for calibration. Samples of catalyst powder were pressed into a cylindrical holder with a thickness chosen to give a total absorbance (μx) at the Pd K (24.350 keV) and Au L_{III} (11.918 keV) edges of ca. 2.0, and an edge step ($\Delta \mu x$) of ca. 0.5. The sample holder was placed in a reactor cell (glass tube, length 18 in., diameter 0.75 in.) fitted at both ends with polyimide windows and stainless steel valves to isolate the reactor from the atmosphere. The reactor was

purged with flowing hydrogen gas for 10 min and then sealed, in order to mimic the hydrogen atmosphere during HDC reactions. All spectra were measured at room temperature.

Experimental phase shifts and back-scattering amplitudes were obtained from reference compounds: Pd foil for Pd-Pd bonding, Pd(NH₃)₄(NO₃)₂ (Aldrich) for Pd-O bonding, and Au foil for Au-Au bonding. Experimental data of Pd and Au foil were used to determine the best fit of Debye-Waller factors (DWF) and amplitude reduction factors (S_0) for phase shifts and back-scattering amplitudes in the FEFF fitting [51]. Along with the bond distances for Pd and Au foil, these values were used for determining the Pd-Au and Au-Pd FEFF phase shifts and back-scattering amplitudes. Standard procedures based on the WINXAS97 software [51] were used to extract the data [52]. The coordination parameters were obtained by a least-square fit in k- and R-space of the nearest-neighbor, k²-weighted Fourier transform (FT) data (k: photoelectron wave number, R: bond distance). The data fitted equally well with both k^1 and k^3 weightings.

2.3. Catalyst testing

Aqueous-phase hydrodechlorination (HDC) of trichloroethene (TCE) at room temperature was chosen as the model reaction for catalytic testing. Batch reactions were performed similar to previous studies [4,26,53]. A screw-cap bottle (250 mL, Alltech), containing 165 mL Nanopure water, 3 mL Na-HCO_{3(aq)} buffer (0.08 mol/L; NaHCO₃, 99%, Fisher), and a magnetic stir bar were sealed with PTFE-sealed threads and a PTFE-silicone septum. Hydrogen gas was bubbled into the bottle for 15 min to displace dissolved oxygen and to fill the headspace with a hydrogen atmosphere (1 atm). Then, 7 µL TCE (99.5%, Sigma-Aldrich) and 0.2 µL pentane (99.7%, Burdick and Jackson) internal standard, were injected into the sealed bottle. The overall solution was stirred for at least 3 h to reach equilibrium. In a separate vial, ~50 mg catalyst powder was dispersed in a mixture of 4.5 mL Nanopure water and 0.5 mL isopropanol with ultrasonication for 1 min. At time t = 0, the catalyst suspension was injected into the bottle. The reactor was magnetically stirred at 600 r/min. The initial TCE concentration in liquid phase was 50.9 ppm, far below the saturation concentration of 1200 ppm in water at 25 °C [54]. The reaction was monitored through headspace gas chromatography (GC) using an Agilent Technologies 6890N GC with a flame ionization detector (FID) and a 60/80 Carbopack B/1% SP-1000 packed column (Supelco 12487, Sigma-Aldrich). Reaction rates were determined from changes of TCE concentrations in the headspace. All reactions were performed at room temperature.

3. Results and discussion

3.1. Elemental analysis and particle morphology

ICP results of Pd and Au loadings are listed in Table 1. Pd loadings remained the same (\sim 1 wt%) for all the samples, compared to the control Sample P0 (1 wt% Pd/C). Au loadings, 0.1, 0.4, 1.1, and 1.7 wt%, matched the amount of Au added to

Table 1

Catalyst compositions (as determined by ICP, treatments, and reaction rates, rate constant k_{cat} and initial turnover frequency (TOF) determined from aqueous-phase TCE HDC with initial $C_{TCE(aq)}$ = 50.9 ppm at room temperature 22 ± 2 °C).

No.	Catalyst	Pd weight loading Au weight		Tracetor	Rate constant k_{cat} (L	Initial TOF (10 ⁻³
		(wt%)	loading (wt%)	Treatment	$g_{Pd}^{-1} \min^{-1}$)	mol _{TCE} mol _{Pd} ⁻¹ s ⁻¹)
D-0.1	PdAu/C	1.0	0.1	Dried	29	20
D-0.4	PdAu/C	1.0	0.4	Dried	85	58
D-1.1	PdAu/C	1.0	1.1	Dried	89	61
D-1.7	PdAu/C	1.0	1.7	Dried	33	22
DA-0.1	PdAu/C	1.0	0.1	Dried/air	39	27
DA-0.4	PdAu/C	1.0	0.4	Dried/air	130	88
DA-1.1	PdAu/C	1.0	1.1	Dried/air	110	75
DA-1.7	PdAu/C	1.0	1.7	Dried/air	22	15
DAH-0.1	PdAu/C	1.0	0.1	Dried/air/H ₂	84	58
DAH-0.4	PdAu/C	1.0	0.4	Dried/air/H ₂	310	210
DAH-1.1	PdAu/C	1.0	1.1	Dried/air/H ₂	490	340
DAH-1.7	PdAu/C	1.0	1.7	Dried/air/H ₂	310	210
DH-0.1	PdAu/C	1.0	0.1	Dried/H ₂	64	44
DH-0.4	PdAu/C	1.0	0.4	Dried/H ₂	71	49
DH-1.1	PdAu/C	1.0	1.1	Dried/H ₂	59	41
DH-1.4	PdAu/C	1.0	1.7	Dried/H ₂	63	43
DHA-0.1	PdAu/C	1.0	0.1	Dried/H ₂ /air	46	32
DHA-0.4	PdAu/C	1.0	0.4	Dried/H ₂ /air	71	49
DHA-1.1	PdAu/C	1.0	1.1	Dried/H ₂ /air	120	82
DHA-1.7	PdAu/C	1.0	1.7	Dried/H ₂ /air	210	140
P0	Pd/C	1.0	0	(Pretreatments only, control sample)	32	22

the different sets of catalysts.

Fig. 1 shows representative TEM images of PdAu/C samples, indicating that metal particles have roughly spherical morphology and a broad size distribution from ~5 nm (Fig. 1(a)) to over 50 nm (Fig. 1(b)). Particle size analysis showed a bimodal size distribution for metal particles on PdAu/C samples, with smaller particles around 5–10 nm (Fig. 1(a)) and larger particles around 30–100 nm (Fig. 1(b)). This is in contrast to the monometallic 1 wt% Pd/C catalyst, which has a relatively uniform size distribution of 3.5 nm Pd particles [55].

3.2. Catalytic activity for TCE HDC reaction

Reaction rates of TCE HDC were quantified using the rate constant k_{cat} and initial turnover frequency (TOF, number of reacted TCE molecules per Pd atom per time), with the implicit assumption of first-order dependence in TCE and zero-order in H₂ [26,27,57,58]. k_{cat} is the Pd-normalized reaction rate constant (with unit of L g_{Pd}-1 min⁻¹), derived from Eqs. (1) and (2):



$$k_{\rm meas} = k_{\rm cat} C_{\rm cat} \tag{2}$$

where k_{meas} is the measured first-order rate constant, and C_{TCE} and C_{cat} are the concentrations of TCE and Pd in the liquid phase in the reactor, respectively. Dilute NaHCO_{3(aq)} (~1.4 mmol/L in the reactor) was chosen as the buffer, and pH was controlled between 8.3–6.0 for all the tests in order to minimize possible effects from salts and pH [58,59]. All reactions reached >90% TCE conversion and showed >90% product selectivity to ethane as previously reported [26].

Results of catalyst activities are listed in Table 1; data points of initial TOF's at different compositions and treatments are plotted in Fig. 2. Most of the bimetallic PdAu/C samples showed higher activities than the monometallic Pd/C (Sample P0), indicating that catalytic enhancement could be achieved by the addition of the Au precursor salt. Sample DAH-1.1 (initial TOF =



Fig. 1. Representative TEM images of sample DAH-1.1 with smaller particles around 5–10 nm (a) and larger particles around 30–100 nm (b).



Fig. 2. TCE HDC reaction activity profiles of PdAu/C catalysts with different Au loadings and treatment processes and Pd/C control.

 $340 \times 10^{-3} \text{ mol}_{TCE} \text{ mol}_{Pd^{-1}} \text{ s}^{-1}$) was the most active, with an initial TOF value >15 times higher than Pd/C (initial TOF = 22 × $10^{-3} \text{ mol}_{TCE} \text{ mol}_{Pd^{-1}} \text{ s}^{-1}$).

3.3. Local atomic information from XAS measurements

XAS is a powerful technique to acquire detailed structural and electronic information at an atomic level for monometallic NPs [60–62] and bimetallic NPs [4,16–22]. The EXAFS region provides local structural information including the types of neighboring atoms, coordination number (N), and bond distance (R). The results of the EXAFS fitting are shown in Table 2.

3.4. Effect of Au loading on catalytic activity

From the Pd edge, coordination numbers of bimetallic Pd-Au bonding (NPd-Au) generally increased with higher Au loadings (Table 2). NPd-Au was as high as 7.0-7.5 which was 60%-70% of total coordination number of Pd (N_{Pd}). Fourier transform (FT) fits from the EXAFS data also exhibited a dependence on bimetallic interaction with Au loadings for the same Dried/Air/H₂ treatments (Fig. 3). FT fits of sample DAH-0.1 (Au 0.1 wt%) were almost the same as Pd foil (Fig. 3(a)), implying little to no Pd-Au interaction. Sample DAH-0.4 (Au 0.4 wt%) showed a change in the ratio of the two characteristic Pd peaks (the two highest FT magnitude peaks) and small shifts in the node positions of the FT imaginary parts (Fig. 3(b)) due to interference from the Pd-Pd and Pd-Au contributions, indicating bimetallic Pd-Au bonding. Sample DAH-1.1 (Au 1.1 wt%) and DAH-1.7 (Au 1.7 wt%) each showed nearly equal ratios of the two characteristic Pd peaks (Fig. 3(c) and (d)), indicating more Pd-Au interaction.

From the Au edge, Au-Pd interaction was not apparent for the majority of PdAu/C samples (Table 2), with the exceptions of DAH-0.1, DA-0.4, DAH-0.4, and DAH-1.1 with small N_{Au-Pd} values (N_{Au-Pd} = 1.7%–2.6%, 14%–22% of total coordination number of Au). This is indicative that for almost all of the catalysts, the majority of Au atoms were present as monometallic Au, as opposed to being in a bimetallic PdAu structure. Conversely, the number of Pd atoms in the bimetallic structure increased with increasing Au loadings. For example, Fig. 4 shows FT results from the EXAFS data of samples with different Au loadings under the same Dried/Air/H₂ treatments. Compared to Au foil, samples with lower Au loadings (DAH-0.1, DAH-0.4, and DAH-1.1) exhibited noticeable differences in shape and relative peak magnitudes and node positions of the imaginary parts (Fig. 4(a)–(c)) due to the Au-Pd interaction.

Sample DAH-1.7, which had the highest Au loading, appeared similar to Au foil (Fig. 4(d)), indicative of insignificant Au-Pd interaction. The small shift in the R_{Au-Au} between DAH-1.7 (2.86 Å) and Au foil (2.88 Å), could possibly be due to the smaller particle size of the Au in DAH-1.7. With increasing Au loadings, the additional Au atoms formed monometallic Au particles, diluting the Au-Pd interaction. Indeed, the Dried/Air/H₂ process enhanced the bimetallic Au-Pd interaction.

No	Catalvet	Edgo	Scattering	Ν	R (Å)
NO.	Catalyst	Euge	path	(±10%)	(±0.02 Å)
D-0.1	PdAu/C	Pd	Pd-Pd	9.7	2.75
		Au	Au-Au	10.8	2.87
DA-0.1	PdAu/C	Pd	Pd-Pd	10.0	2.74
		Au	Au-Au	10.3	2.84
DAH-0.1	PdAu/C	Pd	Pd-Pd	11.1	2.75
		Au	Au-Au	10.1	2.87
			Au-Pd	2.0	2.79
DH-0.1	PdAu/C	Pd	Pd-Pd	9.8	2.79
		Au	Au-Au	9.4	2.83
DHA-0.1	PdAu/C	Pd	Pd-Pd	10.2	2.75
		Au	Au-Au	9.4	2.84
D-0.4	PdAu/C	Pd	Pd-Pd	9.2	2.75
		Au	Au-Au	11.0	2.86
DA-0.4	PdAu/C	Pd	Pd-Pd	6.1	2.75
			Pd-Au	5.3	2.79
		Au	Au-Au	9.1	2.86
			Au-Pd	2.6	2.80
DAH-0.4	PdAu/C	Pd	Pd-Pd	6.4	2.75
			Pd-Au	5.5	2.80
		Au	Au-Au	9.7	2.84
			Au-Pd	2.2	2.79
DH-0.4	PdAu/C	Pd	Pd-Pd	6.6	2.76
			Pd-Au	5.2	2.79
		Au	Au-Au	10.9	2.85
DHA-0.4	PdAu/C	Pd	Pd-Pd	9.0	2.75
		Au	Au-Au	10.8	2.86
D-1.1	PdAu/C	Pd	Pd-Cl	3.8	2.33
		Au	Au-Au	10.7	2.86
DA-1.1	PdAu/C	Pd	Pd-Pd	3.5	2.75
			Pd-Au	7.0	2.79
		Au	Au-Au	10.3	2.83
DAH-1.1	PdAu/C	Pd	Pd-Pd	4.8	2.75
			Pd-Au	6.4	2.79
		Au	Au-Au	10.3	2.86
			Au-Pd	1.7	2.79
DH-1.1	PdAu/C	Pd	Pd-Pd	4.4	2.75
			Pd-Au	7.0	2.79
		Au	Au-Au	11.0	2.86
DHA-1.1	PdAu/C	Pd	Pd-Pd	4.4	2.75
			Pd-Au	7.0	2.79
		Au	Au-Au	10.9	2.84
D-1.7	PdAu/C	Pd	Pd-Cl	4.0	2.33
		Au	Au-Au	9.5	2.86
			Au-Cl	0.8	2.29
DA-1.7	PdAu/C	Pd	Pd-Pd	2.1	2.75
			Pd-Au	5.7	2.80
			Pd-O	1.3	2.04
		Au	Au-Au	11.1	2.86
DAH-1.7	PdAu/C	Pd	Pd-Pd	4.5	2.75
			Pd-Au	6.5	2.79
		Au	Au-Au	11.0	2.86
DH-1.7	PdAu/C	Pd	Pd-Pd	4.3	2.74
			Pd-Au	7.5	2.79
		Au	Au-Au	11.0	2.86
DHA-1.7	PdAu/C	Pd	Pd-Pd	2.9	2.75
			Pd-Au	5.4	2.80
			Pd-O	0.9	2.04
		Au	Au-Au	10.9	2.85
P0	Pd/C	Pd	Pd-Pd	10.5	2.80

N: coordination number, R: bond distance, RT: room temperature.

tion (see Sec. 3.5) while other processes led to no or little Au-Pd

Table 2 EXAFS fit parameters.



Fig. 3. Fourier transform (k^2 weighted, $\Delta k = 2.7-11.8$ Å⁻¹; solid line: magnitude, dotted line: imaginary components) of Pd K edge EXAFS data for Pd foil (blue) and PdAu/C samples (red). (a) DAH-0.1; (b) DAH-0.4; (c) DAH-1.1; (d) DAH-1.7.



Fig. 4. Fourier transform (k^2 weighted; solid line: magnitude, dotted line: imaginary components) of Au L_{III} edge EXAFS data for Au foil (blue) and PdAu/C samples (red). (a) Sample DAH-0.1 ($\Delta k = 2.7-11.8 \text{ Å}^{-1}$); (b) Sample DAH-0.4 ($\Delta k = 2.6-11.7 \text{ Å}^{-1}$); (c) Sample DAH-1.1 ($\Delta k = 2.6-11.5 \text{ Å}^{-1}$); (d) Sample DAH-1.7 ($\Delta k = 2.6-12.0 \text{ Å}^{-1}$).

interaction even at low Au loadings. This implies that most of the Pd-Au interaction was in smaller particles, while larger particles were mostly monometallic Au, in accordance with the observed bimodal size distribution from TEM. This interpretation is consistent with the work by Hutchings and co-workers [50], who synthesized supported PdAu catalysts by co-impregnation also resulting in bimodal size distribution with Au forming large clusters.

Significantly (Table 2), Au stabilized metallic Pd under high-temperature calcination. Based on our previous studies[4], Pd/C was fully oxidized after calcination in flowing air at 400 °C, could not be reduced in H₂ at room temperature, and showed no activity for TCE HDC. However, addition of Au, as low as 0.1 wt%, significantly improved Pd oxidization resistance. Samples DA-0.1 DHA-0.1, DA-0.4, DHA-0.4, DA-1.1, and DHA-1.1 exhibited no detectable oxidized Pd, and also had enhanced catalytic activities (Table 1 and 2). This stabilization effect was also found in our previous investigation of colloidal Pd-on-Au NPs [4]. Curiously, the air-treated samples with the highest Au loading, DA-1.7 and DHA-1.7, did have partial Pd oxidation (~33% for DA-1.7, ~23% for DHA-1.7; percentages calculated from the ratio between N_{Pd-O} of the sample and N_{Pd-O} (= 4) of fully oxidized PdO). We speculate that this may be due to the Cl- ions from the gold salt; Cl- ions can be oxidatively adsorbed to Pd under acidic conditions and reduce Pd activity [53,63]. Indeed, adding the Au precursor to these samples also added 0.73 mmol Cl resulting in a Cl:Pd atomic ratio of 3.9:1.

The Au-Au bond distances of all PdAu/C samples were similar (2.83–2.87 Å) and slightly less than Au foil (2.88 Å), which is typical for NPs. The Pd-Pd bond distance of Pd/C (2.80 Å) was larger than Pd foil (2.75 Å) and similar to Pd-H [64], which was expected since XAS measurements were conducted under hydrogen atmosphere. In general, the hydride disappeared with the addition of Au, and the bimetallic PdAu/C samples (N_{Pd-Pd} = 2.74–2.76 Å) became similar to Pd foil with the exception of the sample with the lowest Au loading, DH-0.1 (N_{Pd-Pd} = 2.79 Å), which was more like Pd-H due to its lack of bimetallic interaction.

Scheme 2 shows our proposed catalyst structures, summarizing the general effect of Au loadings and Fig. 5 shows profiles of reaction activities and bimetallic interaction (Pd-Au and



Scheme 2. Illustration of proposed cross-section structures of PdAu/C samples with different Au loadings. (a) 0.1 wt%; (b) 0.4 wt%; (c) 1.1 wt%; (d) 1.7 wt%.



Fig. 5. Relationship between TCE HDC reaction activities and bimetallic interaction (Pd-Au and Au-Pd) at different Au loadings under the Dried/Air/H₂ process (dotted line: initial TOF ($22 \times 10^{-3} \text{ mol}_{TCE} \text{ mol}_{Pd}^{-1} \text{ s}^{-1}$) value of the control Sample P0 Pd/C).

Au-Pd) at different Au loadings under the same treatment process (dried/air/H₂, as an example). Higher Au loadings led to more Pd-Au interaction (higher N_{Pd-Au}) but less Au-Pd interaction (lower N_{Au-Pd}). Sample DAH-1.1 ($N_{Pd-Au} = 6.4$, $N_{Au-Pd} = 1.7$) was the most active (initial TOF = $340 \times 10^{-3} \text{ mol}_{\text{TCE}} \text{ mol}_{\text{Pd}^{-1}}$ s⁻¹). The dried/air/H₂ process provided the highest activities than other processes, and exhibited a volcano-shape curve for activities among different Au loadings. While initial TOFs increased with Au loadings for samples up to 1.1 wt% Au, higher loadings resulted in a decrease in activity. DAH-1.7 had an initial TOF = 210×10^{-3} mol_{TCE} mol_{Pd⁻¹} s⁻¹; a 50% decrease compared to DAH-1.1. An EXAFS comparison of DAH-1.1 and DAH-1.7 (Table 2 and Fig. 6) showed that DAH-1.1 and DAH-1.7 coordination numbers were similar from the Pd edge (DAH-1.1: NPd-Pd = 4.8, NPd-Au = 6.4; DAH-1.7: NPd-Pd = 4.5, NPd-Au = 6.5), however, the higher loaded sample showed a higher Au-Au interaction and almost no measurable Au-Pd interaction from the Au edge (DAH-1.1: NAu-Au = 10.3, NAu-Pd = 1.7; DAH-1.7: $N_{\text{Au-Au}} = 11.0$, $N_{\text{Au-Pd}} = 0$). This suggests Au interacted with Pd



Fig. 6. Relationship between TCE HDC reaction activities and bimetallic interaction (Pd-Au and Au-Pd) with different treatment processes at the same 1.1 wt% Au loading (dotted line: initial TOF value ($22 \times 10^{-3} \text{ mol}_{TCE} \text{ mol}_{Pd}^{-1} \text{ s}^{-1}$) of the control Sample P0 Pd/C).

such that DAH-1.1 and DAH-1.7 were similar from the Pd edge; on the other hand, the excess Au in DAH-1.7 could have resulted in the formation of large Au clusters which possibly blocked the PdAu bimetallic particles, which is consistent with the lower catalytic activity and higher *N*_{Au-Au} of DAH-1.7.

3.5. Effect of treatment on catalytic activity

As shown in Fig. 2, catalytic activities were influenced by different treatments, even at the same PdAu composition, and could be explained by changes in the bimetallic interaction as shown from EXAFS. Fig. 6 shows activity and coordination numbers as a function of treatment for the 1.1 wt% Au samples. Samples with drying only (D-0.1, D-0.4, D-1.1, D-1.7) showed no bimetallic interaction since the temperature (90 °C) was low and no significant Pd-Au or Au-Pd bonding was observed (Table 2); the catalytic activities were only slightly promoted (D-0.4, D-1.1) or remained similar to Pd/C (D-0.1, D-1.7, Table 1). Au has a higher reduction potential than Pd, and galvanic replacement of Pd by Au was expected. This can be seen in the EXAFS results, Pd-Cl (Table 2) was present for the higher loaded Au samples (D-1.1 and D-1.7). In addition, for the dried samples Au was in the Au-Au form except for D-1.7. At this loading, the amount of electrons necessary to reduce all of the added Au3+ (0.516 mmol e-) was in excess of that available upon oxidizing Pd⁰ to Pd²⁺ (0.376 mmol e⁻ in 2g of catalyst), resulting in incomplete reduction of the Au as exhibited by the existence of Au-Cl bonding. The slightly higher activities for D-0.4 and D-1.1 were likely due to promotion from a small amount of Au⁰ atoms. At the extremes, the lowest loaded sample, D-0.1 may have had too few Au⁰ atoms for measurable promotion, while D-1.7 might have had excess Cl- ions so that Au promotion was not obvious.

Samples with the dried/air process (DA-0.1, DA-0.4, DA-1.1, DA-1.7) generally exhibited significant bimetallic interaction from both the Pd and Au edges (e.g. increased Pd-Au and Au-Pd) and also showed the Au stabilization effect for Pd oxidization resistance. Pd and Au are thermodynamically miscible over their entire composition; thus, it is not unexpected to have bimetallic interaction from alloying more after high-temperature treatment. DA-0.1 did not have detectable Pd-Au and Au-Pd probably due to its low Au loading. DA-1.1 and DA-1.7 had Pd-Au but no Au-Pd because most Au presented in the larger Au-rich particles, as mentioned in Sec. 3.4. As such, any Au-Pd interaction was undetectable due to the high Au-Au at high Au loadings. The Au stabilization effect, also mentioned in Sec. 3.4, led to no detectable Pd-O except for DA-1.7 with effects from initial excess Cl- ions. The catalytic activities were promoted for DA-0.4 and DA-1.1 most likely due to bimetallic interaction. DA-0.1, with the low Au loading, remained similar to Pd/C. DA-1.7 had a slightly lower activity than Pd/C because of initial excess Cl- ions and resulting Pd-O and lower Pd-Au.

Samples with the dried/air/H₂ process (DAH-0.1, DAH-0.4, DAH-1.1, DAH-1.7) also had significant bimetallic interaction, with the exception of DAH-0.1, which had the lowest Au loading. DAH-0.4 and DAH-1.1 had both Pd-Au and Au-Pd interactions while no Au-Pd could be observed from DAH-1.7, likely due once again to the presence of larger Au-rich particles. Compared to the dried/air samples, where only DA-0.4 had measurable Pd-Au and Au-Pd, the dried/air/H₂ process might be more amenable toward the alloying of Pd and Au atoms, as the high temperature H₂ treatment seems to promote this. As expected, following the high temperature H₂ treatment no oxidized Pd or Au was detected in the DAH samples. Compared to all the other treatment protocols, the catalytic activities of the dried/air/H₂ samples were generally higher across compositions.

Samples with the dried/ H_2 process (DH-0.1, DH-0.4, DH-1.1, DH-1.4) also showed Pd-Au bimetallic interaction except for the lowest loaded sample, DH-0.1. No Au-Pd bonding was detected in any of the samples. No oxidized Pd or Au was detected, as was expected under the high-temperature H_2 treatment. The catalytic activities of the dried/air/ H_2 samples were slightly promoted compared to Pd/C, but were similar regardless of Au loading.

Samples with the dried/H₂/air process (DHA-0.1, DHA-0.4, DHA-1.1, DHA-1.7) showed bimetallic interaction with only Pd-Au for DHA-1.1 and DHA-1.7. Like the dried/H₂ samples, no Au-Pd bonding was detected, indicating that most Au atoms were still in large Au-rich particles and had little interaction with Pd atoms. DHA-1.7 had some Pd–O bonding, which may be due to excess Cl- ions preventing Pd atoms from contacting Au atoms, leading to less Pd oxidization resistance and similar EXAFS results as DA-1.7 synthesized with the dried/air process. However, different from DA-1.7 and other dried/air samples, the catalytic activities of the dried/H₂/air samples increased with Au loadings, and DHA-1.7 was the most active one. The explanation for this difference is not understood. Fig. 6 and Scheme 3 illustrate these effects.

Several researchers observed that, for PdAu materials under high-temperature calcination in air, Pd tends to be in the shell of particles, and Au in the core, due to the lower reduction potential of Pd [49,65]. We speculate that the Au and Pd in the samples prepared with the air calcination process may migrate to form a Pd-rich shell and Au-rich core structure. On the other hand, samples synthesized with the H₂ reduction process had little migration; since there was no air present, addition of Au should only lead to Au atoms deposited on the surface of Pd



Scheme 3. Schematic illustration of proposed cross-section structures of PdAu/C samples with different treatments. (a) Dried; (b) Dried/Air; (c) Dried/Air/H₂; (d) Dried/H₂; (e) Dried/H₂/Air.

particles.

To summarize, we hypothesize that the dried/air process led to a Pd-rich shell/Au-rich core structure due to atomic migration in air at high temperature (Scheme 3(a)), but led to little increase in activity. Addition of the H₂ treatment step to the dried/air process (dried/air/H₂ Scheme 3(b)) caused local alloying of the core-shell particles, resulting in better bimetallic interaction and the highest activities of all the different treatment methods. The dried/H₂ process resulted in only a small amount of Au atoms interacting with Pd atoms to form a possible Au-rich shell/Pd-rich core structure since no air was present during calcination; the activities were therefore only slightly promoted. The dried/H₂/air process might increase surface Pd amount due to atomic migration in calcination; so the activities became higher than the dried/H₂ samples. As shown in Scheme 3, different treatments might lead to similar bimetallic interaction but also very different reaction activities, which could be explained by the above analysis.

4. Conclusions

Bimetallic supported PdAu catalysts, synthesized by adding gold salt to existing supported Pd catalysts, were investigated for the higher activities and corresponding nanostructures. Bimetallic PdAu/C catalysts were successfully synthesized with well-established industrial processes of catalyst manufacture, including impregnation, drying. Catalyst composition and post-treatments revealed were both important to the resulting metal nanostructure. The most active PdAu/C catalyst (Pd 1.0 wt%, Au 1.1 wt%, dried/air/H₂ process, initial TOF = 340 × 10^{-3} mol_{TCE} mol⁻¹ s⁻¹) showed an activity >15 times higher than Pd/C (Pd 1.0 wt%, initial TOF = 22×10^{-3} mol_{TCE} mol_{Pd⁻¹} s⁻¹) for aqueous-phase TCE HDC. TEM images indicated that PdAu/C catalysts might have a bimodal size distribution with smaller particles around 5–10 nm and larger particles around 30–100 nm. XAS results further suggested that larger particles may be Au-rich, and bimetallic smaller. Au stabilized metallic Pd against oxidation under calcination up to 400 °C; however, initial excess Cl- ions inhibited this stabilization effect. Nanostructure models were proposed for effects of Au loading and treatment, in accordance with EXAFS data and catalytic results, exhibiting the structure-activity relationships. Among all the treatments tested, the Dried/Air/H₂ process led to a probable Pd-rich shell/Au-rich core structure with higher bimetallic interaction and the most active catalytic performance.

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PdAu catalysts of varied bimetallic structure and activity were prepared using simple impregnation techniques on commercially available Pd on carbon catalysts. Au loading and catalyst post-impregnation treatment conditions dramatically affect structure and hydrodechlorination activity.

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