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# Aerobic oxidation of $\alpha$ , $\beta$ -unsaturated alcohols using sequentially-grown AuPd nanoparticles in water and tetraalkylphosphonium ionic liquids

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## A R T I C L E I N F O

# ABSTRACT

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Keywords: Nanoparticles Alcohol oxidation Ionic liquids Quasi-homogeneous catalysis EXAFS Metallic and bimetallic nanoparticles (NPs) (Au, Pd, and AuPd) were synthesized in water with poly(vinylpyrroldine)(PVP) as a polymer stabilizer, as well as in tetraalkylphosphonium chloride ionic liquids (ILs). A borohydride reduction technique was used for the preparation of the monometallic NPs, while a sequential reduction strategy was seen to generate the putative core–shell varieties. Pd and sequentially grown Au–Pd NPs were seen to serve as efficient catalysts for the oxidation of  $\alpha$ , $\beta$ -unsaturated alcohols, while the Au NPs themselves showed minimal activity. However, a system with both Au NPs and a Pd(II) salt (K<sub>2</sub>PdCl<sub>4</sub>) also efficiently catalyzed the oxidation reaction in water. A number of aliphatic and aromatic unsaturated alcohols were oxidized using oxygen as an oxidant with these as-prepared catalysts at 60 °C in the absence of base. TEM and EXAFS studies of the nanoparticle catalysts before and after the oxidation reaction revealed that the Pd(II) salt was reduced in situ during catalytic conditions, and that there was large changes in particle size and morphology after catalysis, which suggests Ostwald ripening and the presence of a redox mechanism. In the IL system, the ease of Pd reduction led to high activities for many  $\alpha$ , $\beta$ -unsaturated alcohols in the absence of the Au promoter.

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# 1. Introduction

The oxidation of alcohols to their respective carbonyl compounds, although known to the scientific community since the 19th century [1], continues to represent a major challenge as far as the industrial implementation of such processes is concerned. Traditionally, in the laboratory, such conversions have been performed using highly toxic transition metal compounds (such as chromium salts) in volatile and flammable organic solvents [2]. Such systems are rife with disadvantages: the reaction mixtures are inherently toxic, often corrosive, and the process can pose a serious threat to the environment if performed regularly on a large scale [3]. Another point worth noting is the probability of "overoxidation" of primary alcohols in such systems, where the reaction proceeds to give the carboxylic acid rather than halt at the aldehyde stage. Moreover, from the standpoint of green chemistry, catalytic processes are preferred over stoichiometric ones. While the application of novel sources of oxygen such as ozone, PhOI, N-morpholine-N-oxide, or urea-hydrogen peroxide have notable utility, for industrial processes either air or oxygen are the oxidants of choice if they can be used safely, simply for the sake of accessibility and cost-effectiveness [4].

Our group and many others are examining the "greening" of important chemical reactions by developing methods by which reactions of industrial importance (such as oxidations, hydrogenations, and so on) can be carried out in solvents ear-marked as "green", and with catalysts that are readily recyclable, with high yields and minimal waste products (e.g. high selectivities). Stable metal nanoparticles (NPs) in solvents such as water, supercritical carbon dioxide, ionic liquids, or eutectic mixtures provide an alternative route to traditional homogeneous or heterogeneous catalysis [5]. In fact, such "guasi-homogeneous" nanocatalysis involving suspended nanoparticle catalysts in liquid media straddles the boundaries between homogeneous and heterogeneous catalysis, combining some of the advantages of both approaches. While the catalytic versatility of metal NPs is well-known, their tendency to agglomerate and precipitate in the absence of stabilizers can restrict their catalytic uses: however, several strategies have been successfully applied to minimize such catalyst deactivation, and many different reactions have been screened for potential application of "quasi-homogeneous" nanocatalysis.

After the pioneering work by Haruta, it is now well-known that Au NPs below a certain critical size are capable of efficient catalysis of oxidation reactions at low temperatures [6]. In 2005, Tsunoyama et al. showed that PVP-stabilized Au NPs in water selectively catalyze the oxidation of benzyl alcohol to benzaldehyde in the



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presence of base [7–9], and many other groups have also reported alcohol oxidations with Au NPs [3,10-15], as well as enhanced activities for AuPd NPs for mild alcohol oxidations [16-26]. We previously studied alcohol oxidations in aqueous solutions using Au, Pd, and bimetallic AuPd NP catalysts in aqueous solutions, and determined that AuPd systems were much more reactive than their monometallic Au and Pd counterparts [18]. Recently, both ourselves [25], and others [21,24], have shown that core-shell AuPd NPs (either as-synthesized or synthesized in situ during reaction conditions) are particularly active for alcohol oxidations, with substantial activities and selectivities for  $\alpha,\beta$ -unsaturated alcohols such as crotyl alcohol at room temperature in the absence of bases. However, it was not apparent how generic such results were to other alcohol systems, and what the dominant mechanism was in the reaction. In addition, little to no studies are available detailing the recyclability of such nanoparticle systems. Catalytic oxidations in ionic liquids (ILs) are rather less-well-known than those in other media: even in cases where such studies have been carried out, the actual catalytic species are often transition metal complexes (such as methyltrioxorhenium [27], OsO<sub>4</sub> [28], RuCl<sub>3</sub> [29], and so on), and/or the oxygen is harvested from novel oxidants rather than using molecular oxygen or air. Heteropolyacids have been immobilized on imidazolium IL modified SBA-15 for alcohol oxidations [30], and ILs such as choline hydroxide have also been used to stabilize Ru NPs on MgO supports for oxidations [31]. However, AuPd systems have not been well explored in IL systems to date

In this study, the oxidation of a variety of  $\alpha$ , $\beta$ -unsaturated alcohols (aliphatic as well as aromatic) in the presence of molecular oxygen have been investigated. The catalytic systems of choice are Au, Pd, Au/Pd(II), and sequentially grown AuPd NPs, while the reaction media include water in the presence of PVP stabilizer as well as a tetraalkylphosphonium chloride IL capable of inherent NP stabilization. Careful growth of Pd shells on Au seeds using mild reductants such as ascorbic acid have been used to generate sequentially grown AuPd NPs while minimizing secondary nucleation of Pd NPs. In situ formation of Pd shells on Au cores may also be achieved by the oxidation of the substrate itself, and concurrent reduction of Pd(II) in the presence of Au NPs, while individually each of these show very little catalytic activity. Similar catalytic NP systems are generated in trihexyl(tetradecyl)phosphonium chloride ILs in the absence of any external stabilizers, and the resulting Pd NPs show high activities even in the absence of the Au promoter. Tentative mechanisms for  $\alpha,\beta$ -unsaturated alcohol oxidation in water and in trihexyl(tetradecyl)phosphonium halide ionic liquids have been suggested. Finally, TEM and EXAFS studies of the core-shell catalyst before and after reaction, as well as of Au NP/Pd(II) salt after reaction has been conducted to study the structure of these NP catalysts, and results suggest that the initial step of the oxidation reaction with Au NPs in the presence of Pd(II) salts leads to in situ formation of AuPd catalysts. Since allylic aldehydes are valuable fine chemicals finding extensive use in the pharmaceutical, agrochemical and cosmetic industries, we believe it is worthwhile to seek clean technologies for their synthesis via atom-efficient oxidations that also address issues of catalyst reusability, environmental impact, waste disposal, and renewable feedstock.

#### 2. Experimental

#### 2.1. Materials

All chemicals except for the ones listed below were purchased from Sigma Aldrich and used as received. Poly(vinylpyrrolidone) (PVP)(M.W. 58,000 g/mol), tetrachloroauric acid, HAuCl<sub>4</sub>·4H<sub>2</sub>O and potassium tetrachloropalladate, K<sub>2</sub>PdCl<sub>4</sub>, (both 99.9%, metals basis) were all obtained from Alfa Aesar, and the metal salts were stored under vacuum and flushed with nitrogen after every use. Commercial samples of the trihexyl(tetradecyl)phosphonium chloride (P[6,6,6,14]Cl) room-temperature ionic liquid (IL) were generously donated by Cytec Industries Ltd. Commercial samples of ILs were dried under vacuum at 70 °C for 10–12 h with stirring before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories. 18 M $\Omega$  cm Milli-Q water (Millipore, Bedford, MA) was used throughout.

# 2.2. Synthesis of PVP stabilized Pd, Au and AuPd NPs in water

PVP-stabilized metallic and sequentially grown bimetallic NPs were synthesized by previously reported procedures [18,25]; metallic NPs were synthesized using sodium borohydride while sequentially grown AuPd NPs were synthesized using ascorbic acid as the selective reducing agent for the Pd shell. To prepare the Au NPs (also used as "seed" particles), 50 mL of 0.35 mM PVP ( $1.75 \times 10^{-5}$  mol) was added to 5 mL of 10 mM HAuCl<sub>4</sub>•3H<sub>2</sub>O  $(5 \times 10^{-5} \text{ mol})$  and stirred at 800 rpm for 30 min. The solution was then placed on ice, stirring set to 1200 rpm, and 5 mL of 100 mM NaBH<sub>4</sub> ( $5 \times 10^{-4}$  mol) was added quickly to the solution. The reaction was left to stir for 30 min on ice, then stirred for another 30 min at room temperature. To quench the reaction, 5 mL of 100 mM HCl  $(5 \times 10^{-4} \text{ mol})$  was added to the solution and stirred for 30 min. To further stabilize the NPs, 35 mL of 1.0 mM PVP  $(3.5 \times 10^{-4} \text{ mol})$ was added to the final solution and stirred for 30 min. The particles were dialyzed overnight using cellulose dialysis membrane with a molecular cut off of 12,400 g/mol under N2. Pd NPs were synthesized using the same procedure, but K<sub>2</sub>PdCl<sub>4</sub> was used instead of HAuCl<sub>4</sub>•3H<sub>2</sub>O. The sequentially-grown 1:3 AuPd NPs were synthesized by mixing 100 mL of previously made Au "seed" particles  $(5 \times 10^{-5} \text{ mol})$  with 15 mL of 100 mM ascorbic acid  $(1.5 \times 10^{-3} \text{ mol})$ on ice, stirring at 800 rpm. To this solution, 15 mL of 10 mM K<sub>2</sub>PdCl<sub>4</sub>  $(1.5 \times 10^{-4} \text{ mol})$  was added then left to stir at 800 rpm on ice for 1 h. Upon completion, the particles were dialyzed overnight in the same manner as the Au seed particles. For the generation of the Au NP/Pd(II) system, an identical procedure was followed, except for the addition of ascorbic acid and the second dialysis step.

#### 2.3. Synthesis of Pd, Au and AuPd NPs in IL

For the synthesis of Pd NPs in IL, 1.6 mg of K<sub>2</sub>PdCl<sub>4</sub>  $(5.0 \times 10^{-6} \text{ mol})$  was added to a 10 mL sample of the trihexyl(tetradecyl)phosphonium chloride IL mixed with 2 mL 1,4-dioxane at room temperature, and vigorously stirred. To this solution, a stoichiometric excess of LiBH<sub>4</sub> reagent (1.0 mL, 2.0 M in THF) was injected drop-wise over a period of five minutes [32]. A brisk effervescence followed, and the entire solution turned brown, indicating nanoparticle formation. After the addition of LiBH<sub>4</sub>, volatile impurities including the dioxane were removed by vacuum-stripping the system at 70 °C. The Pd NP solution thus obtained was stored under nitrogen in capped vials until use. For the synthesis of Au NPs, a similar procedure was followed. Tetrachloroauric acid (2.0 mg,  $5.0 \times 10^{-6}$  mol) was dissolved in 10 mL P[6,6,6,14]Cl diluted with 2 mL 1,4-dioxane at room temperature to give a golden yellow solution which turned colorless, violet and then wine-red upon drop-wise addition of 1.0 mL of a 2.0 M LiBH<sub>4</sub> reagent. Excess LiBH<sub>4</sub> was quenched with methanol and volatiles were subsequently removed by vacuum-stripping. For the synthesis of sequentially grown AuPd NPs, a sequential reduction procedure was followed using the Au NP seeds as synthesized above, followed by the addition of 200 mg ascorbic acid to the reaction medium. While stirring this mixture under ice, a 5 mL solution of  $K_2PdCl_4$  (15.0 × 10<sup>-6</sup> mol) dissolved in methanol was added to



Fig. 1. TEM images of PVP-stabilized (A) as-synthesized Au NP seeds and (B) as-synthesized sequentially-reduced 1:3 AuPd NPs and (C) Au NP/Pd(II) 1:3 mixture after 24h reaction with cinnamyl alcohol and (D) sequentially-grown 1:3 AuPd NPs after 24h reaction with cinnamyl alcohol.

it all at once. The mixture was then stirred under ice for  $\sim 1$  h, and volatiles were removed from it by vacuum-stripping. For the generation of the Au NP/Pd(II) system, an identical procedure was followed, except for the addition of ascorbic acid.

# 2.4. General procedure for oxidation reactions

Oxidation reactions were carried out in a round-bottomed flask, sealed with a septum. In a general procedure, 10 mL of the NP solution (in water or IL) was stirred and heated to 60 °C under a flow of oxygen for about 10 min for aqueous systems, and for about 1 h in IL systems to compensate for the higher viscosity of the IL. After this, 500 or 5000 equivalents (based on one equivalent of metal catalyst) of the alcohol substrate was injected into the flask. For aqueous work, at incremental times 1.0 mL of the reaction mixture was sampled and the products were then extracted by two, 0.5 mL aliquots of ethyl acetate, shaking in 1 min intervals for 5 min per extraction. For IL samples, after  $\sim$ 12 h, the reaction vessel was removed from the constant temperature bath, and subjected to vacuum-stripping while being heated for extraction of the products and/or unreacted substrate. Conversion and selectivity were obtained from GC using a FID detector (Agilent Technologies 7890A) and a HP-Innowax capillary column. Two reactions were typically run for each sample. The neat organic liquids extracted were subsequently characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC-FID techniques. For GC-FID analysis,  $25 \,\mu$ L of a neat extract was mixed with 1 mL ethyl acetate in a GC-vial, and subjected to analysis.

#### 2.5. Characterization

UV-Vis spectra were obtained using a Varian Cary 50 Bio UV-Visible spectrophotometer with a scan range of 200-800 nm and an optical path length of 1.0 cm. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker 500 MHz Advance NMR spectrometer; chemical shifts were referenced to the residual protons of the deuterated solvent. TEM analyses of the NPs in IL and water, both before and after catalytic cycles, were conducted using a Philips 410 microscope operating at 100 kV. The samples in IL were prepared by ultrasonication of a 1% solution of the NP/IL solution in DCM followed by drop-wise addition onto a carbon-coated copper TEM grid (Electron Microscopy Sciences, Hatfield, PA). To determine average particle diameters, a minimum of 100 particles from each sample were manually measured from several TEM images using the ImageJ program. The Hard X-ray MicroAnalysis beamline (HXMA) 061D-1 (energy range, 5–30 keV; resolution,  $1 \times 10^4 \Delta E/E$ ) at the Canadian Light Source was used for recording X-ray absorption spectra at the Pd K-edge and the Au  $L_{III}$ -edge. The beamline optics include water-cooled collimating KB mirrors (Rh for the Au L<sub>III</sub>-edge and Pt for Pd K-edge), and a liquid nitrogen cooled double crystal monochromator housing two crystal pairs [Si(111) and

Table 1		
Summary of nanoparticle sizes	obtained by	TEM.

Nanoparticle	Size (nm)	
	Water	Ionic liquid
Au NPs	2.9 (1.4)	2.2 (0.8)
Pd NPs	2.7 (1.0)	4.3 (1.3)
1:3 AuPd Seq. grown NPs	3.9(1.7)	3.7 (1.0)
1:3 AuPd Seq. grown NPs after reaction	_a	8.0 (5.0) <sup>b</sup>
1:3 Au NPs/Pd(II) after reaction	6.4 (7.8) <sup>b</sup>	8.7 (3.9)
Pd NPs after reaction	-	9.0 (2.9)

<sup>a</sup> Particles formed worm-like structures.

<sup>b</sup> Bimodal distribution of particles.

Si(220)]. The X-ray measurements were conducted in ion chamber filled with a helium and nitrogen mixture for the Au L<sub>III</sub>-edge and pure helium for the Pd K-edge. The energy scan range for the measurement was between -200 eV and +1000 eV at each edge. Pd and Au foils were used for the respective edges as references. All EXAFS measurements were conducted in transmission mode at room temperature using samples trapped in alumina at 2.5% by weight metal and pressed into pellets [33]. The software package IFEFFIT was used for data processing which included fitting the preedge region to a straight line, and the background above the edge was fit to a cubic spline function [34,35]. The EXAFS function,  $\chi$ , was obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge jump step. The EXAFS fitting was performed in *R*-space between 1.4 and 3.4 Å for the Au edge and 1.4–3.0 Å for the Pd edge using theoretical phase-shifts and amplitudes generated by FEFF. fcc bulk lattice parameters (i.e., first shell coordination numbers of 12) were used to determine the amplitude reduction factor,  $S_0^2$ , for Au and Pd by analyzing Au and Pd reference foils [36].

# 3. Results and discussion

#### 3.1. Oxidation reactions in water

PVP-stabilized Au, Pd, sequentially grown 1:3 AuPd NPs and Au NP/Pd(II) 1:3 mixtures were synthesized. Fig. 1(A) and (B) shows representative TEM images of samples of PVP-stabilized Au NPs and sequentially grown 1:3 AuPd NPs. Average particle sizes were found to be  $2.9 \text{ nm} \pm 1.4 \text{ nm}$  and  $3.9 \text{ nm} \pm 1.7 \text{ nm}$  for these systems, respectively, which is in general agreement with previous work, although the Au NP sample showed some larger particles present and thus were not as monodisperse as could be desired. Pd NPs were  $2.7 \text{ nm} \pm 1.0 \text{ nm}$ , which within error is similar to that of the Au NPs; particle sizes of all samples by TEM are listed in Table 1. The ca. 1 nm increase of size for the sequentially-grown particles is consistent with, but does not in itself prove, core-shell type growth of the particles. The UV-Vis spectra of Au, Pd, and sequentially grown 1:3 AuPd NPs are shown in Fig. 2. There is a slight plasmon shoulder at ~530 nm in the Au NP sample, which is no longer apparent in the sequentially grown AuPd NP sample, which is similar to results seen before in this system [25,33,37], and is in agreement with TEM results which suggest Pd growth on the Au NP seeds. However, no information about whether the final particles have specific structures (core-shell, cluster on cluster, etc.) can be obtained from this TEM and UV-Vis information alone.

We have previously shown that sequentially-grown PVPstabilized 1:3 AuPd NPs were optimal catalysts for the roomtemperature oxidation of crotyl alcohol in water in the absence of base [25]; however, it was noted in the previous study that crotyl alcohol was an unusual substrate in this regard (e.g. room temperature/base free activation) and other allyl and benzyl alcohols showed much lower activity at these conditions. We also noted in



Fig. 2. UV-Vis spectra of PVP-stabilized Au, Pd, and sequentially-grown 1:3 AuPd NPs.

the previous study that Au NPs in the presence of Pd(II) salts (specifically K<sub>2</sub>PdCl<sub>4</sub>) also showed tremendous activity for crotyl alcohol oxidation activation at room temperature while the individual Au NPs and Pd(II) salts showed next to no activity, and hypothesized that in situ reduction of Pd onto the Au NPs was responsible for this activity [25]. Thus in this study we wished to test the generality of both the high activity of sequentially-grown 1:3 AuPd NPs for other allylic and benzylic alcohols (e.g.  $\alpha$ ,  $\beta$ -unsaturated alcohols) and whether the Au NP/Pd(II) salt mixtures showed strong activities for other substrates as well. In order to activate other allylic and benzylic alcohols with moderate conversions, it was necessary to increase reaction temperatures to 60 °C using 1 atm oxygen as the oxidant (but no external base has been added to the system). Catalysis results for the five chosen  $\alpha$ ,  $\beta$ -unsaturated alcohols are shown in Table 2, and the major and minor products are shown in Scheme 1. For all the systems studied, Au NPs showed no or next to no activity under these conditions. Results for the K<sub>2</sub>PdCl<sub>4</sub> salt by itself were non-uniform; both cinnamyl alcohol and crotyl alcohol showed significant conversions over 24 h in the presence of the Pd(II) salt alone, while the other substrates did not react to any significant extent. Similarly, Pd NPs by themselves did not show significant activities for many substrates, although nearly 12% conversion was seen for allyl alcohol. Interestingly, both the sequentially-grown 1:3 AuPd NPs and the 1:3 Au NP/Pd(II) mixtures showed moderate activity for most substrates, typically with similar conversions and selectivities towards the aldehyde (or ketone in the case of 1-hexen-3-ol) product. For 1-hexen-3-ol, the 1:3 Au NP/Pd(II) mixture showed significantly higher reactivity, for reasons that are not known at this time. High selectivities towards the aldehyde product were seen for benzyl and cinnamyl alcohols, while moderate selectivities were seen in the crotyl alcohol reaction, in which significant hydrogenation and isomerization products were also seen at short time periods. For 1-hexen-3-ol, the major product of the reaction was actually the saturated ketone, 3-hexanone, which is an isomerization/tautomerization product (or a hydrogenation+oxidation product) [38,39]; while the expected oxidation product, 1-hexen-3-one was formed in much lower amounts. Similarly, the major product for the allyl alcohol oxidation reaction was the isomerization/tautomerization product, 1-propanal. Similar reactivity of allyl alcohol to give large amounts of 1-propanal has been previously documented by our group using Pd catalysts under hydrogenation conditions [39]. The formation of minor hydrogenation products in many reactions can be attributed to a partial hydrogen coating on the NP surface, since it has been shown by Schwabe that even

# Table 2

Summary of catalytic results for the oxidation of  $\alpha$ , $\beta$ -unsaturated alcohols using PVP-stabilized NPs in water.<sup>a</sup>

Substrate	NP catalyst	Conversion <sup>b</sup>	Selectivity (%)		
			Aldehyde or ketone	Other	
Allyl alcohol	Au NPs	0	0	0	
-	K <sub>2</sub> PdCl <sub>4</sub>	2	66	34	
	Pd NPs	11.6	29	71 <sup>d</sup>	
	1:3 AuPd Seq. NPs	19.9	14	86 <sup>d</sup>	
	1:3 Au/Pd(II)	17.1	9	91 <sup>d</sup>	
Benzyl alcohol	Au NPs	0	0	0	
benzyraconor	K <sub>2</sub> PdCl <sub>4</sub>	2.3	100	0	
	Pd NPs	2.7	100	0	
	1:3 AuPd Seq. NPs	4.3	100	0	
	1:3 Au/Pd(II)	3.1	100	0	
Cinnamyl alcohol	Au NPs	0	0	0	
	K <sub>2</sub> PdCl <sub>4</sub>	34.3	96	4	
	Pd NPs	6.8	100	0	
	1:3 AuPd Seq. NPs	34.2	89	11	
	1:3 Au/Pd(II)	29.3	90	10	
Crotyl alcohol	Au NPs	-	-	-	
Crotyl alcohol	K <sub>2</sub> PdCl <sub>4</sub>	14.0	34	66	
	Pd NPs	-	-	-	
	1:3 AuPd Seq. NPs	36.9	73	27	
	1:3 Au/Pd(II)	37.9	65	35	
1-Hexen-3-ol	Au NPs	0	0	0	
	K <sub>2</sub> PdCl <sub>4</sub>	Trace amounts	~97	~3	
	Pd NPs	Trace amounts	~37	~63	
	1:3 AuPd Seq. NPs	17.3 <sup>c</sup>	29	71 <sup>e</sup>	
	1:3 Au/Pd(II)	35.1 <sup>c</sup>	27	73 <sup>e</sup>	

<sup>a</sup> Reaction conditions: All reactions are carried out at 60 °C with a substrate: catalyst ratio of 500:1.

<sup>b</sup> Conversions and selectivities listed over 24 h.

<sup>c</sup> Conversions and selectivities listed after 4 h.

<sup>d</sup> Major product for allyl alcohol reaction 1-propanal (isomerization product),  $\alpha$ , $\beta$ -unsaturated ketone (prop-2-en-1-al) was minor product.

e Major product for 1-hexen-3-ol reaction is 3-hexanone (isomerization product), α,β-unsaturated ketone (1-hexen-3-one) was minor product.

during oxidation of alcohols, the potential of Pt-group metals lie in the "hydrogen region" [40].

Interestingly, for crotyl alcohol, which we have previously shown can be activated at room temperature in the absence of base with excellent conversions and a high selectivity to crotonalde-hyde [25], the harsher reaction conditions ( $60 \,^\circ C$ ) here generally

lead to lower overall conversions for both the AuPd NPs and Au NP/Pd(II) systems with moderate selectivities to crotonaldehyde; also, moderate decompositions to CO and propene were seen after 8 h [21,41]. The reaction has a TOF of 120 moles product/moles catalyst  $h^{-1}$  over the first hour, which is comparable to earlier room-temperature work [18,25], followed by a drastic reduction



Scheme 1.

in the reaction rate after 1 h. We believe that the decrease in TOF after 1 h and thus the lower overall conversions after 24 h seen at these higher temperature conditions are due to significant Ostwald ripening of the particles during the catalyst experiment. To further explore this, the nanoparticle catalysts were examined after the catalytic reaction, Fig. 1(C) and (D) shows the final TEM images of the Au NP/Pd(II) and sequentially-grown AuPd NP systems, respectively, after 24 h reaction. Significant growth in the NPs are seen in both systems; the Au NP/Pd(II) system showed a bimodal distribution with the presence of extremely large particles and an average particle size of 6.4 nm  $\pm$  7.8 nm, while the sequentially-grown AuPd NP system showed wormlike particles after the 24 h reaction (no particle size is reported due to the change in morphology). In the absence of a catalytic reaction (e.g. just heating to 60 °C) there is typically no change in average particle sizes in these systems. Both of these results suggest significant ripening of particles during the catalytic reaction, likely due to an Ostwald ripening mechanism. Previously we indicated that the mechanism for this reaction may be a redox mechanism in which the Pd is oxidized to Pd(II) and reformed upon reaction with the alcohol substrate [25]; and others have also supported an Pd(II) oxidation mechanism [24]. Such a mechanism is likely to lead to homogeneous Pd(II) species in solution during the catalytic reaction which would greatly enhance Ostwald ripening. Indeed, others have shown that Pd(II) species can react stoichiometrically with many  $\alpha$ , $\beta$ -unsaturated alcohols [42,43]. Thus the lower activities seen for crotyl alcohol at 60 °C seems mostly due to the large changes seen in particle size during the reaction; at lower temperatures the Ostwald ripening is much slower, thus allowing for higher-surface area NPs to remain active for longer periods of time. We believe the role of the Au in this reaction is to destabilize the Pd to oxidation by oxygen, thus allowing the reaction to turnover.

Finally, in order to further examine both the structure of the sequentially grown AuPd NPs and the reaction product in the Au NP/Pd(II) system, these systems were examined via EXAFS analysis. Fig. 3 shows the Au Lui-edge and Pd K-edge EXAFS spectra in *k*-space for the pure Au and Pd NPs, sequentially grown AuPd NPs, and the final nanoparticles in the Au NP/Pd(II) system (after 24 h reaction with crotyl alcohol); high quality data was collected over a k-range from 0 to 14 for the Au edge and 0 to 10 for the Pd edge. Both the Pd and Au edge k-space data show that the reaction product in the Au NP/Pd(II) system has similar chemical environments around the Au and Pd absorber atoms as the as-synthesized sequentially grown AuPd NPs. The shift in periodicity on the Au k-space data suggests some alloying of Au and Pd in both the bimetallic samples [33,44,45]. Fig. 4 shows the experimentally obtained EXAFS data in R-space with the single-shell theoretical fits for sequentially grown AuPd NPs and the final nanoparticles in the Au NP/Pd(II) system. For the bimetallic NPs, the Au and Pd EXAFS data of the same sample were simultaneously fit using the IFEFFIT software package [35]. High-quality fits have been obtained for both the bimetallic AuPd samples. We note that the Pd data shows significant Pd-Pd and Pd-Au coordination environments but minimal Pd-O and/or Pd-Cl contributions (a very small shoulder can be seen on the low *r*-side of the Pd data); thus during the reaction, the Pd(II) is definitively reduced to form bimetallic NPs in the Au NP/Pd(II) system. The structural fit parameters for the sequentially grown AuPd NPs and the reaction 0 to 10 product in the Au NP/Pd(II) system generated from the EXAFS fitting parameters are presented in Table 3. In both cases, reasonable fits were obtained; however, higher errors in coordination number for the Pd nearest neighbour were seen, which is likely both due to the lower quality of Pd edge data and inhomogeneities in the actual samples (which are particularly evident in the TEM of the reaction product in the Au NP/Pd(II) system). Higher Pd loadings in sample may allow for quality data acquisition to higher k-space values in the future, though heterogeneity



**Fig. 3.** EXAFS spectra in *k*-space for monometallic Au, Pd and sequentially-grown 1:3 AuPd NPs and Au NP/Pd(II) 1:3 mixture after 24 h reaction with crotyl alcohol. (A) Pd K-edge, (B) Au L<sub>III</sub>-edge.

problems will likely compromise data quality regardless. We note that because of these errors one cannot make any definitive conclusions regarding the final structures of the AuPd particles; however, the EXAFS data unambiguously indicates that nearly all the Pd is in the zerovalent state in both systems, and that core–shell morphologies are unlikely as the total first shell Au coordination number (e.g.  $N_{Au-Au} + N_{Au-Pd}$ ) is significantly below the bulk fcc value of 12 for both systems. The moderate  $N_{Au-Pd}$  and  $N_{Pd-Au}$  values (albeit with high errors on the latter) also indicates that significant Au/Pd mixing is seen in both these systems.

# 3.2. Oxidation reactions in ILs

We have recently shown that the trihexyl(tetradecyl) phosphonium chloride (P[6,6,6,14]Cl) IL is an excellent stabilizer for both Au and Pd NPs for hydrogenation reactions [32]. In this IL, the source of NP stabilization is thought to be twofold: the halide ions that interact with the NP surface, and the long-chain hydrocarbons that provide steric protection in the form of a secondary coordination shell. Weaker coordinating anions such as triflate were found to have much lower stabilizing effects in previous work [32]. As AuPd NP recyclability is a major challenge in the water system above (since the products need to be extracted using ethyl acetate or a similar solvent), we were curious as to



Fig. 4. EXAFS single-shell fits in *R*-space for sequentially-reduced 1:3 AuPd NPs at the (A) Au L<sub>III</sub> and (B) Pd K-edges and Au NP/Pd(II) 1:3 mixture after 24 h reaction with crotyl alcohol at the (C) Au L<sub>III</sub> and (D) Pd K-edges.

whether the reaction could proceed in a more recyclable solvent system such as an IL. This system is attractive as it would allow for the products and un-reacted substrates to be removed from the reaction mixture by vacuum extraction, allowing for a potential re-use of the IL/NP catalyst system.

TEM images in Fig. 5 show the Au, Pd NPs and sequentially grown 1:3 AuPd NPs before and after reaction. Before reaction, the Au, AuPd and Pd average NP sizes are 2.2 nm  $\pm$  0.8 nm, 3.7 nm  $\pm$  1.0 nm, and  $4.3 \text{ nm} \pm 1.3 \text{ nm}$ , respectively (see Table 1). The Pd NPs are larger than those formed in the aqueous system above, but in general agreement with our previous work [32]. The larger size of the NPs is confirmed by UV-Vis spectroscopy as shown in Fig. 6; a significant plasmon band at 530 nm is seen for the Au NPs, which dampens significantly upon sequential Pd deposition. However, there is a significant growth of particles during a 12h catalytic cycle, as seen in Fig. 5(D–F); the Pd and Au NP/Pd(II) system grow to  $9.0 \text{ nm} \pm 2.9 \text{ nm}$  and  $8.7 \text{ nm} \pm 3.9 \text{ nm}$ , respectively, while the sequentially grown AuPd system shows a bimodal distribution with a significant number of particles above 10 nm. Since halide ions are also known to promote oxidative etching of Pd, NPs in halide ILs in the presence of oxygen form an unique system in which both Pd and Au oxidation can occur [46]. Evidently an Ostwald ripening mechanism in which Pd (and potentially Au as well) are oxidized and re-reduced upon stoichiometric reactions with the alcohol substrates is occurring to an even greater extent in the IL system as compared to the aqueous system above, due to the extremely high chloride environment in these ILs.

Table 4 shows the product distributions for the catalytic oxidations of four of the various  $\alpha$ , $\beta$ -unsaturated alcohols in trihexyl(tetradecyl)phosphonium chloride. We note that 5000:1 ratios of substrate to catalyst were used for the IL work, rather than the 500:1 ratios in the aqueous work, as vacuum stripping of the products and leftover substrates was more reliable at higher substrate levels and IL-stabilized NPs were still quite stable in the presence of larger amounts of substrate. While the Au NPs showed almost no catalytic activity in the absence of Pd(II) salts, but were active with Pd(II) salts present, Pd NPs and 1:3 AuPd NPs showed variable degrees of conversion for most of the substrates under the reaction conditions. Several things can be noted from the catalyst data; first, the overall conversions over 12 h for reactions in the IL are in most cases much higher than their respective aqueous systems. In particular, aromatic systems such as benzyl alcohol and

#### Table 3

EXAFS fitting parameters for AuPd NP systems.

Nanoparticle sample	Shell	Ν	<i>R</i> (Å)	$\Delta E^0 (\mathrm{eV})$	$\sigma^2$ (Å <sup>2</sup> )	<i>R</i> -factor
1:3 AuPd sequentially grown NPs	Au–Au	5.9 (0.8)	2.812 (0.008)	4.4	0.010 (0.001)	0.020
	Au–Pd	2.4 (0.4)	2.768 (0.009)	(0.5)	0.008 (0.001)	
	Pd–Pd	6.0 (2.6)	2.73 (0.02)	-4.1	0.008 (0.004)	
	Pd–Au	3.8 (2.5)	2.768 (0.009)	(2.6)	0.008 (0.001)	
1:3 Au NPs/Pd(II) after reaction	Au–Au	6.4 (0.7)	2.814 (0.007)	4.9	0.009 (0.001)	0.014
	Au–Pd	3.4 (0.4)	2.777 (0.007)	(0.4)	0.007 (0.001)	
	Pd–Pd	7.0 (3.1)	2.76 (0.02)	3.0	0.008 (0.004)	
	Pd-Au	2.9 (2.7)	2.777 (0.007)	(1.2)	0.007 (0.001)	



Fig. 5. TEM images of as-synthesized P[6,6,6,14]Cl IL-stabilized (A) Pd NPs, (B) sequentially-reduced 1:3 AuPd NPs, and (C) Au NPs; and after 24 h reaction with cinnamyl alcohol: (D) Pd NPs, (E) sequentially-reduced 1:3 AuPd NPs, and (F) Au NP/Pd(II) 1:3 mixture.

cinnamyl alcohol show extremely high conversions with high and moderate selectivities towards the aldehyde, respectively. Again, the major product for the allyl alcohol oxidation reaction is actually the isomerization/tautomerization product, 1-propanal (which could also be formed as a hydrogenation + oxidation product). The activities towards crotyl alcohol oxidation are somewhat similar to that of the aqueous system, albeit with significantly lower selectivities. In order to ensure that the change in substrate:catalyst ratio did not adversely affect the comparison of aqueous/IL systems, crotyl alcohol oxidation was examined in the IL system with a 500:1 substrate:product ratio, and similar yields and selectivities to crotonaldehyde were seen for both Pd NPs (62% conversion, 43% selectivity) and sequentially grown 1:3 AuPd NPs (66% conversion, 56% selectivity) systems. The major finding is that AuPd NPs show



Fig. 6. UV-Vis spectra of P[6,6,6,14]Cl IL-stabilized Au, Pd, and sequentially-grown 1.3 AuPd NPs

#### Table 4

Summary of catalytic results for the oxidation of  $\alpha$ , $\beta$ -unsaturated alcohols using P[6,6,6,14]Cl-stablized NPs.ª

Substrate	NP catalyst	Conversion <sup>b</sup>	Selectivity (%)	
			Aldehyde	Other
Allyl alcohol	Pd NPs	66	17	83 <sup>c</sup>
	1:3 AuPd Seq. NPs	47	21	79 <sup>c</sup>
	1:3 Au/Pd(II)	45	27	73 <sup>c</sup>
Benzyl alcohol	Pd NPs	97	99	1
	1:3 AuPd Seq. NPs	84	97	3
	1:3 Au/Pd(II)	90	98	2
Cinnamyl alcohol	Pd NPs	99	70	30
	1:3 AuPd Seq. NPs	81	91	9
	1:3 Au/Pd(II)	98	74	26
Crotyl alcohol	Pd NPs	53	47	53
	1:3 AuPd Seq. NPs	50	46	54
	1:3 Au/Pd(II)	50	58	42

<sup>a</sup> Reaction conditions: All reactions are carried out at 60 °C with a substrate: catalyst ratio of 5000:1.

<sup>b</sup> Conversions and selectivities listed over 12 h.

<sup>c</sup> Major product for allyl alcohol reaction is 1-propanal (isomerization product),  $\alpha$ . $\beta$ -unsaturated ketone (prop-2-en-1-al) was minor product.

no exceptional abilities in terms of catalytic performance and/or product selectivity compared to Pd NPs in this particular system, likely due to the ease at which Pd can be oxidized in this IL as compared to water. Indeed, we have previously noted facile oxidation of Pd NPs upon heating in the P[6,6,6,14]Cl ILs [32]. This easier oxidation of Pd in the IL system allows for higher turnovers of the redox catalytic cycle even in the absence of the Au promoter. Thus the Pd NP/IL system has some promise for the possibility of high activities for mild alcohol oxidations; however, in order to optimize the system, it would be desirable to attempt to minimize the particle growth occurring in the system. Alternatively, we have previously shown that complete oxidation of Pd NPs can allow for a facile reformation of Pd NPs in P[6,6,6,14]Cl systems by re-addition of a reducing agent such as LiBH<sub>4</sub> [32]. This would, in principle, allow for the recycling of the Pd NP/IL system over a large number of cycles. We will continue to explore this system for recyclable oxidation reactions in the future.

# 4. Conclusions

In summary, the present study considers the NP-catalyzed oxidation of  $\alpha,\beta$ -unsaturated alcohols in water and in a tetraalkylphosphonium IL at 60 °C. In water sequentially grown AuPd NPs, either formed intentionally or in situ, were found to be active for most  $\alpha$ ,  $\beta$ -unsaturated alcohols; although particle size growth due to Ostwald ripening was problematic. TEM and EXAFS studies of sequentially grown AuPd NPs and Au NP/Pd(II) mixtures indicated that both systems led to the formation of AuPd NPs with some mixing of Pd and Au in their structures. Conversely, we found that Pd NPs alone have significant catalytic activity in tetraalkylphosphonium chloride ILs, likely due to the ease of oxidation of Pd in the high chloride environment. As such, Au promoters have little to no effect on Pd catalytic activity in the IL system. The concept of using a recyclable solvent in catalytic alcohol oxidations still remains a problem worthy of intensive research.

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