# Alcohol oxidations in aqueous solutions using Au, Pd, and bimetallic AuPd nanoparticle catalysts

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## Abstract

Alcohol oxidations under mild conditions using polyvinylpyrrolidone (PVP)-stabilized Au, Pd and bimetallic AuPd nanoparticle catalysts in aqueous solutions have been investigated. The catalytic activities of the nanoparticles towards the oxidation of benzyl alcohol, 1-butanol, 2-butanol, 2-buten-1-ol and 1,4-butanediol indicate that bimetallic 1:3 Au:Pd nanoparticles have higher catalytic activities than Au, Pd and other bimetallic AuPd nanoparticles, and that selectivities towards specific products can often be tuned using bimetallic particles. In addition, advantages and disadvantages for the use of such nanoparticle catalysts as mild, environmentally-friendly oxidation catalysts are examined.
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## 1. Introduction

Oxidation of alcohols to their respective aldehyde or ketone is a useful and fundamental organic reaction [1,2]. Traditionally, this oxidation is performed using stoichiometric amounts of oxidants, such as permanganate [3], chromate [2,4], or bromate [5]. These methods produce a large amount of waste, and are unacceptable in view of green chemical practices. Recently, transition metal nanoparticle-catalyzed aerobic alcohol oxidations have been investigated, and many have shown high catalytic activities and good selectivities [6–17]. However, despite this progress, there are still persistent problems in this field. First, many oxidation reactions are conducted in organic solvents or solvent-less conditions [6,7,10,12,13], and the resulting mixtures of the organic substrates, products, solvents and molecular oxygen can be quite dangerous. Also, some oxidation reactions have to be performed under severe conditions, such as high temperature and high oxygen pressure [6,7,14]. Finally, a number of catalysts have only been shown to be active for specific types of alcohols. For example, Biffis et al. [8] have

shown that microgel-stabilized Pd nanoclusters are effective for the selective oxidation of secondary alcohols, while Abad et al. [6,7] have noted that ceria-supported Au nanoparticle catalysts are most suitable for the aerobic oxidation of allylic alcohols and can effectively prevent the isomerization and hydrogenation of C=C double bonds. Therefore there is still significant demand for catalyst systems which can activate a wide range of substrates and can be used under mild, aqueous conditions [15,16,18].

Herein, we show that polyvinylpyrrolidone (PVP)-stabilized bimetallic AuPd nanoparticle catalysts in aqueous solutions can be used as effective catalysts for a wide range of alcohol oxidation reactions under mild conditions. This work builds on the earlier observations by Tsunoyama and coworkers [18] that PVP-stabilized Au nanoparticles could be successfully used for the aerobic oxidation of benzylic alcohols in water. The Au nanoparticles had high catalytic activities, and the PVP stabilizer effectively prevented the agglomeration of nanoparticles during the course of the catalytic oxidations in aqueous solution. Several groups have also recently examined supported-bimetallic PdAu nanoparticles as catalysts with increased activity and product selectivity of alcohol oxidation reactions. Specifically, Enache et al. [10] and Dimitratos et al. [19] have both observed that supported-AuPd bimetallic catalysts have

improved activity and selectivity of desired products for aerobic oxidations of alcohols, presumably due to synergetic electronic interactions between Au and Pd atoms in the individual nanoparticles [20]. Thus we wished to investigate whether polymer-stabilized, solution-phase bimetallic AuPd nanoparticles would also show significantly enhanced activities and desirable product selectivities for aerobic alcohol oxidations. Herein we report the synthesis of PVP-stabilized Au, Pd and AuPd bimetallic nanoparticle catalysts, and show that the resulting nanoparticles can catalyze the oxidation of benzyl alcohol, 1-butanol, 2-butanol, 2-buten-1-ol and 1,4-butanediol in aqueous solutions under an oxygen atmosphere.

## 2. Experimental and methods

### 2.1. Materials

Poly($N$-vinyl-2-pyrrolidone) (M.W. 40,000), hydrogen tetrachloroaurate hydrate (99.9%), potassium tetrachloropalladate (99.99%), benzyl alcohol (99+%, ACS), 2-butanol (99.9%), 1,4-butanediol (99.9%) and 2-buten-1-ol (predominantly trans, 97%) were purchased from Alfa and were used without further purification. Sodium borohydride powder (98%) was obtained from Aldrich and was used as obtained. $K_2CO_3$ (anhydrous) was obtained from EMD Chemicals Inc. and was used without further purification. $n$-Butanol (ACS) was obtained from EM Science and was used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories. 18 M$\Omega$ cm Milli-Q water (Millipore, Bedford, MA) was used throughout.

### 2.2. Preparation of PVP stabilized 1:3 Au:Pd nanoparticles

The following procedure was used to prepare PVP stabilized 1:3 Au:Pd nanoparticles [18]. First, 0.188 ml of a 10 mM potassium tetrachloropalladate solution ($1.88 \times 10^{-6}$ mol) and 0.062 ml of a 10 mM hydrogen tetrachloroaurate trihydrate solution ($0.62 \times 10^{-6}$ mol) was added to 2 ml of deionized water with stirring. Next, 0.5 ml of a 1.39 mM PVP solution ($6.95 \times 10^{-7}$ mol) was added. This mixture was then stirred for 30 min at 0 °C. Finally, 0.25 ml of a fresh 0.10 M sodium borohydride solution ($2.5 \times 10^{-5}$ mol) was added. After stirring for an additional 30 min the PVP stabilized 1:3 Au:Pd NPs were diluted to 5.0 ml. Au, Pd and other bimetallic Au:Pd nanoparticles were prepared as stated above keeping the total molar amount of metal salt constant.

### 2.3. Oxidation reactions

The following procedure was used to oxidize benzyl alcohol [18]. First, 5.0 ml of the previously prepared nanoparticles, 51.9 mg of potassium carbonate ($3.75 \times 10^{-4}$ mol) and 2.5 ml of deionized water were mixed together with vigorous stirring at 1080 rpm with a magnetic stir bar. Next, 129 μl of benzyl alcohol ($1.25 \times 10^{-3}$ mol) was added (for a substrate:catalyst ratio of 500:1). For alternative substrates the catalytic reactions were performed as above but substituting the benzyl alcohol

with other alcohols. For these studies, both the nanoparticle catalyst and substrate amounts were increased by a factor of five, which necessitated a doubling of the PVP stabilizer in order to keep the particles stable during the oxidation of benzyl alcohol and 1-butanol.

NMR, GCMS and GC samples were prepared as follows: 1 ml of the solution was taken out from the oxidation reaction system and placed in a vial and 500 μl of 1.0 M hydrochloric acid ($5 \times 10^{-4}$ mol) was added. Then 1 ml of $CDCl_3$ was added, and the vial was shaken to transfer the substrates and products into the organic phase. The $CDCl_3$ was then extracted and characterized by $^1$H NMR and/or GCMS, GC. Turnover frequencies (TOFs), conversions and selectivities were determined from NMR. Turnover frequencies (TOFs) were determined from the slope of linear plots of turnover (mol product (aldehyde + acid + benzoate)/mol Pd + Au) vs time for initial studies and calculated using the molar ratio of the converted substrate over the catalyst divided by the reaction time for subsequent studies. Turnover numbers generated from NMR results were verified by GC or GCMS for several substrates; in all cases, both methods gave comparable results. Control experiments in which no nanoparticles were present showed no background alcohol oxidation was occurring over 24 h.

### 2.4. Characterization

UV–vis spectra were obtained using a Varian Cary 50 Bio UV–Visible spectrophotometer with a scan range of 300–900 nm with an optical path length of 1.0 cm. $^1$H NMR spectra were obtained using a Bruker 500 MHz Avance NMR spectrometer; chemical shifts were referenced to the residual protons of the deuterated solvent. Transmission electron micrographs (TEM) were obtained with a Philips 410 microscope operating at 100 keV. To prepare samples for TEM, a drop of the solution containing the nanoparticles was placed on a carbon-coated Cu grid which had been pretreated by plasma discharge. Gas chromatography data was obtained using a HP 4890D gas chromatograph and a HP 3393A Integrator using pure acetophenone as an internal standard. The identity of products was confirmed by GC-MS (GC EI + Magnet VG 70SE) in subsequent studies.

## 3. Results and discussion

Poly($N$-vinyl-2-pyrrolidone) (PVP) stabilized Pd, Au, and bimetallic AuPd particles were synthesized via $NaBH_4$ reduction of aqueous solutions of the metal salts in the presence of the polymer. TEM images of the resulting Pd, Au, and AuPd nanoparticles stabilized with PVP are shown in Fig. 1. The average size of the PVP stabilized Au and Pd nanoparticles that were synthesized were measured through TEM was found to be $3.3 \pm 0.8$ nm and $3.9 \pm 2.8$ nm, respectively, while the bimetallic AuPd nanoparticles had average particle sizes of $2.7 \pm 0.7$ nm (Au:Pd = 1:3), $2.7 \pm 1.2$ nm (Au:Pd = 1:1) and $4.0 \pm 1.7$ nm (Au:Pd = 3:1). The PVP stabilized metal nanoparticles are known to be weakly stabilized through multiple coordination of the amido sites of the PVP [18,21]. Fig. 2
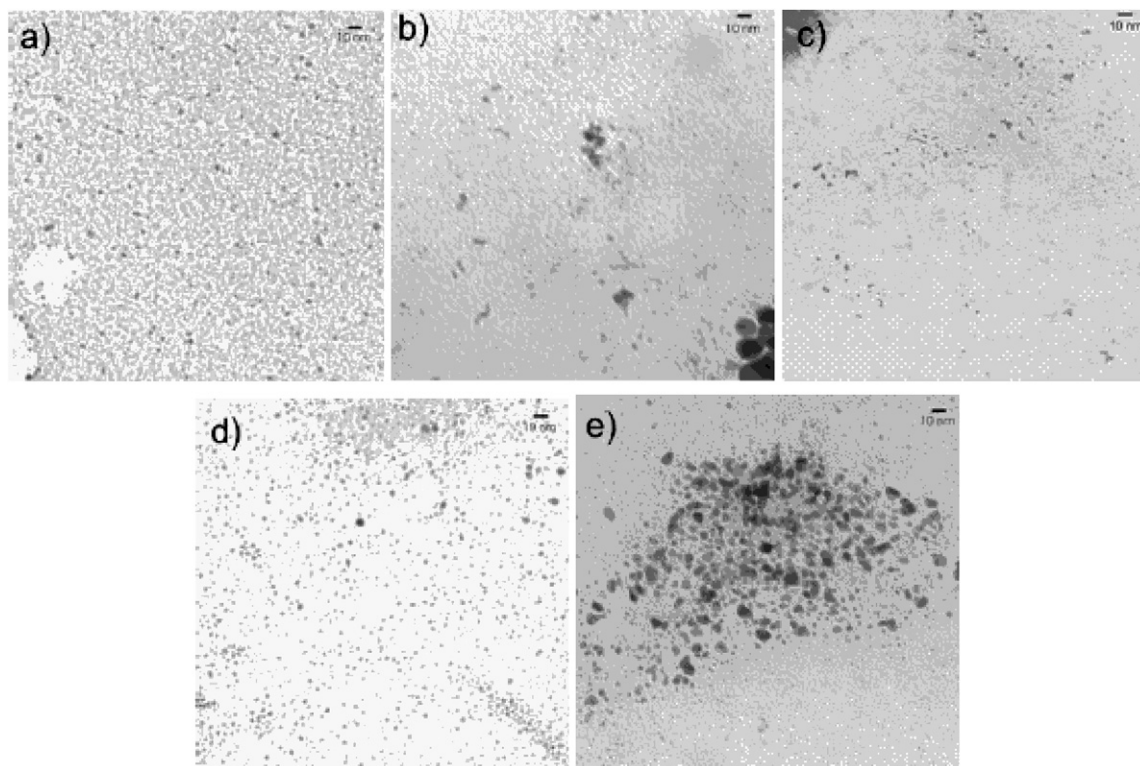
Fig. 1. TEM images of PVP-stabilized (a) Au nanoparticles, (b) Pd nanoparticles, (c) 1:3 Au:Pd nanoparticles, (d) 1:1 Au:Pd nanoparticles, (e) 3:1 Au:Pd nanoparticles.
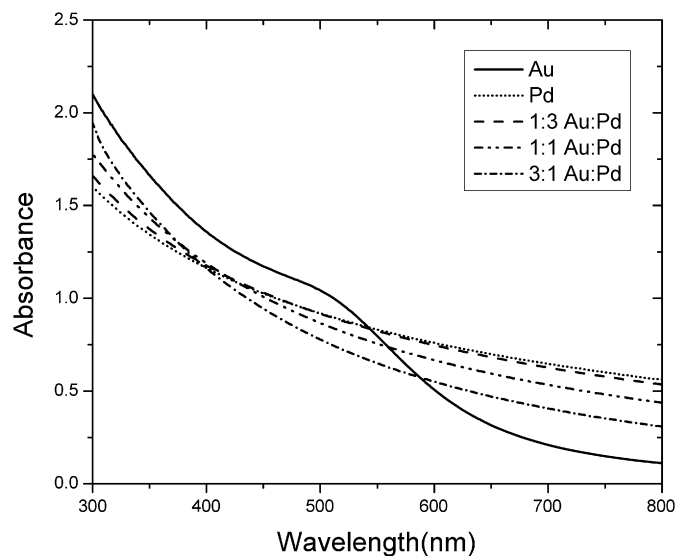


Fig. 2. UV–vis spectra of PVP-stabilized Au, Pd, and Au:Pd nanoparticles.

shows representative UV–vis spectra of the AuPd bimetallic series after reduction with sodium borohydride. UV–vis spectra of the AuPd nanoparticles show an exponentially increasing absorbance toward higher energy; this is a consequence of interband transitions of the newly formed bimetallic AuPd nanoparticles [22,23]. In contrast, the PVP-stabilized Au nanoparticles show a broad plasmon band around 515 nm after reduction, which is in general agreement with TEM results (3.3 ± 0.8 nm). These results show that as-synthesized nanoparticles with similar particle sizes (2.5–4.0 nm) can be stabilized with the PVP

stabilizers over all Au:Pd bimetallic ratios. Of note is the absence of any plasmon bands in the bimetallic nanoparticles, which suggests that all particles are bimetallic with no separate formation of pure Au nanoparticles [24].

The catalytic activity of the nanoparticles towards the oxidation of benzyl alcohol was measured over seven hours (see Section 2), and the formation of benzaldehyde and benzyl benzoate was observed. GC and GCMS results confirmed the presence of benzyl benzoate and absence of benzylic acid as a product. Quantitative yields and turnover frequencies of the two products were determined based on the integration of the respective peaks of the pure alcohol, aldehyde and benzoate. For the PVP stabilized bimetallic nanoparticles (Table 1, entries 1–5) the 1:3 Au:Pd nanoparticles showed the highest turnover frequency for the oxidation of benzyl alcohol in air at room temperature. Such enhancements of catalytic activity have previously been seen for many AuPd systems [19,24], and are thought to be due to synergistic electronic effects in which Au atoms draw electron density away from Pd atoms, thereby enhancing the interaction of Pd atoms with the substrate [20]. The selectivity of each oxidation reaction was also determined, and the results can be seen in Table 1 entries 1–5 for each different type of nanoparticle. When pure Au nanoparticles were used for the oxidation of benzyl alcohol, nearly equal amounts of benzaldehyde and benzyl benzoate were produced, in agreement with previous work by Tsunoyama et al. [18]. However, when Pd and AuPd bimetallic nanoparticles were used for the oxidation, benzaldehyde was produced preferentially with nearly 100% selectivity. Enache and coworkers [10] previously investigated the oxidation of benzyl

Table 1

Turnover frequencies and selectivities for benzyl alcohol oxidation with PVP stabilized Au, Pd and Au:Pd bimetallic nanoparticles

| Entry | Type of NP | Conditions | Turnover frequency $(h^{-1})$[a] | Selectivity | |
|---|---|---|---|---|---|
| | | | | Benzal-dehyde | Benzyl benzoate |
| 1 | Au | 298 K, air | 8.6 | 52.8 | 47.2 |
| 2 | 3:1 Au:Pd | 298 K, air | 8.6 | 86.1 | 13.9 |
| 3 | 1:1 Au:Pd | 298 K, air | 7.1 | 96.9 | 3.1 |
| 4 | 1:3 Au:Pd | 298 K, air | 11.5 | 97.9 | 2.1 |
| 5 | Pd | 298 K, air | 6.2 | 100 | 0 |
| 6 | Au | 298 K, $O_2$ | 3.9 | 100 | 0 |
| 7 | 1:3 Au:Pd | 298 K, $O_2$ | 26.2 | 98.1 | 1.9 |
| 8 | Pd | 298 K, $O_2$ | 3.7 | 100 | 0 |
| 9 | Au | 358 K, $O_2$ | 14.3 | 97.3 | 2.7 |
| 10 | 1:3 Au:Pd | 358 K, $O_2$ | 57.3 | 100 | 0 |
| 11 | Pd | 358 K, $O_2$ | 32.0 | 100 | 0 |

*Note.* Conditions: moles $(Pd + Au) = 2.5 \times 10^{-6}$ mol, $Pd + Au$:substrate = 500:1.

[a] The turnover frequency is the mean value over 6 h measured by plots of mol product (aldehyde + acid + benzoate)/mol Pd + Au vs time. The values do not include alcohol consumed via esterification with benzoic acid to form the benzoate.

alcohol at 373 K with $O_2$ as oxidant in the absence of solvent using $TiO_2$-supported PdAu catalysts, and also found that the bimetallic catalysts were very active for this reaction with high selectivity to benzaldehyde ($\geqslant 96\%$) at high conversion rates.

The conditions were varied in order to maximize the catalytic activity of the nanoparticles. Interestingly, it was found that the TOF for the oxidation of benzyl alcohol by the 1:3 Au:Pd nanoparticles increased to 26.2 h$^{-1}$ from 11.5 h$^{-1}$ upon replacing the atmosphere with pure $O_2$ at 298 K, while slight decreases were seen for both the pure Au and Pd nanoparticles (Table 1, entries 6–8). While we are still uncertain as to the origin of the decreasing catalytic activities for the pure Au and Pd nanoparticles, the results for the 1:3 Au:Pd nanoparticle catalysts suggest that under these experimental conditions the solubility of oxygen in water was a rate-limiting step in the catalytic oxidation reaction. Increasing the reaction temperature to 358 K led to even further increases in the catalytic activity for all three catalysts (Table 1, entries 9–11), with the 1:3 Au:Pd nanoparticles showing a TOF of 57.3 h$^{-1}$ with 100% selectivity towards benzaldehyde under these conditions, which is four times greater than the activity of the Au nanoparticles under these conditions and nearly two times greater than the corresponding Pd nanoparticles. Interestingly, for reactions under pure $O_2$, the selectivity of PVP-stabilized Au nanoparticles shifted nearly completely towards the formation of benzaldehyde, though we are still investigating the source of this selectivity change. Finally, the catalysts retained their activity over 24 h reaction cycles under these conditions, and no precipitation of the PVP-stabilized particles was seen over the course of the reaction. Indeed, after undergoing an oxidation reaction for 24 h under $O_2$ at 358 K; the particle size as determined by TEM increased only very slightly from $2.7 \pm 0.7$ nm to $2.8 \pm 0.6$ nm.

The kinetics of the above reaction were carefully examined to attempt to determine whether the final conditions used (1 atm
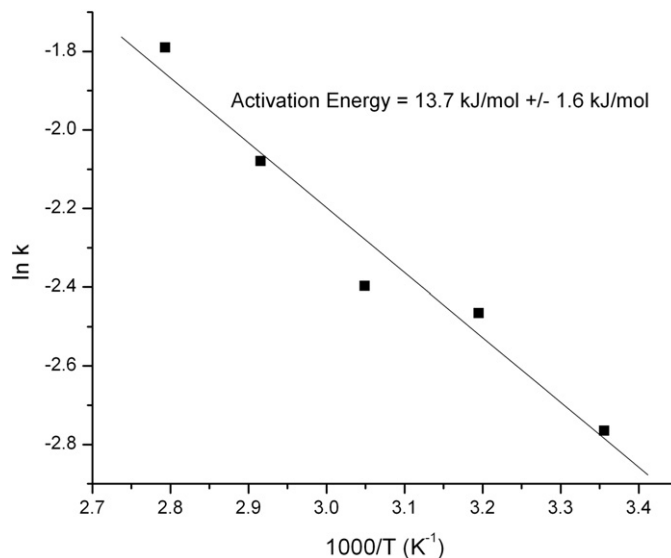


Fig. 3. Arrhenius plot of PVP-stabilized 1:3 Au:Pd nanoparticles at 358 K in 1 atm $O_2$.

$O_2$, 358 K) were kinetically-limiting at the catalyst concentration chosen, or if there was still a mass-transport limitation with respect to $O_2$ under these conditions. Lowering the stirring speed (from 1080 to 720 rpm) led to falling TOFs over time, suggesting that mass-transport limitations become quite strong at lower stirring rates. Attempts to lower the catalyst concentration to ensure the reaction was under kinetically-limiting conditions invariably led to de-activation of the PdAu nanoparticle catalysts within an hour. Indeed, others have previously shown for Pd and Pt nanoparticle catalysts that kinetically-limiting conditions can lead to over-oxidation and poisoning of the particle surface, and that alcohol oxidations can be considerably faster under mass-transport-limiting conditions, in which just enough oxygen is present to clean the surface but not to oxidize the metal surface [25,26]. Thus it is likely that mild mass transport limitations exist for the reaction under these conditions. Such mass-transport-limited conditions appear unavoidable as nanoparticle stability is severely problematic under kinetically-limiting conditions. Finally, the measured effective activation energy for the 1:3 Au:Pd nanoparticles was found to be ca. 14 kJ/mol (Fig. 3), which is much lower than that seen previously for pure PVP-stabilized Au and Pd nanoparticles (20 and 33 kJ/mol, respectively), [18] which lends further support to the likelihood that mass-transport limitations exist under these conditions.

Intrigued by these initial results, we wished to examine the generality of the alcohol oxidation reaction using the 1:3 Au:Pd catalysts at scaled-up conditions. The catalytic activity of the 1:3 Au:Pd nanoparticles toward other alcohol substrates (1-butanol, 2-butanol, 2-buten-1-ol and 1,4-butanediol) were subsequently examined under 1 atm $O_2$ at 335 K; the results are summarized in Table 2 and Scheme 1. For these studies, both the amount of nanoparticle catalyst and the substrate were increased by a factor of five from earlier studies; this necessitated a further doubling of the amount of PVP stabilizer in order to keep the particles stable during the oxidation of benzyl alcohol
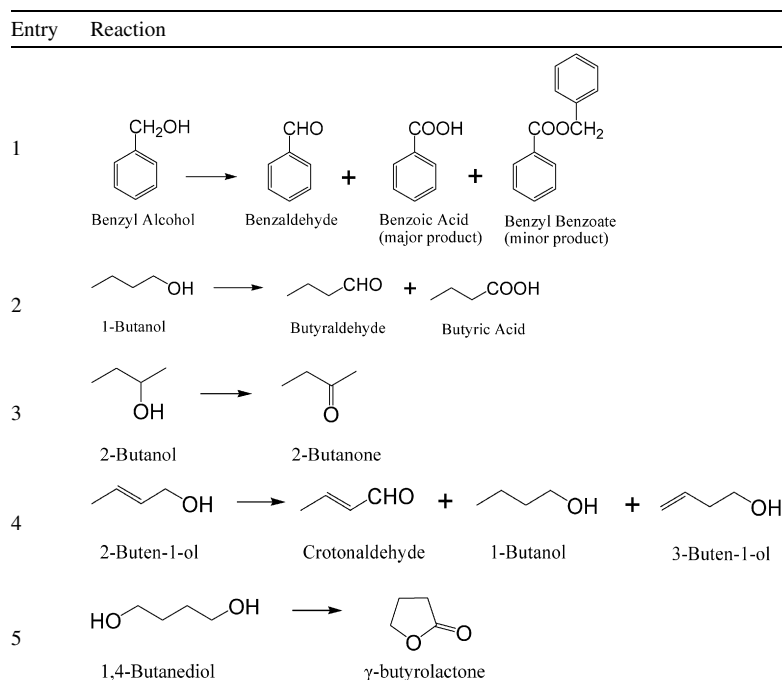
| Entry | Reaction |
|-------|----------|



Scheme 1. Alcohol oxidation reactions over 1:3 Au:Pd bimetallic nanoparticles.

Table 2
Turnover frequencies and selectivities for diverse substrate oxidations with PVP stabilized 1:3 Au:Pd bimetallic nanoparticles

| Entry | Substrate | Conversion (%) | | Turnover frequency $(h^{-1})^a$ | Aldehyde or ketone selectivity (%) | |
|-------|-----------|------|------|------|------|------|
| | | 1 h | 8 h | | 1 h | 8 h |
| 1 | Benzyl alcohol | 14.8 | 33.6 | 74 | 90.5 | 39.7[b] |
| 2 | 1-Butanol | 14.8 | 24.6 | 74 | 26.4 | 23.1 |
| 3 | 2-Butanol | 25.0 | 65.0 | 125 | 100 | 100 |
| 4 | 2-Buten-1-ol | 13.3 | 38.5 | 67 | 34.0 | 77.6 |
| 5 | 1,4-Butanediol | 46.7 | 84.7[c] | 234 | 100[d] | 100 |

*Note*. Conditions: [Pd + Au] = $1.25 \times 10^{-5}$ mol, Pd + Au:substrate = 500:1.
[a] Turnover frequency was calculated over the first hour.
[b] After 24 h.
[c] After 5 h.
[d] $\gamma$-Butyrolactone selectivity.

and 1-butanol. Substantial oxidations of all the alcohols studied were seen under these conditions. The rate of oxidation of benzyl alcohol and 1-butanol were quite similar after one hour, with conversions of 14.8%, but the oxidations of both substrates slowed considerably over time, likely due to mass-transport limitations at these higher catalyst concentrations. In addition, we note that while after 1 h, the major product for the benzyl alcohol oxidation was benzaldehyde (90.5%), a great deal of the aldehyde was subsequently oxidized to benzoic acid over 24 h (final selectivity 39.7% for the aldehyde). Note that benzyl benzoate was a minor product under these new conditions; unlike the earlier room temperature reactions with PVP-stabilized Au nanoparticles in which benzyl benzoate was seen. Control experiments with benzaldehyde in the absence of nanoparticles indicate that disproportionation of the aldehyde over the course of 24 h occurs, and may be a source of the lowered selectivity of the benzyl alcohol oxidation.

No selectivity towards the aldehyde was seen at any point for the oxidation of 1-butanol, as butyric acid was always the predominant product (>75% butyric acid, negligible amounts of butyl butyrate were detected by GC). We speculate that the catalytic oxidation of benzyl alcohol and 1-butanol reactions slow down due to the buildup of benzoic acid and butyric acid on the surface of nanoparticles, lowering the availability of catalyst sites for alcohol oxidation. Alternatively, acid buildup tends to lower the pH of the solution (typically around 11.5–11.6 to start), and we have found that alcohol oxidations over PVP-stabilized nanoparticles are much less effective at pHs below 11. We note that no nanoparticle precipitation was seen for either of these systems during the 24 h reaction. Strong deactivation of AuPd and AuPt catalysts owing to the carboxylic acid production has also been observed by others [19]. Support for this conjecture is seen in the data for the oxidation of 2-butanol and 1,4-butanediol using the 1:3 Au:Pd nanoparticle catalysts; 100% selectivity towards 2-butanone and $\gamma$-butyrolactone, respectively, were seen at substantially higher TOFs than any of the other substrates, with only very gradual changes in the TOF over time.

The oxidation of 2-buten-1-ol using 1:3 Au:Pd nanoparticles shows some interesting features. Three separate reactions were seen: the oxidation reaction of 2-buten-ol to crotonaldehyde, the hydrogenation reaction of 2-buten-1-ol to 1-butanol and the isomerization of 2-buten-1-ol into 3-buten-1-ol. After one hour, the product selectivities were 34% crotonaldehyde, 26% 1-butanol, and 40% 3-buten-1-ol. After the first hour, no further 3-buten-ol and very little 1-butanol were firmed, as the reaction became much more selective towards the oxidation of 2-buten-ol to crotonaldehyde. Similar C=C double bond isomerization and hydrogenation products were reported by Abad et al. [6,7], who suggested that Pd–H species were formed dur-

ing the aerobic alcohol oxidation which promote C=C double bond isomerization and hydrogenation. We found that no isomerization and hydrogenation products were formed using PVP stabilized Au nanoparticle catalyst at the same conditions. However, it should be noted the pure Au nanoparticle catalyst has a low catalytically-activity for this substrate, with a conversion of 2-buten-1-ol to crotonaldehyde of 1.7% was seen after one hour, followed by apparent deactivation of the catalyst.

The actual mechanism of alcohol oxidation of the AuPd catalysts may involve several pathways, given that both pure Au and Pd nanoparticles show activity (albeit lower for the pure metals) for this reaction [6,18]. It has been postulated that alcohol oxidation over Pd nanoparticles involves $\beta$-H elimination of a dissociated alcohol on the Pd surface, followed by reaction of oxygen with Pd–H species, while alcohol oxidation over Au surfaces involves primarily superoxo species via oxygen activation over the Au surface [18]. The appearance of the hydrogenation and isomerization products seen for the AuPd catalysts for the oxidation of 2-buten-1-ol above (which are not seen for pure Au catalysts), along with the maximum activity of bimetallic catalysts with high Pd contents, both suggest that surface Pd atoms are predominately the catalytically-active species in these particles. This would be consistent with a synergetic electronic effect, which has been used to explain enhancements in other AuPd catalysts. However, it should be noted no further buildup of the hydrogenation and isomerization products of 2-buten-1-ol are seen after 1 h, suggesting that other catalytic pathways (such as activation over Au atoms) may be more predominant over longer time scales. In-situ production of $H_2O_2$ over AuPd catalysts is another possible mechanism, particularly given the presence of Pd–H species during catalytic reactions. Others have observed the formation of hydrogen peroxide from $H_2/O_2$ over AuPd bimetallic nanoparticles [27], and that the addition of hydrogen peroxide to PVP-stabilized AuPd nanoparticles led to significant increases in product turnovers over short (1 h) time periods.

## 4. Conclusions

In summary, PVP-stabilized 1:3 Au:Pd nanoparticles have been shown to have higher catalytic activities than pure Au, pure Pd nanoparticles and other bimetallic nanoparticles for alcohol oxidation reactions. These particles have been shown to catalyze the aerobic oxidations of aliphatic, allylic, phenylic alcohols and diols in aqueous solution under mild conditions. In most cases, selective oxidations to aldehydes (or ketones) were seen; however, alkanoic acids were the major products for primary aliphatic alcohols and $\gamma$-butyrolactone was the only product observed for the oxidation of 1,4-butanediol. Future work will be focused on how to prevent catalyst poisoning in this system, understanding structure–property relationships in AuPd bimetallic nanoparticles, as well as attempting to elucidate the mechanism(s) of alcohol oxidation reactions over bimetallic catalysts.

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