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COMMUNICATION

Reductive amination of ethyl levulinate to pyrrolidones over AuPd nanoparticles at ambient hydrogen pressure

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Herein, we describe a AuPd catalyst for selective and solventless conversion of ethyl levulinate (EL) and amines to pyrrolidones under ambient pressure. The optimized $Au_{66}Pd_{34}$ nanoparticle catalyst was stable and reusable over 10 runs. AuPd catalysis was extended to reductive amination of levulinic acid and 4-acetylbutyric acid, providing a green chemistry approach under milder conditions not only to pyrrolidones, but also to piperidines, both of which are important scaffolds in designing polymers, natural products and pharmaceuticals.

Biomass is a class of renewable organic materials containing cellulose, hemicellulose and lignin that come from wood and agricultural crops. It is a conventional source of energy that has been utilized for ages and has recently been restudied as a sustainable source of fuels or value-added chemicals. Biomass can be hydrolyzed in acid to produce platform chemicals like levulinic acid (LA) and furfural.[1] Further selective conversion of these platform chemicals to more useful value-added chemicals is essential for biomass conversion to be practical.[2] One class of such value-added chemicals are pyrrolidones that can be obtained from the reductive amination of LA or its ester derivative ethyl levulinate (EL). Pyrrolidones are useful not only as solvents and surfactants, but also as precursors for preparing fiber and pharmaceutical chemicals.[3]

Conventional methods used to convert LA/EL to pyrrolidones require the presence of Pt- and Ru-based catalysts.[4-5] Pd-based catalysts coupled with ZrO_2 have also been studied for the LA, but not EL, conversion to pyrrolidones.[6] Some efforts have been made in acid-catalyzed metal-free conversions, but require harmful solvents like DMSO or acetonitrile to be successful as well as autogenous pressure formation.[7] In almost all reported metal-catalyzed conversions, pressurized (5-55 atm) hydrogen (H_2) and moderate temperatures (90 - 180 ˚C) are required,[4,6,8] of which the use of pressurized H_2 is especially worrisome as it leads not only to safety concerns, but also to undesirable side reactions, lowering the reaction selectivity.

Recently, we demonstrated that Pd-based nanoparticles (NPs) can serve as very active catalysts for the hydrolysis of ammonia borane (AB, NH_3BH_3) and formic acid (FA, HCOOH) to generate H_2 under ambient conditions.[9] When Pd was alloyed with Ag or Au, the alloy NPs showed very interesting catalysis not only for the dehydrogenation of AB and FA to produce H_2, but also for the tandem hydrogenation of a nitro-compound to primary amine, which can further be converted to a cyclic benzoxazole when reacted with an aldehyde.[10] This AgPd or AuPd catalyzed cyclization to form benzoxazoles, along with other studies on AgPd or AuPd catalysis,[11] inspired us to study their abilities in catalyzing the reductive amination of EL to pyrrolidones using 1 atm H_2.

Here we report our studies on AuPd NP catalyzed reductive amination of EL. We prepared 3.8 nm AuPd NPs on simple carbon support and found their catalysis for the reductive amination reaction was Au/Pd composition dependent. The $Au_{66}Pd_{34}$ alloy NPs were the most active and stable for the reactions between primary amines and EL, forming pyrrolidones under 1 atm H_2 at 85 ˚C with the reaction turnover frequency (TOF) reaching as high as 200 mol mol^{-1}_{metal} h^{-1} and isolated product yields > 90%. The AuPd catalysis could be further extended to the reductive amination of LA/4-acetylbutyric acid to pyrrolidone/piperidine derivatives. Our study demonstrates an exciting new AuPd NP catalytic approach for the reductive amination of EL or LA/4-acetylbutyric acid to pyrrolidones/piperidines under ambient H_2 pressure.

Monodispersed 3.8 nm AuPd alloy NPs were synthesized as reported.[12] Palladium acetylacetonate ($Pd(acac)_2$) and gold tetra-chloroaurate ($HAuCl_4$) were co-reduced with borane morpholine in oleylamine. The compositions of the alloy NPs

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were controlled by the amount of metal precursors added and were measured by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). As a control, 4.5 nm Pd NPs (Figure S1A) or 4 nm Au NPs (Figure S1B) were also prepared by the reduction of $Pd(acac)_2$ in oleylamine or $HAuCl_4$ in tetralin/oleylamine with borane tert-butylamine.[13] Figure 1A and Figure S2A-C show the transmission electron microscope (TEM) images of as-synthesized 3.8 ± 0.4 nm $Au_{66}Pd_{34}$ and other $Au_{24}Pd_{76}$ (3.7 ± 0.4 nm), $Au_{40}Pd_{60}$ (3.8 ± 0.4 nm), and $Au_{84}Pd_{16}$ (4.1 ± 0.4 nm) NPs. Figure 1B shows the high-resolution TEM (HR-TEM) image of a single $Au_{66}Pd_{34}$ NP; the (111) spacing was measured to be 0.231 nm, which is smaller than that of face-centered cubic (fcc) Au (0.235 nm) and larger than that of fcc Pd (0.223 nm).[14] The x-ray diffraction (XRD) patterns of AuPd NPs are similar to those of the fcc structured Au (ICSD 52249) and Pd (ICSD 52251) with the (111) peaks of all the AuPd alloys falling between those of pure Au and Pd (Figure S2D). Further, the plasmonic absorbance of Au disappears upon its alloying with Pd, indicating that AuPd forms a well-alloyed system rather than core-shell architecture (Figure S3).[15-16]

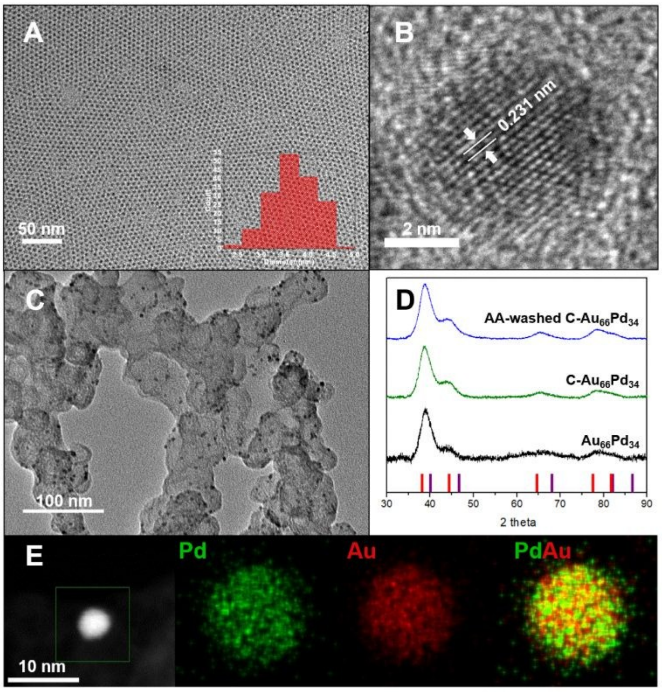

Figure 1. Characterization of $Au_{66}Pd_{34}$ NPs. (A) TEM image of the as-synthesized 3.8 ± 0.4 nm $Au_{66}Pd_{34}$ NPs, (B) HR-TEM image of the $Au_{66}Pd_{34}$ NP on carbon after acetic acid washing, (C) TEM image of the acetic acid washed C-$Au_{66}Pd_{34}$, (D) XRD patterns of $Au_{66}Pd_{34}$, C-$Au_{66}Pd_{34}$, and acetic acid washed C-$Au_{66}Pd_{34}$ compared with ICSD standards for Au (ICSD 52249, red) and Pd (ICSD 52251, purple), and (E) HAADF-STEM image of a selected $Au_{66}Pd_{34}$ NP and STEM-EELS elemental mapping to show Pd (green) and Au (red) distribution within the NP.

As-synthesized NPs were loaded onto carbon support (C) and treated with acetic acid (AA) overnight to remove oleylamine, denoted as C-AuPd, or C-Au, or C-Pd. Figure 1C shows the C-$Au_{66}Pd_{34}$ NPs after AA washing with 15 wt% NP loading; the AA treatment does not change the size and morphology of the NPs. XRD analyses further indicate that the alloy fcc structure is maintained during the processes of NP deposition on C and the AA washing, as evidenced by the stable fcc patterns of the as-synthesized $Au_{66}Pd_{34}$, C-$Au_{66}Pd_{34}$, and the AA-washed C-$Au_{66}Pd_{34}$ (Figure 1D). The alloy structure of the C-NPs after AA-washing was further characterized by high-angle annular dark field (HAADF) scanning TEM (STEM) and electron energy-loss spectroscopy (EELS), showing indeed AuPd is present as an alloy (Figure 1E).

We first screened the reaction between EL and octylamine to form 5-methyl-1-octylpyrrolidin-2-one over C-AuPd with or without solvent under 1 atm H_2 balloon at different reaction temperatures (Table S1). We found solventless at 85 ˚C to be ideal to form the pyrrolidone with > 90% yield after 12 h reaction time. Under the same 1 atm H_2 and 85 ˚C, C-Au showed no activity for the pyrrolidone formation after 48 h reaction time. C-Pd was moderately active, giving 62% yield after 48 h of reaction. We further studied Au/Pd composition dependent catalysis and obtained turnover frequency (TOF) of the reaction by measuring the amount of pyrrolidone formed over a set period with the same metal mol% (Figure 2). Figure 2A shows the pyrrolidone formation yield in a 12 h reaction period when different C-NP catalysts were present with constant metal mol%. Figure 2B is the calculated pyrrolidone formation TOFs of the different C-NP catalysts studied. We can see that C-Au is inactive and C-Pd is moderately active, but not as active as C-AuPd. When Pd is alloyed with Au, its catalytic activity is improved. The most active

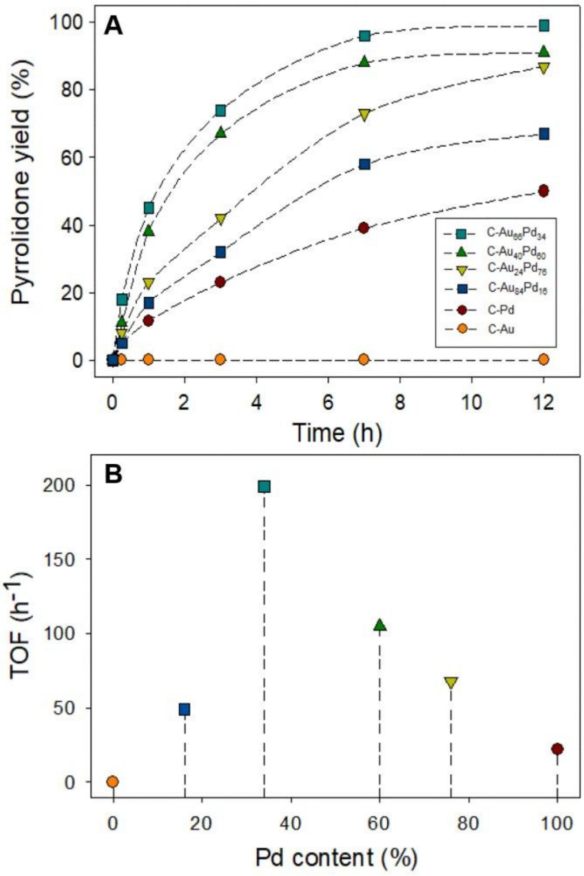

Figure 2. Catalytic data for Au/Pd NPs of varying compositions. (A) Time-dependent formation of 5-methyl-1-octylpyrrolidin-2-one on different C-Au, C-Pd, and C-AuPd NPs, and (B) TOF values of the formation of 5-methyl-1-

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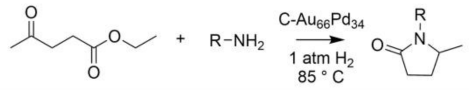
octylpyrrolidin-2-one on different C-NPs. The reaction condition: EL = 3 mmol, octylamine = 3 mmol, catalyst = 0.3 mol%, 1 atm H_2, 85 ˚C. Pyrrolidone yield was calculated from NMR using mesitylene as the internal standard.

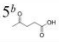
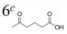
AuPd alloy is $Au_{66}Pd_{34}$ with a TOF of 200 mol mol^{-1}_{metal} h^{-1}, which is about ten times higher than that of C-Pd (22 mol mol^{-1}_{metal} h^{-1}). While adding more Pd to $Au_{66}Pd_{34}$ slows down the reaction kinetics, alloying extra Au with $Au_{66}Pd_{34}$ results in an even sharper drop in AuPd activity, indicating that the right control of metal composition of AuPd NPs is essential to achieve optimal catalytic reductive amination of EL.

A series of amines were chosen to react with EL to test the scope of the C-$Au_{66}Pd_{34}$ catalyzed reactions. The reaction results are summarized in Table 1. The product yields listed in the table were calculated through ^1H NMR using mesitylene as the internal standard, while the isolated yields are given in parentheses (^1H and ^{13}C NMR spectra of purified products are provided in the SI). From this table, we can see that the C-$Au_{66}Pd_{34}$ catalyst is most effective in converting aliphatic amines and EL to the corresponding pyrrolidones (Table 1, entries 1-8). The catalysis is nearly equally effective when a hydroxyl or methoxy group is present (Table 1, entries 9-10). However, when cyclohexylamine was used to react with EL, the pyrrolidone yield was decreased to 35% (Table 1, entry 11). As the cyclohexyl group is aliphatic, this low yield formation of pyrrolidone cannot be attributed to an electronic effect, rather it is more likely caused by the steric effect of the cyclohexyl group, preventing the ring-closure to form the pyrrolidone (Scheme 1). When phenethylamine, benzylamine, or aniline reacted with EL, the pyrrolidone yield was decreased dramatically from 92%, to 55%, down to 13% (Table 1, entries 12-14). There is a clear trend that the closer the -NH_2 group is to the benzene-ring, the lower the product yield. In these cases, electronic effect must dominate the reaction process, along with contributions from steric effect. In the first step of AuPd-catalyzed reductive amination of EL, -NH_2 undergoes a nucleophilic addition to EL to form an imine intermediate; the imine is hydrogenated to an amine which then acts as a nucleophile reacting with the ester portion of the molecule to form pyrrolidone (Scheme 1). The closer the -NH_2 group is to the benzene-ring, the stronger the p-π conjugation between N and C(sp_2), which disperses the electron pair from N to C(sp_2), reducing R-NH's nucleophilicity for the cyclic nucleophilic addition and pyrrolidone ring formation. The negative effect of the electron conjugation between N and C(sp_2) was overcome in a pressurized condition, in reported similar conversions.[6,8]

The C-$Au_{66}Pd_{34}$ catalysis is not limited to the reductive amination of EL but can be extended to reductive amination of LA as well. Under the same 1 atm H_2 and 85 ˚C condition as in the EL conversion, LA could react with octylamine to give 5-methyl-1-octylpyrrolidin-2-one in 91% yield (Table 1, entry 15). The catalysis could be further extended to reductive amination of 4-acetylbutyric acid to form a six-membered N-heterocycle, piperidine derivative, in 89% yield (Table 1, entry 16). Piperidines are important scaffolds in designing pharmaceuticals for cancer treatments and natural products.[17] We should note that the H_2 we used for the current reductive amination reaction could be obtained directly from C-$Au_{66}Pd_{34}$ catalyzed ammonia borane (AB) methanolysis. Our work demonstrates an efficient use of C-$Au_{66}Pd_{34}$ catalyst for dual reactions, both generation of ambient pressured H_2 and reductive amination (Figure S4). We should also note that AB could not be mixed with EL for reductive amination as AB could reduce EL's ketone C=O to C-OH,[18] lowering the C=O amination reaction efficiency.

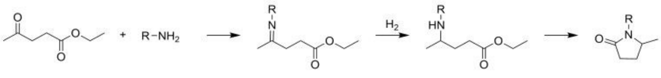
Table 1. C-$Au_{66}Pd_{34}$ catalyzed reductive amination of EL to form pyrrolidone derivatives[a]



entry	R	yield (%)	entry	R	yield (%)
1	-C_8H_{17}	99 (93)	9	-$CH_2CH_2OCH_3$	88 (85)
2	-C_5H_{11}	98 (91)	10	-$CH_2CH_2CH_2OH$	85 (79)
3	-C_6H_{13}	99 (93)	11	-Cy	35 (29)
4	-C_4H_9	99 (89)	12	-CH_2CH_2Ph	92 (86)
5	-$C_{12}H_{25}$	99 (93)	13	-CH_2Ph	55 (50)
6	-$C_{16}H_{33}$	99 (95)	14	-Ph	13 (10)
7	-$C_{18}H_{37}$	99 (96)	15[b] 	-C_8H_{17}	91 (87)
8	-$CH_2CH_2CH(CH_3)_2$	98 (93)	16[c] 	-C_8H_{17}	89 (84)

[a] Reaction conditions: R-NH_2 (3 mmol), EL (3 mmol), C-$Au_{66}Pd_{34}$ (0.3 mol%), 85 ˚C, 12 h, 1 atm H_2. Isolated yields are in parentheses
[b] LA (3 mmol) was used instead of EL; product formed was same as entry 1
[c] 4-acetylbutyric acid (3 mmol) was used instead of EL; product formed was 6-methyl-1-octylpiperidin-2-one

The enhanced activity of $Au_{66}Pd_{34}$ over elemental Au, Pd, and other AuPd NPs may be attributed to the alloy interaction between Au and Pd, in which Pd becomes "electron-deficient", promoting reductive reactions.[19] This was supported by X-ray photoelectron spectroscopy (XPS) analyses (Figure S5). When compared to C-Au, C-$Au_{66}Pd_{34}$ exhibits a negative binding energy shift in both Au $4f_{5/2}$ (-0.3 eV) and Au $4f_{7/2}$ peaks (-0.2 eV). This negative shift is caused by electron build-up on Au as Au is more electronegative than Pd. The C-$Au_{66}Pd_{34}$ also has a small positive binding energy shift (+0.1 eV) in the Pd $3d_{3/2}$ peak, consistent with what was observed from other AuPd-based systems.[20] Therefore, Pd-catalysis is enhanced for this reaction by its alloying with Au. However, when too much Au is present, as in $Au_{84}Pd_{16}$, AuPd catalytic ability drops sharply. Therefore, there is a structure balance in AuPd to show a proper degree of Pd Lewis acidity and Pd exposure, and $Au_{66}Pd_{34}$ is the best Au/Pd combination for catalyzing the reductive amination. This differs from recent arguments about isolated and dilute Pd being the most active AuPd catalysts for both hydrosilylation and selective catalytic oxidations.[16,21] To understand the importance of Au in the AuPd catalytic reaction, we synthesized $Cu_{52}Pd_{48}$ and



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Scheme 1. Reductive amination of EL to pyrrolidone through an imine intermediate.

$Ag_{48}Pd_{52}$ NPs of comparable sizes and morphologies as previously described,[10,13] and tested their catalysis for the reaction between EL and octylamine under the same 1 atm H_2 and 85 °C condition, but for 16 h (Table S2). We can see that the pyrrolidone yield obtained from the $Ag_{48}Pd_{52}$ NP catalysis (75%) is higher than that from $Cu_{52}Pd_{48}$ (37%), but lower than that from either $Au_{66}Pd_{34}$ (99%) or $Au_{40}Pd_{60}$ catalysis (91%). CuPd is even a poorer catalyst than Pd. These provide strong evidence that the Lewis acidity of Pd in the Pd alloy NPs helps to improve Pd catalysis for the reductive amination.

Another important feature of the $Au_{66}Pd_{34}$ catalyst is its stability in the reductive amination condition. When used to catalyze the reaction of EL and octylamine, the C-$Au_{66}Pd_{34}$ catalyst could easily be recycled 10 times without obvious change in the NP's morphology, composition, loading amount on support, and catalysis (Figure S6). C-$Au_{66}Pd_{34}$ could also be used for the same reaction after 1 year exposure to air (Table S1). To further demonstrate that the observed catalysis is originated from the alloy NPs, not from the leached Pd in the reaction solution, we performed the reductive amination of EL with octylamine first in the presence of the AuPd catalyst, then 3 h later, we filtered off the catalyst from the reaction mixture and continued to monitor the solution phase reaction for another 12 h. We found that there was no additional pyrrolidone formation in this extra 12 h reaction period (Figure S7), confirming that our C-$Au_{66}Pd_{34}$ is active and stable for the reductive amination reaction and the observed catalysis is solely from the alloy NPs, not from the leached Pd.

Conclusions

In summary, we have reported our studies on AuPd NP catalyzed reductive amination of EL to pyrrolidones. We prepared 3.8 nm AuPd NPs on simple carbon support with composition control and found that their catalysis for the reductive amination reaction was Au/Pd composition dependent. The $Au_{66}Pd_{34}$ alloy NPs showed the highest activity in catalyzing the reactions between primary amines and EL under 1 atm H_2 at 85 ˚C, forming pyrrolidones with the reaction turnover frequency (TOF) reaching as high as 200 mol mol^{-1}_{metal} h^{-1} and isolated product yields > 90%. The AuPd catalysis was further extended to reductive amination of LA/4-acetylbutyric acid to pyrrolidone/piperidine derivatives. This, combining with the reductive amination of EL, provides a general green chemistry approach with efficient and reusable catalysis to convert EL/LA/4-acetylbutyric acid selectively without solvent to pyrrolidones/piperidines under ambient H_2 pressure generated by a solid H_2 source. These pyrrolidones/piperidines are important scaffolds in designing polymers, natural products and pharmaceuticals for functional materials and biomedical applications. Taking advantage of the interactions of metals in alloy nanoparticles may provide a promising new green chemistry approach to biomass conversions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

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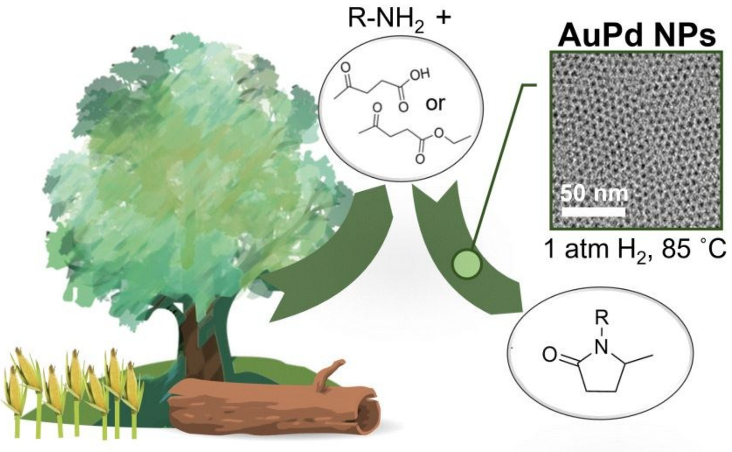

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