

# A PdAg bimetallic nanocatalyst for selective reductive amination of nitroarenes†

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Herein we have identified an optimal catalyst, Pd<sub>1</sub>Ag<sub>1.7</sub>, for the tandem reductive amination between nitroarenes and aldehydes (selectivity > 93%). Key to the success is the ability to control the compositions of the investigational Pd<sub>1-x</sub>Ag<sub>x</sub> (x = 0–1) catalysts, as well as the clear composition dependent activity/selectivity trend observed in this study. This catalyst features a wide substrate scope, excellent recyclability, activity and selectivity under ambient conditions.

Bimetallic nanoparticles have attracted enormous attention in the past decade.<sup>1–5</sup> They provide exciting opportunities for developing novel catalysts with unique or improved activities.<sup>6–11</sup> They also serve as ideal model systems to probe the nature of industrial catalysts.<sup>12</sup> In the past years, notable breakthroughs have been made toward the controlled syntheses of bimetallic nanoparticles.<sup>13–18</sup> These well-defined nanoparticles fueled the ongoing research aimed at elucidating the underlying relationship between catalytic activity and catalyst properties such as size, shape and composition.<sup>19,20</sup> Coupled with increasing ability to synthesize and characterize catalysts,<sup>21</sup> the accumulated knowledge renders it possible to tailor bimetallic nanoparticles of desired activity and selectivity.<sup>22</sup> Herein we report the discovery of an optimal catalyst, Pd<sub>1</sub>Ag<sub>1.7</sub>, for the tandem reductive amination between nitroarenes and aldehydes through tuning the composition of bimetallic Pd<sub>1-x</sub>Ag<sub>x</sub> (x = 0–1) nanoparticles without change in particle size (~3 nm).

Secondary amines are ubiquitous building blocks of functional materials, additives, dyes, agrochemicals and pharmaceuticals.<sup>23</sup> Because controlled monoalkylation of primary amines remains a challenge,<sup>24–26</sup> syntheses of secondary amines rely heavily on the

reductive amination reactions.<sup>27,28</sup> As such, tandem reductive amination using nitroarenes is conceived to be especially attractive as it does not require prior reduction of the nitroarenes.<sup>29–34</sup> It is desirable to develop an effective catalyst for the title transformation.

We envisioned that controlled introduction of an inert metal (*e.g.* Ag) into the intrinsically active Pd might lead to a catalyst of fine-tuned activity suitable for the selective formation of secondary amines. In addition, the formation of the Pd–Ag bond was reported to alter the selectivity of hydrogenation of acetylene over ethylene.<sup>35</sup> To this end, we synthesized a series of Pd<sub>1-x</sub>Ag<sub>x</sub> (x = 0–1) nanoparticles by co-reduction of Pd(acac)<sub>2</sub> and AgOOCF<sub>3</sub> using a borane-*tert*-butylamine complex in oleylamine (OAM) (for details, see the ESI†). The compositions of the bimetallic nanoparticles were to be controlled by varying the ratios of the Pd and Ag precursors. Transmission electron microscopy (TEM) images of the as-obtained Pd<sub>x</sub>Ag<sub>1-x</sub> bimetallic nanoparticles showed that they were monodispersed particles of narrow size distribution (average diameter around 3 nm) (Fig. 1a–f). Fig. 1g shows the powder X-ray diffraction (XRD) patterns of Pd<sub>1-x</sub>Ag<sub>x</sub> bimetallic nanoparticles. The peaks were noted to continuously shift from the Ag standard peak to those of Pd when the content of Pd increased (Fig. 1g). Importantly, inductively coupled plasma atomic emission spectrometry (ICP-AES) further confirmed that the exact Pd/Ag ratios in the as-obtained bimetallic NPs closely followed the trend of the designed compositions (Table S1 in the ESI†).

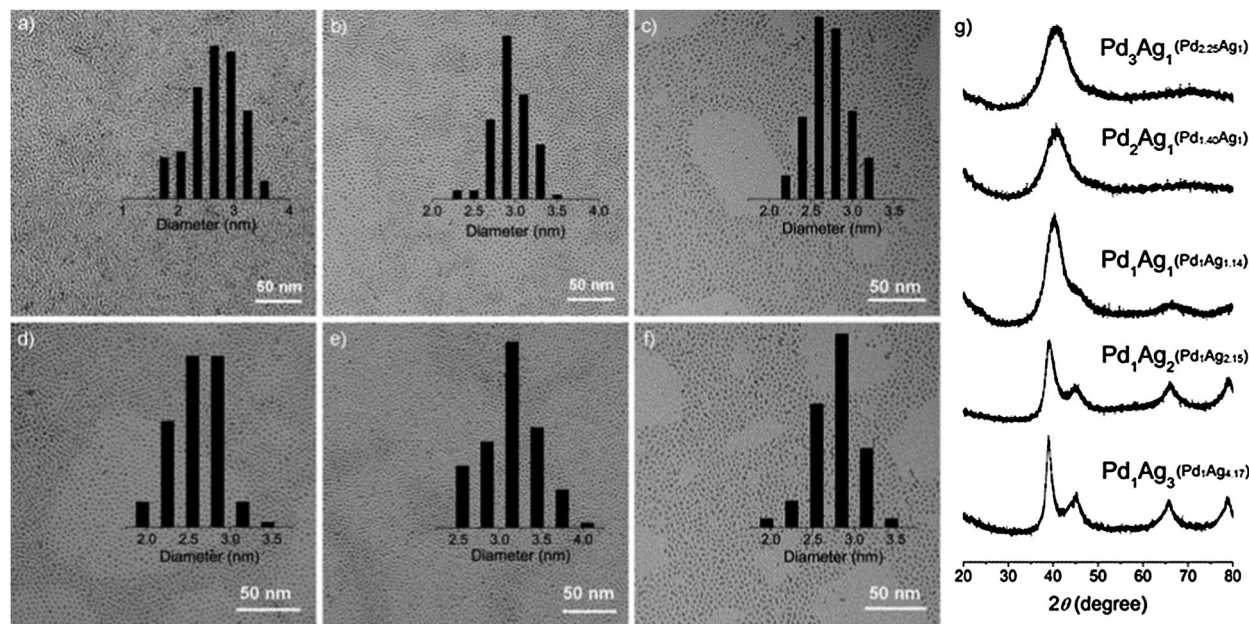
Having these bimetallic NPs in hand, we set out to evaluate their catalytic properties using benzaldehyde (**1a**) and nitrobenzene (**2a**) as the model system (Table 1). Two benchmark catalysts, commercial Pd/C (entry 1) and Pd nanoparticles (~3 nm) (entry 2), were found to have high activity but low selectivity. This observation is consistent with their intrinsic high activity in the benzaldehyde hydrogenation.<sup>36</sup> Not surprisingly, Ag nanoparticles (~4 nm) were inactive (entry 3). In general, Pd<sub>1-x</sub>Ag<sub>x</sub> bimetallic nanoparticles showed a lower activity but a higher selectivity (entries 4–8) compared to Pd nanoparticles (entry 3). As the ratio of Ag increased, a clear trend of decreased activity but increased selectivity was observed. We noted a turning point between Pd<sub>1</sub>Ag<sub>1.40</sub> and Pd<sub>1</sub>Ag<sub>2.15</sub>. In other words,

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**Fig. 1** (a–f). TEM of the as-obtained PdAg nanoparticles: (a) Pd<sub>3</sub>Ag<sub>1</sub>; (b) Pd<sub>2</sub>Ag<sub>1</sub>; (c) Pd<sub>1</sub>Ag<sub>1</sub>; (d) Pd<sub>1</sub>Ag<sub>2</sub>; (e) Pd<sub>1</sub>Ag<sub>3</sub>; (f) Pd<sub>1</sub>Ag<sub>3</sub>; (g) XRD of the as-obtained PdAg nanoparticles. The annotations in the parentheses reflect the compositions found by ICP.

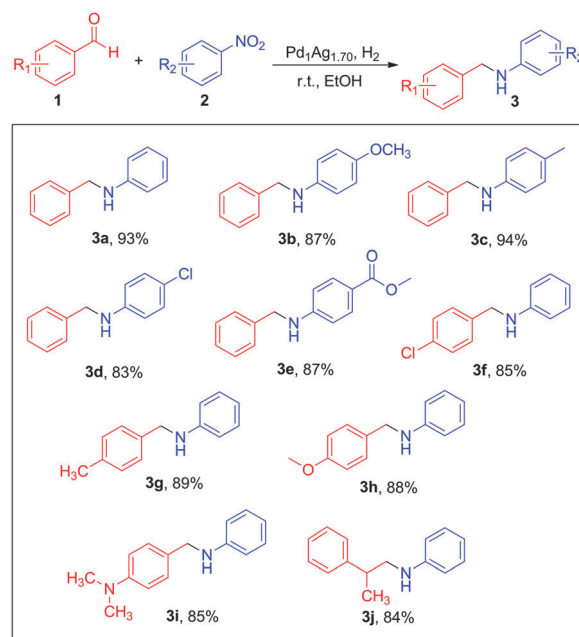
**Table 1** Screening of Pd<sub>1-x</sub>Ag<sub>x</sub> (x = 0–1) bimetallic nanocatalysts<sup>a</sup>

Entry	Catalyst	Time [h]	Conversion of <b>1a</b> [%]	Selectivity <sup>b</sup> [%]			
				<b>3a</b>	<b>4</b>	<b>5</b>	<b>6</b>
1	Pd/C	2	>99	—	58	—	42
2	Pd NCs	3	>99	45	28	—	27
3	Ag NCs	48	—	—	—	—	—
4	Pd <sub>2.25</sub> Ag <sub>1</sub>	4	>99	71	29	—	—
5	Pd <sub>1.40</sub> Ag <sub>1</sub>	4	>99	80	20	—	—
6	Pd <sub>1</sub> Ag <sub>1.14</sub>	4	>99	86	14	—	—
7	Pd <sub>1</sub> Ag <sub>2.15</sub>	24	78	93	—	7	—
8	Pd <sub>1</sub> Ag <sub>4.17</sub>	24	33	89	—	11	—
9	Pd <sub>1</sub> Ag <sub>1.70</sub>	4	>99	93	7	—	—

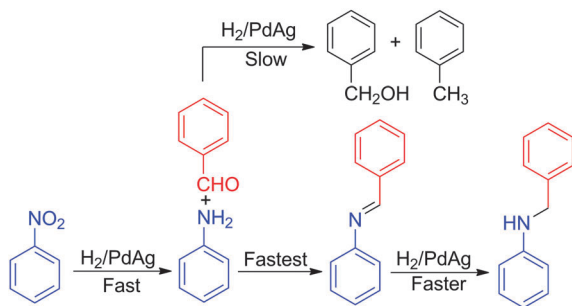
<sup>a</sup> Reaction conditions: substrate **1a** (1.0 mmol), **2a** (1.0 mmol), 0.16 mol% catalyst (based on Pd) in 4 mL ethanol under room temperature/H<sub>2</sub> balloon conditions. <sup>b</sup> Conversion and selectivity were analyzed by GC and *n*-tridecane was used as the internal standard.

when changed from Pd<sub>1</sub>Ag<sub>1.40</sub> to Pd<sub>1</sub>Ag<sub>2.15</sub> the hydrogenation of benzaldehyde was no longer observed but accumulation of imine was detected (entry 7). Similar selectivity with further decreased activity was associated with Pd<sub>1</sub>Ag<sub>4.17</sub> (entry 8). This clear trend prompted us to synthesize Pd<sub>1</sub>Ag<sub>1.70</sub> bimetallic nanoparticles whose Pd content falls midway between Pd<sub>1</sub>Ag<sub>1.40</sub> and Pd<sub>1</sub>Ag<sub>2.15</sub>. To our great delight, the obtained Pd<sub>1</sub>Ag<sub>1.70</sub> nanoparticles showed the best selectivity (93%) without loss in activity (>99% conversion in 4 h) under ambient conditions (entry 9).

Next we examined the utility of the Pd<sub>1</sub>Ag<sub>1.70</sub> catalyst with other substrates (Fig. 2). Nitrobenzenes bearing either an electron donating group (**3b**, **3c**) or an electron withdrawing group (**3e**) gave excellent isolated yields. Various substituted benzaldehydes with different electron demands (**3f**, **3g**, **3h**, **3i**) were also capable substrates. Importantly, reducible groups such as arylhalides (**3d**, **3f**) and ester (**3e**) were intact. Reaction of an aliphatic aldehyde such as **3j** also proceeded very smoothly.



**Fig. 2** Products and isolated yields of Pd<sub>1</sub>Ag<sub>1.70</sub> catalyzed reductive amination. Conditions: **1** (1.0 mmol), **2** (1.0 mmol) and the catalyst (0.16 mol%) in ethanol (4 mL) under room temperature/H<sub>2</sub> balloon conditions.



**Scheme 1** Possible explanation of the observed selectivity.

Overall, the Pd<sub>1</sub>Ag<sub>1.70</sub> catalyst has excellent functional group compatibility and the reaction provides rapid access to an array of secondary amines.

Importantly, leaching of soluble Pd or Ag from the Pd<sub>1</sub>Ag<sub>1.70</sub> catalyst into the reaction filtrate was not detected by ICP-AES. TEM studies showed that the spent catalyst had no observable structural change relative to the fresh catalysts. The catalyst could be recovered by centrifugation and reused at least 6 times without decay in activity and selectivity, consistent with its stability mentioned above (ESI<sup>†</sup>).

Evidence from control experiments (ESI<sup>†</sup>) led us to postulate the reaction mechanism as shown in Scheme 1. The selective formation of the secondary amine could be understood by invoking a dynamic selection, where the favored hydrogenation of nitrobenzene and rapid imine formation helped catalyst turnover and minimized benzyl alcohol formation. Studies to uncover the underlying reason for favored nitrobenzene hydrogenation are being actively carried out in our laboratories.

In conclusion, we successfully identified a general, selective and recyclable bimetallic Pd<sub>1</sub>Ag<sub>1.70</sub> nanocatalyst for the reductive amination between aldehydes and nitroarenes. The clear composition–activity/selectivity relationship observed in this study helped us to design and identify the optimal catalyst, underscoring the possibility of “rational” heterogeneous catalyst design. We envision that such an approach could be extended to the development of novel heterogeneous catalysts for other important transformations given increasing understanding and control of nanoparticle catalysis.<sup>37,38</sup>

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