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## COMMUNICATION

## Oxidative imination of toluenes catalyzed by Pd–Au/silica gel under mild reaction conditions†

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A Pd–Au/SiO<sub>2</sub> catalyst was prepared for the oxidative imination of toluenes with up to 99% yields in the absence of dehydrating agents under mild conditions. Nanoparticles with a PdO layer and Pd–Au core may be the active structure for the reaction.

Aromatic imines are important motifs in the synthesis of many natural and medicinal compounds with various structures and properties.<sup>1</sup> Commonly, the condensation of benzaldehydes with amines is a straightforward and effective route for the formation of imines. However, this process is usually carried out under acidic conditions and limited by the use of dehydrating agents or apparatus.<sup>2</sup> Moreover, in industry, benzaldehydes are mainly obtained as by-products from the oxidation of toluenes to benzoic acids<sup>3</sup> or *via* the chlorination–hydrolysis process.<sup>4</sup> The rigorous reaction conditions or the use of chlorine make these processes environmentally unfriendly and lead to high energy consumption. Apart from the condensation reaction, aromatic imines could also be synthesized through the oxidative coupling of an amine with an alcohol,<sup>5</sup> nitrobenzene reduction and condensation with aldehyde,<sup>6</sup> oxidative dehydrogenation of an *N,N*-disubstituted amine<sup>7</sup> and hydroamination of an alkyne, *etc.*<sup>8</sup> However, from the fundamental and practical points of view, an ideal route for the clean synthesis of aromatic imines is through the direct coupling of toluenes with amines by catalytic activation of the primary C–H bonds, which remains one of the most important and challenging subjects in the clean synthesis of chemicals.<sup>9</sup>

In order to realize this target, the crucial step is the controllable oxidation of toluenes to the corresponding aldehydes because over-oxidation to the acid will result in the formation of ammonium salt with amine. With respect to this transformation, several catalytic systems, such as Cu, Co, V–Ag, Mn, Ce and N–OH imides, *etc.* have been reported in the past decades.<sup>10</sup> Unfortunately, the rigorous reaction conditions used in the above systems, which are normally performed at > 150 °C, caused low selectivity and highly selective syntheses

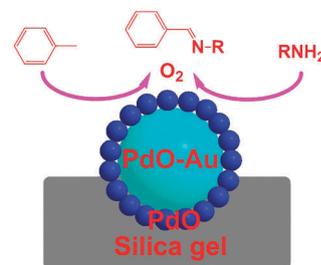


Fig. 1 Toluene imination over Pd–Au/SiO<sub>2</sub>.

of benzaldehydes were difficult. Recently, Au based nanoparticles have emerged as an effective catalyst for many oxidation reactions<sup>11</sup> and the selective oxidation of alkanes<sup>12</sup> has also been realized, although the activity and selectivity were still low. Moreover, due to the lower oxophilicity and larger electronegativity, the segregation of the metallic Au phase could occur in an oxidizing atmosphere, which provided a useful tool for Au–M bimetallic catalyst designation because the catalytic behaviour of gold-containing bimetallic catalysts could be fine-tuned by controlling Au–M structure.<sup>13</sup> As a successful example, the Au–Pd alloy was a good catalyst for toluene oxidation to yield benzyl benzoate at 160 °C and 1 MPa O<sub>2</sub>.<sup>14</sup> Meanwhile, surface Pd(O) was also an active species in liquid phase aerobic oxidation reactions.<sup>15</sup>

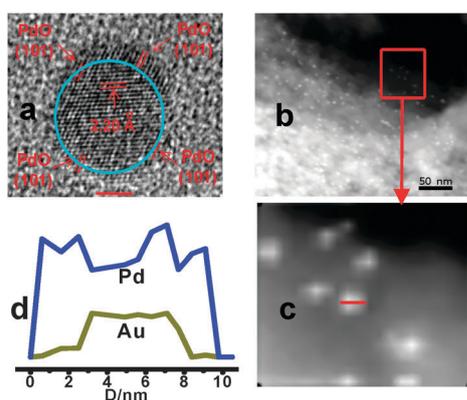
Herein, we show the preparation and catalytic performance of Pd–Au/SiO<sub>2</sub> in the oxidative imination of toluenes with sulfonamides and amines (Fig. 1). The catalysts were prepared by a modified solvent thermal method. In a mixed solvent of water and ethanol (*V*:*V* = 1:5), suitable amounts of polyvinylpyrrolidone (PVP) and cetyltrimethylammonium bromide (CTAB) as surfactants were added and stirred until they had dissolved completely. Then, the metal salt solution, ethyl silicate (TEOS), and urea were added to the above solution and stirred at 40 °C for 30 min. Subsequently, the mixture was transferred into a Teflon-lined stainless steel autoclave and hydrothermally treated at 140 °C for 12 h. The reaction mixture was cooled to room temperature, centrifuged, washed with deionized water, dried at 120 °C for 4 h and calcined at 400 °C for 4 h in air to obtain the catalysts.

TEM characterization showed that the co-addition of PVP, CTAB and Pd was necessary to gain uniformly dispersed nanoparticles. The average particle sizes of samples Pd/SiO<sub>2</sub>–P–C, Pd–Au/SiO<sub>2</sub>–P–C and Pd–Au/SiO<sub>2</sub>–P–C–1 were 4, 7 and 7 nm,

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**Fig. 2** (a) HR-TEM image of Pd-Au/SiO<sub>2</sub>-P-C (scale bar = 2 nm), (b) HAADF-STEM image of Pd-Au/SiO<sub>2</sub>-P-C, (c) HAADF-STEM image of Pd-Au/SiO<sub>2</sub>-P-C, (d) cross-sectional compositional line profiles of the line in (c).

Fig. S1a, e and g.† Larger particles formed (20–60 nm) in Au/SiO<sub>2</sub>-P-C, Pd-Au/SiO<sub>2</sub>-P, Pd-Au/SiO<sub>2</sub>-C and Pd-Au/SiO<sub>2</sub>. Fig. S1b–d and f.† Interestingly, a unique PdO/PdO–Au structure formed in Pd-Au/SiO<sub>2</sub>-P-C, Fig. 2a, which contains a core of PdO (101,  $d = 2.64$  Å) and Au ( $d = 2.20$  Å) surrounded with PdO (101). The lattice distance of Au is smaller than Au (111,  $d = 2.35$  Å) but bigger than Au (200,  $d = 2.04$  Å), which suggests its interaction with PdO. HR-TEM imaging revealed that the PdO–Au core diameter was  $\sim 5$  nm and the PdO shell thickness was  $\sim 1$  nm, Fig. 2a. HAADF-STEM and EDX spectroscopy line-scan characterization confirmed the observation from HR-TEM images, *i.e.* the particle size was 6–8 nm, Fig. 2b and Fig. S2.† The EDX line-scan over a randomly selected nanoparticle also indicated the formation of a Au–PdO core and PdO shell, Fig. 2c and d and Fig. S3.† The Au–PdO core of this particle was  $\sim 5$  nm and the PdO shell was  $\sim 2$  nm. However, if more Au was added to prepare a catalyst with a higher Au: Pd ratio, *i.e.* sample Pd-Au/SiO<sub>2</sub>-P-C-1, the PdO shell disappeared and a mixed structure of Au and PdO formed, Fig. S4e–h.† XPS characterization showed that the binding energy of Pd3d<sub>5/2</sub> in Pd-Au/SiO<sub>2</sub>-P-C, *i.e.* 336.98 eV, was 0.14 eV, lower than that of Pd/SiO<sub>2</sub>-P-C, *i.e.* 337.12 eV, which suggested the formation of Au–Pd alloy in Pd-Au/SiO<sub>2</sub>-P-C, Fig. S8.†<sup>16</sup>

Powder X-ray diffraction (XRD) characterization revealed the crystal structure of PdO and Au, Fig. S5.† Interestingly, the co-addition of Pd and Au resulted in significant changes in the diffraction peaks according to the molar ratio of Pd to Au. When Pd: Au  $\approx$  2: 1, the major changes from the XRD patterns were the shifting of the diffraction peak of Au (111) from 38.1° to 38.8° and the shifting of the Au (200) diffraction peak from 44.4° to 45.1°. This might correspond to the lattice distance of Au ( $d = 2.20$  Å) in the HR-TEM image, Fig. 2a. In reverse, if Au: Pd  $\approx$  2: 1, the diffraction peaks of Pd (101) disappeared, and Au (111) and Au (200) diffraction peaks appeared again. It is also possible that the diffraction peak of PdO is overlapped with Au (111).

Subsequently, the activities of these catalysts were tested, Table 1. Only 35% and 5% conversions of benzenesulfonamide were obtained if Pd/SiO<sub>2</sub>-P-C and Au/SiO<sub>2</sub>-P-C were employed, entries 1 and 2. Similar results were obtained if Pd-Au/SiO<sub>2</sub>-P or

**Table 1** Catalyst screening for oxidative imination of toluene<sup>a</sup>

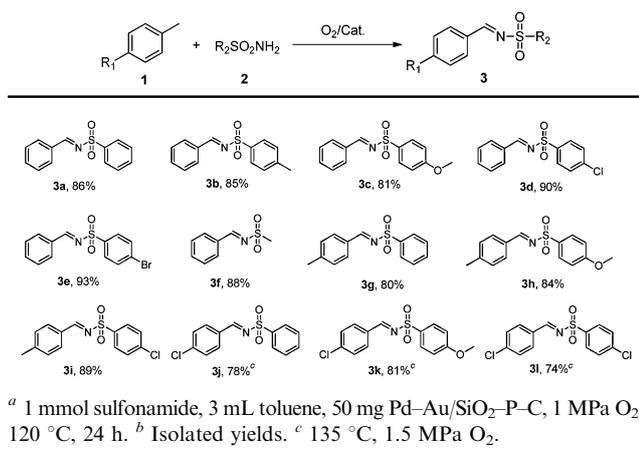
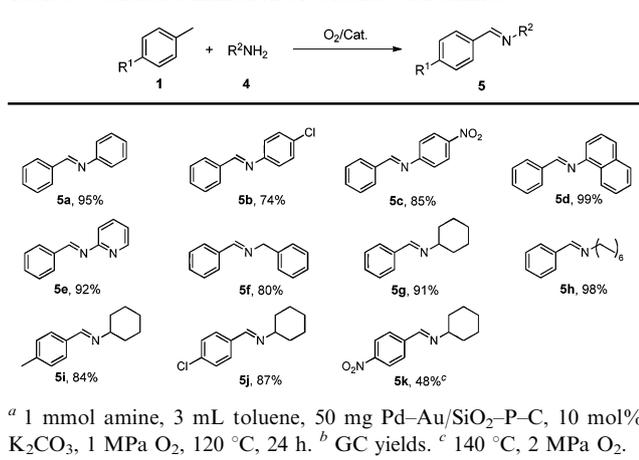
Entry	Catalyst	Pd/Au (mol/mol)	Conversion (%) <sup>b</sup>	TON/TOF <sup>c</sup>
1	Pd/SiO <sub>2</sub> -P-C	0.42/0	35	83/3.5
2	Au/SiO <sub>2</sub> -P-C	0/0.21	5	24/1
3	Pd-Au/SiO <sub>2</sub>	0.42/0.21	13	21/0.9
4	Pd-Au/SiO <sub>2</sub> -P	0.41/0.21	4	6/0.3
5	Pd-Au/SiO <sub>2</sub> -C	0.41/0.21	30	48/2
6	Pd-Au/SiO <sub>2</sub> -P-C	0.42/0.21	92/(86 <sup>d</sup> /83 <sup>e</sup> )	148/6.2
7	Pd-Au/SiO <sub>2</sub> -P-C-1	0.16/0.32	30	63/2.6

<sup>a</sup> 1 mmol sulfonamide, 5 mL toluene, 50 mg catalyst, 1 MPa O<sub>2</sub>, 120 °C, 24 h. <sup>b</sup> Sulfonamide conversion determined by GC-FID. <sup>c</sup> TON = mmol sulfonamide converted per mol Pd + Au; TOF = mmol sulfonamide converted per mol Pd + Au per hour. <sup>d</sup> Isolated yields. <sup>e</sup> Reused at the 5th run.

Pd-Au/SiO<sub>2</sub>-C was used, in which only PVP or CTAB itself was used as the surfactant in catalyst preparation, entries 3–5. By applying Pd-Au/SiO<sub>2</sub>-P-C, the conversion reached 92% with 86% isolated yield, entry 6. However, Pd-Au/SiO<sub>2</sub>-P-C-1 showed lower catalytic activity and only  $\sim 30\%$  conversion of benzenesulfonamide was obtained, entry 7. The TON value of Pd-Au/SiO<sub>2</sub>-P-C reached 148 but only 6, 48 and 63 TON values were obtained for Pd-Au/SiO<sub>2</sub>-P, Pd-Au/SiO<sub>2</sub>-C and Pd-Au/SiO<sub>2</sub>-P-C-1. By tracing the reaction with GC-MS, benzaldehyde was observed as the intermediate, which was also the major by-product, and no phenol by-product formed. Notably, the catalyst could be easily separated, and 83% isolated yield was maintained when it was used for the 5th time, entry 6 and Table S1.† ICP-AES measuring of the filtered solution showed that the Pd and Au concentrations were out of the detection limits and no further reaction could be observed if the catalyst was filtered off and another portion of benzenesulfonamide added, Tables S1 and S2.† Moreover, similar Au and Pd loadings were observed in the used catalyst if comparing with the fresh sample, Table S2.† Thus the catalytic activity was derived from Pd-Au/SiO<sub>2</sub>-P-C but not leached Pd and Au in the solution. However, HRTEM pictures of the used catalyst indicated its restructuring, although no aggregation occurred, Fig. S6.† XRD characterization indicated the presence of PdO crystal and thus PdO was not reduced, Fig. S7.†

The scope screening of the imination reaction of toluenes was further investigated using Pd-Au/SiO<sub>2</sub>-P-C as catalyst, Table 2. For the reaction of toluene with benzenesulfonamide, 86% isolated yield was obtained (**3a**). The reactions of toluene with other sulfonamides were tested. It was clear that electron-rich as well as electron-poor groups were all tolerated (**3b–3e**). As a typical aliphatic sulfonamide, 88% yield was obtained using methanesulfonamide as starting material (**3f**). In addition, 74–89% yields were obtained with toluenes and aromatic sulfonamides contain different substituent groups as starting materials (**3g–3l**).

With the addition of a catalytic amount of K<sub>2</sub>CO<sub>3</sub>, the imination of toluenes with amines could also be realized with Pd-Au/SiO<sub>2</sub>-P-C as catalyst, Table 3. The catalyst system had

**Table 2** Oxidative imination of toluenes with sulfonamides<sup>a,b</sup>**Table 3** Oxidative imination of toluenes with amines<sup>a,b</sup>

a nice functional group tolerance on the structure of the amine and 74–99% yields were obtained for the amination reactions of toluene (**5a–5h**). The variation of substituent groups on the aromatic ring of the toluene had a remarkable effect on the coupling reaction. First, 84% and 87% yields were obtained for the reactions of *p*-xylene and *p*-chlorotoluene with cyclohexyl amine (**5i**, **5j**). The incorporation of an electron-withdrawing nitro group resulted in a much lower reactivity to yield the imination product although higher temperature and oxygen pressure were used (**5k**).

In conclusion, for the first time, the oxidative imination of toluenes was realized using a heterogeneous Au–Pd bimetallic catalyst. This catalyst could be easily recovered and reused several times without deactivation. It provides a successful example to improve fine chemical synthesis, and extends the application of heterogeneous catalysis.

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