## *In situ* hydrogen from aqueous-methanol for nitroarene reduction and imine formation over an Au–Pd/Al<sub>2</sub>O<sub>3</sub> catalyst<sup>†</sup>

Yizhi Xiang, Qiangqiang Meng, Xiaonian Li\* and Jianguo Wang

Received 22nd March 2010, Accepted 7th June 2010 DOI: 10.1039/c0cc00531b

In situ hydrogen from aqueous-methanol, instead of  $H_2$  or CO, was used to synthesize imines with a high selectivity from nitroarenes and carbonyl compounds over an Au-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

Direct synthesis of complex molecules from simple starting materials in a single reaction without separation of intermediates is an important issue in chemistry.<sup>1</sup> The direct synthesis of N-containing compounds (*e.g.*, amines, *N*-alkylamines, and imines) from the reduction of nitroarenes followed by alkylation or condensation of aryl amines is an important aspect of this issue. Currently, the synthesis of *N*-alkylamine from nitroarenes and aldehydes, ketones, or nitriles in the presence of reductants (B<sub>10</sub>H<sub>14</sub>, H<sub>2</sub>, and metallic zinc or tin) has been extensively investigated.<sup>2</sup> The one-pot synthesis of *N*,*N*-dimethylaniline and *N*-ethylaniline from nitrobenzene and methanol or ethanol in an atmosphere of N<sub>2</sub> or Ar over a RANEY<sup>®</sup> Ni catalyst has also been reported.<sup>3</sup> But there are only few reports on the direct synthesis of imines.

Imines are bioactive N-containing compounds and often used as intermediates for the synthesis of herbicides, pharmaceuticals, and other fine chemicals.<sup>4</sup> Generally, imines are produced from the condensation of primary amines with carbonyl compounds,<sup>5</sup> or from the oxidative dehydrogenation of secondary amines using  $O_2$ ,<sup>6</sup> iodosylbenzene,<sup>7</sup> or persulfate<sup>8</sup> as the oxidants. Imines were also synthesized from amines and alcohols in the presence of  $O_2$ .<sup>9</sup> Recently, the direct synthesis of imines from nitroarenes and carbonyl compounds was realized using Au/TiO<sub>2</sub><sup>10</sup> or Ni/SiO<sub>2</sub><sup>11</sup> as catalyst in the presence of H<sub>2</sub>, or using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>–SnCl<sub>2</sub> as catalyst in the presence of CO,<sup>12</sup> or using Fe–HCl as both catalyst and reductant.<sup>13</sup> But these processes were not desirable due to the use of H<sub>2</sub>, CO, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>–SnCl<sub>2</sub>, and Fe–HCl.

$$R_1 - NO_2 + \bigvee_{R_2} + CH_3OH \longrightarrow R_1 - N + CO_2 + 2H_2O$$
(1)

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$
(2)

$$R_1 - NO_2 + 3H_2 \rightarrow R_1 - NH_2 + 3H_2O$$
 (3)

$$R_1 - NH_2 + \mathcal{O}_{R_2} \longrightarrow \mathcal{R}_1 - \mathcal{N} + H_2O$$
 (4)

$$\underset{R_1 - N}{\bigwedge} R_2 + H_2 \longrightarrow R_1 - NH$$
 (5)

$$R_2 \xrightarrow{O} + H_2 \xrightarrow{R_2} OH$$
 (6)

In this study, we report a new catalysis system for the direct synthesis of imines from nitroarenes and carbonyl compounds in the absence of  $H_2$  or CO over an Au–Pd/Al<sub>2</sub>O<sub>3</sub> catalyst (eqn (1)). *In situ* hydrogen, produced from aqueous-phase reforming of methanol, or hydrogen transfer from methanol as donor (in both routes CO<sub>2</sub> was the only gas effluent product, eqn (2), Fig. S1 and S2†), was used to reduce nitroarenes into aryl amines (eqn (3)).<sup>14</sup> The amines condensed with carbonyl compounds and finally produced imines (eqn (4)). High selectivity of the imine was reached because only limited *in situ* hydrogen from aqueous-methanol reforming could be used to selectively reduce nitroarenes (Table S1†) without the occurrence of side reactions as illustrated in eqn (5) and (6). Methanol in this process acted as both the solvent and hydrogen source.

Table 1 shows the results of imines synthesized from a model system composed of "nitrobenzene (1 mL)/furfural (1 mL)/methanol (40 mL)/water (10 mL)". As shown in entry 1, the formation rate of imine was 14.1  $\mu$ mol g<sup>-1</sup> min<sup>-1</sup> with the conversion of nitrobenzene and furfural at 30.6 and 29.6%, respectively. The selectivity for the imine based on furfural was 98.9% when the reaction was carried out over Au-Pd/Al<sub>2</sub>O<sub>3</sub> at 408 K and 2.0 MPa Ar-pressure (Au-Pd/Al2O3 was not deactivated, see Fig. S3<sup>†</sup>). H<sub>2</sub> was not detected in the gas effluent under this condition with a CO<sub>2</sub> yield of 5.2  $\mu$ mol g<sup>-1</sup> min<sup>-1</sup>, indicating the nitrobenzene was reduced by the *in situ* hydrogen from aqueous-methanol. When the temperature increased from 408 K to 453 K, H<sub>2</sub> was detected with a yield of 1.3  $\mu$ mol g<sup>-1</sup> min<sup>-1</sup> in the gas effluent. Accordingly, the selectivity for the imine based on furfural decreased to 87.4% with conversions of nitrobenzene and furfural being 93.7 and 79.5%, respectively (the formation rate of the imine was 33.5  $\mu$ mol g<sup>-1</sup> min<sup>-1</sup>), as shown in entry 2. The use of H<sub>2</sub> gas, instead of the in situ hydrogen from aqueous-methanol, for the reduction of nitrobenzene showed the formation rate and selectivity of imine were only  $0.2 \ \mu mol \ g^{-1} \ min^{-1}$  and 0.4%, respectively while the conversions of nitrobenzene and furfural were both 100% (entry 3). These results implied that the utilization of excessive amounts of hydrogen, either from H2 or from aqueous-phase reformation of methanol at high temperature, was not favored in the synthesis of imines.

Entries 4–7 in Table 1 show the effects of Au–Pd on the synthesis of imines. Obviously, both nitrobenzene and furfural

State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Industrial Catalysis Institute of Zhejiang University of Technology, Hangzhou 310032, P.R. China. E-mail: xnli@zjut.edu.cn; Fax: +86 571-88320409; Tel: +86 571-88320409 † Electronic supplementary information (ESI) available: Experimental

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures, catalyst evaluation, DFT calculations. See DOI: 10.1039/ c0cc00531b

Table 1 Experimental results of the direct synthesis of imine from nitrobenzene and furfural<sup>4</sup>

Entry	Factors affecting <i>S</i> (%)	Catalysts	Imine formation rate/ $\mu$ mol g <sup>-1</sup> min <sup>-1</sup>	<i>x</i> (%)			Products composition (%) <sup>c</sup>		
				NB	FF	$S(\%)^b$	Imine	AL + NMA	FA + THFA + AM
1		Au-Pd/Al <sub>2</sub> O <sub>3</sub>	14.1	30.6	29.6	98.9	89.4	9.6	1.0
$2^d$	(1) Hydrogen	Au-Pd/Al <sub>2</sub> O <sub>3</sub>	33.5	93.7	79.5	87.4	76.2	12.8	11.0
$3^e$		Au-Pd/Al <sub>2</sub> O <sub>3</sub>	0.2	100	100	0.4	0.3	30.5	69.2
4	(2) Active	Ru-Pd/Al <sub>2</sub> O <sub>3</sub>	10.1	26.2	23.3	90.2	74.6	17.3	8.1
5	components	Fe-Pd/Al <sub>2</sub> O <sub>3</sub>	7.8	19.5	18.1	89.7	76.8	4.9	18.3
6	*	Pd/Al <sub>2</sub> O <sub>3</sub>	4.2	9.7	9.4	92.9	79.4	13.6	7.0
7		$Au/Al_2O_3$	0	_				_	_
8	(3) Support	Au-Pd/MgO	3.2	27.3	6.7	100	72.6	27.4	_
9		Au-Pd/TiO <sub>2</sub>	12.5	27.8	25.9	100	81.0	19.0	—

<sup>a</sup> Reactions were carried out at 408 K, 2.0 MPa (Ar pressure). The load of Au-Pd/Al <sub>2</sub> O <sub>3</sub> was 0.5 g. A mixed solution (methanol 40 mL + water
10 mL + nitroarenes 1 mL + furfural 1 mL) was fed at 0.1 mL min <sup>-1</sup> . <sup>b</sup> Selectivity of imine based on furfural. <sup>c</sup> AL: aniline; NMA: N-methylaniline;
FA: furfural alcohol; THFA: tetrahydro furfural alcohol; AM: amines. <sup>d</sup> Reaction temperature: 453 K. <sup>e</sup> Molecular H <sub>2</sub> was co-fed at 10 mL min <sup>-1</sup>
with the liquid solution.

conversions and the formation rate of imine as well as the selectivity were decreased in the absence of Au as a catalytically active component. The formation rate of imine over Ru–Pd/Al<sub>2</sub>O<sub>3</sub>, Fe–Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were 10.1, 7.8 and 4.2  $\mu$ mol g<sup>-1</sup> min<sup>-1</sup>, respectively. The corresponding selectivities for the imine based on furfural were 90.2, 89.7 and 92.9%, respectively, at 408 K and 2.0 MPa Ar-pressure with *in situ* hydrogen from aqueous-methanol. Additionally, no imine was produced from the monometallic Au/Al<sub>2</sub>O<sub>3</sub> catalyst (entry 7), but Au–Pd on MgO and TiO<sub>2</sub> supports showed relatively lower imine formation rates (entries 8, 9). These results indicated that the bimetallic Au–Pd was the catalytically active component and necessary for the formation of imines.

The characteristics of the Au–Pd/Al<sub>2</sub>O<sub>3</sub> catalyst were examined to identify its catalytic mechanism. The IR spectra of CO adsorbed on Au–Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts (Fig. S4<sup>†</sup>) indicated the presence of Pd (111) on the catalyst surface.<sup>15</sup> The X-ray photoelectron spectroscopy (XPS) analysis of Au–Pd/Al<sub>2</sub>O<sub>3</sub> revealed that the Au  $4f_{7/2}$  and  $4f_{5/2}$  core levels showed binding energies of 83.5 and 87.1 eV respectively, and the Pd  $3d_{5/2}$  and  $3d_{3/2}$  core levels showed binding energies of 335.1 and 339.8 eV, respectively. Representative HRTEM images of Au–Pd/Al<sub>2</sub>O<sub>3</sub> taken from several different particles are shown in Fig. 1. The lattice spacings of most particles were in the range of 0.227 to 0.229 nm and 0.233 to 0.236 nm, which were close to the Pd (111) planes (0.225 nm) and the Au (111) planes (0.235 nm), respectively. Some particles were multiply twinned in a form of truncated decahedron (Fig. 1(d)). Similar TEM results have also been reported by Wang *et al.*<sup>15</sup>

From the above analysis, the proposed mechanism for the direct synthesis of imine from nitrobenzene and furfural is shown in Fig. 2. The availability of limited hydrogen is the vital factor to control the reaction selectivity. Too much available hydrogen will result in a series of side reactions



**Fig. 1** Representative HRTEM images of the Au–Pd/Al<sub>2</sub>O<sub>3</sub> catalyst obtained from several different particles.



Fig. 2 The catalytic mechanism of the direct synthesis of imine from nitrobenzene and furfural over the  $Au-Pd/Al_2O_3$  catalyst with (a) hydrogen from the aqueous-phase reforming of methanol, (b) molecular  $H_2$  as a reducing agent.

(Table 1 entries 2, 3). One important role of the Pd in Au-Pd is the catalytic reforming or dehydrogenation of methanol (step (1) in Fig. 2a), which cannot happen on a monometallic Au catalyst (Table 1, entry 7). This proposition can be further confirmed by a density functional calculation of the adsorption energy of methanol on pure Au (111), pure Pd (111), Au (111) with a surface of Pd, and Pd (111) with a surface of Au (Table 2). Methanol was found not to adsorb on Au (111) at all. The in situ formed hydrogen from the reformation of methanol will immediately reduce the nitroarenes adsorbed on the Au-Pd particles (step (2) in Fig. 2a). It is well known that Au has excellent selectivity for the catalytic hydrogenation of nitroarenes into aryl amines.<sup>16</sup> When Au was replaced with Fe or Ru, the selectivity of imine significantly decreased. It should be also pointed out that the Au and Pd particles alone without the modification of each other are not active for the selective reduction of nitroarenes using methanol as a hydrogen source and the direct synthesis of imines from nitroarenes and carbonyl compounds. Therefore, Pd and Au, respectively, played a major role in steps (1) and (2). Pd also enhanced the adsorption of nitrobenzene on the Au-Pd particles. Imine

**Table 2** The adsorption energy of methanol, nitrobenzene and furfural on Au (111), Pd (111), Au (111) with a surface of Pd, and Pd (111) with a surface of Au (eV).



	Pd (111)	Pd (111)–Au	Au (111)–Pd	Au(111)
Methanol	0.50	0.45	0.40	0.18
Nitrobenzene	1.36	1.25	0.35	0.33
Furfural	1.06	0.96	0.40	0.40

 Table 3
 Experimental results of the direct synthesis of imines from nitroarenes and carbonyl compounds over the Au–Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>a</sup>

	Nitroarenes conversion (%)	Carbonyl compounds conversion (%)	Imines formation rates/ $\mu$ mol g <sup>-1</sup> min <sup>-1</sup> and composition (%)
Entry	R <sub>1</sub> -NO <sub>2</sub>	R2O	$n = \frac{1}{N} R_2$
1	x = 19.5	x = 18.3	Ph N <sup>Ph</sup> 6.7 and 74.8
2	x = 22.6	x = 21.2	Ph N <sup>Ph</sup> 7.5 and 83.7
3	x = 16.6	x = 15.9	Ph N 5.4 and 87.2
4	x = 18.4	x = 18.1	Ph N 6.3 and 94.6

<sup>*a*</sup> Reactions were carried out at 408 K, 2.0 MPa (Ar pressure). The load of  $Au-Pd/Al_2O_3$  was 0.5 g. A mixture of 40 mL methanol, 10 mL water, 1 mL nitroarenes, and 1 mL carbonyl compounds was fed at 0.1 mL min<sup>-1</sup>.

was finally obtained from the condensation of aniline with furfural at the Lewis acid site on  $Al_2O_3$ .

In order to extend the applicability of the current method, the direct syntheses of imines from nitrobenzene and benzaldehyde or cinnamaldehyde, 3-methylnitrobenzene and cinnamaldehyde, or 4-methylnitrobenzene and cinnamaldehyde were also investigated. As shown in Table 3, the formation rates of the corresponding imines are 6.7, 7.5, 5.4 and 6.3  $\mu$ mol g<sup>-1</sup> min<sup>-1</sup>, respectively. These results are comparable to those in the reaction of nitrobenzene with furfural.

In conclusion, the direct synthesis of imines from nitroarenes and carbonyl compounds was realized over the Au–Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of methanol. The available limited *in situ* hydrogen, from the aqueous-phase reformation of methanol or hydrogen transfer using methanol as the donor, was the vital factor controlling the selectivity of imines. Pd and Au, respectively, played a major role in generating limited hydrogen and *in situ* hydrogenation of nitroarenes. The produced aryl amine from nitroarenes finally condensed with carbonyl compounds to form imines at the Lewis acid sites on Al<sub>2</sub>O<sub>3</sub>.

This work was supported by National Nature Science Foundation of China (NSFC-20976164).

## Notes and references

- N. Hall, Science, 1994, 266, 32; J. C. Wasilke, S. J. Obrey, T. Baker and G. C. Bazan, Chem. Rev., 2005, 105, 1001.
- J. W. Bae, Y. J. Cho, S. H. Lee, C. O. M. Yoon and C. M. Yoon, *Chem. Commun.*, 2000, 1857; E. Byun, B. Hong, K. A. D. Castro, M. Lim and H. Rhee, *J. Org. Chem.*, 2007, **72**, 9815; X. J. Zhou, Z. W. Wu, L. Lin, G. J. Wang and J. P. Li, *Dyes Pigm.*, 1998, **36**, 365; L. W. Bieber, R. C. da Costa and M. F. da Silva, *Tetrahedron Lett.*, 2000, **41**, 4827.
- 3 X. N. Li, J. H. Zhang, Y. Z. Xiang, L. Ma, Q. F. Zhang, C. S. Lu, H. Wang and Y. Bai, *Sci. China Chem.*, 2008, **51**, 248; L. Xu, X. N. Li, Y. F. Zhu and Y. Z. Xiang, *New J. Chem.*, 2009, **33**, 2051.
- 4 R. W. Layer, *Chem. Rev.*, 1963, 63, 489; V. Alexander, *Chem. Rev.*, 1995, 95, 273; M. Higuchi and K. Yamamoto, *Org. Lett.*, 1999, 1, 1881; M. Kimura, T. Tamaki, M. Nakata, K. Tohyama and Y. Tamaru, *Angew. Chem., Int. Ed.*, 2008, 47, 5803.
- J. H. Billman and K. M. Tai, J. Org. Chem., 1958, 23, 535;
   J. A. Castellano, J. E. Goldmacher, L. A. Barton and J. S. Kane, J. Org. Chem., 1968, 33, 3501; F. Texier-Boullet, Synthesis, 1985, 679;
   K. Tanaka and F. Toda, Chem. Rev., 2000, 100, 1025; K. Tanaka and R. Shiraishi, Green Chem., 2000, 2, 272; J. S. Bennett, K. L. Charles, M. R. Miner, C. F. Heuberger, E. J. Spina, M. F. Bartels and T. Foreman, Green Chem., 2009, 11, 166.
- A. J. Bailey and B. R. James, *Chem. Commun.*, 1996, 2343;
   K. Mori, K. Yamaguchi, T. Mizugaki, K. Ebitani and K. Kaneda, *Chem. Commun.*, 2001, 461; B. Zhu, M. Lazar, B. G. Trewyna and R. J. Angelici, *J. Catal.*, 2008, 260, 1; B. Zhu and R. J. Angelici, *Chem. Commun.*, 2007, 2157.
- 7 F. Porta, C. Crotti and S. Cenini, J. Mol. Catal., 1989, 50, 333.
- 8 G. Green, W. P. Griffith, D. M. Hollinshead, S. V. Ley and M. Schrder, J. Chem. Soc., Perkin Trans. 1, 1984, 681.
- 9 S. Sithambaram, R. Kumar, Y. C. Son and S. L. Suib, J. Catal., 2008, 253, 269; H. Sun, F. Z. Su, J. Ni, Y. Cao, H. Y. He and K. N. Fan, Angew. Chem., Int. Ed., 2009, 48, 4390.
- L. L. Santos, P. Serna and A. Corma, *Chem.-Eur. J.*, 2009, **15**, 8196.
   Y. Zheng, K. Ma, H. Li, J. Li, J. He, X. Sun, R. Li and J. Ma, *Catal. Lett.*, 2009, **128**, 465.
- 12 M. Akazome, T. Kondo and Y. Watanabe, J. Org. Chem., 1994, 59, 3375.
- 13 A. L. Korich and T. S. Hughes, Synlett, 2007, 2602.
- 14 X. N. Li and Y. Z. Xiang, *Sci. China Chem.*, 2007, **50**, 746; Y. Z. Xiang, X. N. Li, C. S. Lu, L. Ma and Q. F. Zhang, *Appl. Catal.*, *A*, 2010, **375**, 289.
- 15 D. Wang, A. Villa, F. Porta, L. Prati and D. S. Su, J. Phys. Chem. C, 2008, 112, 8617.
- 16 A. Corma and P. Serna, Science, 2006, 313, 332.