DOI: 10.1002/adsc.201000621

Highly Chemo- and Regioselective Transfer Reduction of Aromatic Nitro Compounds using Ammonium Formate Catalyzed by Supported Gold Nanoparticles

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Received: August 5, 2010; Revised: November 23, 2010; Published online: February 9, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000621.

Abstract: A highly chemo- and regioselective reduction of a wide diversity of aromatic nitro compounds to the corresponding amines has been achieved by a combination of gold nanoparticles supported on titania and ammonium formate ($HCOONH_4$) in ethanol at room temperature. Furthermore, a direct and mild route to formanilides from aromatic nitro compounds bearing different functional groups by reductive N-formylation using the gold-mediated transfer reduction protocol is also established.

Keywords: ammonium formate; chemoselectivity; gold; heterogeneous catalysis; N-formylation; nitro group reduction

The reduction of aromatic nitro compounds to the corresponding amines is an important step in the industrial synthesis of dyes, biologically active compounds, pharmaceuticals, rubber chemicals, and agricultural chemicals.[1] A wide variety of methods have been developed for this purpose. As opposed to the commonly used reduction processes, which involve hazardous Fe/HCl[2] or Sn/HCl[3] or molecular hydrogen (H_2), catalytic transfer hydrogenation (CTH)[4] employing cheap and easily accessible hydrogen donors, e.g., ammonium formate ($HCOONH_4$), is simpler, safer, highly selective, and ecofriendly.[5] Furthermore, unlike conventional hydrogenation methods, CTH reactions do not require any elaborate experimental set-up or high-pressure reactors.[6] Practically, almost all relevant results have been achieved using palladium supported on activated charcoal (Pd/C) as the catalysts.[7] More recently, a facile selective reduction of nitro compounds catalyzed by $HCOONH_4$-Cu nanoparticles (NPs) has also appeared.[8] One critical limitation of these processes, however, is the pyrophoric or air-sensitive nature of the involved catalysts, which presents additional handling problems. Moreover, these catalysts generally lack the desired chemoselectivity over other functional groups that are often present in the substrates such as acid, aldehyde, ester, alkene, halide and nitrile moieties and also, the desired regioselectivity in the reduction of dinitro compounds. In addition, the reduction of aromatic nitro compounds often stops at an intermediate stage, yielding hydroxylamine, hydrazine, and azoarene products.[9] In this sense, there is a strong incentive to develop new simple, efficient, easily-handled procedures that can allow the highly chemo- and regioselective reduction of the nitro group under mild conditions.

In recent years, supported gold NPs have emerged as excellent catalysts for a broad range of organic transformations under mild conditions.[10] Gold was originally considered catalytically inactive. However, when finely divided as small particles (≤ 5 nm) and associated with a suitable support, Au could be active and highly selective in a variety of hydrogen-involving reactions.[11] Notably, the seminal work by Corma and Serna has shown that TiO_2-supported Au NPs are highly selective for the hydrogenation of a nitro group by H_2 in the presence of other reducible functions.[12] Despite its efficiency, this method suffers from some drawbacks or limitations such as the need of relatively high temperature/pressure, complicated equipment, and unfavourably low hydrogen-delivery rate. Very recently, we have described a facile Au-catalyzed, CO/H_2O-mediated method that circumvented

Table 1. Reduction of nitrobenzene to aniline under CTH conditions.[a]

Entry	Catalyst	Solvent	Hydrogen donor	Conversion[b] [%]	Selectivity[b] [%]
1	Au/TiO_2	ethanol	$HCOONH_4$	>99	>99
2[c]	Au/TiO_2	ethanol	$HCOONH_4$	>99	>99
3	TiO_2	ethanol	$HCOONH_4$	–	–
4	Au/TiO_2	ethanol	–	–	–
5	Au/TiO_2	ethanol	HCOOK	37	84
6	Au/TiO_2	ethanol	HCOOH	–	–
7	Au/TiO_2	2-propanol	2-propanol	–	–
8[d]	Au/TiO_2	ethanol	$HCOONH_4$	>99	98
9	Au/TiO_2	THF	$HCOONH_4$	35	59
10	Au/TiO_2	DCM	$HCOONH_4$	7	71
11	Au/TiO_2	DMSO	$HCOONH_4$	10	45
12	Au/TiO_2	CH_3CN	$HCOONH_4$	54	92
13[e]	Au/TiO_2	H_2O	$HCOONH_4$	>99	>99
14	Au/CeO_2	ethanol	$HCOONH_4$	71	52
15	Au/ZnO	ethanol	$HCOONH_4$	24	>99
16	Au/HAP	ethanol	$HCOONH_4$	59	56
17	Au/SiO_2	ethanol	$HCOONH_4$	13	59
18	Au/Al_2O_3	ethanol	$HCOONH_4$	23	61
19	Pd/C	ethanol	$HCOONH_4$	59	97
20	Ru/TiO_2	ethanol	$HCOONH_4$	–	–

[a] *Reaction conditions:* $PhNO_2$ (1 mmol), catalyst (metal: 1 mol%), solvent (10 mL), hydrogen donor (5 mmol), N_2 protection, 25 °C, 3 h.
[b] Conversion and selectivity were determined by GC (internal standard: *n*-decane) and GC-MS.
[c] Results for the third run.
[d] Reaction at 0 °C for 30 h.
[e] 12 h.

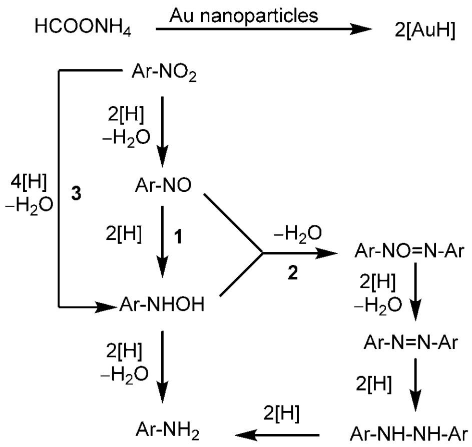
the difficult H_2 activation thus enabling more efficient and selective nitro reduction.[13] In continuation of our interest in the use of supported Au as greener catalysts to facilitate new functional transformations under mild conditions, we wish to report here an efficient, convenient and high-yield $HCOONH_4$-mediated protocol using safe and easily-handled supported Au NPs as a robust catalyst for the reduction of aryl nitro compounds at ambient temperature. Our results have shown that a wide diversity of the functionalized nitro compounds could be selectively reduced to the corresponding amines under mild conditions while the other reducible functions remained intact. To the best of our knowledge, this study also represents the first direct one-pot conversion of aryl nitro compounds to formanilides by reductive N-formylation using gold catalysts.

First of all, a mixture of solid Au/TiO_2 (supplied by Mintek), nitrobenzene (**1**), and $HCOONH_4$ in ethanol was stirred at room temperature under an N_2 atmosphere for 3 h (Table 1, entry 1). Selective reduction of **1** occurred to quantitatively yield aniline (**2**) without any by-products such as hydroxylamine, azo or azoxy compounds. The reaction was not initiated at all using $HCOONH_4$ in the absence of Au/TiO_2. No conversion of **1** was observed with Au/TiO_2 without $HCOONH_4$. Thus, a combination of Au/TiO_2 and $HCOONH_4$ is essential to carry out the reduction (Table 1, entries 3 and 4). Other hydrogen sources such as HCOOK showed much lower activity, whereas HCOOH and 2-propanol were not reactive (Table 1, entries 5, 6, and 7). As shown in the Supporting Information (Table S2), the turnover frequency (TOF) of the catalyst was dramatically improved by increasing the reaction temperature. An excellent yield was also obtained even at 0 °C although a longer reaction time was required (Table 1, entry 8). Among the solvents tested, high yields of **2** were obtained using ethanol as solvent (Table 1, entry 1). In contrast, low yields were obtained using tetrahydrofuran (THF), dichloromethane (DCM), dimethyl sulfoxide (DMSO) and acetonitrile as solvents (Table 1, entries 9–12). Interestingly, the Au/TiO_2-catalyzed reduction can also be carried out in water (Table 1, entry 13).

Next, we investigated the influence of the inorganic support on the performance of Au NPs in more detail. As observed with other gold-catalyzed processes, the choice of the solid support had a significant influence on the catalytic activity. Among the tested supports, TiO_2 was the best. CeO_2 was also effective (Table 1, entry 14), whereas Au/ZnO, Au/hydroxyapatite (Au/HAP), Au/SiO_2 and Au/Al_2O_3 resulted in low yields of **2** (Table 1, entries 15–18). Moreover, the use of other metal particles with catalytic potential, such as Pd and Ru, resulted in significantly lower or no yield of **2** for the reduction of **1** under similar reaction conditions (Table 1, entries 19 and 20). These results clearly indicate that TiO_2-supported Au NPs, a versatile material that has shown its high activity in a variety of reduction reactions involving H_2[11,12] or CO/H_2O[13] as the hydrogen source, has the optimum activity for the reduction of **1** by using $HCOONH_4$ as the reductant. Thus, under optimized conditions, the average TOF and the TON reached up to 33.3 h^{-1} and 100, respectively (Table 1, entry 1). These values are one or two orders of magnitude greater than those in previously reported catalyst systems, such as $HCOONH_4$-Cu nanoparticles (TOF: 0.1 h^{-1}, TON: 20, reaction at 120 °C).[8]

To determine whether Au/TiO_2 worked as a heterogeneous catalyst, Au/TiO_2 was removed from the reaction mixture by simple filtration at 50% conversion of **1**. Continued stirring of the filtrate under similar conditions did not give any products. The absence of Au ions in the filtrate was verified using ICP analysis (detection limit: 0.10 ppm). These results clearly demonstrate that reduction took place only on the Au NPs deposited on TiO_2. Furthermore, the Au/TiO_2 catalyst was recoverable by simple filtration after the transfer reduction without any loss in their activity or selectivity after several uses (Table 1, entry 2). TEM images of Au/TiO_2 after the reuse revealed that the average diameter and size distribution of the gold NPs were similar to those of the fresh Au/TiO_2 (see Supporting Information, Figure S1), and that no aggregation of the used gold NPs was apparent. In addition, XPS analysis of Au/TiO_2 showed virtually no change in the surface Au/Ti ratio (see Supporting Information, Figure S2, Table S1), corroborating the observation that the gold NPs after reuse were the same size after recycling compared to the original sample. These results are consistent with the retention of the catalytic activities of Au/TiO_2 during recycling experiments.

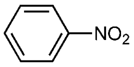
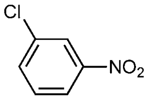
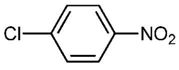
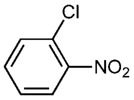
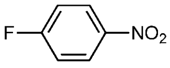
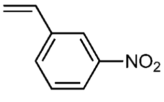
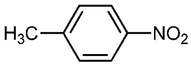
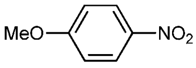
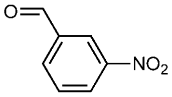
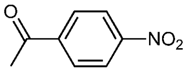
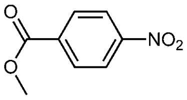
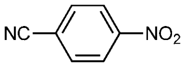
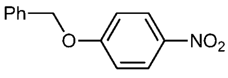
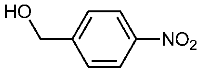
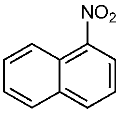
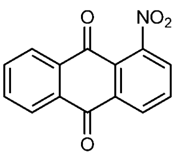
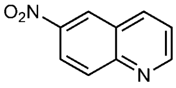
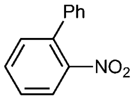
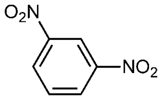
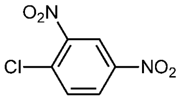
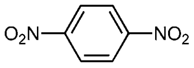
Given the observed high activity and selectivity, it is of interest to clarify the catalytic origin of the present $HCOONH_4$-Au/TiO_2 system. In line with our recent proposal for gold-catalyzed nitro reduction using CO/H_2O as the reductant, a facile transfer dehydrogenation from $HCOONH_4$ leading to crucial Au–H formation could be the key factor for achieving rapid nitro reduction under mild conditions.[13] On the other hand, it is known that the reduction of aromatic nitro compounds can proceed by two different routes (Scheme 1) in which a couple of consecutive elemental steps are involved.[14] In path **1**, the nitro compound is first reduced to a nitroso compound which further proceeds to provide the hydroxylamine and finally gives rise to amine. In path **2**, the initially formed nitroso compound may condense with hydroxylamine to produce the azoxy compound, which then may undergo further reduction to azo, hydrazo, and finally to amine. Recently, Corma et al. have proposed a more straightforward route (path **3**) involving the direct formation of the intermediate hydroxylamine for Au-catalyzed nitro hydrogenation by H_2.[14] To obtain an insight into the reaction pathways involved in the $HCOONH_4$-mediated nitro reduction, we carried out a series of experiments using the above intermediates. When phenyl hydroxylamine, obtained by a different route, was subjected to reduction by this procedure, aniline was obtained in 60% yield (Supporting Information, Table S3, entry 1). However, when nitrosobenzene, azobenzene and hydrazobenzene, also obtained separately, were reduced under identical reaction conditions, aniline was formed only in substantially lower yields of 3%, 12% and 3%, respectively (Supporting Information, Table S3, entries 2–4). Therefore, it seems that the present $HCOONH_4$-Au/TiO_2-mediated nitro reduction occurs mainly through path **3**.



Scheme 1. Proposed reaction pathways for reduction of aromatic nitro compounds by the $HCOONH_4$-Au/TiO_2 system.

With these findings in hand, we then extended our studies to various kinds of nitro compounds to establish the scope of the CTH reaction with the $HCOONH_4$-Au/TiO_2 system. Table 2 shows that the catalyst system was surprisingly versatile. Various structurally diverse aryl nitro compounds, regardless of the presence of electron-withdrawing or electron-donating functions (Table 2, entries 2–14), could be selectively reduced to the corresponding amine compounds. Unlike the catalytic hydrogenation of nitro compounds with halogens (Table 2, entries 2–5) on other metal surfaces, the substrates were reduced cleanly to the corresponding anilines without any dehalogenation over Au/TiO_2. In the transformations of chloronitroaromatics, the lower reaction rate of *o*-chloronitrobenzene relative to the *m*- and *p*-analogues indicated a steric effect (Table 2, entries 2–4). Strikingly, all of the reducible functions such as alkene, aldehyde, nitrile, ketone and ester as well as O-benzyl moieties remained intact during the reduc-

Table 2. Transfer reduction of aromatic nitro compounds to the corresponding amines by HCOONH$_4$-Au/TiO$_2$.[a]

Entry	Substrate	Time [h]	Yield [%][b]
1		3	99 (95)
2		6	99 (92)
3		3.5	98 (95)
4		8	90 (80)
5		3	99 (96)
6		3.5	98 (93)
7		5	99 (83)
8[c,e]		1.7	94 (77)
9[d]		3	90 (82)
10		2.5	99 (91)
11[c]		3	98 (94)
12		2	65 (61)
13[d]		3	90 (81)
14		3	99 (96)
15		5.2	99 (85)
16[c]		1.7	96 (92)
17[e]		3	99 (89)
18		3.5	99 (96)
19		0.25	88 (85)[f]
20		0.4	91 (87)[f]
21		3	75 (71)[f]

[a] *Reaction conditions:* substrate (1 mmol), Au/TiO$_2$ catalyst (Au: 1 mol%), ethanol (10 mL), HCOONH$_4$ (5 mmol), N$_2$ protection, 25 °C.

[b] Yields were determined by GC analysis; values in parenthesis are the yields of the isolated products. The structures of the products were established from their GC-mass spectra.

[c] Methanol (10 mL) as solvent.

[d] CH$_3$CN (10 mL) as solvent.

[e] 50 °C.[f] Yield for nitroaniline.

tion process (Table 2, entries 6, 9–14). 6-Nitroquinoline was reduced to 6-aminoquinoline (an important intermediate in synthesizing several dyes) which indicated that the heterocyclic ring would not be affected under these CTH conditions (Table 2, entry 17). The relatively higher reduction rate of 1-nitroanthroquinone (Table 2, entry 16) to 1-aminoanthroquinone (another important intermediate in the dye industry) showed that the electron-withdrawing group might facilitate the reduction process.

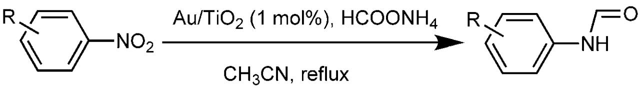
The origin of the high chemoselectivity for the specific reduction of nitro group was confirmed by an intermolecular competitive reaction between nitrobenzene and other unsaturated substrates, such as styrene, acetophenone, benzaldehyde, and benzonitrile under the conditions described above (see Supporting Information). The result showed that while the yield of aniline was >99% (GC yield), all other unsaturated substrates exhibited no conversion at all. Therefore, the higher intrinsic rate for the reduction of the nitro group than that of the other reducible functions over the HCOONH$_4$-Au/TiO$_2$ system is responsible for the high chemoselectivity observed.

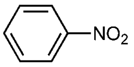
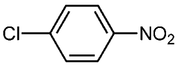
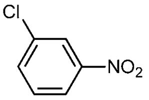
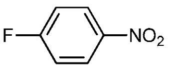
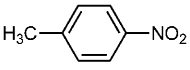
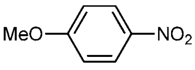
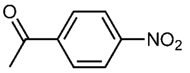
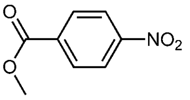
The catalyst also shows promise for regioselective reduction of dinitrobenzenes with high to excellent yields (Table 2, entries 19–21). Many conventional procedures involving hydride reducing agents, hydrogenation, or indium failed to give such a high regioselectivity.[9,15] Recently, the regioselective reduction of *o*-, *m*-, and *p*-dinitrobenzenes has been carried out by using silane/oxo-rhenium complexes.[15] However, the use of a toxic silane as hydrogen source, costly metal complexes as catalyst, long reaction times (24–38 h), and low yields (58–76%) limit the scope of the method. Very recently, we have demonstrated that a more efficient regioselective reduction of dinitrobenzenes could be achieved with Au/TiO_2 in the presence of CO/H_2O.[13] Nevertheless this method was inconvenient to some extent due to the fact that the toxic CO gas is highly dangerous and difficult to handle. Thus, we have been able to further proceed along these green lines. Notably, the convenient and safer chemo- and regioselective reduction of the nitro compounds can be achieved with the $HCOONH_4$-Au/TiO_2 system under mild CTH conditions.

Finally, taking into account that $HCOONH_4$ in an aprotic solvent like acetonitrile has previously been reported as a formylating agent,[17] we envisioned that the present $HCOONH_4$-Au/TiO_2 system could afford a green and efficient protocol for the direct synthesis of formanilides from nitro compounds. Formanilides are widely used in the synthesis of biologically active compounds as well as catalyzing several organic transformations as Lewis bases.[18] Various methods have been reported for the selective reduction of aryl nitro compounds to anilines as well as the N-formylation of anilines with different formylating agents.[19] However, the direct conversion of aryl nitro compounds to formanilides would be an ideal choice for this class of important compounds. The efficacy of the one-step gold-catalyzed reductive N-formylation methodology can be seen from Table 3. A variety of aromatic nitro compounds having different sensitive functional groups can be converted into the corresponding formanilides in high yields following the procedure as depicted in Table 3. While Baskaran and co-workers[20] have reported an efficient one-step synthesis of formanilides from aromatic nitro compounds with $HCOONH_4$-Pd/C, this system requires prolonged reaction times (up to 10–24 h) and a large excess of $HCOONH_4$ to achieve high yields of the products (>90%). In contrast, the present Au-based system has the following significant advantages: 1) only 7 equivalents of $HCOONH_4$ was employed; 2) the reaction was much more efficient even at much lower metal loadings; and 3) the reaction uses the non-pyrophoric Au/TiO_2 catalyst that is easy to handle.

In summary, we have developed an efficient and highly chemo- and regioselective gold-catalyzed, $HCOONH_4$-mediated CTH methodology for the reduction of a great variety of multifunctionalized aromatic nitro compounds to the corresponding amines. Moreover, this gold-based CTH system could also accomplish the direct conversion of aromatic nitro compounds bearing different functional groups to the corresponding N-formanilides chemoselectively. In this valuable transformation, $HCOONH_4$ serves two distinct functions: as hydrogen source for nitro reduction and as a formylating agent. The mild reaction conditions and associated low cost of ammonium formate will greatly facilitate the synthesis of functionalized amines and formanilides in both laboratory and industrial production.

Table 3. Reductive N-formylation of aryl nitro compounds under catalytic transfer hydrogenation conditions.[a]



Entry	Substrate	Time [h]	Yield [%][b]
1		4.5	94 (87)
2		6	94 (85)
3		7	95 (90)
4		5	92 (83)
5		3	95 (88)
6		2.5	97 (93)
7		8	70 (66)
8		9	77 (71)

[a] *Reaction conditions:* substrate (1 mmol), Au/TiO_2 catalyst (Au: 1 mol%), $HCOONH_4$ (7 mmol), N_2 protection, in CH_3CN (3 mL) under reflux conditions.

[b] Yields were determined by GC analysis; values in parenthesis are the yields of the isolated products.

Experimental Section

General Procedure for the Reduction of Aromatic Nitro Compounds

The mixture of nitro compound (1 mmol), metal catalysts (metal: 1 mol%), ethanol (10 mL), and anhydrous $HCOONH_4$ (5 mmol) was put into a flask (100 mL) fitted with a gas inlet tube for introducing N_2 by bubbling (10 mL min^{-1}). The reaction mixture was magnetically stirred (1000 rpm) at 25 °C. The conversion and product selectivity were periodically determined by GC analysis [Shimazu GC-17 A equipped with an HP-FFAP column (30 m ×

0.25 mm) and a flame ionization detector (FID)] using *n*-decane as an internal standard. After completion of the reduction, the reaction mixture was filtered and the catalyst was washed thoroughly with ethanol. Then the filtrate was concentrated under vacuum and extracted by CH_2Cl_2 (3× 3 mL). The combined CH_2Cl_2 fractions were concentrated under reduced pressure using a rotatory evaporator. The crude product was purified by column chromatography [silica 200–300; petroleum ether (60~90 °C)/ethyl acetate mixture] to afford the amine product. All the products were characterized by GC-MS and further confirmed by the comparison of their GC retention time, mass with those of authentic samples.

General Procedure for the Formylation of Aromatic Nitro Compounds

The mixture of nitro compound (1 mmol), Au/TiO_2 catalyst (Au: 1 mol%), anhydrous CH_3CN (3 mL) and anhydrous $HCOONH_4$ (7 mmol) was added to a flask (10 mL) equipped with a reflux condenser. The resulting mixture was allowed to reflux with vigorous stirring under a nitrogen atmosphere. After completion of the reaction, the reaction mixture was filtered and the catalyst was washed thoroughly with CH_3CN. Then the filtrate was concentrated and dried under reduced pressure using a rotatory evaporator. The crude product was purified by column chromatography [silica 200–300; petroleum ether (60~90 °C)/ethyl acetate mixture] to afford the product. All the products were characterized by GC-MS and further confirmed by the comparison of their GC retention time, mass with those of authentic samples.

Acknowledgements

Financial support by the National Natural Science Foundation of China (20721063, 20873026 and 21073042), New Century Excellent Talents in the University of China (NCET-09-0305), and the State Key Basic Research Program of PRC (2009CB623506), FDUROP (09018) as well as Science & Technology Commission of Shanghai Municipality (08DZ2270500) is kindly acknowledged.

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