

Novel chemoselective hydrogenation of aromatic nitro compounds over ferric hydroxide supported nanocluster gold in the presence of CO and H₂O†

Lequan Liu,^{ab} Botao Qiao,^{ab} Zhengjian Chen,^{ab} Juan Zhang^{ab} and Youquan Deng^{*a}

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Chemoselective hydrogenation of aromatic nitro compounds were first efficiently achieved over Au/Fe(OH)_x at 100–120 °C for 1.5–6 h (depending on different substrates) in the presence of CO and H₂O.

Anilines and their derivatives, especially with functionalized groups, are important industrial intermediates for pharmaceutical, organic synthesis and fine chemicals, thus exploring new catalysts or methods to achieve chemoselective hydrogenation of nitro compounds has attracted considerable attention.^{1–3} Though many studies have been made, the efficient hydrogenation with high selectivity, as well as with high activity, for nitro compounds has not so far been reported. Generally, the process is approached by three methods. One is stoichiometric reduction of corresponding aromatic nitro compounds by using iron, tin, zinc or a metal sulfide such as Na₂S. However, this method is of low selectivity for nitro group, and large amounts of waste acids and residues are generated during the reaction. The second is catalytic hydrogenation of nitro compounds with H₂ over supported noble metal catalysts, *e.g.* Pd,^{4,5} Pt,⁶ Ru catalysts,⁷ *etc.* Nevertheless, hydrogenation byproducts from other groups are often inevitable in most cases. Another method is chemoselective hydrogenation of aromatic nitro compounds catalyzed by carbonyl or organic metals in the presence of CO and H₂O.^{8,9} Much research has been done in this area as it offered a new way to afford aniline, especially in the presence of other functional groups, and utilization of CO is one of the important subjects in C₁ chemistry. However, its disadvantages are also obvious: relatively low efficiency (TOF values in the range of 300 h⁻¹),⁹ involving toxic carbonyl or organic metal compounds as catalysts and the indispensability of basic conditions resulting from addition of organic or inorganic bases restrict its further industrial application especially when environmental considerations play an increasingly important role. It is therefore desirable to develop a more efficient and environmental process to achieve chemoselective hydrogenation for obtaining valuable functionalized anilines.

Supported Au catalysts have attracted considerable experimental and theoretical attention in the chemistry

community,^{10–14} and numerous studies have been carried out to study new reactions. Recently, Corma *et al.* first reported that chemoselective hydrogenation of aromatic nitro compounds could be achieved over TiO₂ and Fe₂O₃ supported Au catalysts with H₂,¹ and our previous work also found that the catalytic activity could be improved by using Fe(OH)_x supported Au nanoclusters (TOF increased to 200–350 h⁻¹).¹⁵ However, the efficiency still needs to be enhanced in view of practical application. On the other hand, one industrial process using CO to produce pure H₂, the low temperature water–gas shift (WGS) reaction (generally in the temperature range of 180–250 °C), has attracted considerable attention, and supported Au catalysts have been found to be very active for this reaction.^{16,17} Thus, supported Au catalysts may show high activity and even selectivity for the chemoselective hydrogenation of aromatic nitro compounds by introducing low temperature WGS reaction. Meanwhile, if this strategy can be implemented, the disadvantages such as use of toxic carbonyls or organometallics and dispensability of produced bases in the traditional processes can be overcome. Herein, we report for the first time that aromatic nitro compounds can be efficiently and chemoselectively hydrogenated over ferric hydroxide supported nanocluster Au catalysts in the presence of CO and H₂O with enhanced catalytic performance.

A series of Au catalysts with different loadings (1.5–1.6%) were prepared with co-precipitation and the final pH was adjusted to *ca.* 8.5 with Na₂CO₃. The resultant precipitates were washed with distilled water and then treated at 200 °C for 5 h or 500 °C for 4 h in static air, and are denoted as Au/Fe(OH)_x and Au/Fe₂O₃, respectively. For comparison, ferric hydroxide supported Pd and Pt catalysts prepared in the same manner, denoted as Pd/Fe(OH)_x and Pt/Fe(OH)_x, respectively, and 4.4% Au/Fe₂O₃ bought from World Gold Council, denoted as Au/Fe₂O₃-W, were also employed. Catalytic testing was carried out in a 90 ml autoclave equipped with magnetic stirring. In general, 0.050 g catalyst, 7.5 mmol substrate (15 mmol for *p*-nitroacetophenone), 7 ml 2-ethoxyethanol as solvent, 3 ml H₂O and 1.5 MPa CO were successively charged into the reactor, then each autoclave was heated to the required temperature (100–120 °C). Detailed procedures can be found in ESI.†

Typical data such as noble metal loadings, BET surface areas and binding energies are summarized in Table S1 of ESI.† As can be seen, Fe(OH)_x supported catalysts possessed relatively higher BET surface (200–230 m² g⁻¹), while after being treated at 500 °C the BET surface decreased substantially to 42.4 for 1.6 wt% Au/Fe₂O₃, which was comparable

^a State Key Laboratory for Oxo Synthesis and Selective Oxidation, Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China. E-mail: ydeng@lzb.ac.cn; Fax: 88-931-4968116; Tel: 88-931-4968116

^b Graduate University of Chinese Academy of Sciences, Beijing, China
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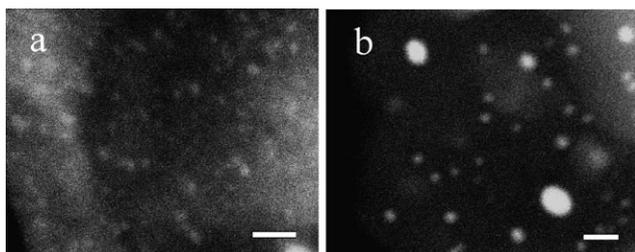


Fig. 1 HAADF-STEM images of supported Au catalysts: (a) 1.5 wt% Au/Fe(OH)_x, (b) 1.6 wt% Au/Fe₂O₃ catalyst; bars correspond to 10 nm.

to that of Au/Fe₂O₃-W, 39.0 m² g⁻¹. XPS analysis (Fig. S1, ESI†) showed that the chemical states of surface Au species in Au/Fe(OH)_x were a mixture of Au⁺ and Au (Au⁺/Au: 0.07), while after being calcined at 500 °C, the Au species changed to metal Au completely (B.E. 4f_{7/2} = 83.8 eV). A mixture of chemical states of Pt⁴⁺ and Pt²⁺ species was also observed in 2.2 wt% Pt/Fe(OH)_x with the corresponding atom ratio of 1.8. As for 2.8 wt% Pd/Fe(OH)_x, only Pd²⁺ species were found. XRD results (Fig. S2, ESI†) showed that ferric hydroxide was amorphous upon treatment at 200 °C for 5 h, and Au, Pd, Pt species in ferric hydroxide were highly dispersed. As for 1.6 wt% Au/Fe₂O₃, formation of α-Fe₂O₃ crystallites was evident. In order to obtain explicit details of Au particle size, 1.5 wt% Au/Fe(OH)_x and 1.6 wt% Au/Fe₂O₃ were examined with high-resolution scanning transmission electron microscopy (STEM) in high angle annular dark field (HAADF) mode. As can be seen from the HAADF-STEM images, Fig. 1(a), small bright spots, images of Au species, can be discerned from the background over 1.5 wt% Au/Fe(OH)_x. Further, Au particle sizes range from 1.0 to 2.5 nm, which agrees with no characteristic diffraction peaks of Au in XRD image, suggesting Au species in Fe(OH)_x are still in homogenous dispersion without no obvious aggregation. Also, this result was similar to the early work of Hutchings *et al.*,¹³ in which specific clusters were identified to be critical for a good performance in CO oxidation. However, after calcination at 500 °C, 3–5 nm and even 6–9 nm Au particles were clearly observed over 1.6 wt% Au/Fe₂O₃ showing that calcination has a remarkable effect for Au particle aggregation.

Catalytic performances of ferric hydroxide supported Au, Pd and Pt catalysts as well as ferric oxide supported Au were tested. First, chemoselective hydrogenation of *p*-nitroacetophenone in the presence of CO and H₂O was tested, Table 1 entries 1–6. As expected, pure Fe(OH)_x exhibited no activity, but after incorporation of Au, the hydrogenation activity increased greatly. With increased CO pressure and reaction time, conversions clearly increased and the percentage of byproducts was reduced to a low level (0.4%), Fig. S3, ESI.† A >99% conversion with selectivity of 99.6% was successfully achieved over 1.5 wt% Au/Fe(OH)_x under mild conditions, entry 2. The evolution of the reaction byproduct showed only a trace of azoxy compound, suggesting *p*-nitroacetophenone was successfully hydrogenated to the corresponding amine without any hydrogenation of acetyl. It is of note that the TOF value showed a marked increase to 2627 h⁻¹ with respect to the hydrogenation process over supported Au catalysts with

H₂ in early reports.^{1,15} For comparison, 1.6 wt% Au/Fe₂O₃ catalyst calcined at 500 °C as well as 4.4 wt% Au/Fe₂O₃-W was also evaluated, and the conversions were decreased to 23 and 58% respectively despite higher Au loadings. This is in accordance with our previous finding that ferric hydroxide supported nanocluster Au showed enhanced catalytic activities as compared with corresponding ferric oxide Au catalysts calcined at elevated temperatures.¹⁵ Combined with HAADF-STEM and XRD characterizations, the superior catalytic activity of 1.5 wt% Au/Fe(OH)_x was speculated to be caused by the nanocluster size of Au particles. Two supported Pd, Pt catalysts, known for their high activity for hydrogenation reactions, were also evaluated for the hydrogenation of *p*-nitroacetophenone. As can be seen from entries 5 and 6, very low conversions were obtained under the same reaction conditions. Nevertheless, these low activities were reasonable as supported Pd and Pt catalysts have been found to be less active for the low temperature WGS,¹⁸ which was speculated to be critical in this hydrogenation process.

The chemoselective hydrogenation of the aromatic nitro compound in the presence of an aldehyde group was also studied by hydrogenation of 4-nitrobenzaldehyde, entries 7–9. Results showed that 4-nitrobenzaldehyde could be efficiently hydrogenated to the corresponding 4-aminobenzaldehyde over 1.5 wt% Au/Fe(OH)_x. Owing to its substantial electro-accepting effect, 4-nitrobenzaldehyde is relatively difficult to hydrogenate as compared with *p*-nitroacetophenone, which was manifested in the required reaction temperature and time. Evaluation of the byproducts showed only a trace of azoxy and no decarbonylated byproduct was detected.

Chemoselective hydrogenations of aromatic nitro compounds with chlorine, methoxy and bromine groups in the presence of CO and H₂O were also investigated. In the case of 2-chloronitrobenzene, 1.5 wt% Au/Fe(OH)_x gave 98% conversion with 98.6% selectivity to 2-chloroaniline (*o*-CAN), and the byproducts were 1-chloro-2-nitrosobenzene and 2-chloro-*n*-ethylbenzenamine resulting from alkylation with the solvent, entry 10. Moreover, TOF of 1379 h⁻¹ over 1.5 wt% Au/Fe(OH)_x in this process was more than five times higher than that of the traditional process in the presence of CO and H₂O catalyzed by Ru₃(CO)₁₂¹⁹ (TOF: 250 h⁻¹) which was conducted at relative harsh reaction conditions (2 MPa CO, 150 °C), indicating the high efficiency of the process catalyzed by supported Au in the presence of CO and H₂O. Similar results were also obtained over 1.5 wt% Au/Fe(OH)_x in chemoselective hydrogenation of 1-methoxy-2-nitrobenzene and 4-bromonitrobenzene to the corresponding amines.

In order to gain a more specific insight into mechanism, the gas after reaction was analyzed by GC equipped with TCD and GC-MS. CO₂ was identified to be formed while no H₂ was detected during the hydrogenation reactions over 1.5 wt% Au/Fe(OH)_x. For comparison, a reaction in the absence of nitro compounds was carried out at 120 °C for 6 h in the presence of CO and H₂O. Still, no H₂ as well as CO₂ was detected in the gas after reaction, indicating independent low temperature WGS could not be ignited over 1.5 wt% Au/Fe(OH)_x even under the harshest reaction conditions in this work. So, in this report, no molecular H₂ formation during the chemoselective hydrogenation process in the

Table 1 Comparison of the catalytic performances for chemoselective hydrogenation of aromatic nitro-compounds

Entry	Substrate	Catalyst	T/°C	t/h	Conv. (%)	Sel. (%)	TOF/h ⁻¹	Other products (sel. %)
1	<i>p</i> -Nitroacetophenone	Fe(OH) _x	100	1.5	0	—	—	—
2		1.5 wt% Au/Fe(OH) _x	100	1.5	>99	99.6	2627	4,4'-Diacetylazoxybenzene (0.4)
3		1.6 wt% Au/Fe ₂ O ₃	100	1.5	23	96.1	566	4,4'-Diacetylazoxybenzene (3.9)
4		4.4 wt% Au/Fe ₂ O ₃ -W	100	1.5	58	98.5	519	4,4'-Diacetylazoxybenzene (1.5)
5		2.8 wt% Pd/Fe(OH) _x	100	1.5	10	92.3	76	4,4'-Diacetylazoxybenzene (7.7)
6		2.2 wt% Pt/Fe(OH) _x	100	1.5	1	94.1	18	4,4'-Diacetylazoxybenzene (5.9)
7	4-Nitrobenzaldehyde	1.5 wt% Au/Fe(OH) _x	120	5.5	>99	97.5	358	Azoxybenzene-4-aldehyde (2.5)
8		2.8 wt% Pd/Fe(OH) _x	120	5.5	11	60.3	11	4-(2-ethoxyethylamino)benzaldehyde (33.7) Azoxybenzene-4-aldehyde (6.0)
9		2.2 wt% Pt/Fe(OH) _x	120	5.5	7	87.1	17	4-(2-ethoxyethylamino)benzaldehyde (12.9)
10	2-Chloronitrobenzene	1.5 wt% Au/Fe(OH) _x	100	1.5	98	98.6	1287	2-Chloro- <i>N</i> -ethylbenzenamine (1.1) 1-Chloro-2-nitrosobenzene (0.3)
11		2.8 wt% Pd/Fe(OH) _x	100	1.5	3	99.5	11	2-Chloro- <i>N</i> -ethylbenzenamine (0.5)
12		2.2 wt% Pt/Fe(OH) _x	100	1.5	1	94.0	9	2-Chloro- <i>N</i> -ethylbenzenamine (6.0)
13	1-Methoxy-2-nitrobenzene	1.5 wt% Au/Fe(OH) _x	100	1.5	>99	99.5	1313	2,2'-Dimethoxyazoxybenzene (0.5)
14		2.8 wt% Pd/Fe(OH) _x	100	1.5	2	98.5	8	2,2'-Dimethoxyazoxybenzene (1.5)
15		2.2 wt% Pt/Fe(OH) _x	100	1.5	1	99.0	9	2,2'-Dimethoxyazoxybenzene (1.0)
16	4-Bromonitrobenzene	1.5 wt% Au/Fe(OH) _x	120	6	95	99.4	312	1,2-Bis(4-bromophenyl)diazene (0.6)
17		2.8 wt% Pd/Fe(OH) _x	120	6	4	98.6	4	1,2-Bis(4-bromophenyl)diazene (1.4)
18		2.2 wt% Pt/Fe(OH) _x	120	6	3	99.1	7	1,2-Bis(4-bromophenyl)diazene (0.9)

presence of CO and H₂O was reasonable. Nevertheless, taking into account the potential activity of supported Au catalysts exhibited in the low temperature WGS reaction and the H source from H₂O, WGS reaction was speculated to occur in the nitro compounds hydrogenation in the presence of CO and H₂O. Furthermore, atomic hydrogen formed during WGS reaction could participate in the hydrogenation of aromatic nitro compounds immediately without release of molecular H₂, which may lead to hydrogenation of aromatic nitro compounds in a more efficient way.

Although the detailed mechanism is not clear at this stage, it was found for the first time that ferric hydroxide supported nanocluster Au catalysts could efficiently and chemoselectively hydrogenate aromatic nitro compounds resulting in the corresponding amines in the presence of CO and H₂O. This process shows enhanced catalytic performance both in activity and selectivity, and the absence of carbonyl metal complexes as well as basic conditions make this process catalyzed by supported Au catalysts more attractive. In evaluation of catalytic activity of different Au catalysts, a size effect is observed, and Au particles of nanocluster size over Au/Fe(OH)_x are speculated to be the key factor for its superior activity as compared with catalysts calcined at elevated temperatures. It is clear that this process catalyzed with Au catalysts in the presence of CO and H₂O show a promising performance, and may open an alternative process of interest for the chemoselective hydrogenation of aromatic nitro compounds.

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