

Highly Chemoselective Reduction of Nitroaromatic Compounds Using a Hydrotalcite-supported Silver-nanoparticle Catalyst under a CO Atmosphere

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Hydrotalcite-supported silver nanoparticles (Ag/HT) acted as an effective heterogeneous catalyst for the reduction of nitroaromatic compounds using CO/H₂O as a reducing reagent. The Ag/HT catalyst system showed complete chemoselectivity for nitro groups in the presence of inter- and intra-molecular olefinic functionalities. Moreover, Ag/HT was reusable without any loss of its activity or selectivity.

Aniline derivatives are valuable intermediates in the production of agrochemicals, pharmaceuticals, and dyes.¹ Although the reduction of aromatic nitro compounds is the most straightforward method for the synthesis of the corresponding anilines,² it is difficult to reduce only the nitro functionality of mother nitro compounds in the presence of other reducible functionalities.³ The chemoselective reduction of nitro compounds bearing C=C bonds to the corresponding anilines has been achieved using a large excess of stoichiometric reducing agents such as Fe, Sn, Zn, and Na₂S₂O₄.⁴ However, these reaction systems have suffered from the production of harmful wastes, the need for neutralization of acid additives as a hydrogen source, and from their low atom efficiencies. From practical and environmental perspectives, some efficient catalysts for the chemoselective reduction of nitroaromatics with C=C double bonds have been developed.⁵ To date, TiO₂-supported gold NPs (Au/TiO₂) may be the best heterogeneous catalyst for the chemoselective reduction of the nitro functionality under an H₂ atmosphere. Thus, reduction of 3-nitrostyrene using Au/TiO₂ gave the desired 3-vinylaniline in 98.5% conversion with 95.9% selectivity.⁶

Recently, we have found that supported silver nanoparticles (Ag NPs) can act as efficient heterogeneous catalysts for versatile functional transformations under liquid-phase conditions such as dehydrogenation of alcohols,⁷ oxidation of silanes to silanols using water,⁸ and hydration of nitriles.⁹ These Ag NP catalysts showed remarkably high and unique activities,¹⁰ although Ag NP catalysts have generally been considered to have low activities for many organic reactions except for the gas-phase epoxidation of ethylene. Herein, we report that Ag NPs, supported on an inorganic material of hydrotalcite (Ag/HT), function as an effective heterogeneous catalyst for the quantitative chemoselective reduction of various nitroaromatics to corresponding anilines with a >99% selectivity in the presence of olefinic bonds, using CO/H₂O as the hydrogen source.^{11,12} This methodology completely suppresses the reduction of C=C double bonds during the reduction of nitro functionalities.

Hydrotalcite [HT, Mg₆Al₂(OH)₁₆CO₃] was synthesized as previously described.¹³ HT (2.0 g) was added to 150 mL of an aqueous solution of AgNO₃ (6.7 × 10⁻³ M), and then the mixed

solution was stirred for 1 h in air at room temperature. The resulting slurry was filtered, washed with deionized water, and dried in vacuo at room temperature to yield HT-supported Ag¹ ions as a gray powder. Next, the obtained solid was reduced with KBH₄ at room temperature for 1 h to give Ag/HT. The X-ray diffraction (XRD) patterns of Ag/HT were similar to those of the parent HT. The fraction of Ag atoms in the Ag/HT composite was determined by elemental analysis to be 2.0 wt % as a dark green powder. *k*³-Weighted Ag K-edge extended X-ray absorption fine structure (EXAFS) study, and transmission electron microscopy (TEM) image of Ag/HT, showed that Ag NPs with a mean diameter of 9.5 nm were formed on Ag/HT.¹⁴

We examined the catalysis of Ag/HT for the reduction of 3-nitrostyrene (**1**) under 9 atm of CO at 150 °C in the presence of water. 3-Vinylaniline (**2**) was formed in over 99% yield in 3 h without reduction products of the C=C double bond such as 3-ethylaniline (**3**) or 3-ethyl-1-nitrobenzene (Table 1, Entry 1). Among the solvents tested, DMA provided the highest yield of **2**. THF and toluene were also good solvents giving **2** with 99% selectivity in moderate yields, while 1,4-dioxane, DMF, and 1,2-dichloroethane were poor solvents (Entries 4–8).

The reductions of **1** using Ag NPs on various inorganic materials showed that HT was the best support and that Ag/Al₂O₃ also had high activity and chemoselectivity toward **2** (Entry 13). On the other hand, Ag/TiO₂, Ag/SiO₂, Ag/MgO, and AgHAP gave low conversions of **1** (Entries 14–17). Individual use of the bulk Ag metal, the catalyst precursor of AgNO₃ or the parent HT did not give any products (Entries 18–20).

Figure 1 shows time courses for the reductions of **1** using Ag/HT and other HT-supported metal NPs: Au/HT, Pd/HT, Pt/HT, and Rh/HT. Although the activity of the Au/HT catalyst was higher than that of Ag/HT, an over reduction to **3** was observed, resulting in lower selectivity toward **2**. Pt/HT and Rh/HT functioned as good catalysts giving **2** in moderate yields with high selectivity, while Pd/HT did not exhibit high activity or chemoselectivity. These results indicate that Ag/HT gives the highest yield of **2**. Notably, the C=C bond of product **2** was maintained intact even after the complete conversion of **1**.

This chemoselectivity of Ag/HT toward **2** in the reduction of **1** is greater than those of previously reported catalyst systems such as Au/TiO₂ with H₂ (98.5% conversion with 96% selectivity),⁶ Au/Al₂O₃ with H₂ (100% with 89%),¹⁵ Au nanoparticle/polyelectrolyte with NaBH₄ (99% with 85%),¹⁶ Sm with 1,1'-dioctyl-4,4'-bipyridinium dibromide (82% with 100%),¹⁷ Cu nanoparticles with HCOONH₄ (76% with 59%),¹⁸ Rh₆(CO)₁₆/TMPDA with CO (91% with 100%),¹⁹ or PdCl₂/BINAS with CO (50% with 100%).²⁰

The high chemoselectivity of Ag/HT for nitro functionalities was further investigated in the intermolecular competitive

Table 1. Reduction of 3-nitrostyrene under a CO atmosphere in the presence of H₂O^a

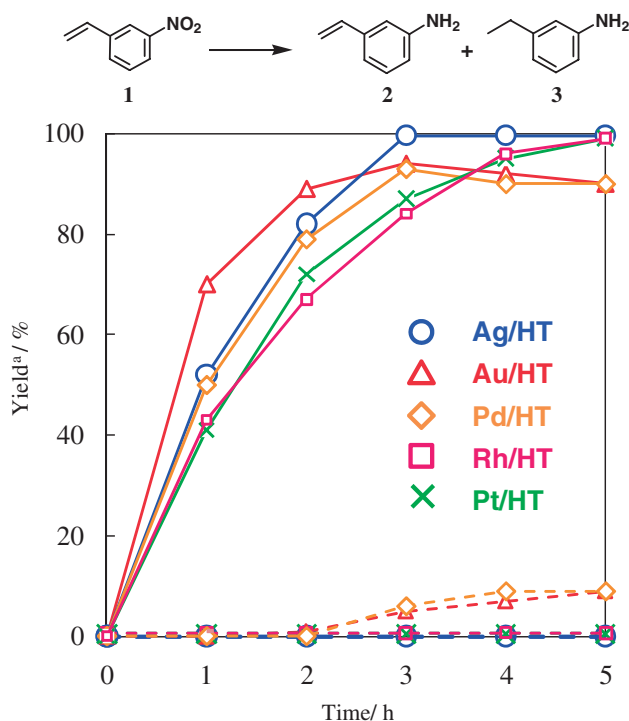
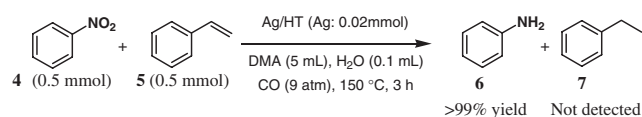
Entry	Catalyst	Solvent	Conversion /% ^b	Selectivity/% ^b	
				2	3
1	Ag/HT	DMA	>99	>99	0
2 ^c	Ag/HT	DMA	99	>99	0
3 ^d	Ag/HT	DMA	95	>99	0
4	Ag/HT	THF	58	>99	0
5	Ag/HT	Toluene	42	>99	0
6	Ag/HT	1,4-Dioxane	10	>99	0
7	Ag/HT	DMF	8	>99	0
8	Ag/HT	1,2-DCE	0	—	—
9 ^e	Ag/HT	DMA	99	0	>99
10 ^f	Ag/HT	DMA	35	90	9
11 ^g	Ag/HT	DMA	42	75	24
12 ^h	Ag/HT	DMA	30	40	59
13	Ag/Al ₂ O ₃	DMA	90	>99	0
14	Ag/TiO ₂	DMA	42	>99	0
15	Ag/SiO ₂	DMA	17	>99	0
16	Ag/MgO	DMA	3	>99	0
17	Ag/HAP	DMA	2	>99	0
18	Ag powder	DMA	8	>99	0
19	AgNO ₃	DMA	1	—	—
20 ⁱ	HT	DMA	0	—	—

^aReaction conditions: **1** (0.25 mmol), catalyst (Ag: 14 mol %), DMA (5 mL), H₂O (0.10 mL), CO (9 atm), 150 °C, 3 h. ^bDetermined by LC using an internal standard. ^c1st reuse. ^d2nd reuse. ^eH₂ (9 atm), 1 h. ^fH₂ (9 atm), 80 °C, 1 h. ^gH₂ (4 atm), 150 °C, 1 h. ^hH₂ (9 atm), 150 °C, 10 min. ⁱHT (0.2 g).

reaction of nitrobenzene (**4**) and styrene (**5**) (Scheme 1). Interestingly, **4** was reduced to give aniline (**6**) with over 99% yield but **5** was not reduced at all. These results clearly demonstrated that the Ag/HT catalyst system using CO/H₂O showed complete chemoselectivity for nitro functionalities *in the presence of inter- and intra-molecular olefinic functionalities*. This is in sharp contrast with a previously reported Au/TiO₂ catalyst system in which reduction of **5** did occur in the competitive reduction of **4** and **5**.²¹ Furthermore, the Ag/HT catalyst was applicable to the reduction of various nitro compounds bearing C=C double bonds, such as 4-nitrostyrene, 4-nitrostilbene, 1-nitro-4-propenylbenzene, and 5-nitroindole, where the corresponding anilines were obtained in high yields with over 99% selectivity.

After the reduction of **1**, Ag/HT was recovered by a simple filtration from the reaction mixture, and was reusable without any loss of its activity or selectivity (Table 1, Entries 2 and 3). TEM and XAFS analyses of the used Ag/HT catalyst revealed that the size and oxidation state of the used Ag NPs on HT did not differ from those of the fresh Ag/HT and no apparent aggregation of used Ag NPs was observed. These data are consistent with the retention of the catalytic activity of Ag/HT during the recycling experiments.²²

In separate experiments under identical conditions without **1**, H₂ was not generated from the water-gas shift reaction.

**Figure 1.** Kinetic plots showing the yield of **2** (solid lines) and **3** (wavy lines) for the reduction of **1** using HT-supported metal NPs: Ag/HT, Au/HT, Pd/HT, Rh/HT, and Pt/HT. Reaction conditions: catalyst (14 mol %), **1** (0.25 mmol), DMA (5 mL), H₂O (0.1 mL), CO (9 atm), 150 °C. ^aDetermined by LC using an internal standard.**Scheme 1.** Intermolecular competitive reaction of nitrobenzene and styrene using Ag/HT in the presence of CO/H₂O.

Moreover, when H₂ was used as a reducing agent instead of CO/H₂O, selective reduction of **1** to **2** did not occur (Table 1, Entries 9–12). These results rule out the participation of H₂ in the Ag/HT-catalyzed reduction reaction described above. It is likely that *in situ* silver hydride species generated from the reaction of H₂O with CO at the surface of AgNPs is an active species that leads to highly chemoselective reduction of nitroaromatics with suppression of the reduction of the olefinic bond.²³

In conclusion, we found that the Ag/HT catalyst showed complete chemoselective reduction of nitroaromatic compounds in the presence of a C=C double bond to give the corresponding anilines in high yields using CO/H₂O as a reducing reagent. This methodology would be a powerful tool for the synthesis of functionalized anilines.

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References and Notes

- 1 G. Booth, *Ullmanns Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag, Weinheim, Germany, **2002**.
- 2 H. U. Blaser, U. Siegrist, H. Steiner, M. Studer, in *Fine Chemicals Through Heterogeneous Catalysis*, ed. by R. A. Sheldon, H. van Bekkum, Wiley-VCH, Weinheim, **2001**, p. 389.
- 3 Houben-Weyl, *Methoden der Organischen Chemie*, Thieme Verlag Stuttgart, **1980**, Vol. 4/1c, p. 511.
- 4 R. S. Downing, P. J. Kunkeler, H. van Bekkum, *Catal. Today* **1997**, *37*, 121.
- 5 H.-U. Blaser, H. Steiner, M. Studer, *ChemCatChem* **2009**, *1*, 210.
- 6 A. Corma, P. Serna, *Science* **2006**, *313*, 332.
- 7 T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem., Int. Ed.* **2008**, *47*, 138.
- 8 T. Mitsudome, S. Arita, H. Mori, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem., Int. Ed.* **2008**, *47*, 7938.
- 9 T. Mitsudome, Y. Mikami, H. Mori, S. Arita, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2009**, 3258.
- 10 Recent silver catalysts reported by other groups: a) P. Claus, H. Hofmeister, *J. Phys. Chem. B* **1999**, *103*, 2766. b) Y. Chen, C. Wang, H. Liu, J. Qiu, X. Bao, *Chem. Commun.* **2005**, 5298. c) H. Zhao, J. Zhou, H. Luo, C. Zeng, D. Li, Y. Liu, *Catal. Lett.* **2006**, *108*, 49. d) U. Halbes-Letinois, J.-M. Weibel, P. Pale, *Chem. Soc. Rev.* **2007**, *36*, 759. e) J. Sun, S. A. Kozmin, *Angew. Chem., Int. Ed.* **2006**, *45*, 4991. f) K. Inazu, T. Koyama, A. Miyaji, T. Baba, *J. Jpn. Petrol. Inst.* **2008**, *51*, 205. g) K. Shimizu, R. Sato, A. Satsuma, *Angew. Chem., Int. Ed.* **2009**, *48*, 3982.
- 11 We first discovered the catalytic chemoselective reduction of nitro functionalities using CO/H₂O as a hydrogen source using Rh carbonyl clusters. See Ref. 19.
- 12 Very recently, Cao et al. also reported that highly chemoselective hydrogenation of nitro compounds under CO/H₂O condition using Au catalyst, see: L. He, L.-C. Wang, H. Sun, J. Ni, Y. Cao, H.-Y. He, K.-N. Fan, *Angew. Chem., Int. Ed.* **2009**, *48*, 9538.
- 13 F. Cavani, F. Trifiró, A. Vaccari, *Catal. Today* **1991**, *11*, 173.
- 14 See Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- 15 K. Shimizu, Y. Miyamoto, T. Kawasaki, T. Tanji, Y. Tai, A. Satsuma, *J. Phys. Chem. C* **2009**, *113*, 17803.
- 16 D. M. Dotzauer, S. Bhattacharjee, Y. Wen, M. L. Bruening, *Langmuir* **2009**, *25*, 1865.
- 17 C. Yu, B. Liu, L. Hu, *J. Org. Chem.* **2001**, *66*, 919.
- 18 A. Saha, B. Ranu, *J. Org. Chem.* **2008**, *73*, 6867.
- 19 K. Kaneda, H. Kuwahara, T. Imanaka, *J. Mol. Catal.* **1994**, *88*, L267.
- 20 A. M. Tafesh, M. Beller, A. G. Hoechst, *Tetrahedron Lett.* **1995**, *36*, 9305.
- 21 A. Corma, P. Serna, P. Conception, J. J. Calvino, *J. Am. Chem. Soc.* **2008**, *130*, 8748.
- 22 To assay potential leaching of the active species into the reaction mixture, the Ag/HT catalyst was separated from the reaction mixture by simple filtration at 50% conversion of **1**, and the filtrate was then stirred again under similar reaction conditions (9 atm of a CO atmosphere at 150 °C), which did not give further reaction products. The absence of any Ag species in the filtrate was confirmed by inductively coupled plasma spectrometry (detection limit; 0.007 ppm). These results clearly support the fact that the reduction occurred at the Ag NPs on the solid HT.
- 23 We think that basicity of HT plays an important role in the facile formation of an active Ag-H⁻ species; a basic site of HT promotes formation of a OH⁻ species from a H₂O molecule, which leads to nucleophilic attack of a OH⁻ species to a CO molecule adsorbed on silver nanoparticles, followed by loss of a CO₂ molecule to give the active Ag-H⁻ species.