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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/H_2O 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 NaS_2O_4.[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, TiO_2-supported gold NPs (Au/TiO_2) may be the best heterogeneous catalyst for the chemoselective reduction of the nitro functionality under an H_2 atmosphere. Thus, reduction of 3-nitrostyrene using Au/TiO_2 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/H_2O 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, $Mg_6Al_2(OH)_{16}CO_3$] was synthesized as previously described.[13] HT (2.0 g) was added to 150 mL of an aqueous solution of $AgNO_3$ (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 Ag^I ions as a gray powder. Next, the obtained solid was reduced with KBH_4 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).

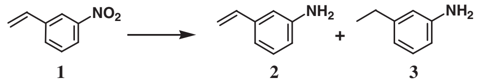
The reductions of **1** using Ag NPs on various inorganic materials showed that HT was the best support and that Ag/Al_2O_3 also had high activity and chemoselectivity toward **2** (Entry 13). On the other hand, Ag/TiO_2, Ag/SiO_2, Ag/MgO, and AgHAP gave low conversions of **1** (Entries 14–17). Individual use of the bulk Ag metal, the catalyst precursor of $AgNO_3$ 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/TiO_2 with H_2 (98.5% conversion with 96% selectivity),[6] Au/Al_2O_3 with H_2 (100% with 89%),[15] Au nanoparticle/polyelectrolyte with $NaBH_4$ (99% with 85%),[16] Sm with 1,1′-dioctyl-4,4′-bipyridinium dibromide (82% with 100%),[17] Cu nanoparticles with $HCOONH_4$ (76% with 59%),[18] $Rh_6(CO)_{16}$/TMPDA with CO (91% with 100%),[19] or $PdCl_2$/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 H_2O[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_2O_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	—	—

[a] Reaction conditions: **1** (0.25 mmol), catalyst (Ag: 14 mol %), DMA (5 mL), H_2O (0.10 mL), CO (9 atm), 150 °C, 3 h. [b] Determined by LC using an internal standard. [c] 1st reuse. [d] 2nd reuse. [e] H_2 (9 atm), 1 h. [f] H_2 (9 atm), 80 °C, 1 h. [g] H_2 (4 atm), 150 °C, 1 h. [h] H_2 (9 atm), 150 °C, 10 min. [i] HT (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/H_2O 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/TiO_2 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**, H_2 was not generated from the water-gas shift reaction.

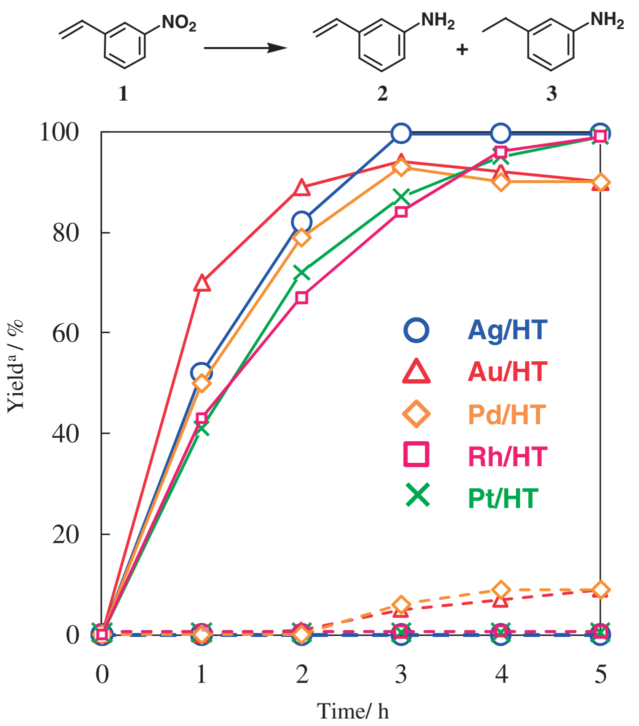
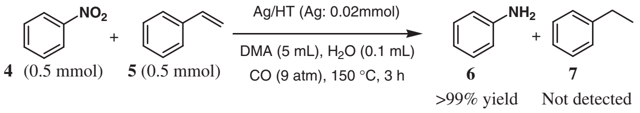


Figure 1. Kinetic plots showing the yield of **2** (solid lines) and **3** (wavy lines) for the reduction of **1** using HT-supported metal NPs: Ag/HT, Au/HT, Pd/HT, Rh/HT, and Pt/HT. Reaction conditons: catalyst (14 mol %), **1** (0.25 mmol), DMA (5 mL), H_2O (0.1 mL), CO (9 atm), 150 °C. [a] Determined by LC using an internal standard.



Scheme 1. Intermolecular competitive reaction of nitrobenzene and styrene using Ag/HT in the presence of CO/H_2O.

Moreover, when H_2 was used as a reducing agent instead of CO/H_2O, selective reduction of **1** to **2** did not occur (Table 1, Entries 9–12). These results rule out the participation of H_2 in the Ag/HT-catalyzed reduction reaction described above. It is likely that in situ silver hydride species generated from the reaction of H_2O 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/H_2O as a reducing reagent. This methodology would be a powerful tool for the synthesis of functionalized anilines.

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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 H_2O molecule, which leads to nucleophilic attack of a OH^- species to a CO molecule adsorbed on silver nanoparticles, followed by loss of a CO_2 molecule to give the active $Ag–H^-$ species.