doi:10.1246/cl.130132

Remarkable Effect of Bases on Core–Shell AgNP@CeO_2 Nanocomposite-catalyzed Highly Chemoselective Reduction of Unsaturated Aldehydes

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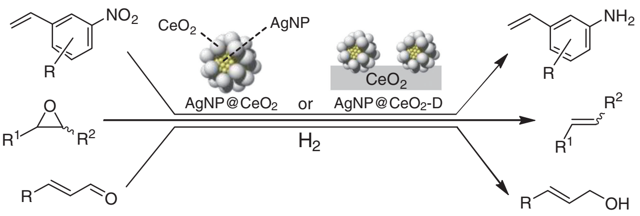
A highly dispersed core–shell silver nanoparticle–ceria nanocomposite catalyst (AgNP@CeO_2-D) was prepared. The addition of bases was found to enhance the catalytic efficiency of AgNP@CeO_2-D significantly in the chemoselective reduction of diverse unsaturated aldehydes to the corresponding unsaturated alcohols.

The selective reduction of a targeted functional group in a molecule having several functional groups is of great utility in organic synthesis.[1] In this context, the chemoselective reduction of unsaturated carbonyl compounds while maintaining the reducible C=C bonds is an important and challenging objective, because the corresponding unsaturated alcohols often serve as valuable intermediates for fragrances, pharmaceuticals, agrichemicals, and resins.[2] Chemoselective reduction has been performed by using stoichiometric reagents such as metal borohydrides,[3] diisobutylaluminum hydride,[4] and zinc metal,[5] which produce large amounts of waste. For the replacement of such traditional stoichiometric reactions, much effort has been devoted to the development of catalytic systems.[6] Among these catalytic methods, heterogeneous catalyst systems using molecular hydrogen (H_2) as a highly atom-efficient reductant represent ideal green protocols. However, the heterogeneous catalysts reported previously still suffer from insufficient selectivity at high conversions, limited substrate scope, and low reusability.[7,8]

Recently, we reported the synthesis of a core–shell silver nanoparticle–ceria nanocomposite (AgNP@CeO_2) consisting of AgNPs with diameters of 10 nm in the core and assembled CeO_2 NPs with diameters of 3–5 nm in the shell. AgNP@CeO_2 acted as a highly efficient reusable catalyst for the completely chemoselective reductions of nitrostyrenes to aminostyrenes and epoxides to alkenes using H_2, where over 99% selectivity for the targeted products was attained.[9] AgNP@CeO_2 highly dispersed on CeO_2 (AgNP@CeO_2-D) was also developed and was found to be applicable to the selective reduction of unsaturated aldehydes to the corresponding unsaturated alcohols (Scheme 1).[10] The obtained selectivity for unsaturated alcohols was much greater than those of previously reported heterogeneous catalyst systems. In these reactions, the combination of AgNPs and a base of CeO_2 is the key. Wrapping AgNPs with CeO_2 can maximize the interfacial interaction between the active AgNP species and the basic sites of CeO_2. The core–shell interface induces the heterolytic cleavage of H_2 to produce an ionic Ag–hydride species and a proton associated with the basic site of CeO_2, which enables the selective reduction of polar functional groups. In a continuing attempt to achieve higher chemoselectivity using AgNP@CeO_2-D, we discovered that the addition of bases such as alkali metal salts and amines to the AgNP@CeO_2-D catalyst system enhanced significantly both the catalytic activity and selectivity for the reduction of unsaturated aldehydes to the unsaturated alcohols.

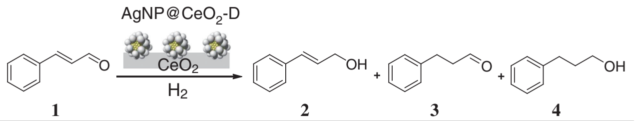


Scheme 1. Chemoselective reductions with AgNP@CeO_2 or AgNP@CeO_2-D.

Inspired by our previous finding that bases exhibited cooperative catalysis with AgNPs in chemoselective reductions,[9–13] we initially focused on various bases as additives for the AgNP@CeO_2-D-catalyzed reduction of cinnamaldehyde (**1**) to cinnamyl alcohol (**2**) under 6 atm of H_2 at 110 °C for 6 h.[14] The results are summarized in Table 1. Interestingly, among the bases tested, the addition of Cs_2CO_3 significantly enhanced the catalytic efficiency to afford over 99% selectivity for **2** with full conversion (Entry 1 vs. 11). Rb_2CO_3 and triethylamine also had a positive effect on the reduction (Entries 6 and 7), and the weaker bases of Na_2CO_3, K_2CO_3, pyridine, and imidazole improved the selectivity slightly (Entries 4, 5, 9, and 10). Notably, when the reaction time of Entry 1 was prolonged, hydrogenation of the olefin moiety of **2** was not observed at all (Entry 2). Furthermore, even at 60 °C, AgNP@CeO_2-D worked well in the presence of Cs_2CO_3, giving **2** in 96% yield with excellent selectivity, while AgNP@CeO_2-D without Cs_2CO_3 hardly promoted the reduction (Entry 3 vs. 12). Next, nonencapsulated AgNPs on CeO_2 (AgNP/CeO_2), which had a similar AgNP size to that of AgNP@CeO_2-D, were synthesized,[15] and the effect of Cs_2CO_3 was investigated. The addition of Cs_2CO_3 also improved the AgNP/CeO_2 catalysis (Entry 13 vs. 14); however, the catalytic performance of AgNP/CeO_2 was inferior to that of AgNP@CeO_2-D (Entry 1 vs. 13). These results revealed that the combination of AgNP@CeO_2-D and Cs_2CO_3 provided an extremely high efficiency for the chemoselective reduction of **1** to **2** with H_2.

The substrate scope of the catalytic system consisting of AgNP@CeO_2-D and Cs_2CO_3 in the chemoselective reduction of aldehydes was investigated next (Table 2). For all the aldehydes tested, Cs_2CO_3 enhanced the activity and selectivity of AgNP@CeO_2-D significantly, affording excellent selectivity for unsaturated alcohols with high conversions. Cinnamaldehydes, which have electron-withdrawing and -donating groups, were converted efficiently to cinnamyl alcohols (Entries 3 and 4). *p*-Chlorocinnamyl alcohol was obtained with over 99%

Table 1. Chemoselective reduction of **1** using AgNP@CeO_2-D with bases[a]



Entry	Base	t/h	Conv./%[b]	Sel./%[b]		
				2	**3**	**4**
1	Cs_2CO_3	6	>99	>99	trace	trace
2	Cs_2CO_3	12	>99	>99	trace	trace
3[c]	Cs_2CO_3	24	96	>99	trace	trace
4	Na_2CO_3	6	58	94	5	1
5	K_2CO_3	6	56	95	2	3
6	Rb_2CO_3	6	78	99	1	trace
7	triethylamine	6	67	>99	trace	trace
8	triethylamine	12	>99	>99	trace	trace
9	pyridine	6	38	93	2	5
10	imidazole	6	25	95	2	3
11	—	6	43	92	2	6
12[c]	—	24	1	trace	trace	trace
13[d]	Cs_2CO_3	6	96	94	2	4
14[d]	—	6	38	73	16	11

[a] Reaction conditions: **1** (0.25 mmol), AgNP@CeO_2-D (Ag: 6 mol %), THF (5 mL), base (1 mmol), H_2 (6 atm), 110 °C. [b] Determined by GC using an internal standard. [c] H_2 (30 atm), 60 °C. [d] AgNP/CeO_2 (Ag: 6 mol %) was used in place of AgNP@CeO_2-D.

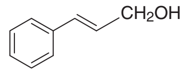
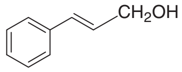
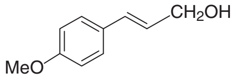
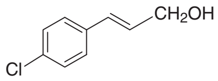
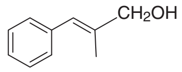
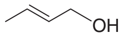
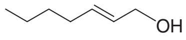
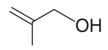
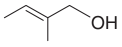
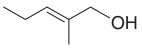
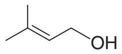
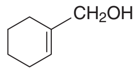
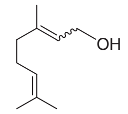
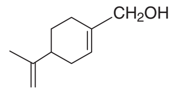
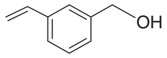
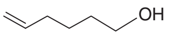
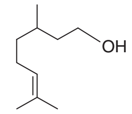
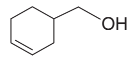
selectivity, and the chloro moiety as well as the C=C bond remained intact during the reduction (Entry 4). Aliphatic conjugated aldehydes including terpenes could also be used in this catalyst system (Entries 6–14). For example, citral gave the corresponding allylic alcohols in quantitative yield (Entry 13). Moreover, unconjugated aldehydes were also found to be good substrates (Entries 15–18). Vinylbenzaldehyde was reduced chemoselectively to vinylbenzyl alcohol with complete retention of the olefinic bond (Entry 15).[16]

After the reduction of **1**, AgNP@CeO_2-D was readily separated from the reaction mixture by filtration, and then, the used AgNP@CeO_2-D catalyst and Cs_2CO_3 were applied to the next run. AgNP@CeO_2 could be reused without loss of activity or chemoselectivity in the reuse experiments (Entry 2).

The dramatic effect of the base additives on both the activity and selectivity of AgNP@CeO_2-D may be due to an increase in the exclusive formation of the ionic hydrogen species. That is, base additives promote the heterolytic cleavage of H_2 to $[Ag–H]^-$ and $[H–base]^+$ and also assist in the cooperative action between AgNP and CeO_2 to generate $[Ag–H]^-$ and $[CeO_2–H–base]^+$. These polar hydrogen species prefer polar aldehyde groups over C=C bonds, enhancing the activity and chemoselectivity in the reduction of unsaturated aldehydes to unsaturated alcohols.

In conclusion, we discovered that the addition of bases greatly enhanced the catalytic efficiency in AgNP-catalyzed chemoselective reduction reactions. The catalyst system consisting of AgNP@CeO_2-D and Cs_2CO_3 provided highly chemoselective reduction of diverse unsaturated aldehydes to the corresponding unsaturated alcohols with excellent selectivity.

Table 2. Chemoselective hydrogenations of unsaturated aldehydes using AgNP@CeO_2-D with Cs_2CO_3[a]

Entry	Product	t/h	Conv./%[b]	Sel./%[b]
1		6	>99	>99 (92)
2[c]		6	>99	>99
3		10	>99	93
4		3	>99	>99
5		6	>99	>99 (96)
6[d]		8	>99	98
7[d]		8	98	96 (91)
8[d]		8	97	95
9[d]		8	98	97
10[d]		8	>99	97
11[d]		8	>99	95
12		8	>99	97
13[e]		6	>99	>99 (94)
14		18	>99	98
15		6	>99	>99 (93)
16[d]		12	>99	96
17[e]		6	>99	>99
18		6	>99	98

[a] Reaction conditions: Substrate (0.25 mmol), AgNP@CeO_2-D (Ag: 6 mol %), THF (5 mL), Cs_2CO_3 (1 mmol), H_2 (6 atm), 110 °C. [b] Determined by GC using an internal standard. Values in parentheses are isolated yields. For the isolation experiments, the reactions were carried out under the following conditions. Substrate (10 mmol), AgNP@CeO_2-D (Ag: 6 mol %), THF (25 mL), Cs_2CO_3 (5 mmol). [c] 2nd reuse. [d] H_2 (15 atm), 60 °C. [e] AgNPs@CeO_2-D (Ag: 3 mol %), H_2 (15 atm), 150 °C.

Furthermore, the AgNP@CeO_2-D catalyst was separable and reusable without loss of efficiency.

This work was supported by JSPS KAKENHI Grant Numbers 23686116, 23360357, 24246129, and 22360339. T. M. thanks the Japan Association for Chemical Innovation and JGC-S Scholarship Foundation for funding.

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14 AgNP@CeO_2-D was prepared as follows: An aqueous solution of silver amine complex (2 mL, 0.15 M) was prepared from silver nitrate (1.5 mmol), ammonia solution (0.3 mL of 28 wt %), and deionized water (10 mL). The aqueous solution and an aqueous solution of cerium nitrate hexahydrate (2 mL, 0.1 M) were added into a cyclohexane/poly(oxyethylene) nonylphenyl ether mixture (20 mL/8 mL), respectively. Next, these two solutions were mixed and stirred for 1 h at 60 °C, giving a black suspension. After that, ethanol (40 mL) was injected into the mixture and then, the obtained precipitate was washed with ethanol, and redispersed in EtOH (100 mL). CeO_2 (JRC-CEO3) (2.0 g) was added into the dispersion solution. After stirring for 1 h at 25 °C, the gray precipitate was filtered and dried in vacuo. The obtained solid was heated at 400 °C for 4 h, giving AgNP@CeO_2-D. Elemental analysis showed that the Ag loading of AgNP@CeO_2-D was 1 wt %. A typical procedure for the reduction of unsaturated aldehydes by AgNP@CeO_2-D is as follows. AgNP@CeO_2-D (0.2 g) and Cs_2CO_3 (0.3 g) were placed in a stainless steel autoclave (with a Teflon inner cylinder) followed by the addition of THF (5 mL) and **1** (0.25 mmol). The reaction mixture was stirred at 110 °C under 6 atm of H_2 for 6 h. After the reaction, AgNP@CeO_2-D was removed by filtration, and the filtrate was analyzed by GC with dibenzyl as an internal standard to determine the conversion and yield.

15 AgNP/CeO_2 was prepared as follows: CeO_2 (JRC-CEO3) (1.0 g) was added into of aqueous silver nitrate solution (30 mL, 0.031 M). After stirring for 2 h at 25 °C, the mixture was evaporated. The obtained solid was treated with KBH_4 (100 mL, 0.094 M). After that, the slurry was filtered, washed with deionized water, and dried in vacuo, yielding AgNP/CeO_2. Elemental analysis showed that the Ag loading of AgNP/CeO_2 was 10 wt %.

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