DOI: 10.1002/ange.201106244

Design of a Silver–Cerium Dioxide Core–Shell Nanocomposite Catalyst for Chemoselective Reduction Reactions[**]

*Takato Mitsudome, Yusuke Mikami, Motoshi Matoba, Tomoo Mizugaki, Koichiro Jitsukawa, and Kiyotomi Kaneda**

The interaction of metals with ligands is the key factor in the design of catalysts and much effort has been devoted to the rational control of metal–ligand interactions in order to exploit catalytic properties. Quite sophisticated heterogeneous catalysts have been produced by controlling the size and shape of active metal species, and by screening and altering the composition of the supports.[1] The supports can be considered as "macro ligands" for supported active metals, and the fine-tuning of the interactions between active metal species and supports is the most important factor through which high catalytic performance can be attained. Despite many intrinsic advantages of heterogeneous catalysts over homogeneous ones, such as their durability at high temperatures and reusability, the fine-tuning of metal–ligand interactions in heterogeneous catalysts is more difficult than in homogeneous catalysts, and remains a challenging objective.

Our research group has recently reported that silver nanoparticles (AgNPs) on a basic support of hydrotalcite (Ag/HT) catalyzed the chemoselective reductions of nitrostyrenes[2] and epoxides[3,4] to the corresponding anilines and alkenes when using alcohols or CO/H_2O as a reducing reagent while retaining the reducible $C{=}C$ bonds. During the reductions, polar species of hydrides and protons were formed in situ at the interface of AgNPs/HT through a cooperative effect between the AgNPs and basic sites (BS) of HT, which were then exclusively active for the reduction of the polar functional groups (Figure 1). However, the use of H_2 instead of alcohols or CO/H_2O in our Ag catalyst system caused reductions of both the polar groups (nitro and epoxide) and the nonpolar $C{=}C$ bonds. This nonselective reduction was due to the formation of nonpolar hydrogen species through the homolytic cleavage of H_2 at the AgNPs surface, which is active for $C{=}C$ bond reduction (Figure 2a).

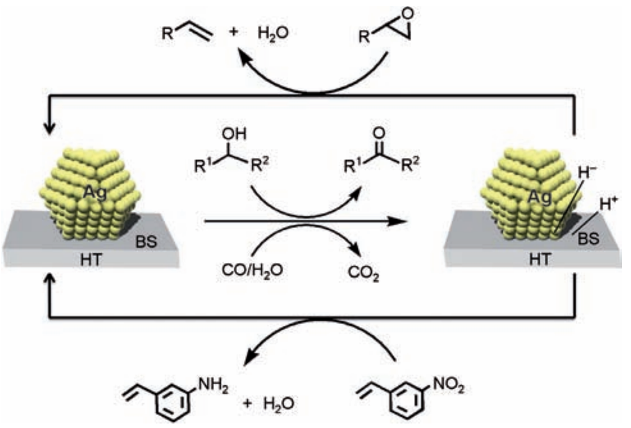

Figure 1. Schematic of Ag/HT-catalyzed chemoselective reductions with alcohols or CO/H_2O.

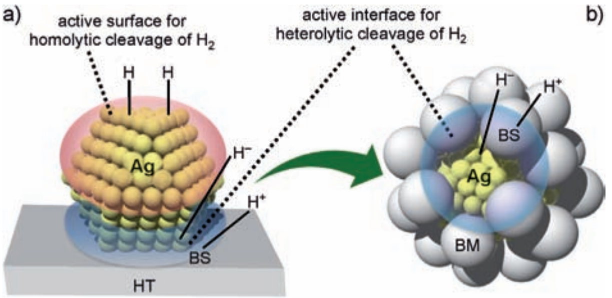

Figure 2. Catalyst design of core–shell nanocomposite for chemoselective reductions with H_2. a) Representation of Ag/HT reacting with H_2; both polar and nonpolar hydrogen species are formed. b) Representation of AgNPs@BM; AgNPs are covered with a basic material (BM), which reacts with H_2 to result in the exclusive formation of polar hydrogen species. A basic site of HT and BM is represented by BS.

We envisioned that AgNPs covered with a basic material (BM), namely, the core–shell nanocomposite AgNPs@BM, would be a reasonable structure for performing the above complete chemoselective reductions (Figure 2b). The AgNPs@BM structure can maximize the interface area of the AgNPs–BM, while minimizing the area of the bare AgNPs. This property would enable the exclusive formation of the heterolytically cleaved hydrogen species through a concerted effect between AgNPs and basic sites of BM that suppresses the unfavorable formation of homolytically cleaved hydrogen species on the bare AgNPs. The resulting Ag hydride and proton species would lead to complete chemoselective reduction of polar functionalities while retaining the $C{=}C$ bonds.

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[**] This work was supported by a Grant-in-Aid for Young Scientists (A) (23686116) from the Japan Society for the Promotion of Science (JSPS). We also thank Dr. T. Uruga, Dr. H. Tanida, and Dr. K. Nitta (SPring-8) for XAFS measurements (2011A1295). T.M. thanks the Japan Association for Chemical Innovation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201106244.

Well-defined hybrid metal nanoparticles with core–shell structures have attracted enormous attention because of their unique optic,[5–7] magnetic,[8] electronic,[9,10] and catalytic[11–19] properties that cannot be obtained in monometallic nanoparticles. In the catalytic field of core–shell bimetals, the core metals can affect the catalytic active metal species in the shell, thus giving rise to improvements in their activities and selectivities for organic reactions. However, the core metals cannot act directly as the active species because the shell covers the core metals entirely, and the access of reactants to the core metals is prevented. Furthermore, the core metals reported to date are often relatively large (>20 nm in diameter), which is generally not suitable for catalytically active species. The solutions to these above issues will generate new approaches toward novel applications of core–shell catalysts.

Herein, we present a new concept for the rational design of a core–shell catalyst that has active metal nanoparticles in the core and an oxide support with nanospaces in the shell. We successfully synthesized a novel core–shell AgNPs–CeO_2 nanocomposite (AgNPs@CeO_2) involving core AgNPs 10 nm in diameter and a shell assembled with spherical CeO_2 NPs 3–5 nm in diameter. The shell has nanospaces between the CeO_2 NPs that permit the access of reactants to the active center of the AgNPs. The AgNPs@CeO_2 catalyst showed complete chemoselectivity for the reduction of both nitrostyrenes to aminostyrenes and epoxides to alkenes by using H_2 while retaining the reducible C=C bonds. The advantages of the core–shell structure are shown in the remarkable improvement of the chemoselectivity compared with AgNPs supported on CeO_2 (AgNPs/CeO_2). Moreover, AgNPs@CeO_2 was easily separable from the reaction mixture and was reusable without loss of catalytic activity or selectivity.

AgNPs@CeO_2 was synthesized by the combination of the reverse micelle technique and the redox reaction between silver(I) and cerium(III).[20] CeO_2 has advantages as a BM because of its basicity and the facile control of its shape and size.[21–23] The scanning electron microscopy (SEM) image of AgNPs@CeO_2 showed uniform spherical nanoparticles 30 nm in diameter (Figure 3a). Transmission electron microscopy (TEM) showed the two areas of an electron-dense core 10 nm in diameter and an electron-poor shell 8 nm thick (Figure 3b). Energy-dispersive X-ray spectroscopy (EDS) analysis clearly demonstrated that the nanocomposite was composed of an Ag core and CeO_2 shell (Figure 3c). Close inspection of the HRTEM image showed that the spherical CeO_2 NPs about 3–5 nm in diameter assembled to form the shell (Figure 3c and Figure 1S in the Supporting Information). The zero-valent state of Ag in AgNPs@CeO_2 was confirmed by the Ag K-edge X-ray absorption near-edge structure (XANES) analysis (Figure 2S in the Supporting Information). The basic nature of AgNPs@CeO_2 were calculated by CO_2 adsorption analysis, which showed that 165 μmol g^{-1} CO_2 was adsorbed. These results conclusively show that a uniform core–shell AgNPs–CeO_2 nanocomposite can be synthesized. The core AgNPs 10 nm in diameter were covered with the shell assembled of spherical basic CeO_2 NPs. The nanospaces between the spherical CeO_2 NPs enable the access of reactants to the AgNPs core. The combination of the reverse micelle technique with the redox reaction between silver(I) and cerium(III) is crucial in forming the nanocomposite; much larger AgNPs@CeO_2 with a 100 nm diameter was obtained when the reverse micelle method was not used.[23]

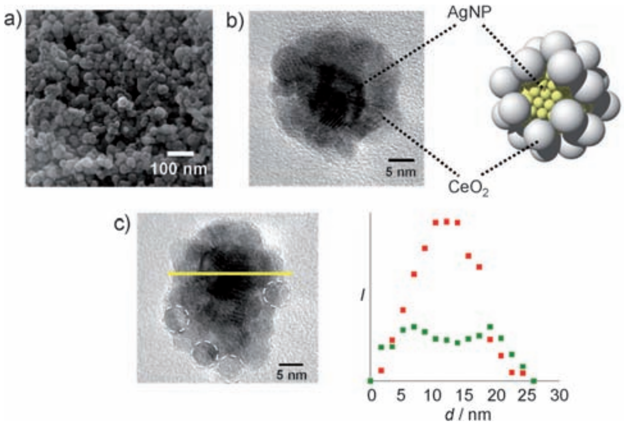


Figure 3. Electron micrographs of AgNPs@CeO_2. a) SEM image of AgNPs@CeO_2. b) HRTEM image of the single AgNPs@CeO_2 nanocomposite. c) The line-scan STEM-EDS across the AgNPs@CeO_2 nanocomposite (Ag: red squares, Ce: green squares). The circled areas correspond to the spherical CeO_2 NPs.

The catalytic activity of AgNPs@CeO_2 was evaluated in the reduction of 3-nitrostyrene (**1**) using H_2. Chemoselective reduction of the nitro moiety of a molecule that contains an easily reduced C=C bond is a challenge. The functionalized products obtained are useful intermediates.[24,25] AgNPs@CeO_2 exhibited complete chemoselectivity toward the reduction of the nitro group of **1**, and afforded the desired 3-aminostyrene product (**2**) in 98% yield without reduction of the C=C double bond to 3-ethylaniline (**3**) or 3,3′-divinylazobenzene (**4**) by dehydrative condensation (Figure 4a). Interestingly, the C=C bond of the desired product of **2** was intact, even after complete conversion of **1**. The complete chemoselectivity cannot be obtained by the conventional catalysts where the hydrogenation of the C=C bonds of the products is unavoidable and results in a decrease in the selectivity with increasing reaction time.

AgNPs similar in size to AgNPs@CeO_2 were supported on CeO_2 (AgNPs/CeO_2) by using the impregnation method, and were employed in the reduction under similar reaction conditions. AgNPs/CeO_2 had low chemoselectivity toward **2** with the formation of undesired products of **3** and **4**, where **2** and **4** were gradually hydrogenated to **3** and **2**, respectively (Figure 4b). The conversion of **4** to **2** was confirmed in a separate experiment in which **4** was employed as a starting material under similar reaction conditions. These results clearly show that the core–shell structure of AgNPs@CeO_2 is suitable for the complete chemoselective reduction of the nitro functionality while retaining the C=C bond. The efficiency of the core–shell structure was also demonstrated in the reduction of nitrobenzene in the presence of styrene (Scheme 1). Notably, nitrobenzene was efficiently converted to aniline while styrene was not reduced at all. This result was in sharp contrast with that obtained using AgNPs/CeO_2, where both nitrobenzene and styrene were hydrogenated.

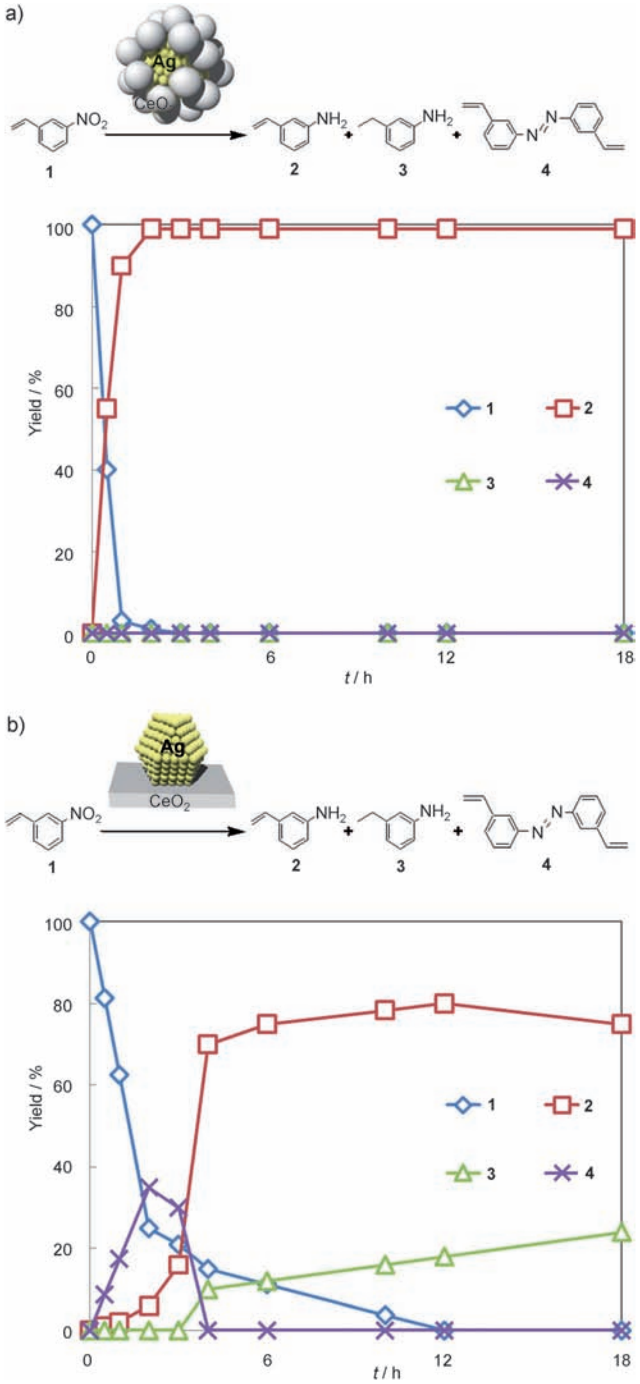
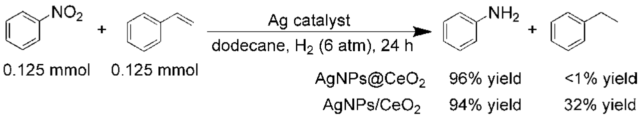


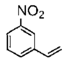
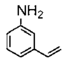
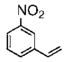
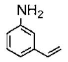
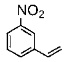
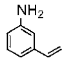
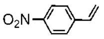
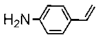
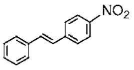
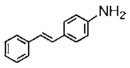
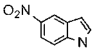
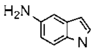
Figure 4. Time course of the reduction of **1** with H_2 using a) AgNPs@CeO_2 and b) AgNPs/CeO_2.



Scheme 1. Competitive reduction of nitrobenzene and styrene using AgNPs@CeO_2 or AgNPs/CeO_2.

The AgNPs@CeO_2 catalyst was also effective in the reduction of other nitro compounds containing C=C bonds to produce the corresponding aniline derivatives in high yields with greater than 99% selectivities (Table 1).

Table 1: Chemoselective reduction of nitro compounds bearing C=C bonds catalyzed by AgNPs@CeO_2.[a]

Entry	Substrate	Product	t [h]	Yield [%][b]	Sel. [%][b]
1			6	98	> 99
2[c]			6	97	> 99
3[d]			6	97	> 99
4			6	98	> 99
5[e]			24	97	> 99
6[e]			24	95	> 99

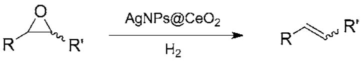
[a] Reaction conditions: AgNPs@CeO_2 (25 mg), substrate (0.5 mmol), dodecane (5 mL), H_2 (6 atm), 110 °C. [b] Determined by GC and LC using an internal standard. [c] Reuse 1. [d] Reuse 2. [e] 150 °C.

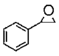
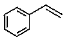
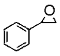
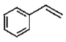
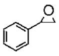
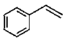
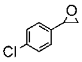
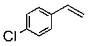
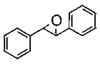
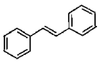
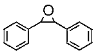
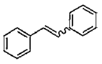
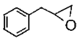
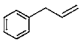
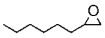
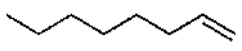
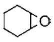
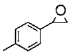
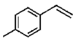
The unique reduction ability of AgNPs@CeO_2 was also investigated in the deoxygenation of epoxides to the corresponding alkenes, which is a valuable reaction in organic synthesis, such as in the deprotection of oxirane rings, and in biological chemistry for the reproduction of vitamin K in the vitamin K cycle.[26,27] AgNPs@CeO_2 showed high efficiency in the deoxygenation reaction. Various epoxides including aromatic, aliphatic, and alicyclic epoxides were smoothly converted to the corresponding alkenes with greater than 99% selectivities, and undesired alkanes that result from hydrogenation of the alkene products were not produced at all (Table 2). *trans*-Stilbene oxide was transformed into *trans*-stilbene, while *cis*-stilbene oxide produced a mixture of *E*/*Z* alkene stereoisomers (Table 2, entries 5 and 6). This is the first demonstration of an Ag-catalyzed chemoselective reduction of epoxides to alkenes using H_2.

In these reactions, AgNPs@CeO_2 was recovered by simple filtration from the reaction mixture and could be reused without any loss of activity or selectivity (Table 1, entries 2 and 3; Table 2, entries 2 and 3). Inductively coupled plasma atomic emission spectra (ICP-AES) analysis of the filtrate revealed the absence of Ag species (detection limit: 0.10 ppm), thus confirming that deoxygenation reactions occurred exclusively on the core AgNPs in AgNPs@CeO_2. TEM and XAFS analysis of the used AgNPs@CeO_2 catalyst revealed that the size and oxidation state of AgNPs of the used AgNPs@CeO_2 did not differ from those of the fresh AgNPs@CeO_2 (Figures 2S and 3S in the Supporting Information). This durability may be due to the successful coating of the active AgNPs with CeO_2.

In conclusion, we have reported a facile synthesis of the core–shell nanocomposite of AgNPs@CeO_2 by combining the reverse micelle technique and a redox reaction. The nanospace-containing shell structure enables the access of reactants to the active metal core. AgNPs@CeO_2 was demon-

Table 2: Chemoselective reduction of epoxides to alkenes catalyzed by AgNPs@CeO$_2$.[a]



Entry	Substrate	Product	t [h]	Yield [%][b]	Sel. [%][b]
1			6	97	> 99
2[c]			6	96	> 99
3[d]			6	97	> 99
4			6	95	> 99
5			12	98	> 99
6			12	96	> 99 E:Z = 3:1
7			24	96	> 99
8			24	95	> 99
9			24	94	> 99
10			6	96	> 99

[a] Reaction conditions: AgNPs@CeO$_2$ (25 mg), substrate (0.5 mmol), toluene (5 mL), 110 °C, H$_2$ (6 atm). [b] Determined by GC and LC using an internal standard. [c] Reuse 1. [d] Reuse 2.

strated to be an effective catalyst for the complete chemoselective reduction of nitro compounds in the presence of C=C bonds using H$_2$ as a clean reductant. Furthermore, AgNPs@CeO$_2$ was applicable to the deoxygenation of epoxides to alkenes with greater 99 % selectivities. In these reactions, AgNPs@CeO$_2$ was reusable while maintaining its catalytic efficiency and particle size. Maximizing the interface interaction between AgNPs and basic sites of CeO$_2$ by the construction of core–shell AgNPs–CeO$_2$ successfully induces the heterolytic cleavage of H$_2$ and leads to the development of highly chemoselective catalytic reduction of polar functionalities. We believe that this strategy for the construction of core–shell nanocomposites can be applied to other selective organic transformations.

Received: September 3, 2011

Keywords: epoxides · heterogeneous catalysis · nanoparticles · nitro compounds · reduction

[1] J. A. Dumesic, G. W. Huber, M. Boudart, *Handbook of Heterogeneous Catalysis*, *Vol. 1*, 2nd ed., Wiley-VCH, Weinheim, **2008**, p. 10.
[2] Y. Mikami, A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Lett.* **2010**, *39*, 223.
[3] Y. Mikami, A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Tetrahedron Lett.* **2010**, *51*, 5466.
[4] T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem.* **2010**, *122*, 5677; *Angew. Chem. Int. Ed.* **2010**, *49*, 5545.
[5] N. S. Sobal, M. Hilgendorff, H. Möhwald, M. Giersig, M. Spasova, T. Radetic, M. Farle, *Nano Lett.* **2002**, *2*, 621.
[6] C. Loo, A. Lowery, N. Halas, J. West, R. Drezek, *Nano Lett.* **2005**, *5*, 709.
[7] K.-S. Lee, M. A. El-Sayed, *J. Phys. Chem. B* **2006**, *110*, 7238.
[8] S. Sun, *Adv. Mater.* **2006**, *18*, 393.
[9] D. V. Talapin, J.-S. Lee, M. V. Kovalenko, E. V. Shevchenko, *Chem. Rev.* **2010**, *110*, 389.
[10] S. Koh, P. Strasser, *J. Am. Chem. Soc.* **2007**, *129*, 12624.
[11] K.-W. Park, J.-H. Choi, B.-K. Kwon, S.-A. Lee, Y.-E. Sung, H.-Y. Ha, S.-A. Hong, H. Kim, A. Wieckowski, *J. Phys. Chem. B* **2002**, *106*, 1869.
[12] X. W. Teng, H. Yang, *J. Am. Chem. Soc.* **2003**, *125*, 14559.
[13] M. Chen, D. Kumar, C.-W. Yi, D. W. Goodman, *Science* **2005**, *310*, 291.
[14] D. Astruc, F. Lu, R. Aranzaes, *Angew. Chem.* **2005**, *117*, 8062; *Angew. Chem. Int. Ed.* **2005**, *44*, 7852.
[15] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362.
[16] S. Alayoglu, A. U. Nilekar, M. Mavrikakis, B. Eichhorn, *Nat. Mater.* **2008**, *7*, 333.
[17] C. Wang, H. Daimon, S. Sun, *Nano Lett.* **2009**, *9*, 1493.
[18] P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C. F. Yu, Z. C Liu, S. Kaya, D. Nordlund, H. Ogasawara, M. F. Toney, A. Nilsson, *Nat. Chem.* **2010**, *2*, 454.
[19] C. J. Serpell, J. Cookson, D. Ozkaya, P. D. Beer, *Nat. Chem.* **2011**, *3*, 478.
[20] See Supporting Information for the preparation of AgNPs@-CeO$_2$.
[21] H.-X. Mai, L.-D. Sun, Y.-W. Zhang, R. Si, W. Feng, H.-P. Zhang, H.-C. Liu, C.-H. Yan, *J. Phys. Chem. B* **2005**, *109*, 24380.
[22] C. M. Y. Yeung, K. M. K. Yu, Q. J. Fu, D. Thompselt, M. I. Petch, S. C. Tsang, *J. Am. Chem. Soc.* **2005**, *127*, 18010.
[23] T. Kayama, K. Yamazaki, H. Shinjoh, *J. Am. Chem. Soc.* **2010**, *132*, 13154.
[24] A. Corma, P. Serna, *Science* **2006**, *313*, 332.
[25] H. Blaser, H. Steiner, M. Studer, *ChemCatChem* **2009**, *1*, 210.
[26] E. J. Corey, W. G. Su, *Tetrahedron Lett.* **1988**, *29*, 3423.
[27] W. S. Johnson, M. S. Plummer, S. P. Reddy, W. R. Bartlett, *J. Am. Chem. Soc.* **1993**, *115*, 515.