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Selective deoxygenation of styrene oxides under a CO atmosphere using silver nanoparticle catalyst

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ABSTRACT

Deoxygenation of styrene oxide derivatives into the corresponding alkenes was efficiently catalyzed by inorganic materials of hydrotalcite-supported silver nanoparticles (Ag/HT) using CO/H_2O as a reductant. The Ag/HT catalyst was reusable without loss of activity or selectivity.

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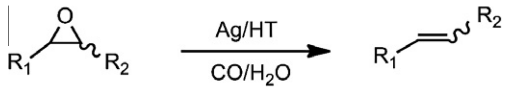
Metal nanoparticles (NPs) often show unique catalytic properties that can dramatically differ from those of metal complex catalysts. Among the various metal NPs, silver nanoparticles (Ag NPs) have a distinguished catalytic ability for the industrial production of ethylene oxide from ethylene in the gas phase[1]. However, Ag NPs are less active catalysts for other organic reactions under liquid phase conditions. Recently, we re-evaluated the catalytic potential of Ag NPs and discovered that inorganic materials-supported Ag NPs exhibited significantly unique and higher catalytic activities than other NPs for several functional transformations, such as dehydrogenation of alcohols,[2] aqueous oxidation of silanes to silanols,[3] and hydration of nitriles to amides under liquid phase conditions.[4] Notably, we found the outstanding reduction ability of Ag NPs for the deoxygenation of nitroaromatic compounds to anilines using CO/H_2O as a reducing reagent.[5] For example, 3-nitrostyrene was chemoselectively reduced to 3-vinylaniline in over 99% selectivity without reduction of the C=C double bond. In the deoxygenation, a Ag-hydride species was generated in situ from the reaction of H_2O with CO, which led to the highly chemoselective reduction.

Epoxides are regarded as efficient protecting groups for alkene functionalities in organic synthesis.[6,7] The deprotection of epoxides has been achieved by stoichiometric reactions using an excess of various reducing reagents, such as phosphines,[8] silanes,[9] iodides,[10] and heavy metals.[11] These reaction systems have suffered from the production of a large amount of waste and/or the need for inert reaction conditions. Therefore, effective catalytic methodology for the deoxygenation of epoxides into the corresponding alkenes has been desired from an environmental standpoint, but these reports have been few.[12,13]

We attempted to extend our deoxygenation methodology using Ag NPs catalyst with CO/H_2O as a reductant to the selective deoxygenation of epoxides. We herein report that inorganic materials of hydrotalcite [HT; $Mg_6Al_2(OH)_{16}CO_3$]-supported Ag NPs exhibited catalytic ability for the selective deoxygenation of styrene oxide derivatives into the corresponding alkenes (Scheme 1). This catalyst system has the following advantages: (1) excellent selectivities for alkenes; (2) CO_2 as the sole byproduct, which can be easily removed from the reaction system; (3) no need for additives; and (4) reusability of the Ag/HT catalyst.

Ag/HT was prepared according to our previous Letter.[5] Initially Ag/HT was examined for deoxygenation of *trans*-stilbene oxide (**1**) at 110 °C in the presence of H_2O under 9 atm of CO. Compound **1** was converted into *trans*-stilbene (**2**) in 99% yield for 3 h accompanied by the generation of CO_2 without formations of 1,2-diphenylethane, 1,2-diphenylethanol, or benzyl phenyl ketone through the hydrogenation and/or isomerization of **1** (Table 1, entry 1).



Scheme 1. Catalytic deoxygenation of epoxide using Ag/HT with CO/H_2O.

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0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
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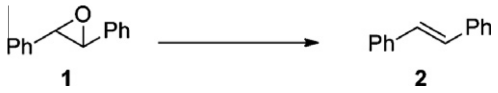
Table 1
Deoxygenation of *trans*-stilbene oxide[a]



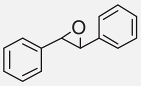
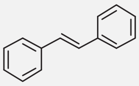
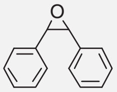
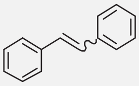
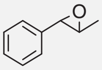
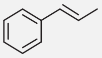
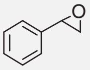
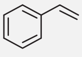
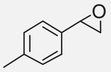
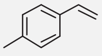
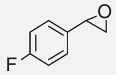
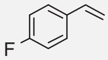
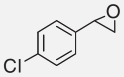
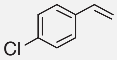
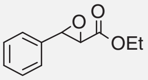
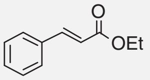
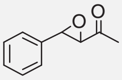
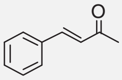
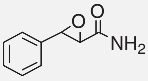
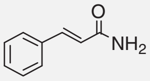
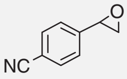
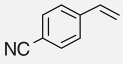
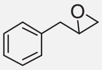
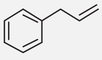
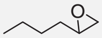
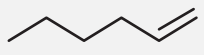
Entry	Catalyst	Solvent	Conv.[b] (%)	Sel.[b] (%)
1	Ag/HT	THF	99	>99
2[c]	Ag/HT	THF	99	>99
3[d]	Ag/HT	THF	99	>99
4	Ag/HT	Toluene	95	>99
5[e]	Ag/HT	Water	92	>99
6	Ag/HT	1,4-Dioxane	10	>99
7	Ag/HT	DMA	0	–
8	Ag/Al_2O_3	THF	62	>99
9	Ag/MgO	THF	33	>99
10	Ag/TiO_2	THF	25	>99
11[f]	Ag/TiO_2	THF	39	>99
12	Ag/SiO_2	THF	4	>99
13	HT	THF	0	–
14	$AgNO_3$	THF	0	–
15	Ag_2O	THF	0	–
16	Ag powder	THF	0	–

[a] Reaction conditions: *trans*-stilbene oxide (0.5 mmol), catalyst (metal: 0.037 mmol), solvent (5 mL), H_2O (0.1 mL), 110 °C CO (9 atm), 3 h.
[b] Determined by LC using internal standard technique.
[c] Reuse 1.
[d] Reuse 2.
[e] Water (4 mL), 150 °C, 3 h.
[f] Na_2CO_3 (1.5 mmol) was added.

Notably, **2** was not hydrogenated even when the reaction time was extended beyond the complete conversion of **1**.[14] Among the various solvents tested, THF and toluene afforded the excellent yields of **2** while 1,4-dioxane and DMA inhibited the reaction (entries 1 and 4 vs 6 and 7). Interestingly, Ag/HT could be used under aqueous conditions without organic solvent. Thus, the deoxygenation of **1** using Ag/HT in water gave **2** in 92% isolated yield (entry 5). The effect of supports on the catalytic activity of Ag NPs was investigated in the deoxygenation of **1** using a series of inorganic supports, such as Al_2O_3, MgO, SiO_2, and TiO_2. HT was found to be the best support, followed by other base supports of Al_2O_3 and MgO (entries 8 and 9), whereas Ag/TiO_2 and Ag/SiO_2 had low activities (entries 10 and 12). Interestingly, the addition of Na_2CO_3 as a base to the above Ag/TiO_2 reaction system improved the yield of **2** (entry 10 vs 11).[15] The parent HT or the silver compounds of $AgNO_3$, Ag_2O, or Ag powder did not promote the deoxygenation at all (entries 13–16). These results indicate that a combination of Ag NPs and base support of HT is essential to obtain high catalytic activity for the deoxygenation of **1**.

The catalyst was filtered off from the reaction mixture after 50% conversion of **1**. Further stirring of the filtrate under identical reaction conditions did not afford any products. ICP analysis of the filtrate confirmed that the leaching of Ag species into the solution was not detected (detection limit: 0.007 ppm). The above phenomenon confirms that the present reaction proceeds on the solid Ag/HT catalyst. The Ag/HT catalyst was separated from the reaction mixture by simple filtration after the deoxygenation of **1**, and then, product **2** could be easily isolated by evaporation of the solvent. The recovered Ag/HT was reusable without any loss of its high catalytic activity or selectivity: 99% yields were obtained in the two recycling reactions of **1** (entries 2 and 3). EXAFS and TEM analysis of Ag/HT revealed that the size and oxidation state of the Ag NPs on HT did not change significantly; the particle sizes of fresh and reused Ag/HTs were 9.5 nm and 9.8 nm, respectively,[17] which is consistent with the retention of the catalytic activity of Ag/HT during the reuse experiments.

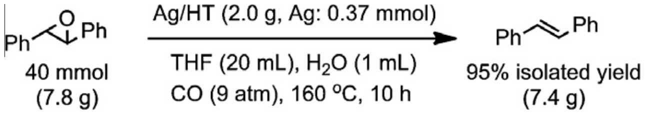
Table 2
Deoxygenation of various epoxides using Ag/HT[a]

Entry	Substrate	Product	Time (h)	Conv.[b,c] (%)	Sel.[b] (%)
1			3	99 (95)	>99
2			3	99 (94)	>99 (*E*/*Z* = 4/1)
3			3	99 (94)	>99
4			2	99 (92)	>99
5			2	95 (90)	>99
6			2	92 (87)	>99
7			2	90 (85)	>99
8			12	92 (88)	>99
9			12	91 (86)	>99
10			12	99 (85)	>99
11			12	85 (80)	>99
12			24	Trace	–
13			24	Trace	–

[a] Reaction conditions: Ag/HT (Ag: 0.037 mmol), substrate (0.5 mmol), THF (5 mL), H_2O (0.1 mL), 110 °C, CO (9 atm).
[b] Determined by GC and LC using internal standard technique.
[c] Values in parentheses are the yields of the isolated products.

The scope and limitations of the Ag/HT-catalyzed deoxygenation of epoxides were explored next (Table 2). Styrene oxides substituted with electron-donating or electron-withdrawing groups were completely converted into the desired alkenes (entries 5–7). Notably, epoxides bearing other reducible functionalities were chemoselectively deoxygenated. The ester, ketone, amide, and cyano moieties remained intact during the deoxygenation of epoxides (entries 8–11). Benzylic and aliphatic epoxides did not show any reactivity (entries 12 and 13). This high activity of Ag/HT toward the aromatic oxirane ring was in contrast to that of previous catalyst systems.[12] In addition, Ag/HT was also applicable for a preparative scale deoxygenation reaction, for example, 40 mmol of **1** was smoothly converted into **2** in 95% isolated yield (Scheme 2).

In conclusion, we have developed a highly efficient catalytic deoxygenation using HT-supported silver nanoparticles with CO/H_2O as a reducing reagent. Various styrene oxide derivatives were



Scheme 2. A 40 mmol-scale deoxygenation of *trans*-stilbene oxide using Ag/HT.

smoothly converted into the corresponding alkenes in high yields without reduction of other reducible functionalities. Ag/HT was easily separated from the reaction mixture and was reusable with retention of its activity and selectivity. This chemoselective deoxygenation system using Ag/HT as a heterogeneous catalyst promises to be a useful methodology for the deprotection of epoxides into alkenes.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.08.031.

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12. For previous reports on the catalytic deoxygenation of epoxides, see: (a) Zhu, Z.; Espenson, J. H. *J. Mol. Catal. A* **1995**, *103*, 87; (b) Gable, K. P.; Brown, E. C. *Synlett* **2003**, 2243; (c) Arterburn, J. B.; Liu, M.; Perry, M. C. *Helv. Chim. Acta* **2002**, *85*, 3225; (d) Itoh, T.; Nagano, T.; Sato, M.; Hirobe, M. *Tetrahedron Lett.* **1989**, *30*, 6387; (e) Isobe, H.; Branchaud, B. P. *Tetrahedron Lett.* **1999**, *40*, 8747.
13. We recently reported a successful example of the catalytic deoxygenation of epoxides using alcohols as reducing reagents, see: Mitsudome, T.; Noujima, A.; Mikami, Y.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5545.
14. The time profile for the reduction of **1** is shown in Fig. 1S in Supplementary data.
15. We previously reported that the positive effect of the additional base and base support was attributed to promote the formation of a metal-hydride species; see: Refs. 13,16.
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17. See Supplementary data for details.