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Supported Gold and Silver Nanoparticles for Catalytic Deoxygenation of Epoxides into Alkenes**

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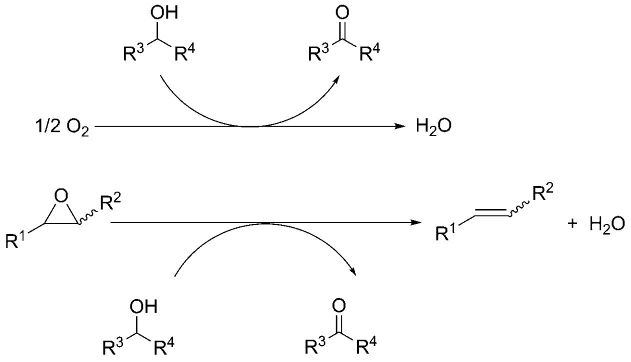
Some metal nanoparticles (NPs) have been shown to have unprecedented catalytic performance which far exceeds those of conventional metal complex catalysts.[1–4] Especially, gold and silver NPs are known to exhibit outstanding catalytic ability in the aerobic epoxidation of propene[5] and styrene,[6] and in the industrial epoxidation of ethylene,[7] respectively. Our recent research has focused on the catalytic potential of coinage-metal NPs under liquid phase conditions, wherein we found that gold, silver, and copper NPs supported on inorganic materials had unique catalytic properties for versatile organic synthesis such as the aerobic oxidation of alcohols,[8,9] oxidation of silanes into silanols using water,[10] and hydration of nitriles.[11] In the course of our study on the coinage-metal NP catalysis for the aerobic oxidation of alcohols, we envisioned that if epoxides could act as hydrogen accepters in place of molecular oxygen, the metal NPs could act as effective catalysts for reverse epoxidation, namely, deoxygenation of epoxides using alcohols as oxygen accepters (Scheme 1).



Scheme 1. The oxidation of alcohols using O_2 versus deoxygenation of epoxides using alcohols.

Deoxygenation of epoxides into alkenes is important reaction in both organic synthesis and biological chemistry; for example, in the deprotection of oxirane rings[12] and in the reproduction of vitamin K in the vitamin K cycle.[13] Stoichiometric deoxygenations of epoxides have been carried out using a variety of reagents[14] including phosphines, silanes, iodides, and heavy metals. However, these reagents are often toxic or employed in large excess, resulting in the production of undesired waste. In addition, most of these methods require special handling and harsh reaction conditions, which may affect other sensitive functional groups in the parent molecules. Several successful catalyst systems have appeared to date such as Re complexes with triphenylphosphine,[15–17] a Fe complex with $NaBH_4$,[18] and a Co complex with Na,[19] but these systems suffer from the need for hazardous reductants, inert conditions, and display low catalytic activities (TOFs $< 13\,h^{-1}$, TONs < 20; TOF = turnover frequency, TON = turnover number), and low atom efficiencies. Therefore, the development of an efficient catalytic system for deoxygenation of epoxides remains of great importance.

Herein, we discovered the intrinsic ability of gold and silver NPs in catalyzing deoxygenation of epoxides; gold and silver NPs supported on an inorganic material of hydrotalcite (HT; Au/HT and Ag/HT) allow highly efficient catalytic deoxygenation of epoxides into alkenes using alcohols. The selectivity for all the alkene products were over 99%, and excellent turnover number was achieved. To the best of our knowledge, this is the first report on the catalytic deoxygenation of epoxides using gold and silver NPs. The Au/HT and Ag/HT catalyst systems described herein offer a green protocol for removing oxygen from epoxides with the following advantages: 1) high catalytic activity and selectivity; 2) the use of safe and easy-to-handle catalysts and reducing reagents; 3) applicability to a wide range of epoxides; 4) a simple purification procedure owing to easy separation of the solid catalysts from the reaction mixtures; and 5) recyclebility of the catalysts without any loss in their efficiency. The discovery of this unique catalysis of gold and silver NPs will open new routes to selective functional transformations in organic synthesis.

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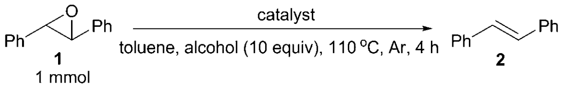
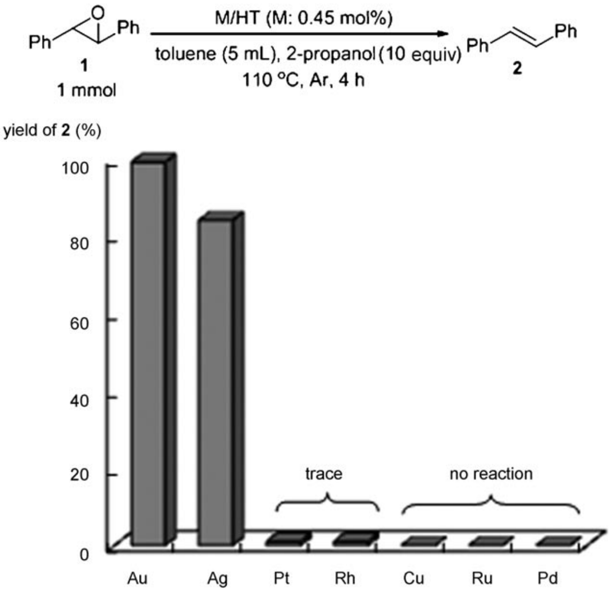
A mixture of solid Au/HT,[20] *trans*-stilbene oxide (**1**), and 2-propanol in toluene was stirred at 110 °C under an Ar atmosphere for 4 hours (Table 1, entry 1). Selective deoxygenation of **1** occurred to afford *trans*-stilbene (**2**) in 99 % yield without any by-products such as 1,2-diphenylethane, 1,2-diphenylethanol, or benzyl phenyl ketone, which could arise from the hydrogenation or isomerization of **1**. Au/HT successfully promoted the deoxygenation reaction even at 60 °C (Table 1, entry 2). Other alcohols such as 1-phenylethanol and benzyl alcohol also worked well, whereas an aliphatic primary alcohol, 1-octanol, was not reactive (Table 1, entries 3–5). The choice in the solid support used was found to significantly influence the catalytic activity; among the tested supports, HT was the best. Al_2O_3 and MgO[21] were also effective (Table 1, entries 1, 6, and 7), whereas Au/TiO_2 and Au/SiO_2 resulted in low yields of **2** (Table 1, entries 8 and 9). Other gold compounds such as $HAuCl_4$, Au_2O_3, and the bulk metal did not result in formation of **2** (Table 1, entries 10–12). Other metal NPs supported on HT, which have catalytic potential for aerobic alcohol oxidation such as Pd, Rh, Pt, Ru, Ag, and Cu, were also examined under similar reaction conditions in the deoxygenation of **1** (Scheme 2). Notably, HT-supported silver NPs also functioned as an efficient catalyst, giving **2** in high yield, and the other metal NPs did not display any catalytic activity.

Table 1: Deoxygenation of *trans*-stilbene oxide (**1**) using Au catalysts.[a]



Entry	Catalyst	Alcohol	Yield [%][b]	Sel. [%][b]
1	Au/HT	2-propanol	99	> 99
2[c]	Au/HT	2-propanol	99	> 99
3	Au/HT	1-phenylethanol	99	> 99
4	Au/HT	benzyl alcohol	91	> 99
5	Au/HT	1-octanol	37	> 99
6	Au/Al_2O_3	2-propanol	60	> 99
7	Au/MgO	2-propanol	43	> 99
8	Au/TiO_2	2-propanol	19	> 99
9	Au/SiO_2	2-propanol	5	> 99
10	$HAuCl_4$	2-propanol	< 1	–
11	Au_2O_3	2-propanol	< 1	–
12	bulk Au metal	2-propanol	0	–

[a] Reaction conditions: catalyst (Au: 0.45 mol %), toluene (5 mL), alcohol (10 mmol). [b] Determined by LC methods using an internal standard technique. [c] At 60 °C, 12 h, Au/HT (Au: 1.4 mol %).



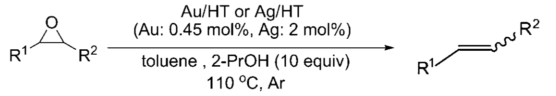
Scheme 2. Deoxygenation of *trans*-stilbene oxide (**1**) using hydrotalcite-supported metal particles. M = metal.

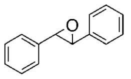
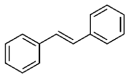
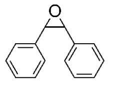
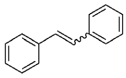
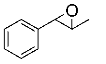
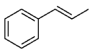
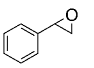
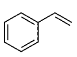
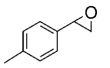
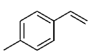
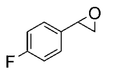
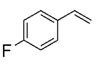
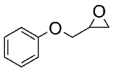
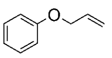
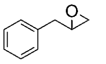
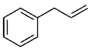
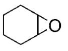
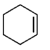
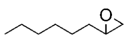
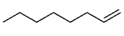
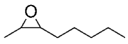
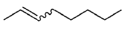
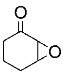
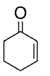
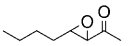
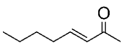
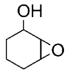
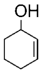
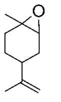
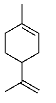
The reaction scope for Au/HT and Ag/HT in the deoxygenation of epoxides is summarized in Table 2.[22] Au/HT could deoxygenate a wide range of epoxides, affording the corresponding alkenes in excellent yields. For example, epoxides having phenyl (Table 2, entries 1, 8, 10, 12, 15, and 17), alkyl (Table 2, entries 23, 25, and 28), ether (Table 2, entry 19), carbonyl (Table 2, entries 30 and 32), hydroxy (Table 2, entry 34), and olefinic (Table 2, entry 36) groups were successfully employed. Deoxygenation of *trans*-stilbene oxide (Table 2, entries 1–7), *trans*-1-phenylpropylene oxide (Table 2, entries 10 and 11), and *trans*-3,4-epoxy-2-octanone (Table 2, entry 32) also proceeded with retention of their configurations. However, *cis*-stilbene oxide and *cis*-2-octene oxide gave a mixture of the *Z*/*E*-alkene stereoisomers (Table 2, entries 8, 9, and 28). Interestingly, Ag/HT showed unique chemoselectivity for the deoxygenation; only styrene oxide derivatives proved to be reactive (Table 2, entries 5, 9, 11, 14, 16, and 18). Such a considerable difference in activity between the gold and silver NPs may be useful as a means for selective de-epoxidation of a compound bearing several epoxide moieties.[23] Furthermore, these solid catalysts were recoverable by simple filtration after the deoxygenation without any loss in their activity or selectivity after several uses (Table 2, entries 2, 3, 6, and 7).

Tunneling electron microscopy (TEM) images of Au/HT after the reuse revealed that the average diameter and size distribution of the gold NPs were similar to those of the fresh Au/HT, and that no aggregation of the used gold NPs was apparent. By using Au L-edge X-ray absorption fine structure (XAFS) methods, atomic-scale analysis of Au/HT showed that the intensity of the Fourier-transform (FT) peak derived from the Au–Au shell at 2.8 Å was unchanged, supporting the observation that the gold NPs after reuse were the same size after recycling compared to that in the original sample.[20] Similar results were also obtained in the analyses of the Ag/HT catalyst. These results are consistent with the retention of the catalytic activities of the NPs during recycling experiments.

The deoxygenation of expoxides using Au/HT was also applicable to a preparative-scale reaction. For example, **1** (3.9 g; 20 mmol) successfully gave **2** [(3.4 g; 95 % (isolated)], wherein the TOF and TON were up to 270 h^{-1} and 20000, respectively (Table 2, entry 4). These values are three orders of magnitude greater than those in previously reported catalyst systems, such as $Tp'ReO_3$ with PPh_3 (TOF, TON: 0.2 h^{-1}, 20),[16] [Re(catecholato)] with PPh_3 (13 h^{-1}, 19),[17]

Table 2: Deoxygenation of various epoxides using Au/HT and Ag/HT.[a]

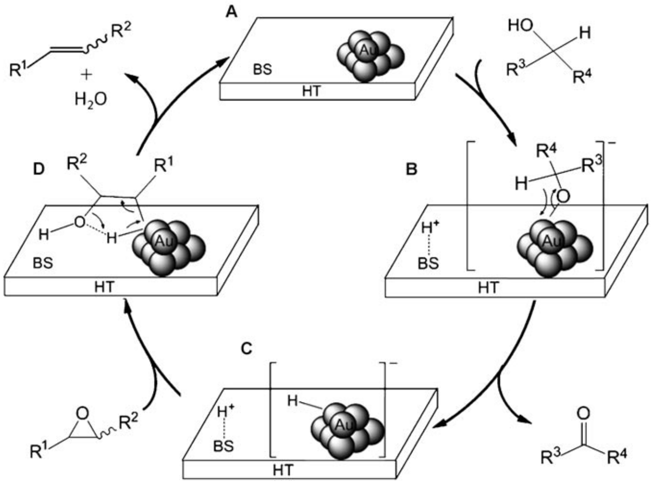


Entry	Substrate	Product	Catalyst	t [h]	Yield [%][b]	Sel. [%][b]
1			Au/HT	4	99	> 99
2[c]			Au/HT	4	99	> 99
3[d]			Au/HT	4	97	> 99
4[e]			Au/HT	72	95	> 99
5			Ag/HT	8	95	> 99
6[c]			Ag/HT	8	93	> 99
7[d]			Ag/HT	8	93	> 99
8			Au/HT	4	99	> 99 (*E*/*Z*=2:3)
9			Ag/HT	4	84	> 99 (*E*/*Z*=4:1)
10			Au/HT	4	98	> 99
11			Ag/HT	8	99	> 99
12[f]			Au/HT	6	> 99	> 99
13[g]			Au/HT	24	95	> 99
14[f]			Ag/HT	6	95	> 99
15			Au/HT	6	96	> 99
16			Ag/HT	6	94	> 99
17			Au/HT	6	94	> 99
18			Ag/HT	6	92	> 99
19			Au/HT	6	93	> 99
20			Ag/HT	6	13	> 99
21			Au/HT	24	89	> 99
22			Ag/HT	24	trace	–
23[h]			Au/HT	24	87	> 99
24[h]			Ag/HT	24	trace	–
25[f]			Au/HT	4	97	> 99
26[g]			Au/HT	48	93	> 99
27[f]			Ag/HT	24	trace	–
28[h]			Au/HT	12	81	> 99 (*E*/*Z*=1:1)
29[h]			Ag/HT	24	trace	–
30[h]			Au/HT	24	88	> 99
31[h]			Ag/HT	24	trace	–
32[h]			Au/HT	24	95	> 99
33[h]			Ag/HT	24	trace	–
34[h]			Au/HT	6	93	> 99
35[h]			Ag/HT	24	trace	–
36			Au/HT	24	72	> 99
37			Ag/HT	24	trace	> 99

[a] Reaction conditions: Catalyst (0.1 g), substrate (1 mmol), toluene (5 mL), 2-propanol (0.6 mL). [b] Determined by GC and LC methods using an internal standard technique. [c] Cycle 1. [d] Cycle 2. [e] Conditions: catalyst (0.02 g), substrate (20 mmol), 2-propanol (20 mL), 150 °C. [f] 80 °C. [g] Conditions: catalyst (0.02 g), substrate (10 mmol), 2-propanol (20 mL). [h] Substrate (0.3 mmol), catalyst (0.2 g).

CH_3ReO_3 with PPh_3 ($0.5\,h^{-1}$, 9),[15] $[Fe_4S_4(SC_6H_5)_4]^{3-}$ with $NaBH_4$ ($1.3\,h^{-1}$, 4),[18] and $[Co(Salen)_2]$ with Na(Hg) ($0.8\,h^{-1}$, 5).[19]

Bearing in mind that the strongly positive effects of basic supports of HT, Al_2O_3, and MgO on the deoxygenation (Table 1, entries 1, 6, and 7), it is considered that the deoxygenation would proceed through cooperation between the gold NPs and a basic site on HT, as proposed in Scheme 3.



Scheme 3. A plausible reaction path for the Au/HT-catalyzed deoxygenation of an epoxide involving participation of the Au NPs and a basic site (BS) of HT.

First, oxidation of the alcohol occurs on Au/HT (**A**) through abstraction of the proton of the alcohol by a basic site of HT to generate $[H\text{-}HT]^+$ and a $[Au\text{-alcoholate}]^-$ species (**B**) at the AuNP-HT interface. The Au-alcoholate species then undergoes β-hydride elimination to give an $[H\text{-}Au]^-$ species (**C**) together with the corresponding carbonyl compound. Next, protonation from the $[H\text{-}HT]^+$ species opens the epoxide, and subsequent attack of the $[H\text{-}Au]^-$ species onto the epoxide gives the intermediate **D**. Subsequent dehydration of **D** provides the alkene, thereby completing the catalytic cycle.[24,25]

The above reaction pathway is supported by the following experimental results: 1) Almost equimolar amounts from acetophenone and H_2O were formed respectively for every mole of styrene (**4**) during the deoxygenation of styrene oxide (**3**) using 1-phenylethanol. 2) When *trans*-2-octenal was used in place of **3**, chemoselective reduction occurred to exclusively afford *trans*-2-octenol, preserving the incipient C=C double bonds; similarly in the case of benzaldehyde, benzylalcohol was formed in quantitative yield.[26–28] 3) Addition of a radical trap, methyl methacrylate, into the reaction medium did not influence the deoxygenation of cyclohexene oxide.[29]

It is well known that all the metal NPs tested can form metal-hydride species in the alcohol oxidation. The distinguished deoxygenation activities of gold and silver NPs from those of other metal NPs should be attributed to their unique reactivity toward an epoxide (**C**→**D**→**A** in Scheme 3). The solid support HT can promote the deoxygenation as a base (**A**$\rightarrow$**B** in Scheme 3) as well as stabilize these metal NPs.

In conclusion, we have demonstrated a new and green catalytic methodology for deoxygenation of a diverse range of epoxides to alkenes through the combination of supported gold or silver NP catalysts using alcohols as reducing reagents. This protocol offers considerable benefits including an extremely simple work-up procedure, significantly higher activity compared with previously reported catalyst systems, and reusability of the catalysts with retention of catalytic efficiency. We believe that such gold and silver NP catalysts for the deoxygenation can be applied not only to epoxides but also to other oxygenated compounds.

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Keywords: epoxides · gold · heterogeneous catalysis · reduction · silver

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[20] The mean diameters (d), and standard deviations (σ) of the gold and silver NPs formed on the surface of the HT support were $d = 2.7$ nm ($\sigma = 0.7$ nm) and $d = 9.5$ nm ($\sigma = 3.9$ nm). See the Supporting Information for detailed preparation methods, characterizations, and their reaction procedures.

[21] MgO was pre-treated with the calcination under a N_2 atmosphere at 1000°C before the preparation of Au/MgO.

[22] To consider the possibility of leaching of active metal species from Au/HT and Ag/HT into the reaction mixtures, these solid catalysts were filtered from the reaction mixtures at 50% conversions of **1**. The filtrates were then stirred under similar reaction conditions, but did not produce additional product. Furthermore, inductively coupled plasma (ICP) analysis gave the result of no metal species in the filtrates (detection limit: 0.1 ppm). These results clearly prove that no leaching occurred and the deoxygenation proceeded on the gold and silver NPs immobilized on HT.

[23] Our previous work has revealed that supported silver NPs strongly interact with phenyl groups to promote oxidation of silanes and hydration of nitriles. See ref. [10a] and [11].

[24] Deoxygenation of **1** using D-benzhydrol ($C_6H_5CD(OD)C_6H_5$) as a reducing reagent was carried out under identical reaction conditions, and all hydrogen atoms in **1** were retained in **2**.

[25] There is another possibility in the reaction mechanism that the generated $[H\text{-}Au]^-$ species attacks an epoxide to form a β-hydroxy gold species. A subsequent protonation from $[H\text{-}HT]^+$ to the intermediate provides an alkene and a H_2O.

[26] For a chemoselective hydrogenation of carbonyl compounds by heterolytic hydrogen species, see: R. M. Bullock, *Chem. Eur. J.* **2004**, *10*, 2366.

[27] The use of 1 atm of H_2 as a reductant in place of 1-phenylethanol results in the formation of the mixture of **4** and ethylbenzene by hydrogenation of **4**. In a separate experiment, the hydrogenation of **4** occurred to afford ethylbenzene in the presence of Au/HT under an atmospheric H_2 conditions. These results indicate the formation of the mixture of the heterolytically and homolytically cleaved H_2 species on Au/HT under a H_2 atmosphere. See the Supporting Information for details.

[28] After the treatment of 1-phenylethanol in the presence or absence of **3**, trace amounts of H_2 (0.16 mol% equivalent to 1-phenylethanol, 0.0046 atm of H_2 atmosphere) in the gas phase was detected. We confirmed a reaction of **3** without 1-phenylethanol under an atmospheric gas mixed Ar with H_2 (H_2 partial pressure: 0.0046 atm) gave no conversion of **3**. See the Supporting Information for details.

[29] It is reported that the addition of methyl methacrylate to the reaction medium gave the corresponding lactone in the reduction of cyclohexene oxide to cyclohexene by Cp_2TiCl, which involves a radical mechanism.[30] See the Supporting Information for details.

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