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Room-Temperature Deoxygenation of Epoxides with CO Catalyzed by Hydrotalcite-Supported Gold Nanoparticles in Water

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Deoxygenation of epoxides to alkenes is useful in organic synthesis because it allows the use of the oxirane ring as a protective group for carbon–carbon double bonds.[1] The transformation is also of great importance in biological chemistry for the reproduction of vitamin K in the vitamin K cycle,[2] and has been recently applied to quantification methods to find the epoxide content in graphite epoxide or oxygenated carbon nanotubes.[3] Although many stoichiometric deoxygenations of epoxides have been developed by using a variety of reagents,[4] catalytic systems are rare[5] and they have suffered from problems such as low catalytic activity and the need for harsh and/or air-sensitive reaction conditions.

Recently, we have discovered that gold nanoparticles (NPs) efficiently catalyze the liquid-phase deoxygenation of epoxides into the corresponding alkenes by using alcohols as reducing reagents in organic solvents.[6] This process can overcome the above problems that have plagued previously reported catalytic systems. However, our reported deoxygenation system required high temperatures (110 °C), which could cause an incompatibility with functionalized epoxides. From the environmental and practical synthetic point of view, our next target is the design of a high-performance catalyst system for the deoxygenation of epoxides under much milder reaction conditions. Herein, we report an alternative green methodology for the catalytic deoxygenation of epoxides with supported gold NPs by using CO/H_2O as a reducing reagent under mild reaction conditions. Namely, an inorganic material of hydrotalcite supporting gold NPs (Au/HT) catalyzes the highly efficient deoxygenation of many epoxides into the corresponding alkenes in water without organic solvents under an atmospheric pressure of CO at room temperature. The use of water in organic reactions instead of organic solvents is attractive[7] because of the low cost, safety (nonexplosive, nonflammable, and nontoxic), and ease of phase-separation of water-insoluble products in the work-up procedure. A further advantage of this deoxygenation method is that only CO_2 is formed as a byproduct, which can be easily released from the reaction system and hence facilitating purification of the alkene products. The solid Au/HT catalyst is also easily separable from the products, and can be reused while maintaining its activity and selectivity. To the best of our knowledge, this is the first report of the catalytic deoxygenation of epoxides in water under organic-solvent-free conditions.

Au/HT was synthesized according to our reported procedure.[8] Au/HT and styrene oxide (**1a**) were added to water and the heterogeneous mixture was stirred under an atmospheric pressure of CO at room temperature. The reduction reaction of **1a** smoothly occurred to give styrene (**2a**) in over 99 % yield accompanied by the formation of an equimolar amount of CO_2 (Table 1, entry 1).[9] No other byproducts, such as a further reduction product of ethylbenzene, a hydration product of styrene glycol, and a CO_2 cycloaddition product of styrene carbonate were formed. Notably, water was found to be the best solvent to promote the deoxygenation efficiently, and lower yields were obtained in organic solvents (Table 1, entry 1 vs. entries 4–6). Among the inorganic materials tested as supports for gold NPs, the HT support afforded the highest yield of **2a**. Other base supports of Al_2O_3 and MgO also gave good yields of **2a** (Table 1, entries 10 and 11). On the other hand, TiO_2 resulted in a low conversion of **1a** (Table 1, entry 9), and SiO_2 and boron nitride were inactive (Table 1, entries 14 and 15). Interestingly,

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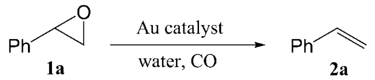
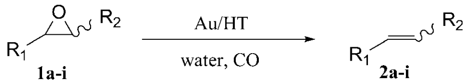
Table 1. Catalytic deoxygenation of styrene oxide.[a]

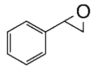
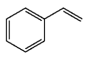
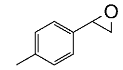
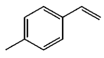
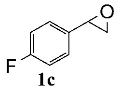
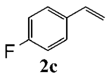
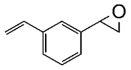
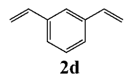
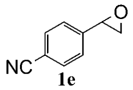
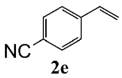
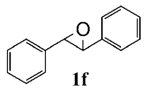
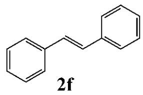
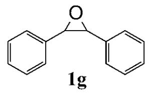
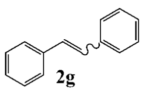
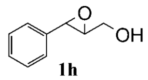
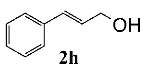
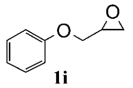
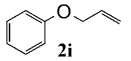
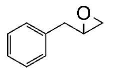
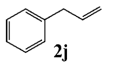
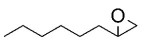
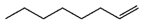
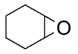
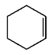
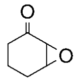
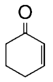


Entry	Catalyst	Yield[b] [%]	Selectivity[b] [%]
1	Au/HT	>99	>99
2[c]	Au/HT	>99	>99
3[d]	Au/HT	97	>99
4[e]	Au/HT	73	>99
5[f]	Au/HT	60	>99
6[g]	Au/HT	6	>99
7	Au_2O_3	<1	–
8	$HAuCl_4$	0	–
9	bulk Au metal	0	–
10	Au/Al_2O_3	79	>99
11	Au/MgO	36	>99
12	Au/TiO_2	18	>99
13[h]	$Au/TiO_2+Na_2CO_3$	57	>99
14	Au/SiO_2	3	>99
15	Au/BN	0	–
16	Ag/HT	0	–
17	Pd/HT	0	–
18	Pt/HT	0	–
19	Rh/HT	0	–
20	Ru/HT	0	–

[a] Reaction conditions: **1a** (0.5 mmol), Au catalyst (Au: 0.9 mol%), water (5 mL), CO (1 atm), 27°C, 6 h. [b] Determined by GC by using an internal standard technique. [c] Reuse 1. [d] Reuse 2. [e] Toluene (5 mL), water (0.1 mL). [f] THF (5 mL), water (0.1 mL). [g] DMA (5 mL), water (0.1 mL). [h] Na_2CO_3 (1.5 mmol) was added.

Table 2. Deoxygenation of various epoxides by using Au/HT.[a]



Entry	Substrate	Product	Time [h]	Yield[b] [%]	Sel.[b] [%]
1	 **1a**	 **2a**	6	>99 (94)	>99
2	 **1b**	 **2b**	12	90 (85)	>99
3	 **1c**	 **2c**	12	99 (94)	>99
4	 **1d**	 **2d**	16	90 (85)	>99
5	 **1e**	 **2e**	24	trace	–
6[c]			12	61	>99
7[c]	 **1f**	 **2f**	3	>99	>99
8[c]	 **1g**	 **2g**	3	>99	>99 (E/Z=38:62)
9[d]	 **1h**	 **2h**	16	96 (90)	96
10[d,e]			16	82	82
11[d,f]			16	36	36
12	 **1i**	 **2i**	24	90 (83)	>99
13	 **1j**	 **2j**	24	75 (69)	>99
14	 **1k**	 **2k**	24	12	>99
15[c]			12	90	>99
16	 **1l**	 **2l**	24	trace	–
17[c]			6	89	>99
18	 **1m**	 **2m**	24	trace	–
19[c]			12	99	>99

[a] Reaction conditions: Substrate (0.5 mmol), Au/HT (0.1 g, Au: 0.9 mol%), water (5 mL), CO (1 atm), 27°C. [b] Determined by GC by using an internal standard technique. Values in parentheses are the isolated yields. [c] THF (5 mL), water (0.1 mL), CO (5 atm), 110°C. [d] Cinnamaldehyde was formed as a byproduct. [e] Toluene (5 mL) was used as a solvent. [f] THF (5 mL) was used as a solvent.

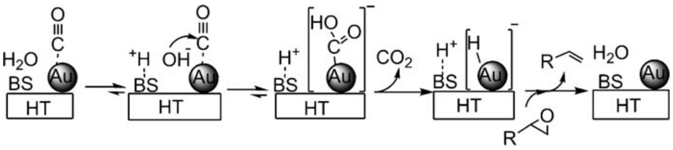
the addition of Na_2CO_3 to the above Au/TiO_2 reaction system significantly improved the yield of **2a** (Table 1, entry 12 vs. 13). Next, HT-supported Ag, Pd, Pt, Rh, and Ru were synthesized and examined in the reduction of **1a** under similar reaction conditions (Table 1, entries 16–20).[10] Interestingly, gold NPs exhibited a unique and distinct catalytic activity for the deoxygenation of **1a**, whereas the other metal NPs did not show any catalytic activities. These results clearly show that a combination of gold NPs and a base support exhibits high catalytic activity for the deoxygenation of **1a**.

After completing the deoxygenation of **1a**, the reaction mixture was separated into the product phase of **2a** and the aqueous phase containing the hydrophilic solid Au/HT, and then **2a** could be easily isolated by extraction using *n*-hexane. The recovered aqueous phase containing Au/HT was reusable without any loss of activity or selectivity during the recycling experiments (Table 1, entries 2 and 3). TEM and EXAFS analyses on the used Au/HT catalyst revealed that the size and oxidation state of gold NPs on HT did not significantly change from the fresh one, nor were aggregated gold species observed.[11] These observations are consistent with the retention of the catalytic activity of Au/HT during the recycling experiments.

The substrate scope of Au/HT for the deoxygenation of epoxides is exemplified in Table 2. Various epoxides were selectively deoxygenated into the corresponding alkenes in excellent yields without the use of organic solvents at room temperature. Many styrene oxide derivatives that have electron-withdrawing or -donating groups were highly reactive (Table 2, entries 2 and 3). In the case of *m*-vinyl styrene oxide, the deoxygenation reaction proceeded with retention of the original C=C bond (Table 2, entry 4). Notably, *trans*-2,3-epoxy-3-phenyl-1-propanol selectively gave cinnamyl alcohol in excellent yield while maintaining the hydroxyl group, and the selectivity for cinnamyl alcohol is much higher in water than in organic solvents (Table 2, entry 9 vs. entries 10 and 11). These phenomena are in sharp contrast with the results from our previously reported system of gold-catalyzed deoxygenation by using alcohols, in which the hydroxyl group was not tolerated and cinnamaldehyde was the main product.[12] An aliphatic epoxide was not applicable to aqueous reaction conditions (Table 2, entries 14 and 16). However, the use of THF as a solvent allowed the deoxygenation of these aliphatic epoxides (Table 2, entries 15 and 17).[13] Some other epoxides also became reactive under similar reaction conditions. 4-Cyanostyrene oxide and 2,3-epoxycyclohexan-1-one, which contain reducible functional groups, were deoxygenated with suppression of reduction of the cyano and carbonyl group (Table 2, entry 5 vs. 6 and entry 18 vs. 19). *trans*-Stilbene oxide was selectively converted into *trans*-stilbene (Table 2, entry 7). On the other hand, *cis*-stilbene oxide afforded a mixture of the alkene stereoisomers (*trans*- and *cis*-stilbene) with 38 % and 62 % yield, respectively (Table 2, entry 8).

In separate experiments under identical conditions without **1a**, H_2 was not detected,[14] but when the reaction temperature was increased to 50 °C, H_2 was observed in the gas-phase of the reactor. In the case of *trans*-2-octenal in place of **1a**, chemoselective reduction occurred to give *trans*-2-octen-1-ol as the sole product.[14] From the above results, we believe that a gold-hydride species generated in situ from the reaction of H_2O with CO is the active species for the deoxygenation of epoxides.[15,16] To verify the above hypothesis, Fourier transform infrared (FTIR) studies of Au/HT were carried out in the presence of CO and H_2O. Au/HT was treated with CO and H_2O vapor at 298 K, and a new band attributed to the formation of a gold-hydride species appeared at 1750 cm^{-1}.[11,17,18] Furthermore, when the treated Au/HT was exposed to the vapor of **1a**, the band attributed to the gold-hydride species gradually disappeared.

A basic site of HT presumably plays an important role in facilitating the formation of the gold-hydride species through the nucleophilic attack of OH^- on a gold–CO species followed by a decarboxylation (Scheme 1),[19] which is well evidenced by the positive effect of the additional base of Na_2CO_3 to the Au/TiO_2 catalyst on the deoxygenation (see above; Table 1, entry 10). The heterolytic hydrogen species of H^+ and H^- generated on Au/HT would deoxygenate the epoxide to form the corresponding alkene and water.[6]



Scheme 1. Concerted effects between HT and Au NPs for the formation of Au−H species (BS represents base site of HT).

In conclusion, we have developed a highly efficient and green catalytic deoxygenation reaction in water by using HT-supported gold NPs with CO/H_2O as a reducing reagent. Epoxides are smoothly converted to the corresponding alkenes under an atmospheric pressure of CO at room temperature in the absence of organic solvents. Moreover, Au/HT can be reused with retention of its activity and selectivity. The cooperative effect between gold NPs and basic sites of inorganic materials promotes the facile formation of a gold-hydride species from CO with water. We believe the generated gold-hydride species can be applied to the selective deoxygenation of other oxygenated compounds.

Experimental Section

Typical reaction procedure: A typical procedure for the deoxygenation of **1a** by the Au/HT catalyst was as follows: Au/HT (0.10 g Au, 0.0045 mmol) was placed in a reaction vessel, followed by addition of water (5 mL) and **1a** (0.5 mmol), and the reaction mixture was vigorously stirred at 27 °C under atmospheric CO for 6 h. After the deoxygenation reaction, the product was extracted by using hexane and was analyzed by GC with naphthalene as an internal standard to determine the conversion and yield.

Characterizations of Au/HT: Elemental analysis showed that gold loading was 0.89 %. X-ray absorption spectra and transmission electron microscopy (TEM) showed that the mean diameter, *d*, and standard deviation (σ) of gold NPs formed on the surface of the HT support were $d = 2.7$ nm ($\sigma = 0.7$ nm).

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Keywords: deoxygenation • epoxides • gold • heterogeneous catalysis • water chemistry

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[8] The synthesis and characterization of Au/HT were carried out in a previous paper, see: T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Green Chem.* **2009**, *11*, 793.

[9] The occurrence of the deoxygenation at gold NPs on Au/HT was confirmed as follows: Au/HT was removed from the reaction mixture at 50% conversion of **1a**. Continued stirring of the filtrate under similar conditions did not give any further products. In addition, no gold ions in the filtrate were confirmed by inductively coupled plasma (ICP) analysis.

[10] See the Supporting Information for the details of the preparation method of various metal NPs supported on HT.

[11] See the Supporting Information for details.

[12] Au/HT-catalyzed deoxygenation of 2,3-epoxy-3-phenyl-1-propanol by using 2-propanol in a toluene was conducted at 110 °C under Ar for 3 h, resulting in the formation of cinnamaldehyde and cinnamyl alcohol in 75% and 12% yield, respectively.

[13] The turnover number (TON) reached 1000 in the deoxygenation of **1a** in a THF solvent. See the Supporting Information for details.

[14] No production of H_2 can rule out the participation of H_2 in the Au/HT-catalyzed deoxygenation reaction. In fact, selective reduction of **1a** did not occur under a H_2 in place of a CO atmosphere; an over-hydrogenated product of ethylbenzene was mainly observed. See the Supporting Information for details.

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

[16] The use of D_2O in place of H_2O under identical conditions significantly affected the reaction rate for the deoxygenation of **1a**; a k_H/k_D value of 3.9 was observed, indicating that not only does CO function as a sole reductant, but also water takes part in the deoxygenation.

[17] Recent IR and theoretical studies on gold–hydride species revealed that a band attributed to the formation of gold-hydride species appeared around 1800 cm^{-1}, see: a) T. Tabakova, M. Manzoli, F. Vindigni, V. Idakiev, F. Boccuzzi, *J. Phys. Chem. A* **2010**, *114*, 3909; b) P. Pyykkö, *Angew. Chem.* **2004**, *116*, 4512; *Angew. Chem. Int. Ed.* **2004**, *43*, 4412.

[18] In the IR study, no peak was observed at 1750 cm^{-1} when Au/HT was treated with CO. The adsorption band at 1750 cm^{-1} also did not appear after the inlet of CO and D_2O vapor in place of H_2O.

[19] The effect of a base on the water gas shift reaction is well known. See: a) A. Basińska, F. Domka, *Catal. Lett.* **1993**, *22*, 327; b) K. Kaneda, K. Fujita, T. Takemoto, T. Imanaka, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 602; c) P. Escaffre, A. Thorez, P. Kalck, *J. Mol. Catal.* **1985**, *33*, 87.

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