

Selective Deoxygenation of Epoxides to Alkenes with Molecular Hydrogen Using a Hydrotalcite-Supported Gold Catalyst: A Concerted Effect between Gold Nanoparticles and Basic Sites on a Support**

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Direct conversion of epoxides into the corresponding alkenes is an important reaction because it allows the use of oxirane rings as protecting groups for carbon–carbon double bonds.^[1] This transformation also occurs in the production of vitamin K in the human body^[2] and is useful for quantification of epoxide moieties in graphite epoxide or oxygenated carbon nanotubes.^[3] Traditionally, the deoxygenation of epoxides to alkenes has been conducted using stoichiometric amounts of reagents, which results in the production of large amounts of undesirable waste. To date, several catalytic deoxygenations using PPh_3 , Na/Hg , and NaBH_4 as reductants have been reported. These catalysts, however, suffer from low activity, low atom efficiency, and tedious work-ups with moisture-sensitive reaction conditions.^[4] An ideal “green” protocol for the catalytic deoxygenation of epoxides is the use of molecular hydrogen (H_2) as a reducing reagent because, theoretically, water is the only by-product. However, the use of H_2 often causes nonselective reduction of epoxides to yield alcohols and alkanes as by-products through hydrogenation of the epoxides and overhydrogenation of the desired alkenes, respectively.^[5] Although there are a few successful reports on the selective deoxygenation of epoxides using H_2 , selectivity for alkenes is restricted to low conversion levels and a limited range of substrates.^[5,6] Therefore, the development of an efficient catalytic system for the selective deoxygenation of

epoxides to the corresponding alkenes using H_2 is highly desired.

Recently, we discovered that heterogeneous gold and silver nanoparticle (NP) catalysts have high activities for the deoxygenation of various epoxides to alkenes with >99% selectivity, using 2-propanol used as an environmentally friendly reductant.^[7] Furthermore, $\text{CO/H}_2\text{O}$ was found to work as an alternative reductant for the selective deoxygenation of epoxides to alkenes in water under mild reaction conditions.^[8]

Herein, we demonstrate that gold NPs supported on hydrotalcite [HT: $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot n\text{H}_2\text{O}$] (Au/HT) can act as a highly efficient heterogeneous catalyst for the deoxygenation of epoxides to alkenes with H_2 used as an ideal reductant. Au/HT is applicable to various epoxides, and selectivities for alkenes are over 99% at high conversions. After the reaction, solid Au/HT can be easily recovered from the reaction mixture and reused with no decrease in its catalytic efficiency.

The deoxygenation of styrene oxide (**1a**) using various inorganic-materials-supported Au NPs was carried out in toluene at 80 °C under 1 atm of H_2 (Table 1). Among the Au NP catalysts tested,^[9] Au/HT exhibited the highest activity toward this deoxygenation to afford styrene (**2a**) in 95% yield with a small amount of the overhydrogenated product ethylbenzene (**3a**; Table 1, entry 1). Au/ CeO_2 and Au/ Al_2O_3 also converted **1a**, but selectivities for **2a** were much lower than that of Au/HT (Table 1, entries 4 and 5). Interestingly, Au/ TiO_2 showed the highest selectivity for **2a**, although the conversion of **1a** was low (Table 1, entry 6). Au/ SiO_2 did not have any catalytic activity for this reaction (Table 1, entry 7). Notably, when the reaction temperature was lowered to 60 °C, Au/HT produced **2a** as the sole product in quantitative yield with >99% selectivity (Table 1, entry 2). Moreover, the carbon–carbon double bond of **2a** was completely intact when the reaction time was prolonged (Table 1, entry 3).

Next, various HT-supported metal NPs were examined in this reaction (Table 1, entries 8–13).^[11] Ag/HT, Ru/HT, Rh/HT and Cu/HT did not function as catalysts (Table 1, entries 10–13). In the case of Pd/HT and Pt/HT, hydrogenation of **1a** occurred to give 2-phenylethanol (**4a**), but no deoxygenated product was obtained (Table 1, entries 8 and 9). These results clearly revealed that the combination of Au NPs and HT had the best catalytic activity and selectivity toward the deoxygenation of epoxides to alkenes using H_2 .

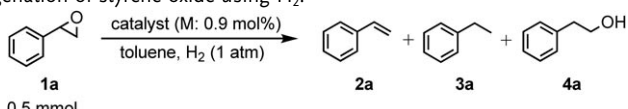
Scheme 1 shows the hydrogenation of **2a** in the presence or absence of *p*-methylstyrene oxide (**1b**) using Au/HT or Au/

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Table 1: Deoxygenation of styrene oxide using H₂.^[a]


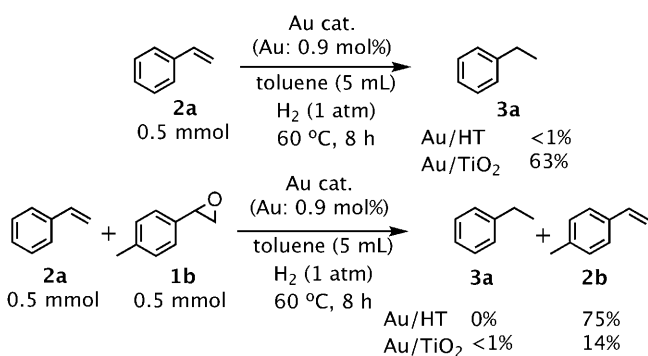
Entry	Catalyst	Conversion [%] ^[b]	Selectivity for 2a [%] ^[b]	Selectivity for 3a [%] ^[b]	Selectivity for 4a [%] ^[b]
1	Au/HT	97	97	3	0
2 ^[c]	Au/HT	> 99	> 99	0	0
3 ^[d]	Au/HT	> 99	> 99	0	0
4	Au/CeO ₂	64	81	19	0
5	Au/Al ₂ O ₃	82	36	64	0
6	Au/TiO ₂	26	> 99	< 1	0
7	Au/SiO ₂	< 1	–	–	–
8	Pd/HT	> 99	0	0	99
9	Pt/HT	87	0	0	99
10	Ag/HT	–	–	–	–
11	Rh/HT	–	–	–	–
12	Ru/HT	–	–	–	–
13	Cu/HT	–	–	–	–

[a] Reaction conditions: Catalyst (M: 0.9 mol%), toluene (5 mL), **1a** (0.5 mmol), 80 °C, 6 h.

[b] Determined by GC using an internal standard technique. [c] 60 °C, 8 h. [d] 60 °C, 24 h.

results show that immobilizing small Au NPs (< 3 nm) is the key to promoting the selective deoxygenation of epoxides to alkenes.

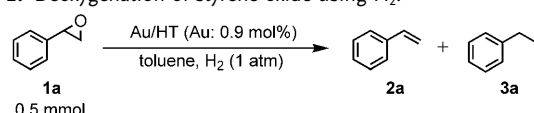
The applicability of this Au/HT-H₂ system was explored using various epoxides (Table 3). In all cases, the epoxides were deoxygenated to the corresponding alkenes with over 99% selectivity, and hydrogenation of the alkene products did not occur. For example, aromatic epoxides were good substrates (Table 3, entries 1, 4–8). *trans*-Stilbene oxide was transformed to *trans*-stilbene with retention of its stereochemistry (Table 3, entry 7), while *cis*-stilbene oxide gave a mixture of *Z/E*-alkene stereoisomers (Table 3, entry 8). Aliphatic epoxides also converted smoothly into



Scheme 1. Hydrogenation of styrene in the presence or absence of *p*-methylstyrene oxide.

TiO₂, which could selectively deoxygenate **1a** to **2a** (Table 1, entries 1 and 6). Neither Au/HT nor Au/TiO₂ hydrogenated **2a** in the presence of **1b**. Notably, Au/HT did not show any catalytic activity for the hydrogenation of **2a** even in the absence of **1b**, but in the case of Au/TiO₂, hydrogenation of **2a** to **3a** occurred. These phenomena indicate that metal-hydride species generated on Au/HT are effective for the deoxygenation of epoxides, but are completely inactive for the hydrogenation of C=C bonds. On the other hand, the high selectivity of Au/TiO₂ for alkenes in the deoxygenation of epoxides (Table 1, entry 6) is attributed to the preferential adsorption of epoxides over alkenes, which is a similar phenomenon to the previous report that the nitro group in 3-nitrostyrene was chemoselectively reduced while C=C bonds were unaffected by a Au/TiO₂ catalyst.^[12]

We next carried out the above deoxygenation using Au/HTs with different sized Au particles (Table 2).^[13] Larger Au NPs (> 3 nm) showed not only lower activities but also lower selectivities for **2a** because of the formation of **3a**. Interestingly, it was found that the yield and selectivity of **2a** increased as the average size of Au NPs decreased. These

Table 2: Deoxygenation of styrene oxide using H₂.^[a]


Particle diameter [nm]	Conversion [%] ^[b]	Selectivity for 2a [%] ^[b]	Selectivity for 3a [%] ^[b]
2.7	97	97	3
5.8	72	95	5
7.9	51	80	20
12	24	59	41
20	10	38	62

[a] Reaction conditions: Au/HT (Au: 0.9 mol%), toluene (5 mL), **1a** (0.5 mmol), 80 °C, 6 h. [b] Determined by GC using an internal standard technique.

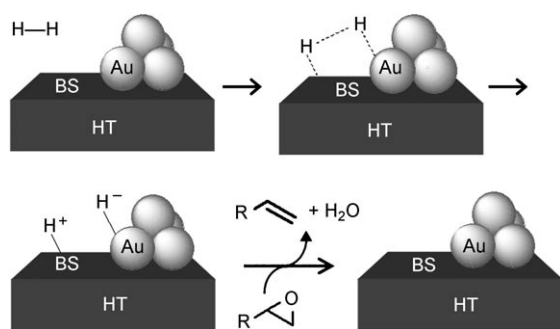
the corresponding alkenes in high yields, although an aliphatic internal epoxide of *trans*-2-octene oxide was not intact (Table 3, entries 9 and 11 vs. 10). An epoxides bearing a hydroxy group was deoxygenated to the corresponding alkene without affecting the functional group (Table 3, entry 12). After the deoxygenation of **1a**, Au/HT could be separated from the reaction mixture and reused without any loss of catalytic efficiency (Table 3, entries 2 and 3).

Bearing in mind that basic ligands of transition-metal complexes promote heterolytic cleavage of H₂ to give metal-hydride species,^[14] we propose a concerted effect between the basic sites of HT and the Au NPs. Namely, heterolytic cleavage of H₂ occurs at the interface between Au NPs and HT as a macroligand of Au NPs to give [Au-H][–] and [HT-H]⁺ species (Scheme 2). These hydrogen species would selectively deoxygenate the epoxides to form the corresponding alkenes and water,^[15] which is supported by the fact that Au/HT is inactive for the hydrogenation of C=C bonds of alkenes (see Scheme 1). Furthermore, bands assigned to the [Au-H][–] and

Table 3: Deoxygenation of various epoxides using Au/HT.^[a]

$\text{R}^1 \text{---} \text{C}_2\text{H}_4 \text{---} \text{O} \text{---} \text{R}^2 \xrightarrow[\text{H}_2 (1 \text{ atm})]{\text{Au/HT (0.9 mol\%)}} \text{R}^1 \text{---} \text{C}_2\text{H}_4 \text{---} \text{R}^2$					
Entry	Substrate	Product	Time [h]	Yield [%] ^[b]	Selectivity [%] ^[b]
1			8	> 99	> 99
2 ^[c]			8	97	> 99
3 ^[d]			8	97	> 99
4			12	81	> 99
5			12	84	> 99
6			24	85	> 99
7 ^[e]			12	98	> 99
8 ^[e]			12	96	> 99 E/Z = 2/3
9			24	84	> 99
10			24	< 1	–
11			24	89	> 99
12			24	92	> 99

[a] Reaction conditions: Au/HT (0.1 g), toluene (5 mL), substrate (0.5 mmol), 60°C. [b] Determined by GC using an internal standard technique. [c] Reuse 1. [d] Reuse 2. [e] At 100°C.



Scheme 2. Heterolytic dissociation of H₂ at the interface between basic sites (BS) of HT and Au NPs in the deoxygenation of epoxides (BS represents OH[–] or CO₃^{2–}).

In conclusion, we have found that Au/HT selectively catalyzed the deoxygenation of epoxides in the presence of H₂ as an ideal reducing reagent to give alkenes. With this system, various epoxides were transformed to alkenes with over 99 % selectivity and high atom efficiency. The selective formation of [Au-H][–] and [HT-H]⁺ species by using H₂ obtained through heterolytic dissociation will be applied to the reduction of other compounds. Moreover, Au/HT could be reused without loss of activity or selectivity.

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[HT-H]⁺ species appeared at around 1748 and 3200 cm^{–1}, respectively, in the FTIR spectrum of Au/HT after treatment with H₂.^[16–18] The band from [Au-H][–] gradually disappeared after treatment with **1a**. These results clearly confirm that active [Au-H][–] and [HT-H]⁺ species are formed in the deoxygenation.

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