Mild and efficient CO-mediated eliminative deoxygenation of epoxides catalyzed by supported gold nanoparticles†

Ji Ni, Lin He, Yong-Mei Liu, Yong Cao,* He-Yong He and Kang-Nian Fan

Received 24th July 2010, Accepted 17th September 2010
DOI: 10.1039/c0cc02783a

Supported gold nanoparticles (NPs), which are well-known epoxidation catalysts, were found to be exceptionally active for the selective deoxygenation of epoxides into alkenes using cheap and easily accessible CO and H_2O as the reductant.

Catalytic epoxidation is a well-documented reaction widely used in organic synthesis and industry.[1] Its prominence is due, in part, to our reliance on petroleum-based feedstocks for the preparation of a number of versatile intermediates that contain heteroatom functionality.[2] In contrast, the reverse reaction, deoxygenation of epoxides to make olefins, is much less developed. The deoxygenation of epoxides to olefins allows the use of the oxirane ring as a protecting group for double bonds, which is an important protocol to control olefin stereochemistry,[3] for conversion of biomass-derived substrates to useful organic compounds[4] and also for structural analysis of natural products.[5] Deoxygenation of epoxides is traditionally carried out with a variety of stoichiometric reducing reagents[6] such as phosphines, silanes, iodides and heavy metals, mostly by multi-step procedures. In spite of their utility, clear drawbacks of these methods are the concomitant formation of undesired waste, difficult work up procedures and harsh reaction conditions, which may affect other sensitive functional groups in the molecule. Therefore, the development of simple and efficient catalytic deoxygenation methods is of high interest. Unfortunately, relevant reports are limited to a few homogeneous systems[7] which are not practically useful because of their low catalytic efficiency, the problem of reusability and the indispensable use of vast amounts of hazardous reductants.

In recent years, supported gold nanoparticles (NPs) have been shown to facilitate catalysis in many organic transformations[8] including selective aerobic epoxidation of olefins using molecular oxygen (O_2) as the sole oxidant.[9] Following the pioneering work by Corma *et al.*[10] that supported Au NPs are highly selective for the reduction of nitroaromatics by molecular hydrogen (H_2) at elevated pressures, we have recently described a more efficient gold-catalyzed approach that can allow rapid and chemoselective reduction of polysubstituted nitro and carbonyl compounds under very mild conditions.[11] The reductant used in this case was CO and H_2O, where the transient Au^0–H formed by the CO-induced H_2O reduction is believed to be the key active species for nitro reduction. An interesting feature of the Au–CO/H_2O-catalyzed reaction is that it tolerates a diverse range of reducible functional groups including alkenes, alkynes, halogens, ketones, aldehydes, esters, and nitriles. Furthermore, this reaction can be carried out under atmospheric CO at room temperature. In view of the prominent efficiency of the gold system for deoxygenation of the nitro functionality, we envisioned that the CO/H_2O-mediated Au-catalyzed reduction strategy could afford a green and efficient protocol for the removal of oxygen from epoxides under mild conditions.

Herein, we report for the first time that very small gold NPs supported on titania (Au/TiO_2-VS) can deoxygenate epoxides exclusively into olefins using cheap and easily accessible CO and H_2O as the reductant.‡ Notably, the reaction can even proceed effectively under a CO atmosphere at sub-ambient temperatures. Compared with those conventional catalytic deoxygenation processes,[6,7] the present Au-catalyzed CO-mediated deoxygenation system has the following advantages: (i) unprecedented high activity under very mild conditions; (ii) high selectivity and functional group tolerance; (iii) the use of safe and easy-to-handle catalysts and reducing reagents; and (iv) a simple workup procedure, namely catalyst/product separation by filtration. The discovery of this unique catalysis of gold NPs can open new routes to selective functional transformations in organic synthesis.

We initially studied the deoxygenation of styrene epoxide (**1**) under a mild CO atmosphere (2 atm) at room temperature over a gold catalyst comprising very small gold NPs (*ca.* 1.9 nm)

Table 1 Deoxygenation of styrene epoxide to styrene with CO/H_2O using various catalysts at 25 °C[a]

Entry	Catalyst	CO/atm	Time/h	Conv. (%)	Sel. (%)
1	Au/TiO_2-VS	2	1.2	99	>99
2[b]	Au/TiO_2-VS	2	15	96	99
3[c]	Au/TiO_2	2	1.2	53.2	>99
4[c]	Pt/TiO_2	2	1.2	trace	—
5[c]	Pd/C	2	1.2	trace	—
6[c]	Ag/TiO_2	2	1.2	trace	—
7[c]	Ir/TiO_2	2	1.2	trace	—
8[c]	Ru/Al_2O_3	2	1.2	trace	—
9[c]	Au/Fe_2O_3	2	1.2	6.5	>99
10[c]	Au/C	2	1.2	trace	—
11[c]	Au/CeO_2	2	1.2	11.4	>99
12	Au/TiO_2-VS	5	1.0	96	>99
13	Au/TiO_2-VS	10	0.7	97	>99
14[d]	Au/TiO_2-VS	—	1.2	23.6	99

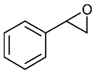
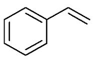
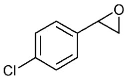
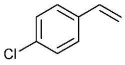
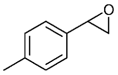
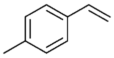
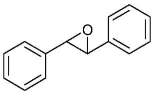
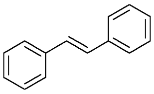
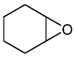
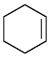
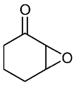
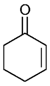
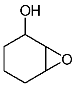
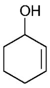
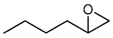
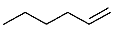
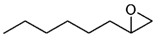
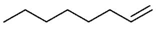
[a] Reaction conditions: 1 mmol styrene epoxide, metal (0.5 mol%), acetone (1 mL), H_2O (0.05 mL), 25 °C. [b] At 5 °C, Au (1 mol%). [c] Au/TiO_2, Au/Fe_2O_3, Au/C provided by the World Gold Council. Au/CeO_2, Pt/TiO_2, Ag/TiO_2, Ir/TiO_2 prepared according to ref. 10*c* and 11, respectively. Pd/C, Ru/Al_2O_3 provided by Alfa Aesar. [d] H_2 (2 atm).

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China. E-mail: yongcao@fudan.edu.cn; Fax: (+86-21) 65643774

† Electronic supplementary information (ESI) available: Experimental section, TEM and XPS data. See DOI: 10.1039/c0cc02783a

supported on TiO_2 (Au/TiO_2-VS, see preparation details in ESI†). Selective deoxygenation of **1** occurred to afford styrene (**2**) in 99% yield without any by-products such as ethylbenzene and 1- or 2-phenylethanol (Table 1, entry 1). Au/TiO_2-VS successfully promoted the deoxygenation reaction even at a sub-ambient temperature of 5 °C (Table 1, entry 2). The reaction does not occur in the absence of the catalyst, or in the presence of just TiO_2. When using gold supported on TiO_2 (Au/TiO_2) supplied by the World Gold Council (WGC) as the catalyst, which has larger average Au particles (*ca.* 3.5 nm, Fig. S1 in ESI†) relative to Au/TiO_2-VS, the catalytic activity and product yield were much lower (Table 1, entry 3). The use of other metals (Pt, Pd, Ag, Ir and Ru) instead of Au did not yield any product (Table 1, entries 4–8). The benefit of using TiO_2 as a support for gold becomes obvious when comparing the activity of Au/TiO_2-VS and Au/TiO_2 with the activity of Au/Fe_2O_3, Au/C, and Au/CeO_2 (Table 1, entries 9–11). Subsequent experiments focused on investigating the effect of pressure revealed that the reaction time was greatly shortened from 1.2 to 0.7 h as the P_{CO} was raised from 2 to 10 atm (Table 1, entries 1, 12 and 13). Among the solvents tested, acetone was the best. Changing the solvent to THF, ethyl acetate and toluene lowered conversion of **1** to 77%, 31.5% and 3.2% (Table S1 in ESI†), respectively.

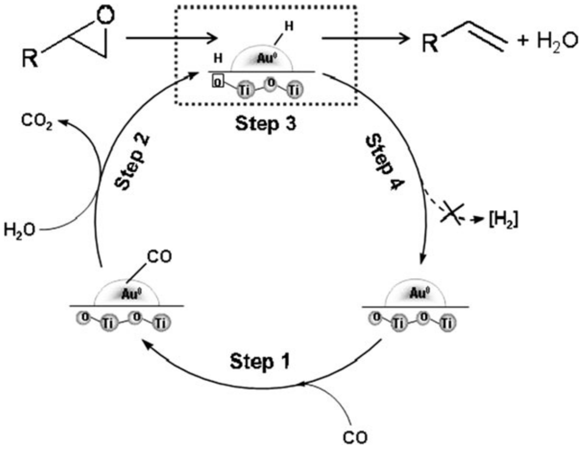
Table 2 Deoxygenation of various epoxides with CO/H_2O^a

Entry	Substrate	Product	Time/h	Conv. (%)	Sel. (%)
1			0.7	99	> 99
2^b			0.7	99	> 99
3^c			24	96	> 99
4^d			1.3	97	> 99
5			2	96	> 99
6			2	97	> 99
7			2	97	> 99
8^e			5	99	> 99
9^e			5	97	> 99
10^e			4	96	> 99
11^e			10	99	> 99
12^e			10	98	> 99

[a] Reaction conditions: substrate (1 mmol), Au/TiO_2-VS (0.5 mol% Au), acetone (1 mL), H_2O (0.05 mL, 2.8 mmol), 25 °C, CO (10 atm). [b] Fifth run. [c] Conditions: substrate (20 mmol), Au (0.01 mol%), acetone (20 mL), H_2O (1 mL), 60 °C, CO (20 atm). [d] H_2O (9 μL, 0.5 mmol). [e] Conditions: substrate (0.3 mmol), Au (3.3 mol%).

Having the optimized conditions in hand, we examined the scope of the deoxygenation of epoxides with Au/TiO_2-VS. As depicted in Table 2, the Au/TiO_2–CO/H_2O protocol was surprisingly versatile. Various structurally diverse epoxides, such as aromatic (Table 2, entries 1, 5–7), alicyclic (Table 2, entries 8–10) and aliphatic (Table 2, entries 11–12) epoxides, could be transformed into the corresponding alkenes in high yields. Halogen-substituted styrene epoxide was cleanly reduced to the corresponding chlorostyrene without any dehalogenation (Table 2, entry 5). Carbonyl and hydroxy groups also remained unaffected during deoxygenation of the corresponding epoxides by this procedure (Table 2, entries 9 and 10). The Au/TiO_2-VS catalyst was stable and could be easily reused in the next reaction without any loss in either activity or selectivity between the first and fifth runs (Table 2, entries 1 and 2). The deoxygenation of epoxide using the Au/TiO_2–CO/H_2O protocol was also applicable to a preparative scale reaction (Table 2, entry 3). For example, the deoxygenation of styrene epoxide (20 mmol) with Au/TiO_2-VS (0.01 mol% Au) gave styrene in 96% yield, wherein the turnover frequency (TOF) was up to 400 h^{-1} at 60 °C. This value compares favorably with 270 h^{-1} for the deoxygenation of **1** to afford **2** achieved at 150 °C reported recently on Au/HT under 2-propanol-driven transfer-hydrogenation conditions.[12]

To obtain information concerning the reaction pathways and mechanism of the CO-mediated epoxide deoxygenation, a couple of test reactions were undertaken. The reduction did not occur for other unsaturated substrates, such as styrene, acetophenone, and benzaldehyde under the conditions described above (Table S2†), which permits a rationalization of the unique reaction exclusivity as seen in Table 2. An almost equimolar amount of CO_2 was formed for every mole of styrene oxide conversion, whereas no styrene was formed when the reaction was conducted in the presence of anhydrous acetone under a CO atmosphere. Based on the above results, a plausible mechanism for the Au-VS/TiO_2-catalyzed



Scheme 1 Proposed mechanism for the Au/TiO_2-VS-catalyzed deoxygenation of epoxides to alkenes by CO/H_2O.

deoxygenation of an epoxide by CO/H_2O is given in Scheme 1. In compliance with our recent proposal for gold-catalyzed carbonylative reduction of nitro groups, a facile CO-induced reduction of H_2O at the Au-support interface results in the formation of transient Au^0–H species, which is considered as the key intermediate for the deoxygenation reaction (Scheme 1). Once formed, the Au^0–H species would be rapidly consumed together with a final formation of the olefin product without liberation of molecular hydrogen. Taking into account this model, one may assume that the deoxygenation of styrene epoxide can proceed with complete conversion even under water-deficient conditions (Table 2, entry 4), owing to the fact that water could be re-generated during the deoxygenation process. Considering the result in Table 1 that the deoxygenation with molecular hydrogen shows a significantly decreased oxygen removal rate as compared to that in the CO atmosphere (Table 1, entry 14), hydrogen gas generation from the low temperature water gas shift (WGS) reaction ($CO + H_2O = CO_2 + H_2$) and subsequent reductive deoxygenation of the epoxides with H_2 is unlikely.

It is well known that supported gold NPs have shown their efficiency for a variety of CO-involving reactions, the most prominent one being the low-temperature CO oxidation. The distinguished catalytic ability of gold compared to that of other metal NPs should be attributed to its unique capability toward CO activation. To gain an insight into the origin of the enhanced deoxygenation activity achieved by using titania as support, the use of O_2 as the hydrogen acceptors in place of epoxides, namely, CO oxidation under similar reaction conditions, has been investigated for Au NPs deposited on different supports (Fig. S2 in ESI†). It is revealed that the CO oxidation over Au/TiO_2 occurred with much higher rates than that over other catalysts, which implies that the CO species adsorbed on the Au–TiO_2 interface could be more active for a relevant transformation. Moreover, a systematic study of the influence of the size of the gold particles in Au/TiO_2 shows that gold NPs with a smaller particle size exhibited higher intrinsic CO oxidation activity (Fig. S3 in ESI†), which showed an excellent correlation with their catalytic activity for epoxide deoxygenation. Therefore, in line with the broad literature documenting the catalytic activity of supported gold NPs, the fact that small gold NPs in combination with the TiO_2 support can substantially facilitate the crucial CO activation in association with H_2O leading to Au–H formation appears to be a key factor for achieving high activity in the CO-mediated epoxide deoxygenation.

In conclusion, we have presented a novel and practical application of TiO_2 supported gold nanoparticles as excellent and reusable catalysts for the deoxygenation of a wide range of epoxides to the corresponding olefins using CO and H_2O as reducing agents under near ambient conditions. A preliminary study using N-oxides and sulfoxides showed that the present Au/TiO_2–CO/H_2O protocol is not limited to the deoxygenation of epoxides (See Table S3 in ESI†). To the best of our knowledge, this CO/H_2O-mediated gold catalysis represents the most efficient, simple, and eco-friendly catalytic system for the selective deoxygenation of oxygenated compounds to date. We believe that the reaction chemistry described herein can open new routes to selective functional transformations in organic synthesis and have important implications in the fundamental understanding of the catalytic origin of Au nanoparticles for low temperature CO oxidation.

This work is supported by the National Natural Science Foundation of China (20633030, 20721063, 20873026, 21073042), National Basic Research Project of China (2009CB623506), New Century Excellent Talents in the University of China (NCET-09-0305), and Science & Technology Commission of Shanghai Municipality (08DZ2270500).

Notes and references

‡ Note: During the course of our study, catalytic deoxygenation of epoxides to olefins using alcohol as a reductant with gold NPs deposited on hydrotalcite (HT) was reported by Kaneda and co-workers.[12] However, the reaction requires elevated temperature (> 100 °C) and environmentally harmful organic solvents to achieve high yields of the products. The potential of CO/H_2O as intermediates for Au-catalyzed deoxygenation of epoxides is further demonstrated by the same group's work that appeared during revision of this communication.[13]

1 R. A. Sheldon and J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.

2 S. T. Oyama, *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis*, Elsevier Science, 2008.

3 (*a*) K. B. Sharpless, M. A. Umbreit, M. T. Nieh and T. C. Flood, *J. Am. Chem. Soc.*, 1972, **94**, 6538; (*b*) P. Dowd and K. Kang, *Chem. Commun.*, 1974, 384; (*c*) P. F. Hudrlik, D. Peterson and R. J. Rona, *J. Org. Chem.*, 1975, **40**, 2263.

4 G. Descotes, *Carbohydrates as Organic Raw Materials II*, VCH, New York, 1993.

5 C. W. Shoppee, S. Sternhell and W. C. Taylor, *Aust. J. Chem.*, 1966, **19**, 1265.

6 (*a*) R. C. Larock, *Comprehensive Organic Transformations*, Wiley, New York, 1999, p. 272; (*b*) M. Mahesh, J. A. Murphy and H. P. Wessel, *J. Org. Chem.*, 2005, **70**, 4118; (*c*) H. Firouzabadi, N. Iranpoor and M. Jafapour, *Tetrahedron Lett.*, 2005, **46**, 4107.

7 (*a*) Z. Zhu and J. H. Espenson, *J. Mol. Catal. A: Chem.*, 1995, **103**, 87; (*b*) K. P. Gable and E. C. Brown, *Synlett*, 2003, 2243; (*c*) T. Itoh, T. Nagano, M. Sato and M. Hirobe, *Tetrahedron Lett.*, 1989, **20**, 6387; (*d*) H. Isobe and B. P. Branchaud, *Tetrahedron Lett.*, 1999, **40**, 8747.

8 (*a*) L. Prati and M. Rossi, *J. Catal.*, 1998, **176**, 552; (*b*) T. Hayashi, K. Tanaka and M. Haruta, *J. Catal.*, 1998, **178**, 566; (*c*) J. E. Bailie and G. J. Hutchings, *Chem. Commun.*, 1999, 2151; (*d*) X. Zhang, H. Shi and B. Q. Xu, *Angew. Chem., Int. Ed.*, 2005, **44**, 7132; (*e*) A. Abad, P. Concepcion, A. Corma and H. Garcia, *Angew. Chem., Int. Ed.*, 2005, **44**, 4066; (*f*) F. Z. Su, L. He, J. Ni, Y. Cao, H. Y. He and K. N. Fan, *Chem. Commun.*, 2008, 3531; (*g*) A. Grirrane, A. Corma and H. Garcia, *Science*, 2008, **322**, 1661.

9 (*a*) M. D. Hughes, Y. J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffin and C. J. Kiely, *Nature*, 2005, **437**, 1132; (*b*) P. Lignier, F. Morfin, S. Mangematin, L. Massin, J. L. Rousset and V. Caps, *Chem. Commun.*, 2007, 186.

10 (*a*) A. Corma and S. Pedro, *Science*, 2006, **313**, 332; (*b*) A. Corma, P. Concepcion and P. Serna, *Angew. Chem., Int. Ed.*, 2007, **46**, 7266; (*c*) A. Corma, P. Serna, P. Concepcion and J. J. Calvino, *J. Am. Chem. Soc.*, 2008, **130**, 8748.

11 (*a*) L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem., Int. Ed.*, 2009, **48**, 9538; (*b*) L. He, F. J. Yu, X. B. Lou, Y. Cao, H. Y. He and K. N. Fan, *Chem. Commun.*, 2010, **46**, 1553.

12 T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem., Int. Ed.*, 2010, **49**, 5390.

13 T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem.–Eur. J.*, DOI: 10.1002/chem.201001387.