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COMMUNICATION

Photocatalytic chemoselective reduction of epoxides to alkenes along with formation of ketones in alcoholic suspensions of silver-loaded titanium(IV) oxide at room temperature without use of reducing gas

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(2,3-Epoxypropyl)benzene was chemoselectively reduced to allylbenzene along with formation of ketones in alcoholic suspensions of a silver-loaded titanium(IV) oxide photocatalyst at room temperature under atmospheric pressure without the use of reducing gas, and various epoxides were also reduced to corresponding alkenes.

Deoxygenation of epoxides is important for transformation from an epoxy group to a C=C double bond as a deprotection reaction.¹⁾ However, conventional deoxygenation requires stoichiometric reagents such as phosphines, silanes, iodides, and heavy metals²⁾ and gives a large amount of undesirable waste, although many efforts have been devoted to improving reaction conditions and minimizing the use of toxic reagents by using catalytic systems.³⁾ Therefore, a “green” method for deoxygenation of epoxides to alkenes is required. Recently, excellent catalysts for deoxygenation of epoxides, i.e., gold (Au) and silver (Ag) supported on hydrotalcite (HT), were reported.⁴⁾ The Au/HT and Ag/HT catalysts exhibited a high selectivity for alkenes free from subsequent hydrogenation to alkanes. However, even in the series of Au/HT and Ag/HT catalysts, temperatures higher than 333 K and/or reducing gas such as carbon monoxide and hydrogen (H₂) are essential. Longer reaction time and/or severe conditions are required for deoxygenation of benzylic epoxide, i.e., (2,3-epoxypropyl)benzene (EPB) to allylbenzene (ALB). Therefore, a new catalytic system working at room temperature without the use of reducing gas is keenly desired.

When titanium(IV) oxide (TiO₂) is irradiated by UV light, charge separation occurs and thus-formed electrons (e⁻) in the conduction band and holes (h⁺) in the valence band cause reduction and oxidation, respectively. TiO₂ has been used for a long time as an indispensable inorganic material such as a pigment and UV absorber because it is inexpensive and not toxic for humans and the environment. Since photocatalytic reaction satisfies almost all of the 12 proposed requirements for green chemistry,⁵⁾ organic synthesis of various compounds using photocatalysts has recently been studied by many researchers,⁶⁾ and the number of papers on photocatalytic reduction of organic compounds by using photogenerated electrons has recently been increasing.⁷⁾ Our research group has recently reported that 3-nitrostyrene was chemoselectively reduced to 3-aminostyrene without reduction of the C=C double bond to 3-ethylaniline in a

suspension of a TiO₂ photocatalyst in the presence of hole scavengers at room temperature under metal-free and reducing gas-free conditions.^{8a)} Subsequently, our group reported that 3-aminostyrene and acetone were simultaneously produced almost stoichiometrically as the reduced and oxidized products, respectively, when 2-propanol was used as a solvent also acting as hole scavenger.^{8b)} In this study, we examined a new photocatalytic redox system, i.e., reductive deoxygenation of epoxides and oxidation of alcohols, and found that epoxides were chemoselectively converted to corresponding alkenes without reduction of the C=C double bond together with formation of corresponding ketones over Ag-loaded TiO₂ at room temperature without the use of reducing gas.

A transmission electron microscope (TEM) image of Ag-TiO₂ is shown in Fig. S1(a) (ESI[†]). Silver particles were observed in the image, indicating that Ag nanoparticles were deposited on the TiO₂ surface. The average diameter of Ag particles in the sample was determined to be 2.4 nm (Fig. S1(b)).

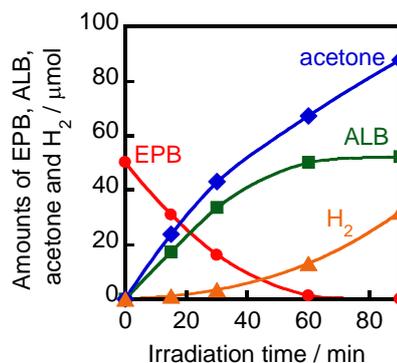
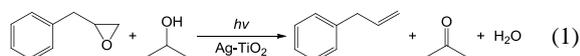


Fig. 1 Time courses of the amounts of EPB, ALB, H₂ and acetone in a 2-propanol suspension of 1.5 wt% Ag-TiO₂ photocatalyst under deaerated conditions.

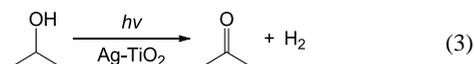
Fig. 1 shows time courses of EPB remaining, ALB formed and acetone formed in a 2-propanol suspension of Ag-TiO₂ under deaerated conditions. The amount of H₂, i.e., another reduced product, was also plotted in Fig. 1. Just after photoirradiation, EPB monotonously decreased, while ALB and acetone were formed as the reduction product of EPB and the oxidation product of 2-propanol, respectively. After 60 min, EPB was almost

completely consumed and ALB was obtained almost quantitatively (99% yield) after 90 min. The reaction, i.e., reductive deoxygenation of EPB to ALB along with oxidation of 2-propanol to acetone, is shown in eqn (1).



We also examined two blank reactions in the absence of Ag-TiO₂ (photochemical reaction) and in the absence of light (thermal reaction) and confirmed that no reaction occurred in either case. The yield of ALB was much larger than the amount of Ag (7.0 μmol) loaded on the TiO₂ surface. These results mean that the observed reaction under the present conditions was photocatalytic, i.e., TiO₂ and light contributed to the formation of ALB and acetone, and Ag worked as a co-catalyst. From the ratio of the amount of ALB and the amount of photons irradiated (eqn (2)), apparent quantum efficiency (AQE) was calculated to be 13% in the experiment using a UV light-emitting diode, indicating that deoxygenation of EPB to ALB occurred effectively over Ag-TiO₂.

$$\text{AQE}(\%) = \frac{2 \times \text{amount of ALB}}{\text{number of incident photons}} \times 100 \quad (2)$$



As shown in Fig. 1, H₂ was also formed, indicating that reduction of protons (H⁺) by photogenerated electrons also occurred. Production of H₂ along with formation of acetone can be regarded as dehydrogenation of 2-propanol (eqn (3)). When bare (Ag-free) TiO₂ was used for dehydrogenation of 2-propanol (in the absence of EPB), H₂ formation was negligible, indicating that Ag loaded on TiO₂ acted as sites for H₂ evolution (H⁺ reduction) as well as ALB formation (EPB reduction).

As shown in Fig. 1, dehydrogenation of 2-propanol (eqn (3)) occurred under excessive photoirradiation after complete consumption of EPB. Simultaneous formation of ALB and H₂ and preservation of ALB after complete consumption of EPB indicate that Ag-TiO₂ had no activity for hydrogenation of ALB even in the presence of H₂. This is an important and excellent performance of the Ag-TiO₂ photocatalyst to maintain a high yield of ALB. We examined another reaction, i.e., thermal reaction of EPB in the presence of Ag-TiO₂ under H₂ (1 atm) in the dark at 298 K, and confirmed that no reaction occurred. This result indicates that H₂ in the gas phase does not contribute to the reduction of EPB.

Fig. 2 shows effects of metal co-catalysts (1.0 wt%) on yields of ALB and H₂ produced in photocatalytic reductive deoxygenation of EPB in 2-propanol suspensions for 30 min. Bare TiO₂ produced a small amount of ALB, while Ag-TiO₂ predominantly produced ALB as shown in Fig. 1. When gold (Au) and copper (Cu) were used as the co-catalysts, only a small amount of ALB was produced and a large amount of H₂ was evolved as the reduction product. Palladium (Pd) and platinum (Pt) had no effect on reduction of EPB to ALB under the present conditions, i.e., only dehydrogenation of 2-propanol (eqn (3)) occurred over Pd-TiO₂ and Pt-TiO₂. The values of material balance of EPB and ALB were close to unity except for Pd-TiO₂,

while the value of Pd-TiO₂ was less than 0.1, indicating that another side reaction consuming EPB and/or ALB occurred over Pd-TiO₂. The results shown in Fig. 2 clearly indicate that Ag was the sole co-catalyst effective for photocatalytic reductive deoxygenation of EPB to ALB in 2-propanol suspensions.

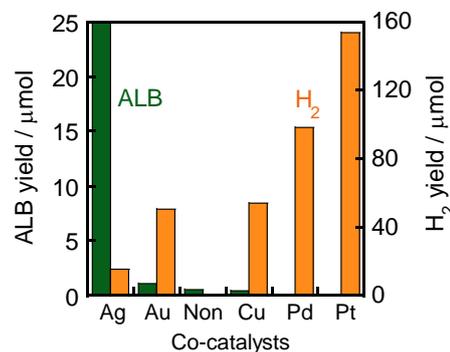
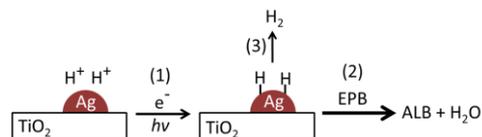


Fig. 2 Effects of metal co-catalysts (1.0 wt%) on the yields of ALB and H₂ produced in photocatalytic reductive deoxygenation of EPB in 2-propanol suspensions for 30 min.



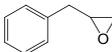
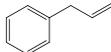
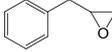
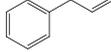
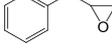
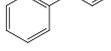
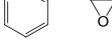
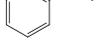
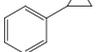
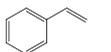
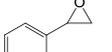
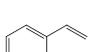
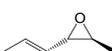
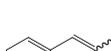
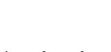
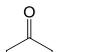
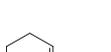
Scheme 1. Expected reaction processes of photocatalytic reductive deoxygenation of EPB to ALB over Ag/TiO₂.

Expected reaction processes of photocatalytic reductive deoxygenation of EPB to ALB over Ag are shown in Scheme 1: 1) surface H species are formed on Ag by reduction of protons by photogenerated electrons under irradiation of UV light, while 2-propanol is oxidized by holes (oxidation process not shown in Scheme 1), 2) EPB is reduced by the surface H species with the aid of Ag co-catalysis, resulting in formation of ALB and water and in regeneration of the photocatalyst, and 3) H₂ formation also occurs as a result of elimination of the surface H species. Reaction rates of 2) and 3) are important to determine the selectivity and yield of ALB in this reaction. In the case of Ag-TiO₂, the reaction rate of 2) is larger than that of 3) probably because of strong interaction between Ag and oxygen of EPB and larger activation energy for H₂ formation. Less production of ALB over other photocatalysts may be explained by weaker or no interaction with oxygen and smaller activation energy for H₂ formation over the other metals.

Applicability of the Ag-TiO₂ photocatalyst for a chemoselective redox system was investigated, and the results are summarized in Table 1. In the re-use in deoxygenation of EPB to ALB, Ag-TiO₂ exhibited activity almost the same as that in the first use (entries 1 and 2). Styrene oxides were reduced to corresponding styrenes selectively with high yields (entries 5 and 7) as well as the deoxygenation of EPB (entry 1). When 2-pentanol was used in place of 2-propanol, ALB was obtained almost quantitatively along with formation of 2-pentanone (entry 4, Fig. S2), indicating that various alcohols can be used for the present chemoselective redox system. We also found that

deoxygenation of styrene oxide occurred even over bare TiO₂ (entry 6), although the performance was slightly lower than that of Ag-TiO₂ (entry 5). The use of metal-free TiO₂ has another advantage of only deoxygenation of epoxides occurring, i.e., Equation (3) does not occur because H₂ evolution requires co-catalysts such as Pt and Ag. However, bare TiO₂ did not show activities for deoxygenation of epoxides other than π -conjugated epoxides such as styrene oxide (entry 3). Ag-TiO₂ was effective for deoxygenation of epoxide of an acyclic compound (entry 8), though longer reaction time was required. In the deoxygenation of epoxides of alicyclic compounds, less selectivity was obtained (entries 9 and 10). Since these compounds are photosensitive, the selectivity may be improved by the use of a gentle light source such as black light.

Table 1 Photocatalytic deoxygenation of epoxides to corresponding alkenes in alcoholic suspension of Ag(1.5)-TiO₂ at 298 K.^a

Entry	Epoxides	Alkenes	t / h	Yield / % ^b	Sel. / % ^b
1			1.5	99	99
2 ^c			1.5	96	99
3 ^d			0.5	1	31
4 ^e			1.5	99	99
5			1	96	97
6 ^d			1	85	85
7			3	85	90
8			5	89	99
9			3	11	11
10			3	26	59

^aReaction conditions: Ag-TiO₂ (50 mg), substrate (50 μ mol), 2-propanol (5 cm³), room temperature, under Ar. ^bDetermined by GC using an internal standard. ^cSecond use. ^dPhotocatalyst (bare TiO₂). ^e2-Pentanol instead of 2-propanol.

In summary, a new photocatalytic chemoselective redox system, i.e., reductive deoxygenation of epoxides to corresponding alkenes and oxidation of alcohols to corresponding ketones, was examined at room temperature without the use of reducing gas. Alkenes and ketones were simultaneously produced over silver-loaded TiO₂, and less reactive (2,3-epoxypropyl)benzene was almost quantitatively reduced to allylbenzene without reduction of the C=C double bond to propylbenzene even in the presence of an H₂ by-product. Chemoselective reduction of styrene oxides to styrenes was achieved even over bare TiO₂. Since alcohols other than 2-propanol can be used as a solvent and hole scavenger (electron donor), various combinations of epoxides and alcohols can be used. The results obtained in this study provide a wide possibility of photocatalytic redox reaction including chemoselective production under gentle conditions such as room temperature and atmospheric pressure without the use of reducing gas.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: [Experimental procedure, Figure S1 and Figure S2]. See DOI: 10.1039/b000000x/.

- a) E. J. Corey and W. G. Su, *J. Am. Chem. Soc.*, 1987, **109**, 7534; b) G. A. Kraus, P. J. Thomas, *J. Org. Chem.*, 1988, **53**, 1395; c) W. S. Johnson, M. S. Plummer, S. P. Reddy, W. R. Bartlett, *J. Am. Chem. Soc.*, 1993, **115**, 515.
- R. C. Larock, *Comprehensive Organic Transformations*, Wiley, New York, 1999, p. 272, and references therein.
- a) Z. Zhu and J. H. Espenson, *J. Mol. Catal. A*, 1995, **103**, 87; b) K. P. Gable and E. C. Brown, *Synlett*, 2003, 2243; c) J. B. Arterburn, M. Liu and M. C. Perry, *Helv. Chim. Acta*, 2002, **85**, 3225; d) T. Itoh, T. Nagano, M. Sato and M. Hirobe, *Tetrahedron Lett.*, 1989, **30**, 6387; e) H. Isobe and B. P. Branchaud, *Tetrahedron Lett.*, 1999, **40**, 8747.
- a) Y. Mikami, A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Tetrahedron Lett.*, 2010, **51**, 5466; b) T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem. Int. Ed.*, 2010, **49**, 5545; c) T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Eur. J.*, 2010, **16**, 11818; d) A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem. Int. Ed.*, 2011, **50**, 2986; e) T. Mitsudome, Y. Mikami, M. Matoba, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem. Int. Ed.*, 2012, **51**, 136.
- P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, 1998.
- M. A. Fox and M. T. Dulay, *Chem. Rev.*, 1993, **93**, 341.
- a) G. Palmisano, V. Augugliaro, M. Pagliaro and L. Palmisano, *Chem. Commun.*, 2007, 3425; b) G. Palmisano, E. Garcia-Lopez, G. Marci, V. Loddo, S. Yurdakal, V. Augugliaro and L. Palmisano, *Chem. Commun.*, 2010, **46**, 7074.
- a) K. Imamura, K. Hashimoto and H. Kominami, *Chem. Commun.*, 2012, **48**, 4356; b) K. Imamura, T. Yoshikawa, K. Hashimoto and H. Kominami, *Appl. Catal. B, Environ.*, 2013, **134-135**, 193.

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