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Photoexcitation ($\lambda > 300$ nm) of TiO₂ loaded with Pt particles promotes selective hydrogenolysis of epoxides with alcohol as a reducing agent.

Reductive ring opening (hydrogenolysis) of epoxides into the corresponding alcohols is one of the most important organic transformations.¹ This facilitates selective hydration of alkenes via the protection of C=C bond by epoxidation (Scheme 1). The hydrogenolysis of epoxides is usually carried out with excess or stoichiometric amount of metal hydrides (H-M; for example: LiAlH₄ and LiEt₃BH), which are explosive and toxic reducing agents, with a concomitant formation of copious amount of wastes.² Catalytic hydrogenolysis is therefore ideal. Pd particles supported on carbon, Al₂O₃, CaCO₃, AlO(OH), or polyurea are well-known heterogeneous catalysts for hydrogenolysis.³ These systems use metal hydride (H-M) species, in-situ generated on the metal surface by the reaction with a reducing agent as active species. They, however, need H₂ or HCOONH₄ as reducing agents, which hold explosion or cost issue. Alternative systems that promote efficient and selective hydrogenolysis with safe and inexpensive reducing agent are therefore desired.



Here we report for the first time a catalytic system that promotes hydrogenolysis of epoxides with safe and inexpensive alcohols as reducing agents. We employed semiconductor TiO₂ loaded with metal particles (M/TiO₂) under UV irradiation (λ >300 nm). Our hypothesis is *in-situ* generation of H-M species with alcohol by photocatalysis: photoexcited TiO₂ produces the electron (e⁻) and positive hole (h⁺) pairs (eq. 1). The h⁺ oxidize alcohols and produce aldehyde (ketones) and H⁺ (eq. 2).⁴ The H⁺ are reduced by the e⁻ on the metal particles and transformed

Pt nanoparticles[†]

Photocatalytic hydrogenolysis of epoxides with

alcohol as a reducing agent on TiO₂ loaded with

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to the H-M species (eq. 3).⁵ The photocatalytically generated H-M species may promote hydrogenolysis of epoxides.

$$\mathrm{TiO}_2 + h\nu \to \mathrm{e}^- + \mathrm{h}^+ \tag{1}$$

 $R_3R_4CHOH + 2h^+ \rightarrow R_3R_4CO + 2H^+$ (2)

> $H^+ + e^- + M \rightarrow H-M$ (3)

We found that the above hypothesis is realized by TiO₂ loaded with Pt particles (Pt/TiO₂). The system produces several kinds of ring-opened products with high selectivity (>72%). The catalytic activity strongly depends on the size of Pt particles; small Pt particles (ca. 3 nm) exhibit the best performance.



Fig. 1 (a) TEM image of Pt_2/TiO_2 prepared by H_2 reduction at 673 K and (b) size distribution of the Pt particles.

 $M_x/TiO_2 [x (wt \%) = M/TiO_2 \times 100]$ catalysts were prepared with JRC-TIO-4 TiO₂ (equivalent to P25, average size, 27 nm; BET surface area, 57 m² g⁻¹; anatase/rutile ratio, 83/17 w/w) supplied from the Catalyst Society of Japan. Pt, Ag, or Pd particles were loaded by impregnation of precursors followed by H₂ reduction at designated temperature.⁶‡ Au particles were loaded by the deposition-precipitation method.⁷§ As shown in Fig. 1, a typical transmission electron microscopy (TEM) image of Pt_2/TiO_2 prepared by H_2 reduction at 673 K shows Pt



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particles with an average size 2.9 nm. As shown in Fig. S1 (ESI[†]), Au₂/TiO₂, Ag₂/TiO₂, and Pd₂/TiO₂ also contain metal particles with similar sizes (3.7, 4.2, and 4.4 nm, respectively). As shown in Fig. S2 (ESI[†]), diffuse-reflectance UV-vis spectra of Au₂/TiO₂ and Ag₂/TiO₂ show characteristic band at ca. 550 and 520 nm, respectively, assigned to the surface plasmon resonance (SPR) absorption,⁸ whereas Pd₂/TiO₂ and Pt₂/TiO₂ show flat absorption at $\lambda >$ 300 nm due to the light scattering by the metal particles.⁴

Hydrogenolysis of trans-stilbene oxide was carried out with 2-PrOH as a reducing agent. The reactions were performed by photoirradiation ($\lambda > 300$ nm) of a 2-PrOH solution (5 mL) containing catalyst (10 mg) and epoxide (50 µmol) under N₂ for 6 h. Table 1 summarizes the conversions of epoxide and yields of stilbene (1), 1,2-diphenylethanol (2), and 1,2-diphenylethane (3). Bare TiO_2 (entry 1) gives a small amount of deoxygenation product (1, 2%), but does not afford the hydrogenolysis product (2).⁹ Au₂/TiO₂ and Ag₂/TiO₂ (entries 2 and 3) are also inactive. Pd₂/TiO₂ (entry 4) produces 2 with 54% yield, but also produces a large amount of byproduct (3, 42%). In contrast, Pt_2/TiO_2 (entry 5) produces 2 with quantitative yield (>99%). Fig. 2 shows the time-profiles for the amounts of substrate and products on Pd₂/TiO₂ and Pt₂/TiO₂. On Pd₂/TiO₂ (Fig. 2a), the epoxide (black) is selectively transformed to 2 (red) at the early stage, but subsequently transformed to 3 (blue). In contrast, Pt₂/TiO₂ (Fig. 2b) selectively produces 2 and does not promote further reaction even after prolonged irradiation. In addition, as shown in Table 1 (entry 5), the catalyst recovered after the reaction exhibits almost the same 2 yields as the fresh one. These data suggest that Pt/TiO₂ specifically promotes efficient and selective hydrogenolysis of epoxide and is reusable without the loss of activity and selectivity.

Mechanism for hydrogenolysis on Pt/TiO₂ is explained as Scheme 2. Photoexcited TiO₂ produces the e⁻ and h⁺ pairs. The e⁻ overcome the Schottky barrier (ϕ_B) created at the interface¹⁰ and are trapped by the Pt particles (a). The h⁺ oxidize alcohol and produce H⁺, while the e⁻ reduce H⁺ and create H–Pt species (b). Epoxide is adsorbed onto the Pt surface and undergoes a homolytic cleavage of the oxirane ring. Subsequent reaction of the intermediates with H–Pt species gives the product (c).

Table 1 Reactions of trans-stilbene oxide on various catalysts under photoirradiation

The formation of H–Pt species by photocatalysis on Pt/TiO₂ is confirmed by diffuse-reflectance infrared Fourier transform (DRIFT) analysis. 2-PrOH was adsorbed onto 18 to 19 to 20 to 2

(DRIFT) analysis. 2-PrOH was adsorbed onto 1987 M_{2}^{View} article Online gas phase and photoirradiated with 360 nm monochromatic light. As shown in Fig. S3 (ESI†), a distinctive absorption band, assigned to the H–Pt species,¹¹ appears at 1975 cm⁻¹. This clearly suggests that, as shown in Scheme 2a→b, photocatalysis on Pt/TiO₂ indeed produces H–Pt species.



Fig. 2 Time-profiles for the amounts of substrate and products during photoreaction of *trans*-stilbene oxide on (a) Pd_2/TiO_2 and (b) Pt_2/TiO_2 catalysts prepared by H_2 reduction at 673 K. The reaction conditions are identical to those in Table 1.



Scheme 2 Proposed mechanism for hydrogenolysis of epoxide on the photoexcited Pt/TiO_2 with alcohol.

3 K. Th	e reacti
b	
	ΓiO ₂
ogenoly	sis of e

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$\frac{h_{\nu}(\lambda > 300 \text{ nm}, 6 \text{ h})}{\text{catalyst (10 mg), 2-PrOH (5 mL)}} + \frac{OH}{2} + \frac{OH}{2} + \frac{OH}{3}$							
entry	catalyst	metal particle size $/ nm^b$	<i>trans-stilbene oxide</i>	1	yield / %	3	
1	TiO ₂		2	2(E/Z = 1/3)	0	0	
2	Au ₂ /TiO ₂	3.7 ± 0.5	<1	0	0	0	
3	Ag ₂ /TiO ₂ ^c	4.2 ± 0.9	9	8 (E/Z = 1/3)	0	0	
4	Pd ₂ /TiO ₂ ^c	4.4 ± 0.8	>99	0	54	42	
5	Pt ₂ /TiO ₂ ^c	2.9 ± 0.8	>99	0	>99	0	
	1 st reuse d		>99	0	>99	0	
	2nd reuse ^d		>99	0	>99	0	

^{*a*} Photoirradiation was carried out with a 2 kW Xe lamp (light intensity at 300–450 nm, 27.3 W m⁻²). ^{*b*} Determined by TEM observations. ^{*c*} Prepared by impregnation followed by H_2 reduction at 673 K. ^{*d*} Catalysts were reused after simple washing with 2-PrOH followed by drying in vacuo.

Au/TiO₂ and Ag/TiO₂ are inactive for hydrogenolysis of epoxide (Table 1, entries 2 and 3). As reported,¹² temperatureprogrammed desorption (TPD) analysis revealed that Pt or Pd surface promotes the oxirane ring cleavage of the adsorbed ethylene oxide via the electron transfer from metal, whereas Au or Ag surface is inactive. This is consistent with no activity of Au/TiO₂ and Ag/TiO₂. This suggests that, as shown in Scheme 2b→c, the oxirane ring cleavage on the Pt surface is indeed involved in the hydrogenolysis on Pt/TiO₂.

As shown in Table 1 (entries 4 and 5), Pd/TiO₂ promotes hydrogenolysis as well as Pt/TiO2 because Pd particles are also active for oxirane ring cleavage.¹² As shown in Fig. 2, Pt/TiO₂ selectively produces 2, but Pd/TiO₂ promotes subsequent hydrogenolysis of -OH group of 2 (formation of 3). This is due to the high nucleophilicity of H-Pd species. It is well known that H atoms are adsorbed onto the Pd surface more strongly than onto the Pt surface.¹³ The e⁻ on the Pd particles are therefore strongly donated to H⁺, producing nucleophilic H-Pd species. This may promote hydrogenolysis of -OH group of 2. Similar hydrogenolysis of -OH group by the H-Pd species is observed for allyl alcohol (propylene formation)¹⁴ and benzyl alcohol (toluene formation),15 whereas the H-Pt species are inactive. These imply that, on Pt/TiO2, less nucleophilic H-Pt species are inactive for hydrogenolysis of -OH group, resulting in selective formation of ring-opened product (2).



Fig. 3 Effect of (a) H_2 reduction temperature of Pt_2/TiO_2 catalysts and (b) amount of Pt loaded (*x*) for Pt_x/TiO_2 catalysts on the **2** yield during photoreaction (2 h) of *trans*-stilbene oxide. Reaction conditions are identical to those in Table 1. Circles denote the average diameter of Pt particles on the catalysts, and the numbers on the top of the figures denote the selectivity of **2**. The H_2 reduction temperature for the catalysts (b) is 673 K. Typical TEM images of catalysts and size distributions of their Pt particles are summarized in Fig. S1 (ESI⁺).

The size of Pt particles strongly affects the catalytic activity. The Pt₂/TiO₂ catalysts were prepared at different H₂ reduction temperatures to create Pt particles with different sizes. As shown in Fig. 3a (circle), the size of Pt particles increases with a rise in temperature due to the migration and sintering of the particles;¹⁶ the treatment at 573, 673, 773, and 873 K creates Pt particles with 2.8, 2.9, 3.6, and 5.9 nm diameters, respectively. These catalysts were employed for photoreaction (2 h) of transstilbene oxide. All of them produce 2 with very high selectivity (>99%), but exhibit different activities. The bar data in Fig. 3a show the 2 yield. The catalysts with ca. 3 nm Pt particles prepared at 573 and 673 K show high activity, but the catalysts with larger Pt particles show lower activity. Larger Pt particles have smaller surface area. The lower activity of these catalysts may therefore be due to the inefficient oxirane ring cleavage of epoxide or formation of H-Pt species.17,18

Fable 2	Photoreaction of vario	ous epoxide	es on Pt ₂ /TiO ₂ ^a	
entry	substrate	t / \mathbf{h}^b	product	yield / %
1		6	OH	>99
2^c		6	\bigcirc	97
3	$\approx A \approx$	6	OH	>99
4 ^{<i>c</i>}	\bigcirc \bigcirc	6		99
5	€ C	6	OH	76
6 ^{<i>d</i>}		6	OH	80
7^d	CI CI	6	CI	84
8^d	Br	6	Br	84
9 ^{<i>d,e</i>}		10	OH	81
10 ^{d,e}		10	OH O	86
11 ^{d,e}	$\bigcirc \circ$	10	OH	72
12 ^{<i>d</i>,<i>e</i>}		10	ОН	73

^{*a*} Reaction conditions: epoxide (50 μmol), Pt₂/TiO₂ catalyst prepared by H₂ reduction at 673 K (10 mg), 2-PrOH (5 mL), N₂ (1 atm), light irradiation (λ >300 nm), temperature (303 K). ^{*b*} Conversions of epoxides in all runs are >99%. ^{*c*} EtOH was used as a solvent in place of 2-PrOH. ^{*d*} Epoxide (20 μmol). ^{*e*} Catalyst (20 mg).

The amount of Pt loaded also affects the catalytic activity. The Pt_x/TiO₂ catalysts with different Pt loadings (x = 0.5-4 wt %) were prepared by H₂ reduction at 673 K. As shown in Fig. 3b (circle), these catalysts possess Pt particles with similar diameters (2.8–3.1 nm). As shown by the bar data, the activity increases linearly with the Pt loadings, where the selectivity of

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2 for all of the catalysts scarcely changes (>99%). The above findings suggest that loading of large number of small Pt particles (ca. 3 nm diameter) exhibit best catalytic performance for hydrogenolysis of epoxide.

The Pt/TiO₂ catalyst is applicable for the hydrogenolysis of several types of epoxides. Table 2 summarizes the results of photoreactions on Pt_2/TiO_2 in 2-PrOH as a reducing agent. Reactions of stilbene oxides (entries 1 and 3), styrene oxides (5–8), and aliphatic epoxides (9–12) successfully produced the corresponding ring-opened alcohols with moderate to high yields (72–99%). In particular, styrene oxides bearing reducible halogen groups (entries 7 and 8) gave the products with high yields (84%) while retaining their substituents. It must also be noted that, as shown by entries 2 and 4, hydrogenolysis is also successfully promoted when using EtOH as a reducing agent, a very cheap alcohol which can be produced from biomass. This suggests that economical hydrogenolysis process can be created by the Pt/TiO_2 system.

In summary, we found that UV irradiation of Pt/TiO_2 with alcohol promotes selective hydrogenolysis of epoxides. The system offers several advantages over conventional processes: (i) safe and inexpensive alcohols can be used as a reducing agent; and, (ii) the reaction is carried out under milder reaction conditions (room temperature). The catalytic system presented here based on photocatalytic *in-situ* generation of H–Pt species may contribute to the catalyst design for photocatalysis-based green organic synthesis.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, supplementary data (Figs. S1–S4). See DOI: 10.1039/c000000x/

[‡] Pt_x/TiO₂ [*x* (wt %) = 0.5, 1, 2, 3, and 4] were prepared as follows: TiO₂ (1.0 g) and H₂PtCl₆·6H₂O (13, 27, 54, 82, or 111 mg) were added to water (20 mL) and evaporated under stirring at 393 K for 12 h. The resultant was dried under air flow and reduced under H₂ flow at the designated temperature (573, 673, 773, or 873 K) with the heating rate and holding time being 2 K min⁻¹ and 2 h, respectively. Pd₂/TiO₂ and Ag₂/TiO₂ were prepared with Pd(NO₃)₂ (44 mg) or AgNO₃ (32 mg) as a precursor.

Au₂/TiO₂ was prepared as follows: HAuCl₄·4H₂O (46 mg) was added to water (50 mL). The pH of the solution was adjusted to 7 by an addition of 1 M NaOH. TiO₂ (1 g) was added to the solution and stirred vigorously at 353 K for 3 h. The solids were recovered by centrifugation, washed with water, and calcined at 673 K for 2 h under air flow.

 (a) N. M. Williamson and A. D. Ward, *Tetrahedron*, 2005, 61, 155– 165; (b) R. Löser, M. Chlupacova, A. Marecek, V. Opletalova and M. Gütschow, Helv. Chim. Acta., 2004, **87**, 2597–2601; (c) T. Hamada and Y. Kobayashi, *Tetrahedron Lett.*, 2003, **44**, 4347–4350; (d) M. R. View Article Online Paleo, N. Aurrecoechea, K.-Y. Jung and H. Rapoports J. Carge Gramk 2003, **68**, 130–138.

- 2 R. C. Larock, *Comprehensive Organic Transformations*, VCH, New York, 1989, p. 505.
- 3 (a) H. Sajiki, K. Hattori and K. Hirota, *Chem. Commun.*, 1999, 1041–1042; (b) E. Thiery, J. L. Bras and J. Muzart, *Green Chem.*, 2007, 9, 326–327; (c) M. S. Kwon, I. S. Park, J. S. Jang and J. Park, *Org. Lett.*, 2007, 9, 3417–3419; (d) S. V. Ley, C. Mitchell, D. Pears, C. Ramarao, J.-Q. Yu and W. Zhou, *Org. Lett.*, 2003, 5, 4665–4668.
- 4 Y. Shiraishi, Y. Sugano, S. Tanaka and T. Hirai, *Angew. Chem. Int. Ed.*, 2010, 49, 1656–1660.
- (a) Y. Shiraishi, Y. Takeda, Y. Sugano, S. Ichikawa, S. Tanaka and T. Hirai, *Chem. Commun.*, 2011, **47**, 7863–7865; (b) A. Maldotti, A. Molinari, R. Juárez and H. Garcia, *Chem. Sci.*, 2011, **2**, 1831–1834; (c) A. A. Gabrienko, S. S. Arzumanov, I. B. Moroz, A. V. Toktarev, W. Wang and A. G. Stepanov, *J. Phys. Chem. C*, 2013, **117**, 7690–7702.
- 6 Y. Shiraishi, H. Sakamoto, Y. Sugano, S. Ichikawa and T. Hirai, ACS Nano, 2013, 7, 9287–9297.
- 7 D. Tsukamoto, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka and T. Hirai, *J. Am. Chem. Soc.*, 2012, **134**, 6309–6315.
- 8 (a) G. L. Chiarello, M. A. Aguirre and E. Selli, *J. Catal.*, 2010, 273, 182–190; (b) A. B. Smetana, K. J. Klabunde, C. M. Sorensen, A. A. Ponce and B. Mwale, *J. Phys. Chem. B*, 2006, 110, 2155–2158.
- 9 Y. Shiraishi, H. Hirakawa, Y. Togawa and T. Hirai, *ACS Catal.*, 2014, 4, 1642–1649.
- 10 T. Uchihara, M. Matsumura, A. Yamamoto and H. Tsubomura, J. Phys. Chem., 1989, 93, 5870–6874.
- 11 H. Ogasawara and M. Ito, Chem. Phys. Lett., 1994, 221, 213–218.
- (a) J. Kim and B. E. Koel, *Langmuir*, 2005, 21, 3886–3891; (b) R. Shekhar and M. A. Barteau, *Surf. Sci.*, 1996, 348, 55–66; (c) C. T. Campbell and M. T. Paffett, *Surf. Sci.*, 1986, 177, 417–430.
- 13 M. Yamauchi, H. Kobayashi and H. Kitagawa, *ChemPhysChem*, 2009, **10**, 2566–2576.
- 14 J. Caner, Z. Liu, Y. Takada, A. Kudo, H. Naka and S. Saito, *Catal. Sci. Technol.*, 2014, 4, 4093–4098.
- 15 (a) T. P. A. Ruberu, N. C. Nelson, I. I. Slowing and J. Vela, J. Phys. Chem. Lett., 2012, 3, 2798–2802; (b) Y. Hong and A. Sen, Chem. Mater., 2007, 19, 961–963.
- 16 Y. Shiraishi, Y. Kofuji, S. Kanazawa, H. Sakamoto, S. Tanaka, S. Ichikawa and T. Hirai, *Chem. Commun.*, 2014, 50, 15255–15258.
- 17 The anatase-to-rutile phase transition of P25 TiO₂ upon heating at higher temperature is not the major factor for decreased activity. As shown in Fig. S4 (ESI†), the anatase/rutile ratios of Pt₂/TiO₂ prepared by H₂ reduction at 573, 673, and 773 K (82/18, 80/20, and 81/19 w/w, respectively), as determined by XRD analysis (ref 18), are similar to those of pure TiO₂ (83/17), although the heating at 873 K increases the ratio to 71/29. As shown in Fig. 3a, the catalyst prepared at 773 K shows activity lower than that prepared at 573 and 673 K, even though their anatase/rutile ratios are similar. This indicates that the phase transition of P25 TiO₂ support is not the major factor for the decreased activity of the catalysts prepared at higher temperatures.
- 18 G. Ramis, G. Busca, C. Cristiani, L. Lietti, P. Forzatti and F. Bregani, Langmuir, 1992, 8, 1744–1749.

Journal Name