

Acetonitrile-assisted highly selective photocatalytic epoxidation of olefins on Ti-containing silica with molecular oxygen†

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Highly selective photocatalytic epoxidation of olefins proceeds on Ti-containing silica with tetrahedrally coordinated Ti-oxide species with molecular oxygen and a simple addition of MeCN.

Epoxidation of an olefin is one of the most important functional group transformations in organic synthesis.¹ Catalytic epoxidation processes driven by heterogeneous catalysts with molecular oxygen (O₂) have attracted a great deal of attention.² Photocatalytic processes have also been studied extensively,³ especially using a semiconductor TiO₂,⁴ but the processes lack sufficient epoxide selectivity. Recently, relatively high selectivity (*ca.* 60%) of epoxidation of olefin (propylene) was attained using a Ti-containing silica with O₂ in a gas/solid (G/S) photocatalytic system.⁵ The catalytic site critical for selective epoxidation is tetrahedrally coordinated Ti-oxide (Ti-O₄) species, which are highly dispersed on a silica matrix.^{5b} On the photoactivated Ti-O₄, O₃^{•-} radical is formed from O₂ and adds directly to the C=C bond of an olefin, affording the corresponding epoxide. This implies a potential role of O₃^{•-} as the oxidant for selective epoxidation. The photoactivated Ti-O₄, however, also produces O₂^{•-} and olefin radicals, which inevitably promotes undesirable side reactions (alcohol and ketone formation). Herein, we describe that a simple addition of *acetonitrile* (MeCN) to this photocatalytic system, forming a conventional liquid/solid (L/S) system, remarkably improves epoxide selectivity. To the best of our knowledge, this is a photocatalytic system achieving the highest epoxide selectivity. We also emphasize a high stereoretivity (> 99%) of the present catalytic system for olefin epoxidation.

We used Ti-containing silica with a hexagonal MCM-41 structure, T-S(*x*) [*x* (mol%) = Ti/(Ti + Si) × 100; *x* = 0.9, 2.2, 5.4],‡ which were prepared by a conventional surfactant-templating method⁶ (catalyst properties: see Table S1 and Figs. S1 and S2†). Bulk TiO₂(anatase) was used as a reference catalyst. Diffuse reflectance UV-vis absorption spectra (Fig. S3†) revealed that T-S(0.9) exhibits a narrow absorption band at λ < 300 nm, which is assigned to LMCT (ligand-to-metal charge transfer) from lattice oxygen (O_L²⁻) to titanium ion (Ti⁴⁺).⁷ This indicates that T-S(0.9) consists predominantly of Ti-O₄ species. In contrast, T-S(2.2) and (5.4) show red-shifted absorption, attributable to aggregated Ti-oxide species,⁷ as does TiO₂. Photoreactions in the presence of MeCN were carried out by photoirradiation (λ > 280 nm, 12 h)⁸ of

a suspension of catalyst in O₂-saturated MeCN within a glass tube (L/S system).† For reactions without MeCN, a G/S system was employed using a conventional flat bottomed cell.†

Reaction of cyclohexene (CHE) in a G/S system using T-S(0.9) (Table 1, run 1) gives rise to the corresponding epoxide with 11% selectivity, together with higher quantities of allylic oxidation products (cyclohexen-2-ol (36%) and cyclohexen-2-one (12%); Table S2†). With MeCN (run 2, L/S system), the CHE conversion is similar to that obtained without MeCN, but surprisingly, the epoxide selectivity is enhanced to 71% (TON: 1.2).⁹ Use of bulk TiO₂ in both G/S and L/S systems (runs 3–5) shows low epoxide selectivity (< 26%). T-S(2.2) and (5.4) catalysts, both containing aggregated Ti-oxide species, in an L/S system (runs 6, 7) also show lower selectivity than does T-S(0.9). The low epoxide selectivities on bulk TiO₂, T-S(2.2), and (5.4) are because the electron–positive hole pairs, which are photoformed on the “semiconducting” aggregated Ti-oxide species, produce O₂^{•-} and cyclohexenyl (‘CHE) radicals, thus promoting the allylic oxidation of CHE.^{4,5b} Addition of MeCN (1 mmol) to a G/S system with T-S(0.9) also enhances the epoxide selectivity (run 8). The results suggest that the enhanced selectivity is triggered by a combination of the presence of MeCN and the catalyst containing Ti-O₄ species.















Photoirradiation of T-S(0.9) (25 mg containing 0.35 μmol Ti-O₄) with MeCN (0.32 μmol) at 77 K shows ESR signals assigned to Ti³⁺ and O_L⁻ (Fig. 1d), as is also observed *in vacuo*.^{5b,8} This indicates that, even in the presence of MeCN, the charge-transfer excited state species [Ti³⁺–O_L⁻]* are formed by photoexcitation of Ti-O₄ and behave as the active site (Scheme 1, II).^{5b} Photoirradiation of Ti-O₄ with O₂ (0.32 μmol) without MeCN at 77 K shows ESR signals assigned to two types of oxygen radicals, O₃^{•-} and O₂^{•-} (Fig. S4†),^{5b,8} where the ratio of the relative amount of the radicals (O₃^{•-}/O₂^{•-}) is determined to be 0.32 by double integration of the signals (see Discussion†). Even with O₂ (0.32 μmol) and MeCN (0.32 μmol) together, O₃^{•-} and O₂^{•-} signals still appear (Fig. S5†), and the ratio is determined to be 0.31 (see Discussion†). This value is similar to that obtained without MeCN, suggesting that MeCN scarcely affects the ratio of these active oxygen radicals. The structures of O₃^{•-} and O₂^{•-} on the Ti-O₄ in the presence of MeCN can therefore be depicted as Scheme 1 (III and IV), as is also the case without MeCN.^{5b,8}

Direct addition of the electrophilic O₃^{•-} to CHE (Scheme 1; route A) should afford the corresponding epoxide in the present system, as it does for propylene.^{5b} The O_L⁻ site on species II and IV, formed *via* an electron transfer from O_L²⁻ to Ti⁴⁺, is also electrophilic and hence acts as a positive hole.^{5b} A proton transfer^{5b} from CHE to O_L⁻ therefore occurs and produces the

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† Electronic supplementary information (ESI) available: methods, discussion, Figs. S1–S5, and Tables S1 and S2. See DOI: 10.1039/b512807b

Table 1 Results of photocatalytic epoxidation of olefins^d

Run	Catalyst System ^b	Substrate	Conversion (%)	Product	Selectivity (%)
1	T-S(0.9) G/S		9		11
2	T-S(0.9) L/S		10		71
3	TiO ₂ G/S ^c		10		21
4	TiO ₂ L/S		27		21
5	TiO ₂ L/S ^c		9		26
6	T-S(2.2) L/S		10		52
7	T-S(5.4) L/S		14		47
8	T-S(0.9) G/S ^d		8		63
9	T-S(0.9) L/S		8		99
10	T-S(0.9) G/S		13		53
11	TiO ₂ L/S	61		47	
12	T-S(0.9) L/S		9		98
13	T-S(0.9) G/S		21		71
14	TiO ₂ L/S	72		76	
15	T-S(0.9) L/S		11		> 99
16	T-S(0.9) G/S		18		31
17	TiO ₂ L/S	26		25	
18	T-S(0.9) L/S		7		98
19	T-S(0.9) G/S		9		38
20	TiO ₂ L/S	20		26	
21	T-S(0.9) L/S		8		> 99
22	T-S(0.9) G/S		11		62(0 ^e)
23	TiO ₂ L/S	32		33(9 ^e)	
24	T-S(0.9) L/S		12		> 99
25	T-S(0.9) G/S		32		67(0 ^f)
26	TiO ₂ L/S	73		12(36 ^f)	

^a Detailed product distribution: see Table S2. ^b L/S system: catalyst, 10 mg; MeCN, 10 ml; olefin, 0.2 mmol; O₂, 1 atm; photoirradiation time, 12 h. G/S system: catalyst, 10 mg; olefin, 0.2 mmol; O₂, 1 atm; photoirradiation time, 12 h. ^c Photoirradiation time, 3 h. ^d With MeCN (1 mmol). ^e Selectivity of *trans* epoxide. ^f Selectivity of *cis* epoxide.

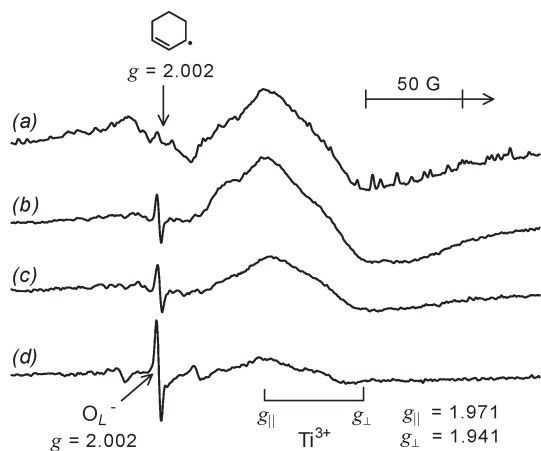
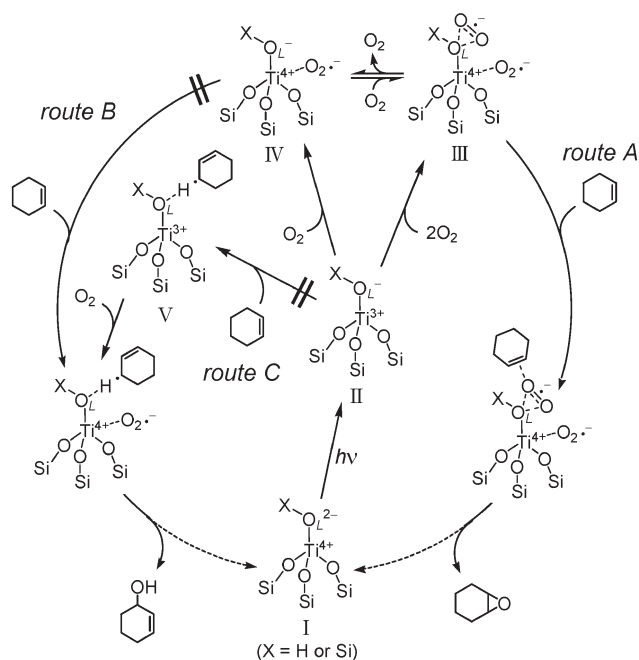


Fig. 1 ESR spectra of T-S(0.9) measured at 77 K after photoirradiation with MeCN and CHE. The ratio of MeCN/CHE ($\mu\text{mol}/\mu\text{mol}$) is (a) 0/0.32, (b) 0.05/0.32, (c) 0.32/0.32, and (d) 0.32/0.

corresponding $\cdot\text{CHE}$ radical, which reacts with $\text{O}_2^{\cdot-}$ to afford allylic oxidation products (routes B and C). As shown in Fig. 1a, photoirradiation of T-S(0.9) with CHE (0.32 μmol), without MeCN and O₂, shows a sine-shaped signal assigned to $\cdot\text{CHE}$ radical ($g = 2.002$),¹⁰ where the Ti^{3+} signal still remains but the O_L^- signal disappears completely. This confirms that O_L^- acts as the site for $\cdot\text{CHE}$ formation. In this case, the Ti^{3+} intensity is



Scheme 1 MeCN-assisted selective olefin epoxidation on photoactivated Ti-O₄ species.

higher than that obtained without CHE (Fig. 1d). This is because CHE consumes the positive hole on O_L^- and hence stabilizes Ti^{3+} (species V).^{5b} However, photoirradiation of T-S(0.9) with CHE and MeCN together leads to flattening of the $\cdot\text{CHE}$ signal (Fig. 1, b and c). This indicates that addition of MeCN leads to a decrease in the quantity of $\cdot\text{CHE}$.

A notable feature of the ESR spectra obtained with MeCN (Fig. 1, b and c) is the appearance of the O_L^- signal, along with the $\cdot\text{CHE}$ signal flattening. As the MeCN quantity increases, the spectrum becomes similar to that obtained with only MeCN (Fig. 1d). This implies that MeCN does not deactivate the $\cdot\text{CHE}$ formed but suppresses the proton transfer from CHE to O_L^- , resulting in suppression of the $\cdot\text{CHE}$ formation. On the O_L^- site, $\text{O}_3^{\cdot-}$ is formed even in the presence of MeCN (Fig. S5[†]). These findings indicate that MeCN allows $\text{O}_3^{\cdot-}$ formation on O_L^- , while suppressing $\cdot\text{CHE}$ formation. The MeCN-assisted selective olefin epoxidation is therefore attributable to the selective suppression of the $\cdot\text{CHE}$ formation on the O_L^- site.

The mechanism of the selective “shield effect” by MeCN must be clarified. As is well known, MeCN acts as a weak Lewis base (donor number, DN = 14.1 kcal mol⁻¹).¹¹ A possible reason for the shield effect is the electron transfer from MeCN to O_L^- , which blocks off the proton transfer from CHE to O_L^- . Photoirradiation of T-S(0.9) with CHE, together with *n*-BuCN (DN = 16.6)¹¹ or THF (DN = 20.0),¹¹ also leads to flattening of the $\cdot\text{CHE}$ signal in the ESR spectrum, but the O_L^- signal scarcely appears (Fig. S6[†]). Photocatalytic CHE oxidation by T-S(0.9) with these solvents shows much lower conversion (< 1% for *n*-BuCN and 2% for THF). The results indicate that electron transfer from these strong bases leads to complete O_L^- deactivation (poisoning), resulting in suppression of both $\text{O}_3^{\cdot-}$ and $\cdot\text{CHE}$ formation. In contrast, electron transfer from MeCN is poor due to its low basicity, resulting in the O_L^- signal appearance in the ESR spectrum (Fig. 1d); this rules out electron transfer from MeCN as the strong

factor triggering the shield effect. Also as is well known, hydrocarbons acting as a Brønsted acid (proton donor) are stabilized by solvation of a basic solvent *via* hydrogen bonding.¹² MeCN, of weak basicity, may stabilize CHE and, hence, suppress the proton transfer from CHE to O_L^- , while keeping O_L^- active. Use of MeCN-*d*₃ (DN = 14.0), with similar DN to MeCN, shows a similar ESR spectrum (Fig. S6†). These findings indicate that the “weak” basicity of MeCN may be the strong factor triggering the shield effect. Neither nonpolar hydrocarbon¹³ nor protic alcohol¹⁴ is suitable; therefore, MeCN is the best solvent for this effect. The mechanism of the MeCN-assisted selective epoxidation can therefore be summarized in Scheme 1, where route A is preferred because routes B and C are suppressed by the shield effect.

Photocatalytic epoxidation of various cyclic and linear olefins on T-S(0.9) using an L/S system also proceeds with excellent selectivity (> 98%, Table 1),¹⁵ whereas the use of T-S(0.9) in a G/S system and bulk TiO₂ in an L/S system shows much lower selectivity. The epoxide selectivities presented here are the highest values among those obtained in the photocatalytic systems reported to date.^{3–5}

Another notable feature of the present photocatalytic system is the retention of the configuration around the C=C moiety of olefins in the resulting epoxide. Reactions of *cis*- and *trans*-2-hexene on T-S(0.9) in an L/S system (runs 21, 24) afford respectively *cis*- and *trans*-2,3-epoxyhexane with > 99% selectivity. Reactions of these olefins on T-S(0.9) without MeCN (runs 22, 25) yield *ca.* 40% byproducts formed *via* route B or C, but *do not yield isomerized epoxides*. This means that $O_3^{\cdot-}$ is a potential oxidant for stereoretentive olefin epoxidation, although this interesting fact has never been reported until now. The results imply that the MeCN-driven shield effect suppresses the undesirable side reactions occurring on Ti-O₄ and maximizes the inherent stereoretentivity of the $O_3^{\cdot-}$ radical for olefin epoxidation.

The photostability of MeCN in the present catalytic system must be checked. Photoirradiation of T-S(0.9) in O₂-saturated MeCN without olefin, in a similar manner to the photocatalytic reaction, reveals that the quantity of CO₂ formed is < 0.1 μmol (12 h), which is less than 1% of the olefin converted (Table 1, run 2). In contrast, use of bulk TiO₂ gives 2.4 mmol CO₂ formation.¹⁶ The results indicate that the MeCN stability on T-S(0.9) is much higher than that on bulk TiO₂.

In conclusion, we found that Ti-containing silica with Ti-O₄ species catalyzes highly selective photocatalytic olefin epoxidation with O₂ and a simple addition of MeCN. This is achieved *via* MeCN-assisted selective suppression of side reactions, the so-labeled “shield effect”. The process has several problems: i) low olefin conversion (< 12%: Table 1) and ii) requirement of UV light (< 300 nm) for catalyst activation. The latter suggests that the process is inapplicable to aryl olefins, which absorb light with wavelength longer than 300 nm. However, the process shows the highest epoxide selectivity of aliphatic olefins among those which have been proposed so far and promotes stereoretentive olefin epoxidation, where stable MeCN may be reusable for further reaction. The basic concept presented here will contribute to the development of a more efficient photocatalytic system for selective epoxide synthesis in an economically- and environmentally-friendly way.

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Notes and references

‡ T-S(x) preparation: a mixture of TEOS (10.4 g) and tetramethylammonium hydroxide (9.1 g) was added slowly to a solution of cetyltrimethylammonium bromide (10.9 g) dissolved in water (32.7 g) with stirring at 278 K and stirred for 0.5 h. Tetrabutyl orthotitanate (0.17 g for *x* = 0.9; 0.35 for *x* = 2.2; 0.71 for *x* = 5.4) dissolved in *i*-PrOH (40 mL) was added slowly to the mixture and stirred for 0.5 h. Water (13.7 g) was added and stirred for 4 h at 358 K. The resulting mixture was transferred into a stainless steel autoclave and heated at 373 K for 10 days under static conditions. The solid obtained was recovered by filtration, washed with water, dried at 333 K for 10 h, and calcined at 813 K for 6 h under air flow, affording white powders.

- (a) *Oxidations in Organic Chemistry*, ed. M. Hudlucky, American Chemical Society, Washington, DC, 1990; (b) *Metal-Catalyzed Oxidations of Organic Compounds*, ed. R. A. Sheldon and J. K. Kochi, Academic Press, New York, 1981; (c) *Encyclopedia of Catalysis*, vol. 3, ed. I. T. Horvath, John Wiley & Sons, Hoboken, 2002.
- (a) Y. Shi, *Acc. Chem. Res.*, 2004, **37**, 488; (b) B. S. Lane and K. Burgess, *Chem. Rev.*, 2003, **103**, 2457; (c) X. Zuwei, Z. Ning, S. Yu and L. Kunlan, *Science*, 2001, **292**, 1139; (d) R. Neumann and M. Dahan, *Nature*, 1997, **388**, 353; (e) B. de Bruin, P. H. M. Budzelaar and A. W. Gal, *Angew. Chem., Int. Ed.*, 2004, **43**, 4142.
- (a) F. Amano, T. Tanaka and T. Funabiki, *Langmuir*, 2004, **20**, 4236; (b) T. Tanaka, H. Nojima, H. Yoshida, H. Nakagawa, T. Funabiki and S. Yoshida, *Catal. Today*, 1993, **16**, 297; (c) C. Murata, H. Yoshida and T. Hattori, *Chem. Commun.*, 2001, 2412.
- (a) M. A. Fox and C. Chen, *J. Am. Chem. Soc.*, 1981, **103**, 6757; (b) Y. Kanno, T. Oguchi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.*, 1980, **21**, 467; (c) T. Ohno, K. Nakabeya and M. Matsumura, *J. Catal.*, 1998, **176**, 76; (d) T. Ohno, T. Kigoshi, K. Nakabeya and M. Matsumura, *Chem. Lett.*, 1998, 877.
- (a) C. Murata, H. Yoshida and T. Hattori, *Chem. Commun.*, 1999, 1551; (b) C. Murata, H. Yoshida, J. Kumagai and T. Hattori, *J. Phys. Chem. B*, 2003, **107**, 4364.
- K. A. Koyano and T. Tatsumi, *Microporous Mater.*, 1997, **10**, 259.
- (a) S. Bordiga, S. Coluccia, C. Lamberti, L. Marchese, A. Zecchina, F. Boscherini, F. Buffa, F. Genoni, G. Leofanti, G. Petrini and G. Vlaic, *J. Phys. Chem.*, 1994, **98**, 4125; (b) X. Gao and I. E. Wachs, *Catal. Today*, 1999, **51**, 233; (c) X. Gao, S. R. Bare, J. L. G. Fierro, M. A. Banares and I. E. Wachs, *J. Phys. Chem. B*, 1998, **102**, 5653.
- Y. Shiraishi, N. Saito and T. Hirai, *J. Am. Chem. Soc.*, 2005, **127**, 8304.
- TON = (amount of epoxide formed)/(amount of Ti on catalyst).
- S. Ohnishi and I. Nitta, *J. Chem. Phys.*, 1963, **39**, 2848.
- (a) *Non-aqueous Solvents*, ed. J. R. Chipperfield, Oxford University Press Inc., New York, 1999; (b) Y. Misono, L. Limantara, Y. Koyama and K. Itoh, *J. Phys. Chem.*, 1996, **100**, 2422.
- (a) E. M. Arnet, E. J. Mitchell and T. S. S. R. Murty, *J. Am. Chem. Soc.*, 1974, **96**, 3875; (b) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, 1971, **75**, 3598.
- Photocatalytic CHE oxidation by T-S(0.9) with *n*-hexane (DN = 0) shows only < 1% conversion. This is because nonpolar *n*-hexane destabilizes the highly polarized $[Ti^{3+}-O_L^-]^*$. K. Ikeue, H. Yamashita, M. Anpo and T. Takewaki, *J. Phys. Chem. B*, 2001, **105**, 8350.
- Photocatalytic CHE oxidation by T-S(0.9) with MeOH (DN = 25) shows 11% conversion, which is comparable to that obtained with MeCN, but epoxide selectivity is only 39%. This is because $\cdot CH_2OH$ radical, formed by proton transfer from MeOH to O_L^- , causes nonselective olefin oxidation: O. I. Micic, Y. Zhang, K. R. Cromack, A. D. Trifunac and M. C. Thurnauer, *J. Phys. Chem.*, 1993, **97**, 13284.
- Much higher epoxide selectivities of these olefins than that of CHE are attributable to the lower activity of the allylic position of the olefins: D. E. Van Sickle, F. R. Mayo and R. M. Arluck, *J. Am. Chem. Soc.*, 1965, **87**, 4824.
- (a) J. Zhuang, C. N. Rusu and J. T. Yates, Jr., *J. Phys. Chem. B*, 1999, **103**, 6957; (b) N. N. Lichtin and M. Avudaitai, *Environ. Sci. Technol.*, 1996, **30**, 2014.