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

Yasuhiro Shiraishi,* Masatsugu Morishita, and Takayuki Hirai

Research Center for Solar Energy Chemistry, and Division of Chemical Engineering,
Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

Electronic Supplementary Information (ESI†)

Methods

1) Photocatalytic Reaction

General: Photoirradiation was performed using a high-pressure Hg lamp (300 W; Eikohsha Co, Ltd., Osaka), filtered through a Pyrex glass to give light wavelengths of $\lambda > 280$ nm.[S1] It was confirmed that all of the substrates used scarcely absorb the light at this range. Concentrations of substrates and products were determined by GC-FID. Identification of the products was carried out on GC-MS (EI).

L/S System: Each catalyst (10 mg) was suspended in dry MeCN (10 ml) containing an individual substrate (0.2 mmol) within a Pyrex glass tube (ϕ 10 mm; capacity, 20 cm^3), and each tube sealed using a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min. O_2 was bubbled through the solution for 5 min. The tube was photoirradiated from side direction with magnetic stirring. The temperature of the solution during photoirradiation was 313 K. The resulting solution was recovered by centrifugation and then analyzed.

G/S System: The reaction was performed with a conventional closed system (capacity, 6 cm^3).[S2] Each catalyst (10 mg) was spread on the flat bottom (2 cm^2) of the quartz vessel. Olefin (0.2 mmol) was introduced to the vessel, and the vessel was then filled with O_2 (1 atm). The sample was photoirradiated from beneath in a static condition. The temperature of the bottom of the vessel during photoirradiation was 315 K. After the reaction, MeCN (5 ml) was added to the vessel, and the catalyst was rinsed well by ultrasonication for 5 min at room temperature. The resulting MeCN was recovered by centrifugation and then analyzed.

2) ESR Measurement

Instruments: ESR spectra were recorded at the X-band using a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 1.0 mW,[S3] where the microwave power saturation of the signals does not occur. The magnetic field was calibrated using a 1,1′-diphenyl-2-picrylhydrazyl (DPPH) as standard. Photoirradiation of the sample was carried out using a 500 W Xe lamp (USHIO Inc.).[S1]

Measurements: T-S(0.9) catalyst (25 mg) was placed in a cylindrical quartz ESR tube (capacity, 6 cm^3) and treated with 100 Torr oxygen (1 Torr = 133.3 Pa) at 703 K for 2 h. The tube was evacuated at 703 K for 2 h and cooled to room temperature. The required quantity of O_2, CHE, and/or MeCN (solvent) was then introduced to the tube. The tube was placed on an ESR sample cavity and photoirradiated at 77 K. After photoirradiation for 0.5 h, the irradiation was turned off, and measurement was started immediately. For determination of the ratio of relative amount of $O_3\cdot^-/O_2\cdot^-$ formed on the catalyst, the tube was then ejected from the cavity and left to stand at room temperature for 1.5 min. The tube was placed on the cavity again, and measurement was then started.[S1,S4]

Discussion

Determination of $O_3\cdot^-/O_2\cdot^-$

In the Absence of MeCN: Photoirradiation of T-S(0.9) in the presence of O_2 (1 Torr; 0.32 μmol) at 77 K gave rise to the ESR signals, consist of two types of oxygen radicals, such as $O_2\cdot^-$ and $O_3\cdot^-$ (Fig. S4.A) The total spectrum of Fig. S4.A is attributed to $O_2\cdot^-$ (g_{xx} = 2.003, g_{yy} = 2.009, g_{zz} = 2.026) and T-type $O_3\cdot^-$ ($g_{\parallel}$ = 2.008, $g_{\perp}$ = 2.002) signals.[S4] As reported,[S4] when the ESR sample is left to stand at room temperature for 1.5 min, the $O_3\cdot^-$ signal disappears and only the $O_2\cdot^-$ signal remains (Fig. S4.B). This is because $O_3\cdot^-$ is unstable at room temperature, while $O_2\cdot^-$ is stable. By subtracting the spectrum B from A, the disappeared $O_3\cdot^-$ signal can be derived (spectrum C). The relative amount of $O_3\cdot^-$ and $O_2\cdot^-$ can therefore be determined by the double integration of the ESR signals, B and C, respectively.[S1,S4] The ratio of $O_3\cdot^-/O_2\cdot^-$ is therefore estimated to be 0.24/0.76 (= 0.32) (total quantity = 1).

In the Presence of MeCN: Photoirradiation of T-S(0.9) in the presence of O_2 (1 Torr; 0.32 μmol) and MeCN (1 Torr; 0.32 μmol) also shows similar ESR spectrum (Fig. S5.A) to that obtained in the presence of only O_2 (Fig. S4.A). Therefore, even in the presence of MeCN, $O_2\cdot^-$ and $O_3\cdot^-$ radicals are also formed on the catalyst. The double integration of the total ESR spectrum (Fig. S5.A) indicated that total quantity of these oxygen radical species is 0.47, which is about half as that obtained in the absence of MeCN (total quantity = 1). This may be because the $[Ti^{3+}–O_L^-]^*$ is destabilized in the presence of MeCN. When the T-S(0.9) sample (Fig. S5.A) is left to stand at room temperature for 1.5 min, disappearance of $O_3\cdot^-$ signal is also observed (Fig. S5.B), suggesting that $O_3\cdot^-$ is less stable than $O_2\cdot^-$ in the presence of MeCN, as is also the case in the absence of MeCN (Fig. S4.B). To evaluate the correct quantities of $O_2\cdot^-$ and $O_3\cdot^-$ radicals, formed from O_2 by photoirradiation in the presence of MeCN, the pure $O_2\cdot^-$ and $O_3\cdot^-$ spectra (Fig. S4, B and C) were summed up with weighting factors, α and β, to produce a simulated spectrum, as below.

$$\text{Simulated spectrum} = \frac{\text{spectrum}\,(O_2\cdot^-)}{0.76}\times\alpha + \frac{\text{spectrum}\,(O_3\cdot^-)}{0.24}\times\beta \qquad (1)$$

$$\alpha+\beta = 0.47 \qquad (2)$$

By trial-and-error method,[S1] the values of α (0.36) and β (0.11), which produce the nearest-shaped spectrum (Fig. S5.C) to the observed spectrum (Fig. S5.A), were determined. The ratio of $O_3\cdot^-$ /$O_2\cdot^-$ was therefore estimated to be 0.11/0.36 (=0.31) (total quantity = 0.47), which is similar to that obtained in the absence of MeCN (0.24/0.76 (= 0.32)). The results suggest that MeCN scarcely affects the ratio of the oxygen radical species and the structures of $O_3\cdot^-$ and $O_2\cdot^-$ on Ti-O_4 can therefore be depicted as Scheme 1 (III and IV).

S1. Y. Shiraishi, N. Saito and T. Hirai, *J. Am. Chem. Soc.,* 2005, **127**, 8304.

S2. Y. Shiraishi, Y. Teshima and T. Hirai, *Chem. Commun.,* 2005, 4569.

S3. Y. Shiraishi, N. Saito and T. Hirai, *J. Am. Chem. Soc.*, 2005, **127**, 12820.

S4. C. Murata, H. Yoshida, J. Kumagai and T. Hattori, *J. Phys. Chem. B,* 2003, **107**, 4364.

Figures

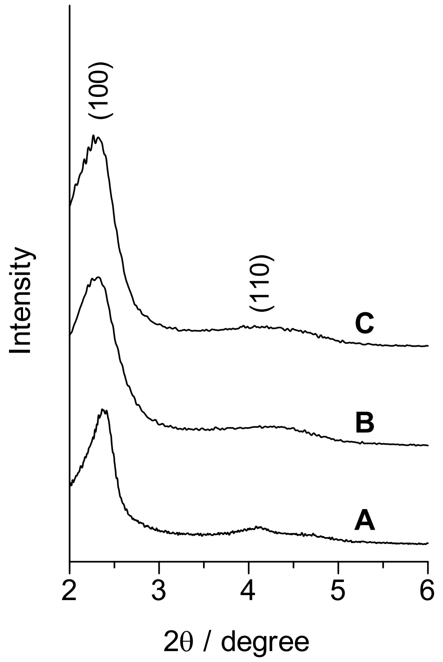


Fig. S1 XRD pattern of (**A**) T-S(0.9), (**B**) T-S(2.2), and (**C**) T-S(5.4) catalysts.

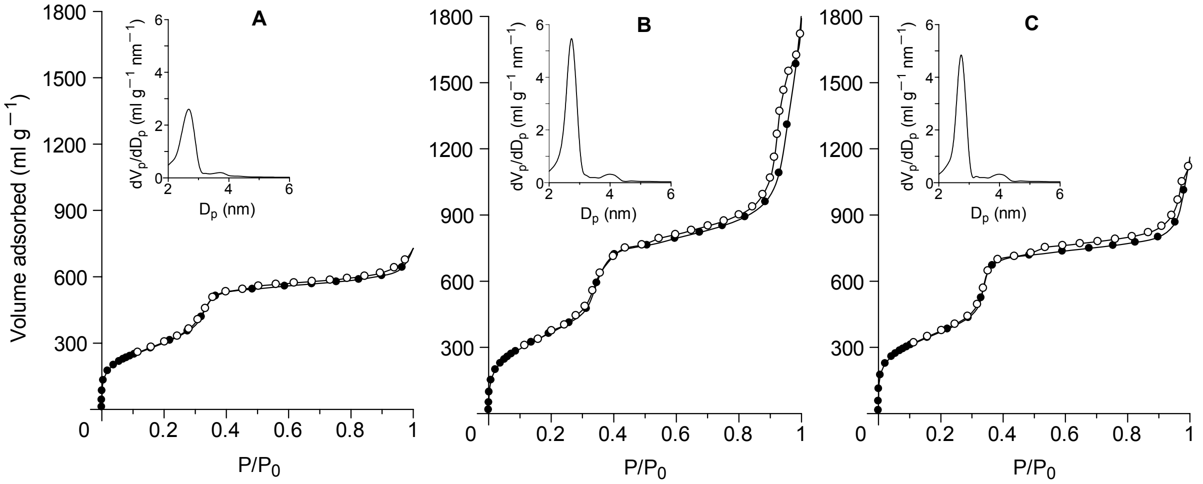


Fig. S2 N_2 adsorption(●)–desorption(○) isotherm and pore size distribution (inset) of the catalysts used. (**A**) T-S(0.9), (**B**) T-S(2.2), and (**C**) T-S(5.4).

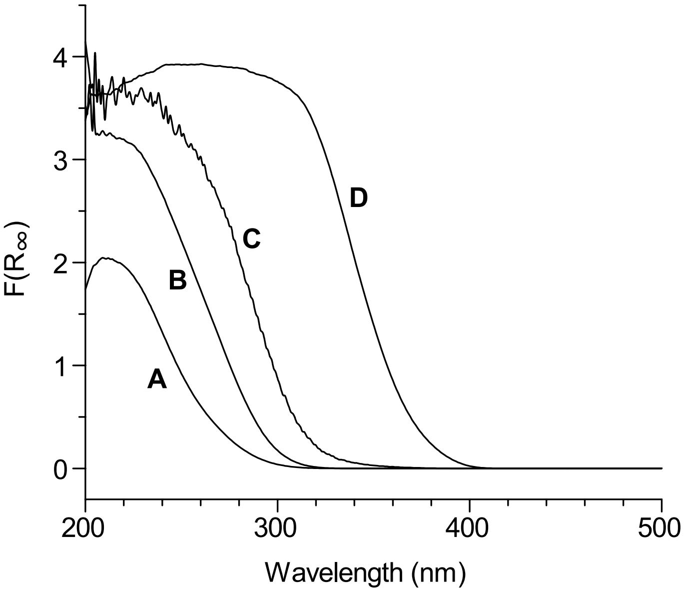


Fig. S3 Diffuse Reflectance UV-vis absorption spectra of (**A**) T-S(0.9), (**B**) T-S(2.2), (**C**) T-S(5.4), and (**D**) bulk TiO_2 catalysts.

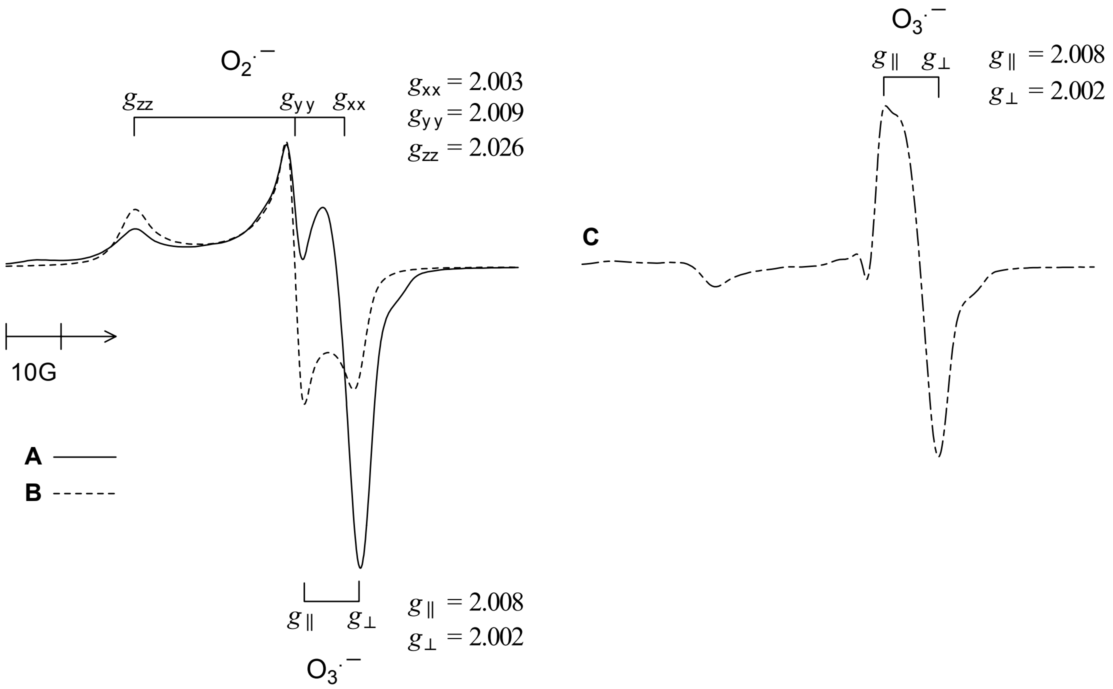


Fig. S4 ESR spectra of T-S(0.9) catalyst at 77 K (**A**) after photoirradiation in the presence of O_2 (0.32 μmol) at 77 K, (**B**) followed by letting to stand at room temperature for 1.5 min. The spectrum (**C**) is obtained by subtracting the spectrum B from the spectrum A.

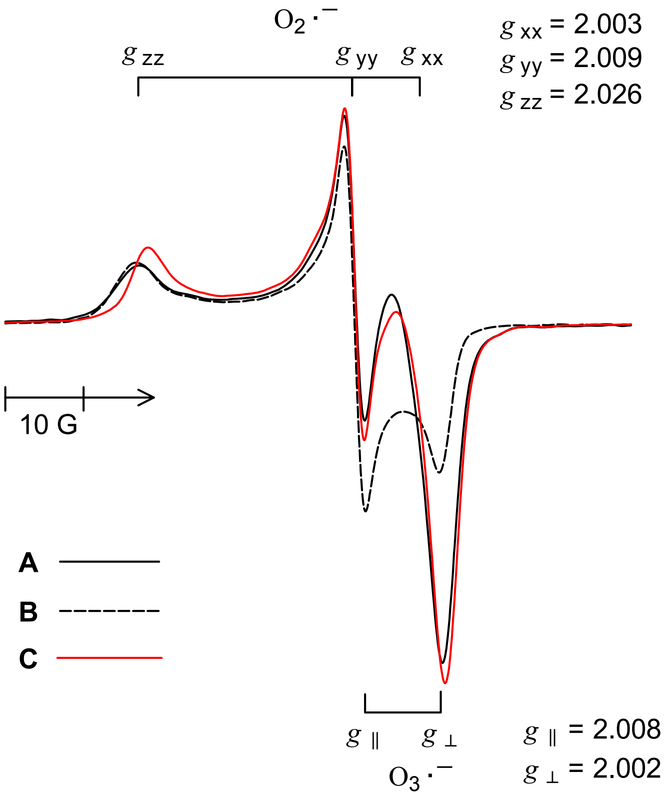


Fig. S5 ESR spectra of T-S(0.9) catalyst at 77K (**A**) after photoirradiation in the presence of O_2 (0.32 μmol) and MeCN (0.32 μmol) at 77 K, (**B**) followed by letting to stand at room temperature for 1.5 min. The spectrum (**C**) is the simulated spectrum obtained by trial-and-error method using eqs. 1 and 2.

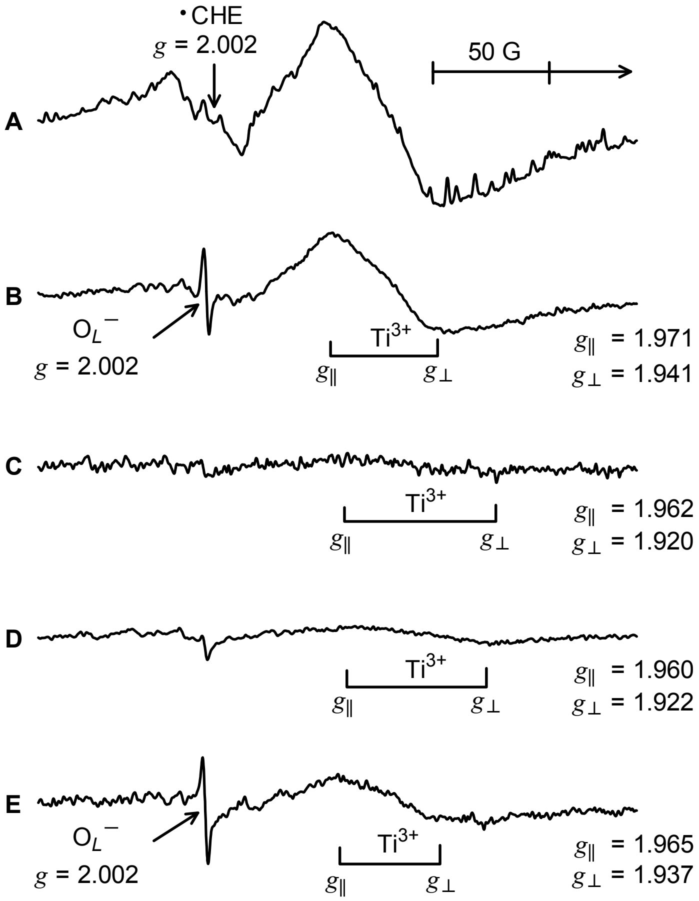


Fig. S6 ESR spectra of T-S(0.9) at 77K after photoirradiation with CHE (0.32 μmol) and (**A**) without solvent, (**B**) with MeCN (0.32 μmol), (**C**) with *n*-BuCN (0.32 μmol), and (**D**) with THF (0.32 μmol), and (**E**) with MeCN-d_3 (0.32 μmol).

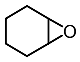
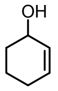
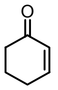
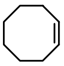
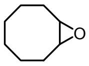
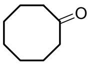
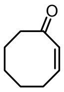
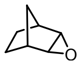
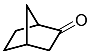
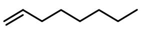
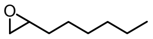
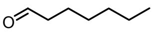
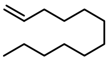
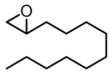
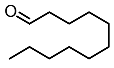
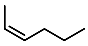
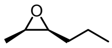
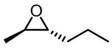
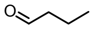
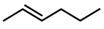
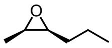
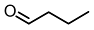
Tables

Table S1 Properties of photocatalysts used.

	Ti/(Ti+Si)×100 (mol %)	d_{100} spacing (nm)	pore diameter [a] (nm)	BET surface area (m^2/g)
T-S(0.9)	0.93	3.70	2.87	1150
T-S(2.2)	2.17	3.78	2.87	1370
T-S(5.4)	5.37	3.80	2.87	1380
TiO_2(anatase)[b]	100			48

[a] determined by DH method. [b] Supplied by Wako.

Table S2 Product distribution in the photooxidation of olefins on various catalysts.^{a}

run	catalyst	system	substrate conv. (%)	product select. (%)			
							others
1	T-S(0.9)	G/S	9	11	36	12	41
2	T-S(0.9)	L/S	10	71	29	0	0
3	TiO$_2$	G/S^b	10	21	13	33	33
4	TiO$_2$	L/S	27	21	7	34	38
5	TiO$_2$	L/S^b	9	26	2	42	30
6	T-S(2.2)	L/S	10	52	18	19	11
7	T-S(5.4)	L/S	14	47	13	24	16
8	T-S(0.9)	G/S^c	8	63	20	11	6
							others
9	T-S(0.9)	L/S	8	99	0	0	1
10	T-S(0.9)	G/S	13	53	25	7	13
11	TiO$_2$	L/S	61	47	3	1	49
						others	
12	T-S(0.9)	L/S	9	98	0	2	
13	T-S(0.9)	G/S	21	71	13	16	
14	TiO$_2$	L/S	72	76	3	21	
						others	
15	T-S(0.9)	L/S	11	>99	0	0	
16	T-S(0.9)	G/S	18	31	42	27	
17	TiO$_2$	L/S	26	25	23	52	
						others	
18	T-S(0.9)	L/S	7	98	0	2	
19	T-S(0.9)	G/S	9	38	17	45	
20	TiO$_2$	L/S	20	26	20	54	
							others
21	T-S(0.9)	L/S	8	>99	0	0	0
22	T-S(0.9)	G/S	11	62	0	18	20
23	TiO$_2$	L/S	32	33	9	11	47
							others
24	T-S(0.9)	L/S	12	>99	0	0	0
25	T-S(0.9)	G/S	32	67	0	22	11
26	TiO$_2$	L/S	73	12	36	7	45

^{a} The reaction conditions are the same as Table 1. ^{b} Photoirradiation time, 3 h. ^{c} With MeCN (1 mmol).