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1. Introduction

Heterogeneous photocatalysis on semiconductor TiO₂ has been studied extensively for decomposition of harmful chemicals in air and water, because it promotes mineralization of these chemicals into CO2 and H2O under milder conditions (room temperature and atmospheric pressure).¹ Application of TiO₂ photocatalysis to selective organic transformation has also attracted much attention.² In most cases, TiO₂ photocatalysis involves the following steps:³ (i) generation of electron (e^{-}) and positive hole (h⁺) pairs by absorption of supra-band gap photons; and (ii) oxidation of substrates by h^+ or surface hydroxyl radicals ($^{\circ}OH_{surf}$) formed by the reaction of h^{+} with water or surface Ti-OH groups. The oxidation step is, however, nonselective and usually promotes oxidation of products (decomposition) as well as oxidation of substrates. Selective photocatalytic transformation therefore requires selective oxidation of substrates while suppressing further oxidation of products.⁴

Selective side-chain oxidation of alkyl-substituted aromatics to the corresponding aldehydes and ketones with molecular oxygen (O_2) as an oxidant is one of the most important

Selective side-chain oxidation of alkyl-substituted aromatics on TiO₂ partially coated with WO₃ as a photocatalyst

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TiO₂ particles partially coated with WO₃ (WO₃/TiO₂) were used as photocatalysts for selective oxidation of toluene to benzaldehyde with molecular oxygen (O₂) under photoirradiation at $\lambda > 300$ nm. The catalysts loaded with 8–10 wt% WO₃ exhibit very high oxidation activity and produce benzaldehyde with *ca.* 50% selectivity, which is the highest selectivity among the photocatalytic systems reported so far. This is achieved because subsequent photocatalytic decomposition of the formed benzaldehyde is suppressed on the catalysts. On the photoactivated WO₃/TiO₂, the exposed TiO₂ surface behaves as the oxidation site, whereas the WO₃ surface is much less active for oxidation. The WO₃ loading decreases the amount of benzaldehyde adsorbed onto the TiO₂ surface. This thus suppresses photocatalytic decomposition of benzaldehyde on the TiO₂ surface, resulting in high benzaldehyde selectivity. The WO₃/TiO₂ catalyst successfully promotes side-chain oxidation of several kinds of alkyl-substituted aromatics and selectively produces aldehydes and ketones.

> transformations in organic synthesis.⁵ Traditional methods using homogeneous⁶ or heterogeneous⁷ catalysts require high O_2 pressures (~10 atm) and reaction temperatures (~463 K). TiO₂ photocatalysis has also been employed for this reaction because it can be operated at atmospheric pressure and room temperature.8 Bouquet-Somrani et al.8b performed photocatalytic oxidation of toluene on a TiO2-zeolite composite in MeCN. Its benzaldehyde selectivity was, however, only 12% at 30% toluene conversion. Ouidri and Khalaf^{8d} used a TiO₂pillared montmorillonite for toluene oxidation in MeCN. Its benzaldehyde selectivity was only 9.5%, although it is higher than that of bare TiO_2 (5.2%). The low selectivity is because the benzaldehyde formed by photooxidation of toluene is subsequently decomposed by photocatalytic reaction. Selective production of benzaldehyde therefore needs to suppress the decomposition of benzaldehyde while promoting oxidation of toluene.

> Earlier, we reported that TiO_2 particles partially coated with WO_3 (WO_3/TiO_2) promote selective photooxidation of benzylic alcohols to benzaldehydes in water.⁹ The mechanism is explained by Scheme 1. On bare TiO_2 (Scheme 1a), the benzaldehyde produced by photooxidation of alcohol is adsorbed onto the TiO_2 surface and decomposed subsequently by photooxidation (formation of CO_2 and water), resulting in low benzaldehyde selectivity. In contrast, on the WO_3/TiO_2 catalyst (Scheme 1b), the exposed TiO_2 surface behaves as the oxidation site, whereas the

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 WO_3 surface is much less active for oxidation. The amount of benzaldehyde adsorbed onto the TiO_2 surface is decreased by the WO_3 loading. This suppresses photocatalytic decomposition of benzaldehyde on the TiO_2 surface, resulting in high benzaldehyde selectivity. This implies that the WO_3/TiO_2 system, if applied to photooxidation of toluene, may promote selective formation of benzaldehyde.

In the present work, the WO₃/TiO₂ catalysts were applied for photooxidation of toluene. The catalysts successfully produce benzaldehyde with *ca.* 50% selectivity at 50% toluene conversion. Adsorption experiments revealed that the enhanced benzaldehyde selectivity is because the amount of aldehyde adsorbed onto the TiO₂ surface is decreased by the WO₃ loadings, suppressing the decomposition of aldehyde. The catalyst successfully promotes selective side-chain oxidation of several kinds of alkyl-substituted aromatics.

2. Results and discussion

2.1 Photocatalytic activity and selectivity

The WO₃/TiO₂ catalysts were prepared according to a procedure described previously,⁹ *via* the impregnation of H₂WO₄ onto the P25 TiO₂ particles by stirring in an ammonia solution at 353 K followed by calcination at 673 K under O₂ flow. Four kinds of WO₃(*x*)/TiO₂ catalysts with different WO₃ loadings [*x* (wt%) = WO₃/(WO₃ + TiO₂) × 100; *x* = 3.4, 7.6, 10.3, 18.5] were obtained as white powders. The properties of catalysts are summarized in Table 1.

Photooxidation of toluene was performed by photoirradiation ($\lambda > 300$ nm, Xe lamp) of a MeCN solution (5 mL) containing catalyst (5 mg) and toluene (50 µmol) under O₂ (1 atm) at 298 K with stirring. Table 1 summarizes the photoirradiation time ($t_{\rm irr}$) required for 50% toluene conversion and the benzaldehyde selectivity at this conversion. In some cases, toluene conversions did not attain 50% even after 72 h photoreaction; therefore, the data obtained by 72 h reaction were given there. Bare TiO₂ (run 1) shows very low benzaldehyde selectivity (12%), but the WO₃/TiO₂ catalysts (runs 2–5) show enhanced selectivity. The selectivity increases with the WO₃ loadings, and the catalysts with \geq 7.6 wt% WO₃ show *ca.* 50% selectivity, which is much higher than those obtained by earlier reported photocatalytic systems (~12%).⁸

During the photocatalytic reaction, the benzaldehyde formed is subsequently decomposed to CO2 and water.¹⁰ As shown in run 1, the amount of CO₂ formed during the reaction with bare TiO₂ is 48 µmol at 27% toluene conversion. In contrast, the WO₃/TiO₂ catalysts with \geq 7.6 wt% WO₃ (runs 3–5) produce a much smaller amount of CO_2 (<16 µmol) even at 50% toluene conversion, suggesting that decomposition of aldehyde is much suppressed. Fig. 1 shows the time-dependent change in the amounts of substrate and products and the benzaldehyde selectivity during the photoreaction. With bare TiO_2 (Fig. 1a), the amount of CO_2 formed is much larger than that of aldehyde, and the aldehyde selectivity is always <25%. In contrast, with WO₃(7.6)/TiO₂ and WO₃(10.3)/TiO₂ catalysts (Fig. 1b and c), the amounts of CO_2 formed are kept very low, and the aldehyde selectivities are always ca. >50% during the reaction. This indicates that the WO3/TiO2 catalysts indeed suppress decomposition of formed aldehyde.

The suppression of aldehyde decomposition on the WO_3/TiO_2 catalyst is confirmed by photoreaction of benzaldehyde as the starting material. As summarized in Fig. 2, the conversion of benzaldehyde and the amount of CO_2 formed decreases with an increase in the WO_3 loadings. These data clearly suggest that, during photooxidation of toluene, WO_3/TiO_2 catalysts indeed suppress subsequent decomposition of aldehydes (complete decomposition to CO_2 and water) and result in high aldehyde selectivity.

It must be noted that, as shown in Table 1, the WO₃/TiO₂ catalysts exhibit much higher activity for toluene oxidation than bare TiO₂. As shown by run 1, bare TiO₂ shows only 27% toluene conversion even after 72 h reaction, but WO₃(7.6)/TiO₂ and WO₃(10.3)/TiO₂ (runs 3 and 4) attain 50% conversion by 30 h reaction. Further WO₃ loading, however, decreases the catalytic activity (run 5). It must also be noted that, as shown by run 6, a physical mixture of TiO₂ and 10.3 wt% WO₃ shows much lower activity and aldehyde selectivity than those of WO₃(10.3)/TiO₂ catalyst (run 4). These data suggest that the WO₃ loading onto the TiO₂ surface is necessary for high catalytic activity and aldehyde selectivity.

2.2 Mechanism for enhanced photocatalytic activity

The structure of WO₃/TiO₂ catalysts has already been clarified in previous work by means of IR, X-ray photoelectron spectroscopy (XPS), X-ray near-edge structure (XANES) spectroscopy, and transmission electron microscopy (TEM).⁹ A brief description is therefore made here. As shown in Scheme 2, the WO₃ species on the TiO₂ surface form a layered structure consisting of branched chains of pentahedral WO₅ units and the terminal tetrahedral WO₄ units.¹¹ The catalysts with lower WO₃ loadings create narrow WO₃ islands, and increased WO₃ loadings lead to

Table 1 Properties of catalysts and results of photocatalytic oxidation of toluene^a

Run	Catalyst	$S_{\rm BET}{}^{b}/{\rm m}^{2}~{\rm g}^{-1}$	$d_{\rm p}{}^c/{\rm nm}$	$E_{\mathrm{bg}}^{\ d}/\mathrm{eV}$	$\theta^{e}/\%$	$t_{\rm irr}^{f/h}$	Toluene conv. ^g /%	Benzaldehyde select. ^{<i>h</i>} /%	CO ₂ /µmol
1	TiO ₂	54.0	23.7	3.13	0	72	27	12	48.3
2	$WO_3(3.4)/TiO_2$	58.2	24.0	3.06	34	72	35	21	39.7
3	WO ₃ (7.6)/TiO ₂	53.1	24.1	3.02	58	29.5	50	49	11.5
4^i	WO ₃ (10.3)/TiO ₂	49.7	25.0	3.02	76	29.5	50	50	11.4
5	$WO_3(18.5)/TiO_2$	44.4	27.2	3.00	89	72	50	48	15.5
6	$WO_3(10.3 \text{ wt\%}) + TiO_2$					72	25	16	35.5
7	WO ₃	3.0	127	2.80		72	6	21	2.3

^{*a*} Reaction conditions: toluene (50 µmol), MeCN (5 mL), catalyst (5 mg), O_2 (1 atm), temperature (298 K), and $\lambda > 300$ nm. ^{*b*} BET surface area. ^{*c*} Particle size determined by dynamic laser scattering (DLS) analysis. ^{*d*} Bandgap energies determined by a plot of the $\{F(R_{\infty}) \times h\nu\}^{1/2}$ versus the energy of light absorbed. ^{*e*} Surface coverage of TiO₂ by WO₃, determined by IR analysis (ref. 9). ^{*f*} The photoirradiation time required for 50% toluene conversion. The maximum photoirradiation time was 72 h. ^{*g*} [Toluene converted]/[initial amount of toluene] × 100. In the case when the toluene conversion did not attain 50%, the data obtained by 72 h are given. ^{*h*} [Benzaldehyde formed]/[toluene converted] × 100. ^{*i*} GC analysis detected benzoic acid (2.1 µmol) and *p*-cresol (0.7 µmol) as byproducts. The carbon balance is 67.8% {= 100 × [toluene + benzaldehyde + benzoic acid + *p*-cresol + (CO₂)/7]/[initial amount of toluene]}. Nonvolatile or thermally-degradable ring-opening products are probably involved as unidentified byproducts.



Fig. 1 Time-dependent change in (top) the benzaldehyde selectivity and (bottom) the amounts of substrate and products during the photocatalytic reaction of toluene with (a) TiO_2 and (b) $WO_3(7.6)/TiO_2$, or (c) $WO_3(10.3)/TiO_2$ catalyst. Reaction conditions are identical to those in Table 1.

a coalescence of these islands producing larger islands. As shown in Table 1, the percent coverage of the TiO₂ surface by the WO₃ layer (θ), determined by IR analysis, increases with the WO₃ loading.⁹ TEM observations also indicate that monolayer WO₃ islands form at \leq 7.6 wt% WO₃ (Scheme 2a and b), whereas multilayer WO₃ islands form at higher WO₃ loadings (Scheme 2c and d).⁹ As shown in Table 1 (run 5), WO₃(18.5)/TiO₂ has much larger surface coverage (θ = 89%) than WO₃(10.3)/TiO₂ (θ = 76%). The photocatalytic activity of WO₃(18.5)/TiO₂, however, is much lower than that of WO₃(10.3)/TiO₂. This suggests that, as described previously,⁹ the exposed TiO₂ surface behaves as the oxidation site, whereas the WO₃ surface is much less active for oxidation.

The higher activity of WO₃(x)/TiO₂ catalysts ($x \le 10.3$) than bare TiO₂ is because the photogenerated e⁻ on TiO₂ is transferred to the WO₃ layer and enhances charge separation between e⁻ and h⁺ pairs.⁹ The e⁻ transfer can be explained by the conduction band potentials of bulk TiO₂ and WO₃, although an accurate conduction band position of the WO₃ layer cannot be determined at present. As shown in Fig. 3, the conduction band potential of TiO₂ (-0.18 V *vs.* NHE) is more negative than that of WO₃ (+0.40 V *vs.* NHE).¹² This may result in the e⁻ transfer from TiO₂ to the WO₃ layer.¹³ If so, the e⁻ on the WO₃ conduction band would not be consumed by oneelectron reduction of O₂, because the reduction potential $(O_2 + e^- \rightarrow O_2^{\bullet-}, -0.13 \text{ V } vs. \text{ NHE})^{14}$ is more negative than the conduction band potential of WO₃ (+0.40 V *vs.* NHE).¹² The e⁻ is, however, consumed by multi-electron reduction of O₂ (O₂ + 2H⁺ + 2e⁻ \rightarrow H₂O₂, +0.68 V *vs.* NHE; O₂ + 4H⁺ + 4e⁻ \rightarrow 2H₂O, +1.23 V *vs.* NHE), as shown in Fig. 3.¹⁵

This mechanism is confirmed by the analysis of $O_2^{\bullet^-}$ and H_2O_2 formed during reaction of toluene. Fig. 4a shows the electron spin resonance (ESR) spectra obtained by photoirradiation of catalysts with toluene and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), a spin trapping reagent. Distinctive signals assigned to the DMPO- $O_2^{\bullet^-}$ spin adduct were observed.¹⁶ The signal intensity decreases with the WO₃ loadings (Fig. 4b), suggesting that the photoformed e^- is indeed not consumed

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Fig. 2 Time-dependent change in the amounts of (a) benzaldehyde and (b) CO₂ during the photoreaction of benzaldehyde in MeCN with TiO₂ or WO₃(*x*)/TiO₂ catalysts. Reaction conditions are as follows: MeCN (5 mL), benzaldehyde (50 μ mol), catalyst (5 mg), O₂ (1 atm), temperature (298 K), and λ > 300 nm.









Fig. 4 (a) ESR spectra of DMPO– $O_2^{\bullet-}$ spin adduct signals obtained by photoirradiation of MeCN solution containing toluene and DMPO with TiO₂ (x = 0) and WO₃(x)/TiO₂. (b) The relative intensity of the signals determined by double integration between 3460–3530 G, where the intensity obtained with TiO₂ (x = 0) was set as 1.



mainly by one-electron reduction of O₂. Fig. 5 shows the amount of H₂O₂ formed during reaction of toluene. The H₂O₂ amount increases with the WO₃ loadings, and WO₃(7.6)/TiO₂ and WO₃(10.3)/TiO₂ produce a very large amount of H₂O₂. The obtained H₂O₂ profile is consistent with the photooxidation activity of toluene (Table 1). In contrast, WO₃(18.5)/TiO₂ with higher WO₃ loading decreases the H₂O₂ formation, which is also consistent with the catalytic activity. This is because the surface coverage of the TiO₂ surface by WO₃ for the WO₃(18.5)/TiO₂ to a surface by WO₃ for the WO₃(18.5)/TiO₂ and Solar the surface to a surface sur

Fig. 5 Amount of H₂O₂ formed during photocatalytic oxidation of toluene in MeCN with respective catalysts. Reaction conditions: MeCN (5 mL), toluene (50 µmol), catalyst (5 mg), O₂ (1 atm), temperature (298 K), λ > 300 nm, and photoirradiation time (3 h and 24 h).

decrease in the exposed TiO_2 surface (decrease in the oxidation site) and, hence, decreases the photocatalytic activity. These findings indicate that, as shown in Fig. 3, the enhanced photocatalytic activity of WO_3/TiO_2 is due to the e^- transfer

from TiO_2 to the WO₃ layer; and appropriate coverage of the TiO_2 surface by WO₃ is important for high photocatalytic activity for toluene oxidation.

As shown in Fig. 5, the WO₃/TiO₂ catalysts produce H_2O_2 during photoirradiation by the reduction of O₂. The amounts of H_2O_2 formed by 4 h and 24 h photoreactions are similar, although the toluene conversion increases with photoirradiation time (Fig. 1). This is because, as reported,¹⁷ H_2O_2 is easily decomposed by UV irradiation. It is also noted that the H_2O_2 is not involved in the benzaldehyde formation. Photoirradiation of a MeCN (5 mL) solution with toluene (50 µmol) and H_2O_2 (10 µmol) in the presence of WO₃(10.3)/TiO₂ (5 mg) under an N_2 atmosphere (1 atm) scarcely produced benzaldehyde. This suggests that O₂ behaves as the oxidizing agent for photocatalytic oxidation of toluene to benzaldehyde.¹⁸

2.3 Mechanism for high aldehyde selectivity

The high benzaldehyde selectivity during the photooxidation of toluene on WO₃/TiO₂ is because the WO₃ loading decreases the amount of benzaldehyde adsorbed onto the TiO₂ surface and suppresses its decomposition. To clarify the adsorption properties of aldehyde onto the catalyst surface, adsorption experiments were carried out in MeCN. Each respective catalyst (5 mg) was added to MeCN (5 mL) containing different amounts of benzaldehyde (1.0–10.0 μ mol) and stirred at 298 K for 3 h in the dark. Fig. 6a shows the adsorption isotherm, where C_e is the equilibrium concentration of aldehyde in solution and Q is the amount of aldehyde adsorbed on the catalysts, respectively. All of the curves show Langmuir-type profiles, and the Q values of WO₃/TiO₂ are higher than those of bare TiO₂. Fig. 6b shows the



Fig. 6 (a) Adsorption isotherms and (b) the linear-transformed Langmuir plots of benzaldehyde, obtained by adsorption experiments in MeCN at 298 K for 3 h with TiO_2 and $WO_3(x)/TiO_2$.

first-order linear transform of the isotherm obtained by the following equation,¹⁹

$$\frac{C_{\rm e}}{Q} = \frac{1}{KQ_{\rm max}} + \frac{C_{\rm e}}{Q_{\rm max}} \tag{1}$$

where Q_{max} and *K* are the total number of adsorption sites on the catalysts and the adsorption equilibrium constant, respectively. Table 2 summarizes these values determined from the slope and intercept of Fig. 6b. The Q_{max} and *K* values of WO₃/ TiO₂ are larger than those of bare TiO₂ and become larger with the WO₃ loadings. This suggests that the WO₃ layer has higher adsorption affinity with benzaldehyde than the TiO₂ surface.

To clarify the adsorption property of benzaldehyde onto the exposed TiO₂ surface of WO₃/TiO₂, the number of adsorption sites on the exposed TiO₂ surface (Q_{TiO_2}) and the WO₃ surface (Q_{WO_3}) were determined. The Q_{TiO_2} values can be obtained from the Q_{max} value of bare TiO₂ (5.09 × 10⁻³ mmol g⁻¹), using the WO₃ loading (*x*) and the surface coverage (θ), as follows:

$$Q_{\text{TiO}_2} = 5.09 \times 10^{-3} \times \left(1 - \frac{x}{100}\right) \times \left(1 - \frac{\theta}{100}\right)$$
 (2)

The Q_{WO_2} values are therefore expressed as follows:

A

$$Q_{\rm WO_3} = Q_{\rm max} - Q_{\rm TiO_2} \tag{3}$$

As shown in Table 2, the Q_{TiO_2} values decrease with the WO₃ loadings, along with an increase in Q_{WO_3} . The percentage of benzaldehyde adsorbed onto the TiO₂ surface in the total amount of the adsorbed benzaldehyde is therefore expressed as follows:

Adsorption selectivity(%) =
$$\frac{Q_{\text{TiO}_2}}{Q_{\text{TiO}_2} + Q_{\text{WO}_3}} \times 100$$
 (4)

As shown in Table 2, the adsorption selectivity decreases with the WO₃ loadings. This suggests that the WO₃ loadings indeed decrease the amount of aldehyde adsorbed onto the TiO₂ surface. The amount of benzaldehyde adsorbed onto the exposed TiO₂ surface (Q_{TiO_2}) of WO₃(10.3)/TiO₂ is *ca.* 20% of that of bare TiO₂. As shown in Fig. 2, the amount of benzaldehyde decomposed on WO₃(10.3)/TiO₂ is *ca.* 20% of that on bare TiO₂. These results are well consistent. This indicates that the enhanced selectivity for benzaldehyde formation during toluene photooxidation on WO₃/TiO₂ (Table 1) is due to the decreased adsorption of aldehyde onto the TiO₂ surface.

It is well known that oxygen radicals such as $O_2^{\bullet^-}$ are often involved in the decomposition of organic substrates.^{1d,4d,15,20} On WO₃/TiO₂, $O_2^{\bullet^-}$ scarcely affects the benzaldehyde decomposition. As shown in Fig. 4b, the intensity of the DMPO- $O_2^{\bullet^-}$ spin adduct signal decreases with the WO₃ loadings due to the multielectron reduction of O_2 (Fig. 3). The signal intensity on WO₃(10.3)/TiO₂ is *ca.* 60% of that on bare TiO₂, meaning that a relatively large amount of $O_2^{\bullet^-}$ is still produced on WO₃(10.3)/ TiO₂. In contrast, as shown in Fig. 2, the amount of benzaldehyde decomposed on WO₃(10.3)/TiO₂ is *ca.* 20% of that on bare TiO₂. This is inconsistent with the decrease in the amount of $O_2^{\bullet^-}$ radical. This clearly suggests that the main factor suppressing benzaldehyde photodecomposition is not the amount of $O_2^{\bullet^-}$ but the adsorption of benzaldehyde onto the catalyst surface.

 Table 2
 Adsorption parameters for benzaldehyde on various catalysts^a

Catalyst	$Q_{\rm max}/{ m mmol}~{ m g}^{-1}$	<i>K</i> /L mmol ⁻¹	$Q_{\rm TiO_2}$ /mmol g ⁻¹	$Q_{\rm WO_3}/\rm mmol~g^{-1}$	Adsorption selectivity on TiO ₂ surface/%
TiO ₂	$5.09 imes10^{-3}$	1.21	$5.09 imes10^{-3}$		
$WO_{3}(3.4)/TiO_{2}$	$7.70 imes10^{-3}$	1.28	$3.24 imes10^{-3}$	$4.46 imes10^{-3}$	42
$WO_3(7.6)/TiO_2$	$8.95 imes10^{-3}$	1.96	$1.97 imes10^{-3}$	$6.98 imes10^{-3}$	22
$WO_{3}(10.3)/TiO_{2}$	$1.04 imes10^{-2}$	2.12	$1.00 imes10^{-3}$	$9.38 imes10^{-3}$	10
$WO_3(18.5)/TiO_2$	1.27×10^{-2}	2.15	4.56×10^{-4}	1.22×10^{-2}	4
^{<i>a</i>} Conditions: MeO	CN (5 mL), benzaldeh	yde (1.0–10.0 μmo	l), catalyst (5 mg), ten	nperature (298 K), and	l time (3 h).

Table 3 Photocatalytic oxidation of various alkyl-substituted aromatics on TiO₂ and WO₃(10.3)/TiO₂^a

Run	Substrate	Catalyst	$t_{\rm irr}{}^b/{\rm h}$	Conv. ^c /%	Product	Select. ^d /%	CO ₂ /µmol
1 2	Br	TiO ₂ WO ₃ (10.3)/TiO ₂	72 19	22 50	Br	32 59	48.1 6.1
3 4	CI	$\begin{array}{l} \mathrm{TiO_2} \\ \mathrm{WO_3(10.3)/TiO_2} \end{array}$	72 20	31 50	CI O	25 48	36.7 14.0
5^e 6^f		TiO_2 WO ₃ (10.3)/TiO ₂	60 12	50 50	0	21 53	62.1 4.9
7 8		$\begin{array}{l} \mathrm{TiO_2} \\ \mathrm{WO_3(10.3)/TiO_2} \end{array}$	72 32	50 50		52 78	65.6 16.7
9 10	Br	TiO ₂ WO ₃ (10.3)/TiO ₂	72 16	52 50	Br	36 54	47.9 3.8
$\frac{11^g}{12^h}$		TiO ₂ WO ₃ (10.3)/TiO ₂	60 12	49 50		45 63	43.7 9.0

^{*a*} Reaction conditions: MeCN (5 mL), substrate (50 μmol), catalyst (5 mg), O_2 (1 atm), temperature (298 K), and $\lambda > 300$ nm. ^{*b*} The photoirradiation time required for 50% substrate conversion. The maximum photoirradiation time was 72 h. ^{*c*} [Substrate converted]/[initial amount of substrate] × 100. ^{*d*} [Product formed]/[substrate converted] × 100. ^{*e*} 4-Methylbenzoic acid (6.0 μmol; 24% select.) was formed. ^{*f*} 4-Methylbenzoic acid (1.3 μmol; 5.4% select.) was formed. ^{*g*} 4-Ethylbenzaldehyde (6.0 μmol; 24% select.) was formed. ^{*h*} 4-Ethylbenzaldehyde (3.4 μmol; 14% select.) was formed.

2.4 Selective oxidation of alkyl-substituted aromatics

The WO₃/TiO₂ catalyst successfully promotes selective sidechain oxidation of several kinds of alkyl-substituted aromatics. Table 3 summarizes the results obtained with bare TiO₂ and WO₃(10.3)/TiO₂. Reactions of halogen-substituted toluenes on WO₃(10.3)/TiO₂ (runs 2 and 4) produce corresponding benzaldehydes with much higher activity and selectivity than those on bare TiO₂ (runs 1 and 3). Reaction of *p*-xylene on WO₃(10.3)/TiO₂ (run 6) produces 4-methylbenzaldehyde with 53% selectivity. As shown in runs 8, 10, and 12, reactions of substituted ethylbenzenes on WO₃(10.3)/TiO₂ produce corresponding acetophenones with much higher activity and selectivity than those on bare TiO₂ (runs 7, 9, and 11). These findings indicate that the WO₃/TiO₂ photocatalytic system is effective for selective side-chain oxidation of alkyl-substituted aromatics.

3. Conclusion

The WO₃/TiO₂ catalysts promote selective oxidation of toluene to benzaldehyde in MeCN with O₂ under photoirradiation ($\lambda > 300$ nm). The catalysts with *ca.* 8–10 wt% WO₃ exhibit high

oxidation activity and benzaldehyde selectivity. The high activity is due to the efficient transfer of e⁻ from the TiO₂ conduction band to the WO₃ layer, leading to enhanced charge separation between e^- and h^+ . The high aldehyde selectivity is due to the decreased area of exposed TiO₂ surface by the coating of WO3 species. This decreases the amount of aldehyde adsorbed onto the TiO₂ surface and suppresses photocatalytic decomposition of formed aldehyde. This system successfully promotes selective side-chain oxidation of several kinds of alkyl-substituted aromatics. The selectivity for toluene to benzaldehyde conversion (ca. 50%) is still insufficient for real application. The present system is, however, successfully carried out under milder reaction conditions (room temperature and atmospheric pressure). The system is therefore potential as one powerful method enabling selective side-chain oxidation in an economically- and environmentally-friendly way.

4. Experimental

4.1 General

All of the reagents were purchased from Wako, Tokyo Kasei, and Sigma-Aldrich and used as received. Japan Reference Catalyst JRC-TIO-4 TiO₂ (equivalent to Degussa P25) was kindly supplied by Catalysis Society of Japan. $WO_3(x)/TiO_2$ catalysts were prepared as follows:⁹ TiO₂ (1 g) was stirred vigorously in an ammonia solution (1 M, 50 mL) containing an appropriate amount of H₂WO₄ at 353 K. The obtained dry powders were calcined at 673 K for 2 h under O₂ flow (0.5 L min⁻¹), affording white powders of catalysts. WO₃ was purchased from Kojundo Chemical Laboratory Co. and used as a reference. Analytical procedures were described in our previous paper.⁹ H₂O₂ concentration was determined by titration with KMnO₄ (detection limit: 0.25 µmol).²¹

4.2 Photoreaction procedure

Each respective catalyst (5 mg) was suspended in MeCN (5 mL) containing the substrate within a Pyrex glass tube (ϕ 10 mm; capacity, 20 mL). The tube was sealed using a rubber septum cap. The catalyst was dispersed by ultrasonication for 5 min and O_2 was bubbled through the solution for 5 min. The solution was photoirradiated under magnetic stirring using a 2 kW Xe lamp (USHIO Inc.),²² and filtered through a Pyrex glass saturated with water to give light wavelength of $\lambda > 300$ nm. The light intensity at 300-400 nm was 2.2 mW cm⁻². After photoirradiation, the gas-phase product was analyzed by GC-TCD (Shimadzu; GC-14B). The catalyst was recovered by centrifugation and washed with MeCN (5 mL). The combined solution was analyzed by GC-FID (Shimadzu; GC-1700), where the substrate and product concentrations were determined using authentic samples. Identification of the products was performed by GC-MS (Shimadzu; GCMS-QP5050A).

4.3 ESR measurement

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 10.5 mW, where microwave power saturation of the signals does not occur.²³ The magnetic field was calibrated using a 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as standard. The measurement was carried out as follows:⁹ each catalyst (1.0 g L⁻¹) was suspended in MeCN containing toluene (10 mmol L⁻¹) and DMPO (100 mmol L⁻¹) and dispersed well by ultrasonication. The 100 µL of the suspension was introduced to a flat ESR cell [10 mm × 20 mm × 0.3 mm (path length)], and O₂ was bubbled through the solution for 1 min. The cell was placed on an ESR sample cavity and photoirradiated using a 500 W Xe lamp through a glass filter to give light wavelengths of λ > 300 nm at room temperature. After photoirradiation for 90 s, the irradiation was turned off, and the measurement was started immediately.

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