## Selective Photocatalytic Oxidation of Alcohols to Aldehydes in Water by TiO<sub>2</sub> Partially Coated with WO<sub>3</sub>

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**Abstract:** Semiconductor TiO<sub>2</sub> particles loaded with WO<sub>3</sub> (WO<sub>3</sub>/TiO<sub>2</sub>), synthesized by impregnation of tungstic acid followed by calcination, were used for photocatalytic oxidation of alcohols in water with molecular oxygen under irradiation at  $\lambda > 350$  nm. The WO<sub>3</sub>/TiO<sub>2</sub> catalysts promote selective oxidation of alcohols to aldehydes and show higher catalytic activity than pure TiO<sub>2</sub>. In particular, a catalyst loading 7.6 wt%  $WO_3$  led to higher aldehyde selectivity than previously reported photocatalytic systems. The high aldehyde selectivity arises because subsequent photocatalytic decomposition of the formed aldehyde is suppressed on the catalyst. The TiO<sub>2</sub> surface of the catalyst, which is

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active for oxidation, is partially coated by the WO<sub>3</sub> layer, which leads to a decrease in the amount of formed aldehyde adsorbed on the TiO<sub>2</sub> surface. This suppresses subsequent decomposition of the aldehyde on the TiO<sub>2</sub> surface and results in high aldehyde selectivity. The WO<sub>3</sub>/TiO<sub>2</sub> catalyst can selectively oxidize various aromatic alcohols and is reusable without loss of catalytic activity or selectivity.

### Introduction

Since the discovery of redox properties of photoirradiated titanium dioxide  $(TiO_2)$ ,<sup>[1]</sup> heterogeneous photocatalysis with  $TiO_2$  has mainly been employed for the decomposition of harmful organic compounds in air and water, promoting mineralization of these compounds into  $CO_2$  and  $H_2O$ .<sup>[2]</sup> Application of  $TiO_2$  photocatalysis for organic synthesis has also attracted much attention. Several  $TiO_2$ -based photocatalytic systems have been proposed so far;<sup>[3]</sup> however, many of these systems need to be performed either in organic solvents or in the gas phase.<sup>[4]</sup> Water is a desirable solvent for chemical reactions, because of environmental concerns, safety, and cost, and organic syntheses in water is currently the focus of much attention.<sup>[5]</sup> There are, however, only a few reports of selective photocatalytic organic transforma-

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tions in water, such as hydrocarbon oxidation,<sup>[6]</sup> aromatic hydroxylation,<sup>[7]</sup> naphthalene oxygenation,<sup>[8]</sup> heterocycle functionalization,<sup>[9]</sup> and cyclization of amino acids.<sup>[10]</sup> In most cases, photocatalytic reactions on TiO<sub>2</sub> in water proceed through the following steps:<sup>[11]</sup> 1) Generation of electron (e<sup>-</sup>) and positive hole (h<sup>+</sup>) pairs by absorption of supra-band gap photons; and 2) oxidation of substrates by h<sup>+</sup> or the hydroxyl radicals ('OH) formed by the reaction of h<sup>+</sup> with surface –OH groups or adsorbed H<sub>2</sub>O molecules. The oxidation step is, however, nonselective and usually promotes further oxidation of substrate. Selective photocatalytic transformation in water therefore requires selective promotion of the substrate reaction while suppressing the product reaction.<sup>[12]</sup>

Selective oxidation of alcohols to aldehydes is one of the most important functional group transformations in organic synthesis.<sup>[13]</sup> Photocatalytic reactions with TiO<sub>2</sub>-based catalysts successfully promote selective alcohol oxidation when using organic solvents.<sup>[14]</sup> Selective photocatalytic oxidation in water is, however, difficult because the formed aldehyde is decomposed by sequential photocatalytic reactions on the TiO<sub>2</sub> surface.<sup>[15]</sup> The highest aldehyde selectivity in water has been achieved by the groups of Augugliaro and Palmisano,<sup>[16]</sup> using low-crystalline TiO<sub>2</sub> particles that are simply prepared by hydrolysis of TiCl<sub>4</sub> in water followed by aging of the resulting gel. The aldehyde selectivity in the reaction of benzyl alcohol, a typical aromatic alcohol, is only 42% at 50% alcohol conversion, although the reaction of 4-methoxybenzyl alcohol produces the corresponding aldehyde with particularly high selectivity (72-74% at 50% alcohol conversion). In addition, the catalytic activity of the catalysts is much lower than that of crystalline TiO<sub>2</sub>.

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*(x* 

(wt%) =

**Results and Discussion** 

**Catalyst preparation**: Five kinds of  $WO_3(x)/TiO_2$  catalysts

 $WO_3/(WO_3+TiO_2) \times 100$ ; x=1.4, 3.4, 7.6, 10.3, 18.5) were

synthesized by impregnation of tungstic acid (H<sub>2</sub>WO<sub>4</sub>) onto

the  $TiO_2$  particles followed by calcination according to a literature procedure<sup>[21]</sup> (see Experimental Section). Japan Ref-

erence Catalyst JRC-TiO-4 TiO<sub>2</sub> particles (equivalent to De-

gussa P25; anatase/rutile=80:20) and the required amount

of H<sub>2</sub>WO<sub>4</sub> were stirred in an ammonia solution at 353 K and

calcined at 673 K under  $O_2$ , affording  $WO_3(x)/TiO_2$  catalysts

as white powders. The properties of the catalysts are sum-

marized in Table 1. Figure 1 shows the diffuse reflectance

loadings

WO<sub>3</sub>

The purpose of the present work was the development of  $TiO_2$  photocatalytic systems that promote selective oxidation of alcohols to aldehydes in water, while maintaining high catalytic activity. It is known that the photocatalytic reactivity of organic compounds depends strongly on the extent of adsorption onto the catalyst surface;<sup>[17]</sup> stronger adsorption usually promotes reactivity enhancement. This implies that one of the possible ways to enhance aldehyde selectivity is the suppression of aldehyde adsorption onto the TiO<sub>2</sub> surface. The easiest way to achieve this is to coat the TiO<sub>2</sub> surface by metal oxide species; a different metal oxide layer, if created on TiO<sub>2</sub> particles, would lead to a decrease in the amount of aldehyde adsorbed on the TiO<sub>2</sub> surface and suppress sequential photocatalytic decomposition of aldehydes.

Several TiO<sub>2</sub> particles coated by metal oxide species such as SiO<sub>2</sub>,<sup>[18]</sup> V<sub>2</sub>O<sub>5</sub>,<sup>[19]</sup> and MoO<sub>3</sub>,<sup>[20]</sup> have been synthesized. In particular, the photocatalytic activity of TiO<sub>2</sub> particles coated with  $WO_3$  ( $WO_3/TiO_2$ ) has been studied extensively for their ability to mediate decomposition of chloroaromatics in water with O2.[21] The WO3/ TiO<sub>2</sub> catalysts show higher activity than pure TiO<sub>2</sub> even though the area of the available TiO<sub>2</sub> surface is reduced by the WO<sub>3</sub> coating. This is because the charge separation between e<sup>-</sup> and h<sup>+</sup> is facilitated by the transfer of e- photoformed on the TiO<sub>2</sub> particles to the surface WO3 species.[22]

In the present work, the  $WO_3/TiO_2$  catalysts were employed for photocatalytic oxidation of alcohols in water. We expected that the  $WO_3$  coating would lead to a decrease in the amount of aldehyde adsorbed

Table 1. Properties of catalysts and the results of photocatalytic oxidation of benzyl alcohol in water.[a]

different

with

	Catalyst	$S_{\rm BET} \ [m^2 g^{-1}]^{[b]}$	$d_{\mathrm{p}}$ [nm] <sup>[c]</sup>	$E_{ m bg} [ m eV]^{[ m d]}$	θ [%] <sup>[e]</sup>	$t_{\rm irr}$ $[h]^{[f]}$	Benzaldehyde select. [%] <sup>[g]</sup>	CO <sub>2</sub> [µmol]
1 <sup>[h]</sup>	TiO <sub>2</sub>	54.0	23.7	3.13	0	9.0	13	121.5
2	WO <sub>3</sub> (1.4)/TiO <sub>2</sub>	56.5	23.8	3.06	15	5.5	28	60.2
3	WO <sub>3</sub> (3.4)/TiO <sub>2</sub>	58.2	24.0	3.06	34	3.3	47	12.3
4 <sup>[i]</sup>	WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	53.1	24.1	3.02	58	5.0	56	6.7
5	WO <sub>3</sub> (10.3)/TiO <sub>2</sub>	49.7	25.0	3.02	76	5.7	53	9.1
6	WO <sub>3</sub> (18.5)/TiO <sub>2</sub>	44.4	27.2	3.00	89	6.0	55	7.7
7 <sup>[j]</sup>	$WO_3(7.6 \text{ wt \%}) + TiO_2$					9.5	28	63.7
8	WO <sub>3</sub>	3.0	127	2.80		$24.0^{[k]}$	61	4.8
9 <sup>[1]</sup>	WO <sub>3</sub> (7.6)/TiO <sub>2</sub>					5.0	55	6.2
10 <sup>[m]</sup>	WO <sub>3</sub> (7.6)/TiO <sub>2</sub>					5.0	54	7.4

[a] Reagents and conditions: benzyl alcohol (0.1 mmol), water (5 mL), catalyst (5 mg), O<sub>2</sub> (1 atm), 298 K,  $\lambda > 350$  nm. [b] BET surface area. [c] Particle size of catalysts determined by dynamic light scattering analysis. [d] Bandgap energies determined by a plot of the Kubelka–Munk function versus the energy of light absorbed (Figure 1). [e] Surface coverage of TiO<sub>2</sub> by WO<sub>3</sub>, determined by FTIR analysis (Figure 5). [f] The photoirradiation time required for 50% alcohol conversion. [g] Calculated as [benzaldehyde formed]/[benzyl alcohol converted] × 100. [h] (*o*-, *m*-, *p*-)Hydroxybenzyl alcohols (trace), (*o*-, *m*-, *p*-)hydroxybenzaldehydes (1.9 µmol), and benzoic acid (20.1 µmol) were detected by GC analysis.<sup>[16a]</sup> The carbon balance {=  $100 \times$  [benzyl alcohol+benzaldehyde+(*o*-, *m*-, *p*-)hydroxybenzyl alcohols+(*o*-, *m*-, *p*-)hydroxybenzaldehydes+benzoic acid +(CO<sub>2</sub> formed)/7]/[initial amount of benzyl alcohol]} was determined to be 92%, in which nonvolatile or thermally-degradable ring-opening products such as carboxylic acids are probably evolved as unidentified products. [i] (*o*-, *m*-, *p*-)Hydroxybenzyl alcohols (0.9 µmol), and benzoic acid (7.2 µmol) were detected by GC analysis. The carbon balance was 80%. [j] TiO<sub>2</sub> (92.4 mg) and WO<sub>3</sub> (7.6 mg) were mixed thoroughly and 5 mg of the mixture was used for reaction. [k] The benzyl alcohol conversion was only 8% even after photoreaction for 24 h. [l] The 1st reuse of the catalyst (entry 4) after washing with MeCN. [m] 2nd reuse.

onto the TiO<sub>2</sub> surface and suppress sequential decomposition, while retaining high catalytic activity. We clarified that the WO<sub>3</sub>/TiO<sub>2</sub> system successfully promotes the selective production of aldehydes with higher catalytic activity than pure TiO<sub>2</sub>. The aldehyde selectivity in benzyl alcohol oxidation is 56% at 50% alcohol conversion, which is higher than obtained in previously reported photocatalytic systems. Surface analysis of the catalysts based on the Fourier-transformed infrared (FTIR) spectroscopy, X-ray absorption near-edge structure (XANES) spectroscopy, and X-ray photoelectron spectroscopy (XPS) indicate that the high aldehyde selectivity is achieved by partial coverage of the TiO<sub>2</sub> by WO<sub>3</sub>. The adsorption of photoformed aldehydes onto the TiO<sub>2</sub> surface is suppressed by the WO<sub>3</sub> coating and the sequential reaction is suppressed significantly.



Figure 1. Diffuse reflectance UV/Vis spectra of respective catalysts: a) TiO<sub>2</sub>, b) WO<sub>3</sub>(1.4)/TiO<sub>2</sub>, c) WO<sub>3</sub>(3.4)/TiO<sub>2</sub>, d) WO<sub>3</sub>(7.6)/TiO<sub>2</sub>, e) WO<sub>3</sub>(10.3)/TiO<sub>2</sub>, f) WO<sub>3</sub>(18.5)/TiO<sub>2</sub>, and g) WO<sub>3</sub>.

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UV/Vis spectra of the catalysts. It can be seen that an increase in WO<sub>3</sub> loading leads to a red shift of the absorptionedge of the catalysts, suggesting that WO<sub>3</sub> is indeed loaded on the TiO<sub>2</sub> surface.<sup>[21]</sup>

Effect of WO<sub>3</sub> loading on photocatalysis: The effect of WO<sub>3</sub> loadings on selective alcohol oxidation in water was investigated by studying the photoreaction of benzyl alcohol. The reaction was performed by photoirradiation ( $\lambda > 350$  nm) of water (5 mL) containing catalyst (5 mg) and benzyl alcohol (100 µmol) under an O<sub>2</sub> atmosphere (1 atm) at 298 K. Table 1 summarizes the photoirradiation time ( $t_{irr}$ ) required for 50% benzyl alcohol conversion and the benzaldehyde selectivity at this conversion. Pure TiO<sub>2</sub> (Table 1, entry 1) showed very low aldehyde selectivity (13%), whereas the WO<sub>3</sub>/TiO<sub>2</sub> catalysts (Table 1, entries 2–6) showed much higher selectivity. The selectivity increased with WO<sub>3</sub> loading, and the catalysts with  $\geq 7.6$  wt% WO<sub>3</sub> show > 53% selectivity, which is higher than the previously reported photocatalytic systems.<sup>[16]</sup>

During photocatalytic reaction with TiO<sub>2</sub> in water, the aldehyde formed is sequentially decomposed to CO<sub>2</sub> and H<sub>2</sub>O.<sup>[15,16]</sup> As shown in Table 1 (entry 1), the amount of CO<sub>2</sub> formed during the reaction with pure TiO<sub>2</sub> was 122 µmol at 50% benzyl alcohol conversion (50 µmol benzyl alcohol reacted). In contrast, the WO<sub>3</sub>/TiO<sub>2</sub> catalysts with  $\geq$ 7.6 wt% WO<sub>3</sub> (entries 4–6) produced much less CO<sub>2</sub> (less than 10 µmol), suggesting that sequential reaction of aldehyde is significantly suppressed. Figure 2 shows the time-dependent change in the amounts of substrate and product, and the benzaldehyde selectivity during the reaction of benzyl alcohol with TiO<sub>2</sub> or WO<sub>3</sub>(7.6)/TiO<sub>2</sub>. In the case of TiO<sub>2</sub> (Figure 2 a), the aldehyde selectivity decreased with photoirradiation time, along with an increase in the amount of  $CO_2$ , indicating that subsequent reaction of the aldehyde results in decreased aldehyde selectivity. In contrast, with WO<sub>3</sub>-(7.6)/TiO<sub>2</sub> (Figure 2b), the amount of CO<sub>2</sub> scarcely increases with time, and the aldehyde selectivity is almost unchanged (ca. 55%).

To further clarify the reactivity of the aldehyde on  $TiO_2$ and  $WO_3/TiO_2$  catalysts, benzaldehyde was used as the starting material in the photocatalytic reactions. As shown in Figure 3 a, the aldehyde conversions on  $WO_3/TiO_2$  are much lower than that on  $TiO_2$ , and catalysts with higher  $WO_3$ loadings suppressed the reaction more significantly. This suggests that  $WO_3$  loading suppresses the subsequent decomposition of the formed aldehydes and results in high aldehyde selectivity. As shown in Figure 3b, the amount of  $CO_2$  formed during the reaction showed a similar trend. This indicates that decomposition of the aldehyde initiates degradation of the aromatic ring (complete decomposition to  $CO_2$ ).

The WO<sub>3</sub>/TiO<sub>2</sub> catalysts show higher catalytic activity for alcohol oxidation than pure TiO<sub>2</sub>. As shown in Table 1, increased WO<sub>3</sub> loadings shorten the photoirradiation time required for 50% benzyl alcohol conversion. Among the catalysts used, WO<sub>3</sub>(3.4)/TiO<sub>2</sub> and WO<sub>3</sub>(7.6)/TiO<sub>2</sub> showed better activity; these catalysts attained 50% alcohol conversion within 3.3 and 5.0 h photoirradiation, respectively, while pure TiO<sub>2</sub> required 9.0 h irradiation. Further WO<sub>3</sub> loadings ( $\geq$ 10.3 wt%), however, decreased the catalytic activity. The aldehyde selectivity and the catalytic activity data suggest that WO<sub>3</sub>(7.6)/TiO<sub>2</sub> shows the best catalytic performance. As shown in Table 1 (entry 7), the physical mixture of TiO<sub>2</sub> and 7.6 wt% WO<sub>3</sub> shows much lower aldehyde selectivity and catalytic activity than WO<sub>3</sub>(7.6)/TiO<sub>2</sub> (entry 4). This sug-

gests that the WO<sub>3</sub> loading on the TiO<sub>2</sub> surface is essential for both high aldehyde selectivity and catalytic activity.

Surface structure of the catalysts: The TiO<sub>2</sub> surface of WO<sub>3</sub>- $(7.6)/\text{TiO}_2$  is partially coated by a WO<sub>3</sub> layer. The impregnation of H<sub>2</sub>WO<sub>4</sub> on the TiO<sub>2</sub> surface followed by calcination leads to the formation of a WO<sub>3</sub> layer consisting of branched chains of pentahedral WO<sub>5</sub> units and terminal tetrahedral WO<sub>4</sub> units,<sup>[23a]</sup> schematically shown in as Scheme 1. Figure 4 shows the W L<sub>1</sub>- and L<sub>3</sub>-edge XANES spectra of WO<sub>3</sub>/TiO<sub>2</sub> catalysts; the spectra for Na<sub>2</sub>WO<sub>4</sub> and WO<sub>3</sub> powders are also shown as reference spectra for the WO<sub>4</sub> and WO<sub>5</sub> units, respectively. In the W L<sub>1</sub>-edge spectra (Fig-

a) b) 60 60 Select. / % Select. / % 30 30 0 0 5 3 ģ 2 4 6 3 ò Time / h Time / h 20 120 20 120 formed / µmol formed / µmol C / mM C / mM 10 10 <sup>S</sup>CO ŝ 0 0 0 3 9 3 5 6 2 Time / h Time / h

Figure 2. Time-dependent change in (top) the benzaldehyde selectivity and (bottom) the concentrations of (open circle) benzyl alcohol and (closed circle) benzaldehyde and (triangle) the amount of  $CO_2$  formed, during photoreaction of benzyl alcohol in water with a) TiO<sub>2</sub> and b) WO<sub>3</sub>(7.6)/TiO<sub>2</sub> catalysts. Reaction conditions are identical to those in Table 1.

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Figure 3. Time-dependent changes in a) the benzaldehyde conversion and b) the amount of CO<sub>2</sub> formed during the reaction of benzaldehyde in water with TiO<sub>2</sub> or WO<sub>3</sub>(*x*)/TiO<sub>2</sub>. Reagents and conditions: water (5 mL), benzaldehyde (0.5  $\mu$ mol), catalyst (5 mg), O<sub>2</sub> (1 atm), 298 K,  $\lambda$  > 350 nm.



Scheme 1. Proposed surface structure of  $WO_3(x)/TiO_2$  catalysts.

ure 4A), Na<sub>2</sub>WO<sub>4</sub> (line a) shows an intense pre-edge peak at approximately 12102.5 eV, which was assigned to the tetrahedral WO<sub>4</sub> units.<sup>[23]</sup> In contrast, WO<sub>3</sub> particles (line e) show a broad pre-edge peak that can be assigned to the pentahedral WO<sub>5</sub> units.<sup>[23a]</sup> As shown by the lines b–d, the peak intensity of WO<sub>3</sub>/TiO<sub>2</sub> becomes broader with increasing WO<sub>3</sub> loadings, indicating that the catalysts with higher WO<sub>3</sub> loadings contain larger numbers of WO<sub>5</sub> units than WO<sub>4</sub> units. This result was also confirmed by the W L<sub>3</sub>-edge spectra



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Figure 4. Normalized A) W L<sub>1</sub>-edge and B) W L<sub>3</sub>-edge XANES spectra of a)  $Na_2WO_4$ , b)  $WO_3(3.4)/TiO_2$ , c)  $WO_3(7.6)/TiO_2$ , d)  $WO_3(18.5)/TiO_2$ , and e)  $WO_3$ .

(Figure 4B). Na<sub>2</sub>WO<sub>4</sub> (line a) shows a sharp absorption at approximately 10210 eV, which can be assigned to tetrahedral WO<sub>4</sub> units.<sup>[23]</sup> In contrast, WO<sub>3</sub> particles (line e) show a broad absorption due to the small number of WO<sub>4</sub> units. The absorption of WO<sub>3</sub>/TiO<sub>2</sub> catalysts (lines b–d) becomes broader with increasing WO<sub>3</sub> loading. This again suggests that the catalysts with higher WO<sub>3</sub> loadings contain larger numbers of WO<sub>5</sub> units than WO<sub>4</sub> units. These data indicate that, as shown in Scheme 1, the catalysts with lower WO<sub>3</sub> loading contain narrow WO<sub>3</sub> islands on the TiO<sub>2</sub> surface, and increases in the WO<sub>3</sub> loading leads to a coalescence of these islands (producing larger WO<sub>3</sub> islands). These data suggest that the TiO<sub>2</sub> surface of the catalyst is covered by a WO<sub>3</sub> layer and that the coverage increases with WO<sub>3</sub> loading.

The percent coverage of the TiO<sub>2</sub> surface by WO<sub>3</sub>, given as  $\theta$ , can roughly be determined by diffuse reflectance FTIR analysis. As shown in Figure 5, the strong absorption at 3691 cm<sup>-1</sup>, assigned to the Ti–OH species on the TiO<sub>2</sub> surface,<sup>[24]</sup> decreases with increasing WO<sub>3</sub> loading due to the adhesion of WO<sub>3</sub>. As shown in the inset of Figure 5, the  $\theta$ value determined from the absorption decrease increases with increasing WO<sub>3</sub> loading; WO<sub>3</sub>(7.6)/TiO<sub>2</sub> has 58% coverage and WO<sub>3</sub>(18.5)/TiO<sub>2</sub> shows much higher coverage (89%).

The catalyst surface was further characterized by TEM and XPS analysis. As shown in Figure 6a and Figure 6b, catalysts with  $\leq$  7.6 wt % WO<sub>3</sub> have a transparent surface, indicating that monolayer WO<sub>3</sub> forms on the TiO<sub>2</sub> surface.<sup>[25]</sup> In contrast, WO<sub>3</sub>(18.5)/TiO<sub>2</sub> shows dark flecks (Figure 6c), sug-



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Figure 5. Diffuse reflectance FTIR spectra of  $TiO_2$  and  $WO_3(x)/TiO_2$ . (Inset) Percent coverage ( $\theta$ ) of  $TiO_2$  surface by  $WO_3$ .



Figure 6. TEM images of catalysts: a) WO\_3(3.4)/TiO\_2, b) WO\_3(7.6)/TiO\_2, and c) WO\_3(18.5)/TiO\_2.

gesting that the adhesion of larger amounts of WO<sub>3</sub> produces multilayered WO<sub>3</sub>. XPS analysis also confirms this. As shown in Figure 7, the intensity ratio of the W 4d and Ti 2p signals  $(I_{W4d}/I_{Ti2p})$  increases linearly with increasing WO<sub>3</sub> loading at  $\leq$  7.6 wt% WO<sub>3</sub>, but becomes gentler at



Figure 7. Relationship between the intensity ratio of W 4d and Ti 2p signals  $(I_{W4d}/I_{T12p})$  and the WO<sub>3</sub> loading, *x*, for WO<sub>3</sub>(*x*)/TiO<sub>2</sub> catalysts, obtained by XPS measurements.

>7.6 wt % WO<sub>3</sub>. This indicates that monolayer WO<sub>3</sub> islands form at  $\leq$ 7.6 wt % WO<sub>3</sub> (Scheme 1b and c), and that multilayer WO<sub>3</sub> islands form at higher WO<sub>3</sub> loadings (Scheme 1d).<sup>[26]</sup> These data suggest that WO<sub>3</sub>(7.6)/TiO<sub>2</sub> catalysts possessing high catalytic activity and aldehyde selectivity have surface structures consisting of an exposed TiO<sub>2</sub> surface (42 %) and a monolayer WO<sub>3</sub> surface (58 %).

**Mechanism for high catalytic activity**: Photoirradiation of  $WO_3/TiO_2$  catalysts promotes excitation of both  $TiO_2$  and  $WO_3$ . The  $WO_3$  surface is, however, inactive for oxidation, and the exposed  $TiO_2$  surface behaves as the oxidation site. The inactivity of the  $WO_3$  layer for oxidation can be explained by the valence band potentials of  $TiO_2$  and  $WO_3$ . As shown in Scheme 2, the valence band potential of  $WO_3$  (+3.20 V vs. NHE) is more positive than that of  $TiO_2$  (+2.95 V vs. NHE),<sup>[27]</sup> indicating that, in the  $WO_3/TiO_2$  system, h<sup>+</sup>, even if formed on the photoexcited  $WO_3$ , is transferred exothermically to  $TiO_2$ .<sup>[22a]</sup> The valence band potentials of  $WO_3$  layer on the  $WO_3/TiO_2$  catalyst is not an oxidation site, leaving the exposed  $TiO_2$  surface as the functioning oxidation site.

As shown in Table 1, the WO<sub>3</sub>/TiO<sub>2</sub> catalysts show much higher activity for alcohol oxidation than pure TiO<sub>2</sub>. This is because the photogenerated  $e^-$  on TiO<sub>2</sub> is transferred to the WO<sub>3</sub> layer, which promotes efficient charge separation between the  $e^-$  and  $h^+$  pairs.<sup>[22]</sup> As shown in Scheme 2, the



Scheme 2. Valence and conduction band potentials for TiO<sub>2</sub> and WO<sub>3</sub>.

conduction band potential of  $TiO_2$  (-0.18 V vs. NHE) is more negative than that of WO<sub>3</sub> (+0.40 V vs. NHE),<sup>[27]</sup> suggesting that the e<sup>-</sup> formed on TiO<sub>2</sub> is transferred exothermically to the WO<sub>3</sub> layer. The  $e^-$  on the conduction band of the WO<sub>3</sub> layer is not consumed by one-electron reduction of  $O_2$  because the reduction potential ( $O_2 + e^- \rightarrow O_2^{--}$ , -0.13 V vs. NHE)<sup>[28]</sup> is more negative than the conduction band potential of WO<sub>3</sub> (Scheme 2). The  $e^-$  is consumed by multielectron reduction of O2, which occurs exothermically because the reduction potentials  $(O_2+2H^++2e^-\rightarrow H_2O_2)$ , +0.68 V vs. NHE;  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O_1$ , +1.23 V vs. NHE)<sup>[29]</sup> are more positive than the conduction band potential of WO<sub>3</sub> (Scheme 2). This mechanism is supported by the analysis of  $O_2^{-}$  and  $H_2O_2$  formed during reaction of benzyl alcohol. Figure 8a shows the electron spin resonance (ESR) spectra obtained upon photoirradiation of a benzyl alcohol solution with respective catalysts in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO), a spin-trapping reagent. All of the systems show distinctive signals that can be assigned to the DMPO-O<sub>2</sub><sup>-</sup> spin adduct ( $a_{\rm N} = 12.9 \,{\rm G}$ ;  $a_{\rm H}^{\beta} =$ 10.4 G;  $a_{\rm H}^{\gamma} = 1.4$  G; g = 2.0059;<sup>[30]</sup> however, the signal intensity decreases with increasing WO<sub>3</sub> loading (Figure 8b). This indicates that, on WO<sub>3</sub>/TiO<sub>2</sub>, the e<sup>-</sup> on the conduction band of the WO<sub>3</sub> layer is not typically consumed by one-electron reduction of  $O_2$ . Figure 9 shows the amount of  $H_2O_2$  formed during the reaction. The amount of H<sub>2</sub>O<sub>2</sub> increases with increasing WO<sub>3</sub> loading, and catalysts with 3.4-7.6 wt % WO<sub>3</sub> produce larger amounts of H<sub>2</sub>O<sub>2</sub>. The obtained profile of  $H_2O_2$  generation is consistent with the oxidation activity of benzyl alcohol (Table 1). These data indicate that the e<sup>-</sup> on the conduction band of WO<sub>3</sub> is consumed by multi-electron reduction of O<sub>2</sub>.

It is known that commercially-available WO<sub>3</sub> particles do not promote multi-electron reduction of O<sub>2</sub> well,<sup>[29]</sup> as also shown in Figure 9; however, the present WO<sub>3</sub>/TiO<sub>2</sub> catalysts do promote such a reduction process. The promotion of multi-electron reduction on WO<sub>3</sub>/TiO<sub>2</sub> is probably due to the large surface area of the WO<sub>3</sub> layer. As shown in



Figure 8. a) ESR spectra of DMPO- $O_2^{-}$  spin adduct signals obtained by photoirradiation of a benzyl alcohol solution containing DMPO with TiO<sub>2</sub> (x=0) and WO<sub>3</sub>(x)/TiO<sub>2</sub> (see Experimental section). b) The relative intensity obtained by double integration of the spin adduct signals between 3405–3455 G, for which the intensity obtained with TiO<sub>2</sub> (x=0) was set as 1.

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Figure 9. The amount of  $H_2O_2$  formed during photocatalytic oxidation of benzyl alcohol in water with respective catalysts.  $H_2O_2$  concentration was determined by titration with KMnO<sub>4</sub>. Reagents and conditions: water (5 mL), benzyl alcohol (0.1 mmol), catalyst (5 mg),  $O_2$  (1 atm), 298 K,  $\lambda >$ 350 nm, irradiation time: 3 h.

Table 1, the surface area of  $TiO_2$  is 54.0 m<sup>2</sup>g<sup>-1</sup>, whereas that of commercial WO<sub>3</sub> is only  $3.0 \text{ m}^2\text{g}^{-1}$ , suggesting that the surface area of the WO<sub>3</sub> layer on TiO<sub>2</sub> is much larger. Several literature reports have shown that WO<sub>3</sub> materials with large surface areas show higher catalytic activity than commercial WO<sub>3</sub> particles.<sup>[31]</sup> The larger surface area of the WO<sub>3</sub> layer on TiO<sub>2</sub> probably promotes efficient multi-electron reduction of  $O_2$ . As shown in Table 1 (entries 5 and 6), catalysts with higher WO<sub>3</sub> loadings (>10.3 wt%) show decreased catalytic activity, which is consistent with the amount of H<sub>2</sub>O<sub>2</sub> formed (Figure 9). Coverage of the TiO<sub>2</sub> surface by the WO<sub>3</sub> layer increases with increasing WO<sub>3</sub> loading, and catalysts with > 10.3 wt % WO<sub>3</sub> have very large coverage ( $\geq$ 76%). This leads to a decrease in the amount of exposed TiO<sub>2</sub> surface (decrease in the oxidation site) and, hence, results in decreased catalytic activity. Choosing a catalyst with an appropriate WO3 coverage is therefore important for high catalytic activity.

Mechanism for high aldehyde selectivity: The high aldehyde selectivity of WO<sub>3</sub>/TiO<sub>2</sub> catalysts arises because the WO<sub>3</sub> loading leads to a decrease in the area of exposed TiO<sub>2</sub> surface. This leads to a decrease in the amount of aldehyde adsorbed onto the TiO<sub>2</sub> surface and suppresses sequential decomposition, as schematically shown in Scheme 3. Adsorption experiments were carried out to clarify the adsorption properties of aldehyde onto the catalyst surface. The respective catalyst (5 mg) was added to water (5 mL) containing different amounts of benzaldehyde  $(0.01-1.0 \text{ mmol } \text{L}^{-1})$  and stirred at 298 K for 3 h. Figure 10 A shows the adsorption isotherm, in which  $C_{\rm e}$  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 for WO<sub>3</sub>/TiO<sub>2</sub> (bf) are higher than that for pure  $TiO_2$  (Figure 10 Aa). Figure 10B shows the first-order linear transform of the isotherm obtained by applying Equation (1),<sup>[32]</sup> in which  $Q_{\text{max}}$ and K are the total number of adsorption sites on the catalysts and the adsorption equilibrium constant, respectively.

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Scheme 3. Schematic representation of surface reactions on a) TiO2 and b) WO<sub>3</sub>/TiO<sub>2</sub> catalysts.



Figure 10. A) Adsorption isotherms and B) the linear-transformed Langmuir plots of benzaldehyde obtained by adsorption experiments in water at 298 K for 3 h with various catalysts: a) TiO<sub>2</sub>, b) WO<sub>3</sub>(1.4)/TiO<sub>2</sub>, c) WO<sub>3</sub>(3.4)/TiO<sub>2</sub>, d) WO<sub>3</sub>(7.6)/TiO<sub>2</sub>, e) WO<sub>3</sub>(10.3)/TiO<sub>2</sub>, and f) WO<sub>3</sub>(18.5)/TiO<sub>2</sub>.

larger than that for pure TiO<sub>2</sub> and become larger with increasing WO<sub>3</sub> loading. This suggests that the WO<sub>3</sub> layer has higher adsorption affinity with benzaldehyde than the TiO<sub>2</sub> surface.

To clarify the adsorption profile of aldehydes on the exposed TiO<sub>2</sub> surface of WO<sub>3</sub>/TiO<sub>2</sub>, the number of adsorption sites on the exposed TiO<sub>2</sub> surface  $(Q_{\text{TiO}_2})$  and the WO<sub>3</sub> surface  $(Q_{\rm WO_3})$  were determined. The  $Q_{\rm TiO_2}$  values were obtained from the  $Q_{\text{max}}$  value for pure TiO<sub>2</sub> (4.33×  $10^{-2} \text{ mmol g}^{-1}$ ), using the WO<sub>3</sub> loading (x) and the surface coverage ( $\theta$ ) in Equation (2) and the  $Q_{WO_3}$  values for WO<sub>3</sub>/  $TiO_2$  can, therefore, be expressed by Equation (3)

$$Q_{\text{TiO}_2} = 4.33 \times 10^{-2} \times (1 - x/100) \times (1 - \theta/100)$$
(2)

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

As summarized in Table 2, the  $Q_{\text{TiO}_2}$  values decrease with increasing WO<sub>3</sub> loading, along with an increase in  $Q_{WO_3}$ . The percentage of aldehyde adsorbed on the TiO<sub>2</sub> surface in the total amount of the adsorbed aldehyde, defined as  $Q_{\rm TiO}$ /  $(Q_{\text{TiO}_2}+Q_{\text{WO}_3})$ , decreases with increasing WO<sub>3</sub> loading. This suggests that the WO<sub>3</sub> loading leads to a decrease in the aldehyde adsorption on the exposed TiO<sub>2</sub> surface, at the same time as increasing the adsorption onto the WO<sub>3</sub> surface, which is inactive for aldehyde decomposition. This suppresses sequential decomposition of the aldehyde on the TiO<sub>2</sub> surface. As shown in Figure 3, photodecomposition of benzaldehyde is suppressed with increasing WO<sub>3</sub> loading, which is consistent with the adsorption results. These data indicate that the increased aldehyde selectivity during photocatalytic alcohol oxidation (Table 1) is due to decreased aldehyde adsorption on the TiO<sub>2</sub> surface.

Selective oxidation of other alcohols: The present photocatalytic system with  $WO_3(7.6)/TiO_2$  is capable of selective oxidation of other benzylic alcohols (Table 3). As shown in entry 1, the aldehyde selectivity in the reaction of 4-methoxybenzyl alcohol with pure TiO<sub>2</sub> is only 23% at 50% alcohol conversion. In contrast, WO<sub>3</sub>(7.6)/TiO<sub>2</sub> produces the aldehyde with >54 % selectivity (Table 3, entries 2 and 3). In addition, WO<sub>3</sub>(7.6)/TiO<sub>2</sub> successfully oxidizes a range of substituted benzylic alcohols to the corresponding aldehydes with higher yields than achieved with pure TiO<sub>2</sub>.

It must be noted that the  $WO_3(7.6)/TiO_2$  catalyst is reusable for further reactions. The WO<sub>3</sub>(7.6)/TiO<sub>2</sub> catalyst used for photocatalytic oxidation of benzyl alcohol was recovered

Table 2. Adsor	ption parameters	for benzaldehy	de on various	catalysts. <sup>[a]</sup>
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			2	-		
$C_{\rm e}/Q = 1/KQ_{\rm max} + C_{\rm e}/Q_{\rm max} $ (1)	Catalyst	$Q_{ m max} \ [{ m mmol}{ m g}^{-1}]$	K [Lmmol <sup>-1</sup> ]	$Q_{ ext{TiO}_2} \ [ ext{mmol} ext{g}^{-1}]$	$Q_{ m WO_3} \ [ m mmolg^{-1}]$	$Q_{\text{TiO}_2}/(Q_{\text{TiO}_2}+Q_{\text{WO}_3}) \times 100 [\%]$
	TiO <sub>2</sub>	$4.33 \times 10^{-2}$	4.67	$4.33 \times 10^{-2}$		
Table 2 summarized these	WO <sub>3</sub> (1.4)/TiO <sub>2</sub>	$4.87 \times 10^{-2}$	5.12	$3.63 \times 10^{-2}$	$1.24 \times 10^{-2}$	75
Table 2 summarizes these	WO <sub>3</sub> (3.4)/TiO <sub>2</sub>	$5.19 \times 10^{-2}$	6.97	$2.76 \times 10^{-2}$	$2.43 \times 10^{-2}$	53
values, which were determined	WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	$5.59 \times 10^{-2}$	7.57	$1.68 \times 10^{-2}$	$3.91 \times 10^{-2}$	30
from the slope and intercept of	WO <sub>3</sub> (10.3)/TiO <sub>2</sub>	$6.04 \times 10^{-2}$	7.58	$0.93 \times 10^{-2}$	$5.11 \times 10^{-2}$	15
the line in Figure 10 B. The $Q_{\text{max}}$	WO <sub>3</sub> (18.5)/TiO <sub>2</sub>	$6.73 \times 10^{-2}$	8.62	$0.39 \times 10^{-2}$	$6.34 \times 10^{-2}$	6
and K values for $WO_3/TiO_2$ are	[a] Reagents and conditions: water (5 mL), benzaldehyde (0.05–5.0 µmol), catalyst (5 mg), 298 K, 3 h.					

[a] Reagents and conditions: water (5 mL), benzaldehyde (0.05–5.0 µmol), catalyst (5 mg), 298 K, 3 h.

Table 3. Photocatalytic oxidation of various alcohols on  $\rm TiO_2$  and WO\_3-(7.6)/TiO\_2^{[a]}

	R	OH $hv (\lambda > 35)$ O <sub>2</sub> , 298 K, photocata	0 nm) water alyst	R	
	R	Catalyst	t <sub>irr</sub> [h] <sup>[b]</sup>	Aldehyde select [%] <sup>[c]</sup>	CO <sub>2</sub> [µmol]
1	p-methoxy	TiO <sub>2</sub>	8.0	23	108
2	-	WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	6.0	54	8.4
3 <sup>[d]</sup>		WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	18.5	62	13.0
4	<i>p</i> -methyl	TiO <sub>2</sub>	5.5	10	55.2
5		WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	4.0	42	4.3
6 <sup>[e]</sup>	<i>m</i> -methyl	$TiO_2$	5.0	19	34.3
7 <sup>[e]</sup>		WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	3.5	44	1.6
8	p-chloro	TiO <sub>2</sub>	6.0	32	52.1
9		WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	2.5	60	3.9
10	m-chloro	TiO <sub>2</sub>	9.5	23	71.6
11		WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	4.8	50	5.5
12 <sup>[e]</sup>	<i>p</i> -bromo	TiO <sub>2</sub>	6.0	23	33.3
13 <sup>[e]</sup>		WO <sub>3</sub> (7.6)/TiO <sub>2</sub>	1.5	41	1.8

[a] Reagents and conditions: water (5 mL), alcohol (0.1 mmol), catalyst (5 mg), O<sub>2</sub> (1 atm), 298 K,  $\lambda > 350$  nm. [b] The photoirradiation time required for 50% alcohol conversion. [c] Calculated as [aldehyde formed]/ [alcohol converted] × 100. [d] 0.5 mmol of alcohol was used. [e] 0.05 mmol of alcohol was used due to low solubility of the alcohol in water.

by simple centrifugation. As shown in Table 1 (entries 9 and 10), the catalyst, when reused for further reaction after washing with MeCN, shows almost the same aldehyde selectivity and catalytic activity as the virgin catalyst (Table 1, entry 4). This indicates that the catalyst can be reused for selective oxidation of alcohols at least twice without loss of selectivity and activity.

### Conclusion

The WO<sub>3</sub>/TiO<sub>2</sub> catalysts promote selective oxidation of alcohols to aldehydes in water with O<sub>2</sub> under photoirradiation at  $\lambda > 350$  nm. Catalysts containing approximately 8 wt % WO<sub>3</sub> show high catalytic activity and possess aldehyde selectivity much higher than the previously reported photocatalytic systems. The high activity is due to the transfer of e<sup>-</sup> from the conduction band of TiO<sub>2</sub> to the surface WO<sub>3</sub>. This leads to a charge separation between e<sup>-</sup> and h<sup>+</sup> and promotes efficient alcohol oxidation on the TiO<sub>2</sub> surface. The high aldehyde selectivity is due to a decrease in the available TiO<sub>2</sub> surface due to the WO<sub>3</sub> coating. This suppresses further reaction of the formed aldehydes on the TiO<sub>2</sub> surface and results in high aldehyde selectivity. It is known that several catalytic (nonphotocatalytic) systems achieve selective alcohol oxidation in water with very high yields.<sup>[33]</sup> The conversion and aldehyde selectivity of the present photocatalytic system is much lower than those of the nonphotocatalytic systems; therefore, further improvement of catalytic performance is necessary for practical application. Nevertheless, the basic concept presented here, which is based on the creation of metal oxide surface behaving as an electron acceptor site on

the semiconducting surface, may contribute to the development of photocatalytic systems promoting selective organic transformations.

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#### **Experimental Section**

**Materials**: All reagents were purchased from Wako, Tokyo Kasei, or Sigma–Aldrich and used without further purification. Water was purified by the Milli-Q system. Japan Reference Catalyst JRC-TIO-4 TiO<sub>2</sub> was kindly supplied by the Catalysis Society of Japan. The WO<sub>3</sub>(*x*)/TiO<sub>2</sub> catalysts with different WO<sub>3</sub> loadings [*x* (wt%) = WO<sub>3</sub>/(TiO<sub>2</sub>+WO<sub>3</sub>)×100; *x*=1.4, 3.4, 7.6, 10.3, 18.5] were synthesized by an impregnation method as follows;<sup>[21]</sup> TiO<sub>2</sub> (1 g) was stirred in an ammonia solution (1.0 molL<sup>-1</sup>, 50 mL) containing an appropriate amount of H<sub>2</sub>WO<sub>4</sub>. The obtained solution was dried at 353 K under vigorous stirring. The powders formed were calcined at 673 K for 2 h under O<sub>2</sub> flow (0.5 Lmin<sup>-1</sup>), affording white powders of catalysts. WO<sub>3</sub> was purchased from Kojundo Chemical Laboratory Co. and used as a reference.

**Photoreaction**: Each catalyst (5 mg) was suspended in water (5 mL) containing the substrate within a Pyrex glass tube ( $\phi$  10 mm; capacity, 20 mL). The tube was sealed with a rubber septum cap. The catalyst was dispersed by ultrasonication for 5 min and O<sub>2</sub> was bubbled through the solution for 5 min. The solution was photoirradiated with magnetic stirring by a 450 W high-pressure mercury lamp (USHIO Inc.), filtered through a glass filter to give light wavelength of  $\lambda > 350$  nm. The light intensity at 350–400 nm was 2.81 mW cm<sup>-2</sup>. The temperature of the solution was kept at 298 K in a water bath during photoirradiation. 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); the substrate and product concentrations were determined with authentic samples. Identification of the products was performed by GC-MS (Shimadzu; GC–MS-QP5050 A) analysis.

Analysis: The total amounts of W and Ti in the catalysts were determined with an X-ray fluorescence spectrometer (Seiko Instruments, Inc.; SEA2110). Diffuse reflectance UV/Vis spectra were measured with a UV/Vis spectrophotometer (Jasco Corp.; V-550 with Integrated Sphere Apparatus ISV-469) with BaSO4 as a reference. FTIR spectra were measured with an infrared spectrophotometer (Jasco Corp.; FTIR-610) using CaF2 as a reference. Particle size distribution was determined with a Horiba LB-500 dynamic light-scattering particle size analyzer. BET surface area was measured at 77 K using an AUTOSORB-1-C/TCD analyzer (Yuasa Ionics Co., Ltd.). The W L-edge XANES spectra were measured with the apparatus at the NW10A, Photon Factory (PF) at the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan (KEK-PF, proposal No. 2009G069). Synchrotron radiation emitted from a 6.5 GeV storage ring with a Si (311) double crystal monochromator. TEM images were recorded with a JEOL JEM-2010 microscope at an acceleration voltage of 200 kV. XPS measurement was performed with a JEOL JPS-9000MX spectrometer using MgKa radiation as the energy source.

**ESR measurement**: ESR spectra were recorded at the X-band with a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 10.5 mW; microwave power saturation of the signals did not occur.<sup>[12]</sup> The magnetic field was calibrated using 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as standard. The measurement was carried out as follows:<sup>[30]</sup> each catalyst (0.5 gL<sup>-1</sup>) was suspended in water containing benzyl alcohol (10 mmolL<sup>-1</sup>) and DMPO (100 mmolL<sup>-1</sup>) and dispersed well by ultrasonication. An aliquot (100 µL) of the suspension and DMSO (900 µL) were introduced into a flat ESR cell [10 × 20 × 0.3 mm (path length)], and O<sub>2</sub> was bubbled through the solution for 1 min. The cell was placed in the ESR sample cavity and photoirradiated using a 500 W Xe lamp through a glass filter to give light wavelengths of  $\lambda > 350$  nm at RT. After photoirradiation for 1 min, the irradiation was turned off and the measurement was started immediately.

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