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Selective photocatalytic oxidation of benzyl alcohol and its derivatives into corresponding aldehydes by molecular oxygen on titanium dioxide under visible light irradiation

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ABSTRACT

The photocatalytic oxidation of benzyl alcohol and its derivatives, such as 4-methoxybenzyl alcohol, 4-chlorobenzyl alcohol, 4-nitrobenzyl alcohol, 4-methylbenzyl alcohol, 4-(trifluoromethyl)benzyl alcohol, and 4-*tertiary*-butylbenzyl alcohol, into corresponding aldehydes proceeded at high conversion and selectivity on a TiO_2 photocatalyst under O_2 atmosphere. The reaction was confirmed to proceed under irradiation with both UV-light and visible light. In particular, the visible light response was observed to be attributed to a characteristic surface complex formed by the adsorption of a benzyl alcoholic compound on the TiO_2 surface. Here, the properties of the surface complex as the active center for this selective photocatalytic oxidation and the mechanism behind the reaction have been investigated.

1. Introduction

Aromatic aldehydes have attracted a great deal of attention as important materials for the production of fine chemicals for such applications as fragrances or flavorings and this work focuses on an approach to their effective production. Two different processes for the formation of aldehydes were investigated in order to develop highly selective catalytic activity. One is the direct catalytic hydrogenation process of carboxylic acids into corresponding aldehydes [1–3] and the other is the direct selective oxidation of alcohols into corresponding aldehydes [4,5].

Yamaguchi and Mizuno [4] have recently reported that a supported ruthenium catalyst, easily prepared by the treatment of $RuCl_3$ with γ-Al_2O_3, is an efficient heterogeneous catalyst for the oxidation of various kinds of alcohols in the presence of O_2. In another case, Tashiro et al. [5] have reported that various salicylaldehyde derivatives were produced from corresponding alcohols in good to excellent yields by aerobic oxidation using a ruthenium salen nitrosyl complex as a photocatalyst under irradiation with visible light. They succeeded in the partial oxidation of various kinds of alcohols into corresponding aldehydes on ruthenium catalysts.

Titanium dioxides (TiO_2) are a promising nano-sized material in photochemical applications [6–9] such as H_2 production by water splitting, the degradation of volatile organic compounds (VOCs), organic synthesis, dye-sensitized solar cells, and super-hydrophilic materials. Since the band gap of TiO_2 with an anatase structure is ca. 3.2 eV, it can only be activated by UV-light; however, only a low percentage reaches the earth's surface from the sun. In order to utilize as much clean and safe solar energy as possible, the development of visible light-sensitive nano-photocatalysts is essential. In the case of organic synthesis, the selective photocatalytic oxidation of aromatic compounds in the presence of O_2 under only UV-light irradiation has previously been reported on TiO_2 in the gas phase [10], in acetonitrile [11,12], or in aqueous solution [13–17].

Here, we have investigated the selective photocatalytic oxidation of benzyl alcohol and its derivatives on TiO_2 in the presence of O_2 under irradiation with both UV-light and visible light. In particular, we have focused on the mechanisms behind the selective photocatalytic oxidation of benzyl alcohol into benzaldehyde on the TiO_2 surface under visible light irradiation.

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2. Experimental

Photo-oxidations of benzyl alcohol and its derivatives were performed on TiO_2 photocatalysts at room temperature in the presence of O_2. The photocatalysts (50 mg each) were dispersed in acetonitrile solution (10 mL) involving the substrates (50 μmol) in a test tube (volume: 20 mL) made of pyrex glass and the gas phase was purged by O_2 at 298 K. The following substrates were used in this work: benzyl alcohol, 4-methoxybenzyl alcohol, 4-chlorobenzyl alcohol, 4-nitrobenzyl alcohol, 4-methylbenzyl alcohol, 4-(trifluoromethyl) benzyl alcohol, 4-*tertiary*-butylbenzyl alcohol, 4-hydroxybenzyl alcohol, and α, α-d2 benzyl alcohol for investigation of the kinetic isotope effect.

The photo-reaction cell was set at a photo-intensity of ca. 0.80 mW cm^{-2} at 365 nm emitted from a black light measured by a CSU-365 radiometer (Cosmo Bio Co., Ltd.) as well as at ca. 1.8×10^4 lux emitted from a blue LED lamp measured by an illumination meter, TMS 870 (TASCO Japan Co., Ltd.).

In order to estimate the quantum yields, the photo-oxidation of benzyl alcohol into benzaldehyde was performed on TiO_2 (10 mg) in acetonitrile solution (2 mL) involving 10 μmol of benzyl alcohol in a quartz cell of 10 × 10 × 44 mm using a 500 W xenon lamp through a monochromator (Koken, SG-100). The resolution of each photo-irradiated wavelength was ca. 13.6 nm and the photo-energy was measured by a power-meter (Ophir, ORION/PD). After the reaction, the catalysts were immediately separated from the solution by filtration through a 0.20 μm membrane filter (Dismic-25, Advantec). The solution was then analyzed by HPLC (Shimadzu LC10ATVP, UV–Vis detector, column: Chemcopak, mobile phase: a mixture of acetonitrile and 1.0% formic acid aqueous solution) and the gas phase was analyzed by GC (Ohkura, Model-802, column: porapak Q).

The infrared spectra of the adsorbed benzyl alcohol were examined by an IR transmission method. A self-supporting pellet (50 mg) of the TiO_2 photocatalyst was placed in an *in situ* infrared cell connected to a closed gas circulation system which was equipped with a vacuum line. The pellet was oxidized under O_2 at 673 K for 6 h and then evacuated at 523 K for 30 min as a pretreatment in the cell. The benzyl alcohol used in the infrared experiment was of analytical grade with a purity level of more than 99%. The adsorption of benzyl alcohol was carried out by introducing a well-evacuated benzyl alcohol vapor (ca. 25 Pa) into the cell at 298 K and the gas phase was then evacuated after adsorption was completed.

The infrared spectra were recorded with a FT-IR (JASCO FT/IR 620) and measured with 100 scans at the resolution of 4 cm^{-1}. The spectrum of the adsorbed benzyl alcohol was obtained by subtracting the spectrum of TiO_2 from that of the benzyl alcohol-adsorbed TiO_2.

3. Results and discussion

3.1. Optical properties of benzyl alcohol-adsorbed TiO_2

In order to understand the optical properties, the UV–Vis absorption spectra of (a) TiO_2 by itself and (b) the benzyl alcohol-adsorbed TiO_2 were investigated and the results are shown in Fig. 1. It was observed that TiO_2 by itself exhibits absorption only in the UV region with a band-gap transition at ca. 385 nm (3.2 eV), as shown in Fig. 1a. In contrast, as can be seen in Fig. 1b, it was confirmed that absorption in the visible region appeared in the spectrum for benzyl alcohol-adsorbed TiO_2. This absorption is due to the surface complex between TiO_2 and benzyl alcohol, and is tentatively assigned to the charge transfer from benzyl alcohol to TiO_2 on the surface complex. On the other hand, neither methanol nor benzene-adsorbed TiO_2 exhibited absorption in the visible region, suggesting that the absorption in the visible region is unique on the benzyl alcohol-adsorbed TiO_2. From these results, absorption in the visible region of the surface complex is expected to lead to photocatalytic reactions under visible light irradiation. Photocatalytic reactions were, therefore, carried out under two different light sources: irradiation with UV-light emitted from the black light having an energy distribution as shown in Fig. 1c; and irradiation with visible light emitted from the LED lamp having an energy distribution as shown in Fig. 1d.

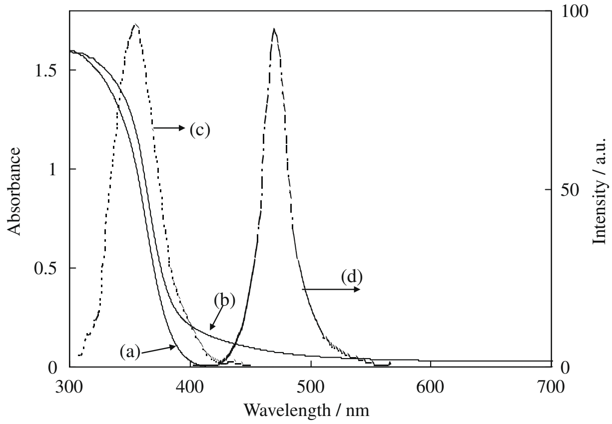


Fig. 1. UV–Vis absorption spectra of (a) TiO_2 by itself; (b) benzyl alcohol-adsorbed TiO_2; energy distribution emitted (c) from the black light; and (d) from the LED lamp used in this experiment.

3.2. Photocatalytic oxidation of benzyl alcohol under UV-light irradiation

The oxidation of benzyl alcohol on a TiO_2 photocatalyst as a function of time under the irradiation with UV-light emitted from the black light is shown in Fig. 2. It was confirmed that the oxidation reaction does not take place under photo-irradiation without a TiO_2 photocatalyst nor with a TiO_2 photocatalyst without irradiation, i.e., both TiO_2 and irradiation are required in combination for the oxidation reaction to occur. Before irradiation, a decrease in the amount of benzyl alcohol originating from its adsorption on TiO_2 was observed. Photo-irradiation

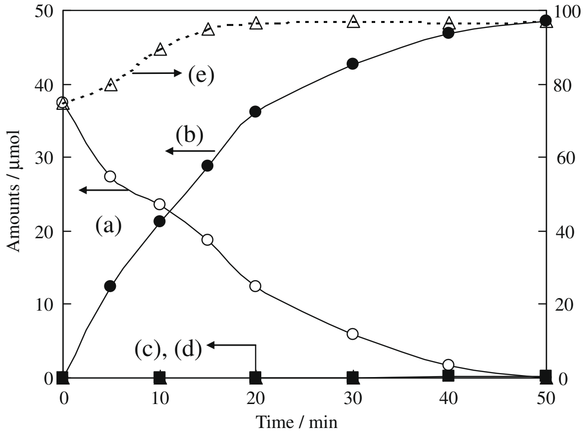


Fig. 2. Photocatalytic oxidation of benzyl alcohol on TiO_2 (50 mg) under irradiation with UV-light emitted from the black light. The initial amount of benzyl alcohol added in the reaction cell was 50 μmol. Amounts of (a) benzyl alcohol; (b) benzaldehyde; (c) benzoic acid; (d) CO_2; and (e) percentage of total organic compounds evolved in solution is plotted.

was carried out after confirming the equilibrium of benzyl alcohol adsorption. As shown in Fig. 2, upon UV-light irradiation, the amount of benzyl alcohol decreased with time. In contrast, benzaldehyde is selectively produced while only negligible amounts of CO_2 or benzoic acid are formed. It was confirmed that the reactions immediately cease when the light is turned off. Subsequently, after the light was turned on again, the reactions immediately proceeded. The yield of benzaldehyde reached >95% and the carbon balance in the liquid phase was >95% after photo-irradiation for 50 min. According to a previous report [11], the photocatalytic oxidation of benzyl alcohol led to the formation of benzaldehyde and benzoic acid in addition to unidentified minor compounds under full arc emitted from a 450-W medium pressure Hg lamp. Therefore, the black light having an energy profile as shown in Fig. 1 (c) seems to be suitable for the selective photocatalytic oxidation reaction. These results clearly demonstrate that the photocatalytic oxidation of benzyl alcohol to benzaldehyde selectively proceeds in the presence of O_2 on a TiO_2 photocatalyst under UV-light irradiation.

3.3. Photocatalytic oxidation of benzyl alcohol under visible light irradiation

Fig. 3 shows the oxidation of benzyl alcohol on the TiO_2 photocatalyst as a function of time under irradiation with visible light emitted from the LED lamp. The photocatalytic oxidation of benzyl alcohol took place on TiO_2 under visible light and this reaction was completed within 240 min, as shown in Fig. 3. Moreover, the yield of benzaldehyde reached ca. 95% and the carbon balance in the liquid phase was ca. 95% after photo-irradiation for 240 min. In order to clarify the contribution of the surface states of TiO_2 on the photocatalytic oxidation, the reactions were carried out on fluorinated TiO_2 (F-TiO_2) on which the surface OH was exchanged to fluoride by diluted HF aqueous solution [18]. Although benzyl alcohol-adsorbed F-TiO_2 exhibits absorption in the visible region, the photocatalytic activity drastically decreased under visible light irradiation. This result suggests that the surface OH groups play a significant role in the photocatalytic oxidation reaction.

Here, the turnover numbers (TONs) were evaluated as the number of benzaldehyde molecules produced per one surface OH group involved on TiO_2. Since the amount of OH groups on the TiO_2 surface is generally estimated to be ca. 10 nm^{-2} [19], the amount of OH groups involved in 50 mg of TiO_2 (BET surface: 300 $m^2\,g^{-1}$) is considered to be ca. 250 μmol. When photo-oxidation was carried out in acetonitrile solution (10 mL) involving 10 mmol of benzyl alcohol on TiO_2 under irradiation with visible light emitted from the LED lamp for 36 h, the photo-formed benzaldehyde was ca. 2.2 mmol, i.e., the TON was estimated to be ca. 9, clearly indicating that this reaction proceeds photocatalytically. From the results shown in Figs. 1 and 3, selective photocatalytic oxidation under visible light irradiation was observed to proceed on an active surface complex initiated by the adsorption of benzyl alcohol on the TiO_2 surface involving OH groups.

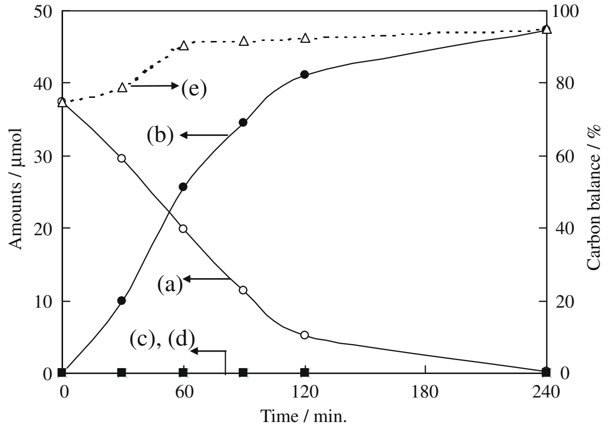


Fig. 3. Photocatalytic oxidation of benzyl alcohol on TiO_2 (50 mg) under irradiation with visible light emitted from the LED lamp. The initial amount of benzyl alcohol added to the reaction cell was 50 μmol. Amounts of (a) benzyl alcohol; (b) benzaldehyde; (c) benzoic acid; (d) CO_2; and (e) percentage of total organic compounds evolved in solution is plotted.

In order to understand the states of benzyl alcohol-adsorbed TiO_2 at 298 K, the infrared spectra were measured and the results are shown in Fig. 4. The infrared spectrum of the benzyl alcohol molecules can be clearly confirmed from Fig. 4a [20]. When the spectrum of the benzyl alcohol adsorbed on TiO_2, as shown in Fig. 4b, is compared with that of the benzyl alcohol by itself in Fig. 4a, the characteristic IR bands for benzyl alcohol adsorbed on TiO_2 are shown to be substantially the same as those for the benzyl alcohol molecules. Moreover, the following unique features caused by the interaction between the benzyl alcohol molecules and TiO_2 surface are observed in Fig. 4a: (i) a downward negative band at 3715 cm^{-1} assigned to $\nu(OH)$ of the surface hydroxyl group is observed; (ii) instead of a negative band at 3715 cm^{-1}, a very broad band attributed to $\nu(OH)$ appears between 3500 and 2500 cm^{-1}; and (iii) a band intensity at 1615 cm^{-1} attributed to the phenyl ring vibration increases markedly. These characteristics indicate that the benzyl alcohol molecules interact with the surface hydroxyl group by the adsorption on the TiO_2 surface. Taking the previous results in the interaction of benzene with surface OH group of TiO_2 into consideration [21], the CH_2OH group and/or phenyl ring of the benzyl alcohol in the form of molecules interacts with the surface OH group of TiO_2.

3.4. Selective photocatalytic oxidation of benzyl alcohol and its derivatives

Photocatalytic reactions of benzyl alcohol and its derivatives into corresponding aldehydes were carried out on TiO_2 under irradiation with both visible light and UV-light. As shown in Table 1, benzyl alcohol and its derivatives substituted by $-OCH_3$, –Cl, $-NO_2$, $-CH_3$, $-CF_3$, and $-C(CH_3)_3$ groups were converted to corresponding aldehydes with a high conversion (>99%) and high selectivity (>99%) on TiO_2, while no other products were observed. Upon UV-light irradiation, benzyl alcohol and its derivatives as mentioned above were also converted to corresponding aldehydes with a high conversion (>99%) and high selectivity (>99%) on TiO_2, while

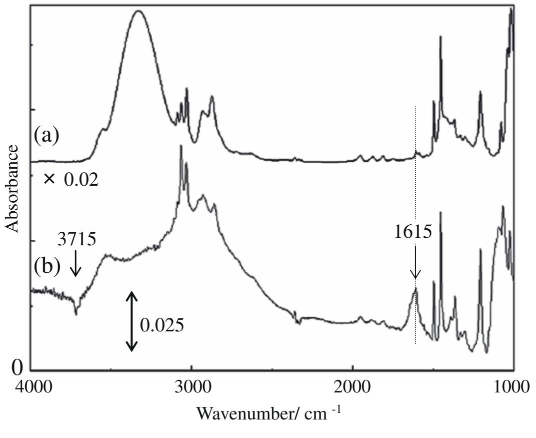
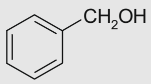
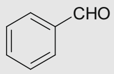
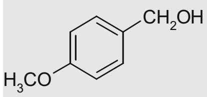
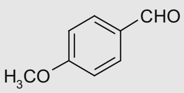
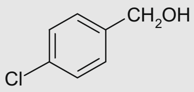
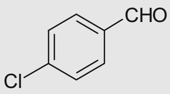
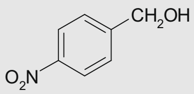
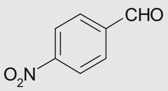
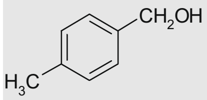
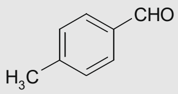
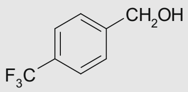
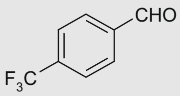
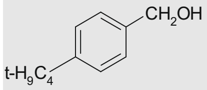
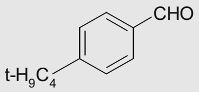
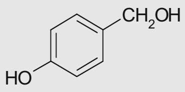
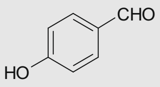


Fig. 4. FT-IR spectra of (a) benzyl alcohol by itself; and (b) benzyl alcohol adsorbed on TiO_2.

Table 1
Selective photocatalytic oxidation of benzyl alcohol and its derivatives into corresponding aldehydes in the presence of O_2 under irradiation with visible light emitted from the LED lamp for 4 h.

Reactants	Products	Conversion (%)	Selectivity (%)
		>99	>99
		>99	>99
		>99	>99
		>99	>99
		>99	>99
		>99	>99
		>99	>99
		>85	23

no other products were observed. Thus, it was confirmed that various kinds of benzyl alcoholic compounds mentioned above were effectively converted to corresponding aldehydes under irradiation with both visible light and UV-light. A kinetic study of the selective photocatalytic oxidation will be discussed in a future report.

On the other hand, the benzyl alcoholic compound substituted by the –OH group such as 4-hydroxybenzyl alcohol was unselectively photo-oxidized into 4-hydroxybenzaldehyde as well as some unidentified products, as shown in Table 1. From now on, we investigate the reasons for the high selectivity on the oxidation of benzyl alcohol, compared with that of 4-hydroxybenzyl alcohol.

3.5. Interaction of 4-hydroxybenzyl alcohol with the TiO_2 surface

The UV–Vis absorption spectra of (a) the TiO_2 by itself, (b) benzyl alcohol-adsorbed TiO_2, and (c) 4-hydroxybenzyl alcohol-adsorbed TiO_2 are shown in Fig. 5. Compared with the spectrum of the benzyl alcohol-adsorbed TiO_2, the 4-hydroxybenzyl alcohol-adsorbed TiO_2 exhibits intensive absorption in the visible region, as shown in Fig. 5c. It is known that the surface OH groups of TiO_2 react with phenolic compounds (Ph–OH) to form a linkage of $\equiv$Ti–O–Ph, which exhibits strong absorption in the visible region due to the ligand-to-metal charge transfer (LMCT) [22]. The 4-hydroxybenzyl alcohol is, therefore, strongly adsorbed on TiO_2 to form the intensive linkage of $\equiv$Ti–O–Ph–CH_2OH. On the other hand, the UV–Vis spectra of the TiO_2 adsorbed benzyl alcoholic derivatives listed in Table 1, with the exception of 4-hydroxybenzyl alcohol, showed absorption in the visible light region in a similar manner as that of benzyl alcohol.

The uptakes in a mixture of benzyl alcohol and benzaldehyde as well as those of 4-hydroxybenzyl alcohol and 4-hydroxybenzaldehyde (50 μmol for each) on TiO_2 as a function of time under dark conditions are shown in Fig. 6. The uptake of every molecule on

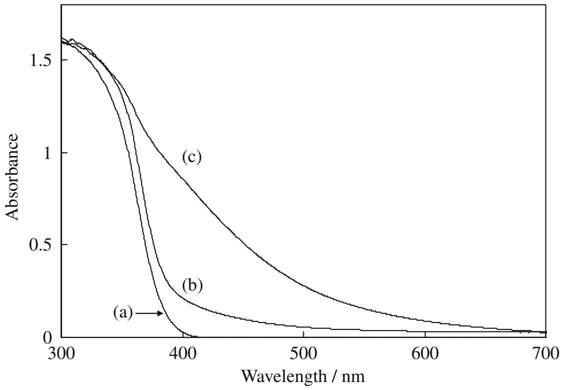


Fig. 5. UV–Vis absorption spectra of (a) TiO_2 by itself; (b) benzyl alcohol-adsorbed TiO_2; and (c) 4-hydroxybenzyl alcohol-adsorbed TiO_2.

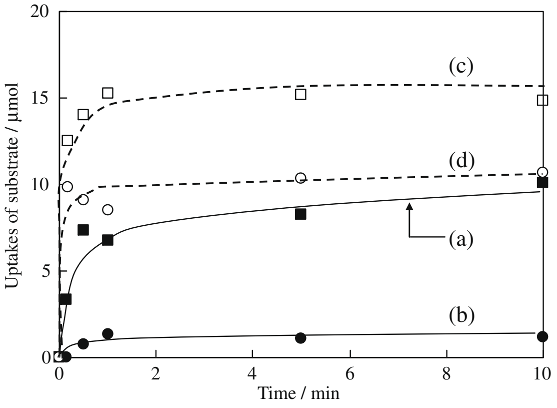


Fig. 6. Uptakes of (a) benzyl alcohol; (b) benzaldehyde; (c) 4-hydroxybenzyl alcohol; and (d) 4-hydroxybenzaldehyde on TiO_2 in the dark. A mixture of benzyl alcohol and benzaldehyde or of 4-hydroxybenzyl alcohol and 4-hydroxybenzaldehyde (50 μmol each), respectively, was added to an acetonitrile suspension involving TiO_2 (50 mg).

TiO_2 is saturated within 1 min. It was noted that the amount of benzaldehyde adsorbed on TiO_2 was negligible compared to that of benzyl alcohol, as is also shown in Fig. 6. These results indicate that the interaction between benzaldehyde and TiO_2 is fairly weak. Therefore, once benzaldehyde is produced by the oxidation of benzyl alcohol, benzaldehyde is immediately released into the bulk solution and may be one of the reasons benzaldehyde is selectively formed.

On the other hand, the amount of 4-hydoxybenzaldehyde adsorbed on TiO_2 is around the same as that of 4-hydoxybenzyl alcohol. This suggests that the adsorbed 4-hydoxybenzaldehyde on TiO_2 produces a stable species due to the formation of strong linkages, as mentioned above. From these results, the reasons for the low activity for the oxidation of 4-hydoxybenzyl alcohol compared with the other benzyl alcoholic derivatives may be considered as follows: 4-hydroxybenzyl alcohol is so strongly adsorbed to form a $\equiv$Ti–O–Ph–CH_2OH linkage that it leads to further oxidation under photo-irradiation; and/or the –CH_2OH group exists far from the TiO_2 surface.

3.6. Action spectrum for the photocatalytic oxidation of benzyl alcohol on TiO_2

Fig. 7 shows the action spectrum for the formation of benzaldehyde in the photocatalytic oxidation of benzyl alcohol into benzaldehyde on TiO_2. The quantum yield (ϕ) is defined in the following Eq. (1):

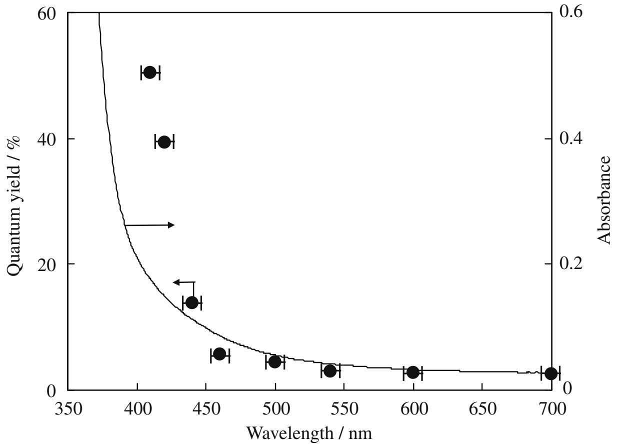


Fig. 7. Action spectrum for the photocatalytic oxidation of benzyl alcohol into benzaldehyde on TiO_2; and the absorption spectrum of benzyl alcohol-adsorbed TiO_2.

$$\phi = \frac{(\text{amount of product formed})}{(\text{amount of photons absorbed})} \times 100 \tag{1}$$

It was observed that the photo-response is extended toward ca. 700 nm and the quantum yields are estimated to be ca. 4.3% under photo-irradiation at 500 ± 6.8 nm, ca. 5.5% at 460 ± 6.8 nm, and ca. 39% at 420 ± 6.8 nm, as shown in Fig. 7. An action spectrum for the photocatalytic activity shows a red-shift from the UV–Vis spectrum, as can be seen in Fig. 7. This result suggests that the surface complex formed by adsorption of benzyl alcohol on the TiO_2 is highly sensitive to the visible light.

3.7. Kinetic isotope effect on the photocatalytic oxidation of α, α-d2 benzyl alcohol

The photocatalytic oxidation of (a) normal benzyl alcohol and (b) α, α-d2 benzyl alcohol into corresponding benzaldehyde is shown in Fig. 8[I]. The reaction rate constants of k_H and k_D for (a) and (b) shown in Fig. 8[I] have been, respectively, evaluated from the first-order rate law in Eqs. (2) and (3):

$$\frac{dx}{dt} = k(a - x) \tag{2}$$

$$kt = \ln\left[\frac{a}{(a - x)}\right] \tag{3}$$

Eq. (3) shows that if $\ln [a/(a - x)]$ is plotted against t, a first-order reaction gives a straight line for slope k. Here, the amount of added benzyl alcohol and that of the photo-formed benzaldehyde as a function of time (t) are defined as a and x, respectively. Although the initial reactions do not completely fit with a first-order reaction due to the induction period, the reaction rate constants for normal benzyl alcohol and α, α-d2 benzyl alcohol were roughly estimated to be $2.06 \times 10^{-4}\ s^{-1}$ and $5.18 \times 10^{-5}\ s^{-1}$ for (c) and (d), respectively (cf. Fig. 8[II]). The ratio of the reaction rates (k_H/k_D) was, therefore, estimated to be ca. 3.9. The first-order isotope effect shows that the C–D bond is cleaved more slowly than the C–H bond. It should be noted that the value of $k_{C\text{-}H}/k_{C\text{-}D}$ is theoretically $\approx$8 when the C–H bond is completely cleaved at the transitional state. Here, from the value of $k_{C\text{-}H}/k_{C\text{-}D}$ at $\approx$3.9, the kinetic isotope effect shows that an abstraction of the α-hydrogen atom from the –CH_2OH group is a rate-determining step while the C–H bond is partially left in the transitional state.

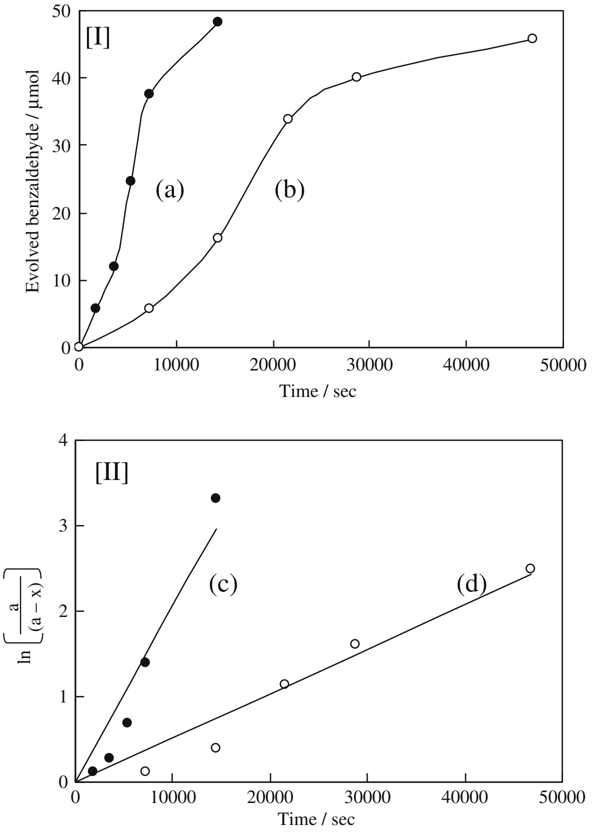


Fig. 8. Photocatalytic oxidation of (a) normal benzyl alcohol and (b) α, α-d2 benzyl alcohol on TiO_2 (50 mg) under irradiation with visible light emitted from the LED lamp [I], and the plots for ln $[a/(a-x)]$ against the time [II] for (c) normal benzyl alcohol and (d) α, α-d2 benzyl alcohol.

3.8. Reaction mechanism for selective photocatalytic oxidation under visible light irradiation

The tentative reaction mechanism for the oxidation of benzyl alcohol on TiO_2 under visible light irradiation into benzaldehyde and H_2O is shown in Fig. 9. The surface complexes, which are formed by the interaction of the $-CH_2OH$ group or possibly the phenyl ring of benzyl alcohol with the surface OH group, induce absorption in the visible region. Upon visible light irradiation, when the surface complex is photo-excited to form holes (h^+) and electrons (e^-), the holes abstract hydrogen atoms from the CH_2OH group of benzyl alcohol. Subsequently, the photo-induced benzyl alcoholic radicals may automatically release another electron to form benzaldehyde due to the current-doubling effect.

On the other hand, the photo-induced electrons are scavenged by O_2 as shown in Fig. 9. The effect of the Ag^+ ions as electron acceptors on the photo-oxidation of benzyl alcohol was also investigated in a suspension of benzyl alcohol with TiO_2 in the absence of O_2 under visible light irradiation. It was observed that only negligible amounts of benzaldehyde were formed by the photo-oxidation of benzyl alcohol under visible light irradiation, while the Ag^+ ions were reduced to Ag particles by the photo-induced electrons. These results indicate that the photo-excited surface complex does not produce benzaldehyde simply by the photo-induced holes, but also in combination with the assistance of O_2 which plays a significant role as electron acceptors; and possibly leads to the re-generation of surface hydroxyl groups on TiO_2, as shown in Fig. 9. Selective photocatalytic oxidation with a high efficiency was, thus, realized on a TiO_2 surface under visible light and a plausible reaction mechanism is proposed.

4. Conclusions

The selective photocatalytic oxidation of benzyl alcohol and its derivatives into corresponding aldehydes proceeded at a high conversion rate of >99% and high selectivity of >99% on TiO_2 in the presence of O_2. To the best of our knowledge, this is the first report of such reactions taking place under visible light irradiation, i.e., a surface complex was formed by the adsorption of benzyl alcohol on TiO_2 involving surface OH groups, leading to the absorption of visible light and the selective photocatalytic oxidation reaction. Moreover, the reaction mechanism behind the photocatalytic oxidation of benzyl alcohol under visible light irradiation was also demonstrated.

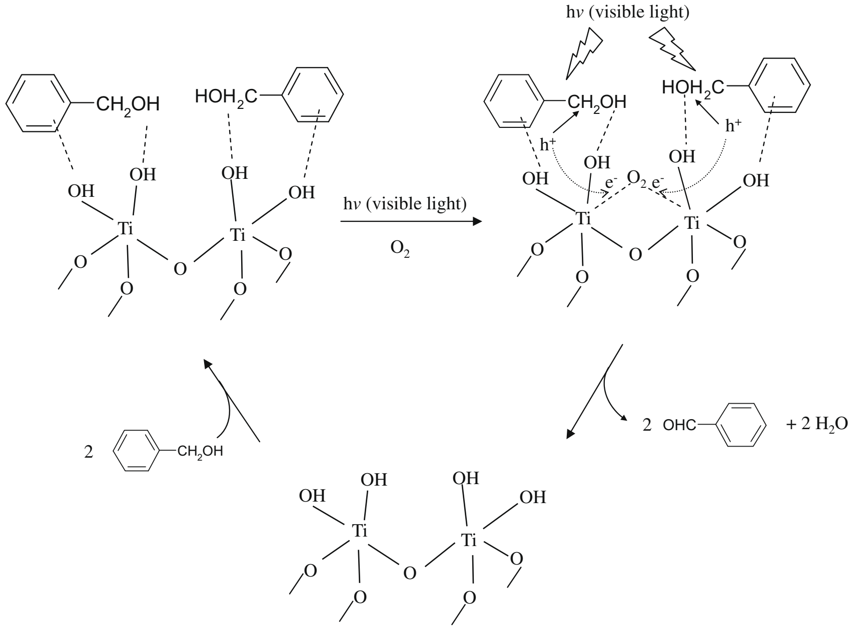


Fig. 9. Tentative reaction mechanism for the selective photocatalytic oxidation of benzyl alcohol in the presence of O_2 on TiO_2 under visible light irradiation.

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