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Benzyl alcohol was converted to benzaldehyde with 97% yield in aqueous suspension of Rh\textsuperscript{3+}/TiO\textsubscript{2} photocatalysts under visible light irradiation.
Selective oxidation of alcohols in aqueous suspensions of rhodium ion-modified TiO$_2$ photocatalyst under irradiation of visible light

Sho Kitano$^a$, Atsuhiro Tanaka$^a$, Keiji Hashimoto$^b$, Hiroshi Kominami$^b$*

$^a$ Interdisciplinary Graduate School of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashiosaka, Osaka 577-8502, Japan

$^b$Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashiosaka, Osaka 577-8502, Japan.

*To whom correspondence should be addressed
Fax: +81-6-6721-2332, Fax: +81-6-6727-2024
E-mail address: hiro@apch.kindai.ac.jp (H. Kominami)

ABSTRACT

Photocatalytic oxidation of benzyl alcohols in aqueous suspensions of rhodium ion-modified titanium(IV) oxide (Rh$^{3+}$/TiO$_2$) in the presence of O$_2$ under irradiation of visible light was examined. In the photocatalytic oxidation of benzyl alcohol, benzaldehyde was obtained in a high yield (97%) at >99% conversion of benzyl alcohol. Rh$^{3+}$/TiO$_2$ photocatalysts having various physical properties were prepared using commercially available TiO$_2$ powders as supporting material for Rh$^{3+}$ to investigate the effect(s) of physical properties of TiO$_2$ on photocatalytic activities of Rh$^{3+}$/TiO$_2$ for selective oxidation. Adsorption properties of benzyl alcohol, benzaldehyde and benzoic acid on TiO$_2$ were also investigated to understand the high benzaldehyde selectivity over the Rh$^{3+}$/TiO$_2$ photocatalyst. The reaction mechanism was discussed on the basis of results of photocatalytic oxidation of various $p$-substituted benzyl
alcohol derivatives.

1. Introduction

Aldehyde compounds are indispensable substances for drugs, fragrances and organic synthesis in the chemical industry, and they are generally produced through reduction of corresponding carboxylic acids or oxidation of corresponding alcohols. The production of aldehydes is conducted in environmentally harmful organic solvents with the use of stoichiometric oxygen donors such as KMnO₄ and CrO₃. Since these reagents are toxic and expensive and produce a large amount of waste, the process should be replaced with a more environmentally friendly method. Recently, selective oxidation of alcohols using oxygen molecules (O₂) instead of oxygen donor agents has attracted attention.¹,²

Titanium(IV) oxide (TiO₂) is known as an excellent photocatalyst.³-⁵ Under irradiation of UV light, TiO₂ is excited and forms holes in the valence band and excited electrons in the conduction band, which induce oxidation and reduction, respectively. Holes have strong oxidation abilities and can mineralize almost all of the organic molecules. Therefore, a TiO₂ photocatalyst has been widely used for oxidative degradation of pollutants, i.e., purification of the atmosphere and water. The TiO₂ photocatalyst has been used not only for simply degradation of molecules but also for organic synthesis by using holes and excited electrons.⁶-¹² Recently, selective oxidation of alcohols to aldehydes in aqueous suspensions of a TiO₂ photocatalyst under irradiation of UV light has been reported.⁶-⁸ These photocatalytic reactions were carried out in water, the “greenest” solvent for the environment, and in the presence of O₂. Photocatalytic selective oxidation over TiO₂ is an environmentally friendly reaction since only harmless substances, i.e., water, O₂ and TiO₂, are used, and solar light can be utilized as an energy source. However, selectivity in the photocatalytic
reaction over TiO$_2$ has been low because the oxidation power of holes in TiO$_2$ is too strong and holes oxidize substances non-selectively, i.e., successive oxidation of aldehydes occurs. In addition, TiO$_2$ only works under irradiation of UV light, which is included only in a small part of solar light. Recently, almost stoichiometric conversion of benzyl alcohol to benzaldehyde was achieved under irradiation of light from a blue LED ($\lambda_{\text{max}}=460$ nm) by a reaction mechanism other than band-gap excitation of TiO$_2$, in which benzyl alcohol species adsorbed on the TiO$_2$ surface itself absorbed visible light and injected its electrons in the conduction band, resulting in oxidation of benzyl alcohol to benzaldehyde.$^{13-16}$

We have reported a new photocatalyst responding to visible light, rhodium ion-modified TiO$_2$ (Rh$^{3+}$/TiO$_2$), that exhibited photocatalytic activities for mineralization of volatile organic compounds (VOC) in gas phase under irradiation of visible light.$^{17-19}$ We have also reported that photocatalytic oxidation abilities of Rh$^{3+}$/TiO$_2$ were enhanced by precise control of the physical properties of TiO$_2$. In addition, we found that the Rh$^{3+}$/TiO$_2$ photocatalyst produced acetone with relatively high selectivity in oxidation of gaseous 2-propanol.$^{17,18}$ Based on these results, we speculated that the Rh$^{3+}$/TiO$_2$ photocatalyst could be used for selective oxidation of alcohols. We also expected that the oxidative power of the sample could be controlled by selecting appropriate TiO$_2$ for selective oxidation. In this study, we examined photocatalytic selective oxidation of benzyl alcohols to benzaldehydes in aqueous suspensions of Rh$^{3+}$/TiO$_2$ under irradiation of visible light and found that the Rh$^{3+}$/TiO$_2$ photocatalyst converted benzyl alcohols to corresponding benzaldehydes with high selectivity. Correlations between catalytic performance and physical properties of photocatalysts, especially adsorption properties, were investigated in detail.
2. Experimental

2.1. Sample preparation

All of the chemicals were used as received without further purification. One of the TiO$_2$ powders was synthesized by the HyCOM (Hydrothermal Crystallization in Organic Media) method at 300°C as reported previously.\textsuperscript{20} HyCOM-TiO$_2$ was calcined at 550°C in a box furnace for 1 h. Hereafter, the HyCOM-TiO$_2$ sample is denoted as HyCOM550. Various TiO$_2$ powders (ST-01, Ishihara Sangyo; MT-150A, TAYCA; F-6, Showa Titanium; P 25, Degussa; HyCOM550) were modified with Rh$^{3+}$ by using the equilibrium adsorption method.\textsuperscript{17-19} Each of the TiO$_2$ powders was suspended in an aqueous solution of rhodium(III) chloride, RhCl$_3$, and stirred and then heated in a water bath at \textit{ca.} 90°C for 1 h. The suspension was filtered and washed repeatedly. The residue was dried \textit{in vacuo} at room temperature. The Rh$^{3+}$-modified TiO$_2$ samples are designated as Rh$^{3+}$/TiO$_2$; for example, the Rh$^{3+}$-modified F-6 TiO$_2$ sample is designated as Rh$^{3+}$/F-6. The amounts of Rh$^{3+}$ on TiO$_2$ were determined by analysis of the filtrate using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500).

2.2. Characterization

Powder X-ray diffraction (XRD) was measured using CuK$\alpha$ radiation by a Rigaku MultiFlex equipped with a carbon monochromator. Specific surface area ($S_{\text{BET}}$) of the samples was obtained using the Brunauer-Emmett-Teller (BET) single-point method on the basis of nitrogen uptake measured at -196°C using a Shimadzu Flowsorb 2300. Diffuse reflectance spectra were measured using a Shimadzu UV-2400 UV-Vis spectrometer equipped with a diffuse reflectance measurement unit (ISR-2000) and recorded after Kubelka–Munk analysis.
2.3. Photocatalytic reaction

Each of the samples (50 mg) was suspended in distilled water (5 cm$^3$) in a test tube (35 cm$^3$), bubbled with O$_2$ for 20 minutes, and sealed with a rubber septum. Substrates (33 µmol) were injected in the suspensions and irradiated with visible light from a blue LED (420-530 nm, 10 mW / cm$^2$, Hayashi Watch Works, Tokyo). The amount of carbon dioxide (CO$_2$) in gas phase (30 cm$^3$) and the amounts of substrates and products in the reaction system were measured by using a Shimadzu GC-8A gas chromatograph with a Porapack QS column and a Shimadzu GC-14B gas chromatograph with a DB-1 capillary column (30 m, 0.25 mm). Substrates adsorbed on photocatalysts were also recovered by repeating washing as possible. Toluene was used as an internal standard sample. The reaction solution (1 cm$^3$) was added to a diethyl ether/water mixture (2:1 v/v, 3 cm$^3$). After the mixture had been stirred for 10 min, aromatic alcohols, aldehydes and carboxylic acid in the ether phase were analyzed. Their amounts were determined from the ratios of their peak areas to the peak area of toluene. The amount of O$_2$ was not measured during the reaction since the amount of O$_2$ (1.21 mmol) was enough larger than that required for complete oxidation of benzyl alcohol (297 µmol).

3. Results and discussion

3.1. Selective oxidation of benzyl alcohol to benzaldehyde in aqueous suspensions of Rh$^{3+}$/F-6 under irradiation of visible light

Fig. 1 shows diffuse reflection spectra of unmodified and 0.5 wt% Rh$^{3+}$-modified F-6 samples and the emission spectrum of visible light from a blue LED. The unmodified F-6 sample exhibited only absorption in the UV range due to band-gap excitation. The Rh$^{3+}$/F-6 sample showed photoabsorption in the visible light region, which originated from the charge transfer from Rh$^{3+}$ to the conduction band of TiO$_2$, as
Fig. 2 shows the time courses of oxidation of benzyl alcohol in an aqueous suspension of 0.5 wt% Rh\textsuperscript{3+}/F-6 in the presence of \text{O}_2 under irradiation of visible light from a blue LED. The amount of \text{CO}_2 evolved in the gas phase is also shown in Fig. 2. Since seven \text{CO}_2 molecules are formed from a benzyl alcohol molecule in the complete mineralization, one-seventh of the amount of \text{CO}_2 is plotted in Fig. 2. The amount of benzyl alcohol decreased while benzaldehyde was formed along with irradiation of visible light. Benzyl alcohol was completely consumed after 30 h and benzaldehyde was obtained in a high yield (97%). We noted that high carbon balances were preserved during the reaction and that neither intermediates such as benzoic acid nor coupling products such as benzoin were detected. This also indicates that the amount of \text{CO}_2 dissolved in the suspension was negligible. These results indicate that the Rh\textsuperscript{3+}/F-6 photocatalyst possessed excellent performance for selective conversion of benzyl alcohol to benzaldehyde in water in the presence of \text{O}_2. In addition, no Rh\textsuperscript{3+} was detected by ICP-AES analysis of the solution after the photocatalytic reaction. The detection limit of ICP-AES used in this study is 0.28 \text{µmol dm}^{-3} for Rh\textsuperscript{3+}. Since the concentration for 100% leaching of Rh\textsuperscript{3+} from TiO\textsubscript{2} corresponds to 490 \text{µmol dm}^{-3}, the maximum leaching ratio was calculated to be 0.058\%, indicating that Rh\textsuperscript{3+} leaching and the effect of the leaching on photocatalytic activity was negligible. Blank experiments were performed to confirm that the reaction proceeded photocatalytically. Table 1 shows the results of oxidation of benzyl alcohol under various conditions. Oxidation of benzyl alcohol did not occur in an aqueous suspension of unmodified F-6 under irradiation of visible light (Entry 2). Higashimoto et al. reported oxidation of benzyl alcohols by the charge transfer from adsorbed benzyl alcohol species to TiO\textsubscript{2} in an acetonitrile suspension.\textsuperscript{13-16} The result (Entry 2) indicates that oxidation of benzyl alcohol does not occur in water. Free
Rh$^{3+}$ species in water did not show homogeneous photocatalytic activity in benzyl alcohol oxidation under irradiation of visible light (Entry 3). Thermal oxidation of benzyl alcohol was not observed in an aqueous suspension of Rh$^{3+}$/F-6 in the presence of O$_2$ at 25°C in the dark (Entry 4). These results indicate that the observed selective oxidation of benzyl alcohol to benzaldehyde in an aqueous suspension of Rh$^{3+}$/TiO$_2$ (Entry 1) was a photocatalytic reaction induced by visible light, not a photocatalytic homogeneous reaction or a thermal aerobic reaction, and that the combination Rh$^{3+}$ with TiO$_2$ and visible light irradiation are indispensable for the selective oxidation. Fig. 3 shows the reaction rate of the selective oxidation of benzyl alcohol to benzaldehyde using the Rh$^{3+}$/TiO$_2$ sample in repeated experiments. A decrease in reaction rate was not observed in the second use and third use of the Rh$^{3+}$/TiO$_2$ sample, suggesting that the Rh$^{3+}$/TiO$_2$ photocatalyst can be repeatedly used for selective oxidation in water. The turnover number, which was defined as the ratio of the amount of benzaldehyde formed at 30 h to the amount of Rh$^{3+}$ fixed on F-6, was calculated to be 13.2, indicating that the reaction was not a quantitative reagent reaction but a photocatalytic reaction.

Copper(II)- and iron(III)-modified TiO$_2$ samples (Cu$^{2+}$/TiO$_2$ and Fe$^{3+}$/TiO$_2$), which exhibited photocatalytic activities for decomposition of VOC in gas phase, were prepared and used for selective oxidation of benzyl alcohol to benzaldehyde under irradiation of visible light. Results are shown in Table S1 (†ESI). The Cu$^{2+}$/TiO$_2$ and Fe$^{3+}$/TiO$_2$, however, exhibited low levels of photocatalytic activities probably because the states of Cu$^{2+}$ and Fe$^{3+}$ modified on the surface of TiO$_2$ might alter in aqueous suspensions. These results indicate that the Rh$^{3+}$/TiO$_2$ photocatalyst exhibited photocatalytic activities for not only mineralization of VOC but also selective oxidation under irradiation of visible light.

3.2. Effects of physical properties of TiO$_2$ on photocatalytic activities of Rh$^{3+}$/TiO$_2$
under irradiation of visible light

Various kinds of TiO₂ powders were used as supporting material for Rh³⁺ to investigate the effects of physical properties of TiO₂ on photocatalytic activities of Rh³⁺/TiO₂ for selective oxidation of benzyl alcohol. TiO₂ samples having various physical properties were used in this study, and the physical properties are shown in Table 2. Fig. 4 shows diffuse reflection spectra of unmodified TiO₂ samples (A) and Rh³⁺-modified TiO₂ samples (B). Photoabsorption in the visible light region was observed for all of the Rh³⁺-modified TiO₂ samples, and the intensity of photoabsorption depended on the kind of TiO₂ as reported previously.¹⁹ Rh³⁺/TiO₂ samples were used for selective oxidation of benzyl alcohol to benzaldehyde in aqueous suspensions under irradiation of visible light from a blue LED. A clear correlation was not observed between the photoabsorption and the rate of benzaldehyde formation. Fig. 5 shows plots of the rate of benzaldehyde formation against the specific surface area of Rh³⁺/TiO₂ samples. The rate increased with increase in the surface area, indicating that the surface area of TiO₂ supports was a decisive factor controlling the reaction rate. For the mineralization of VOC in gas phase under irradiation of visible light, both the specific surface area and the crystallinity of TiO₂ affected the activities, and balance of them was important for higher activities.¹⁷⁻¹⁹ Therefore, the most contributory physical properties of TiO₂ were dependent on the type of reaction, and the photocatalytic performance of Rh³⁺/TiO₂ can be controlled by selecting appropriate TiO₂.

3.3 Correlations between amounts of adsorbed and reaction rates of benzyl alcohol, benzaldehyde and benzoic acid over TiO₂

Each photocatalytic oxidation of benzaldehyde and benzoic acid on Rh³⁺/F-6 was also examined (not competitive oxidation of benzyl alcohol, benzaldehyde and
benzoic acid) under the same conditions to clarify the high benzaldehyde selectivity in the oxidation of benzyl alcohol over Rh\textsuperscript{3+}/TiO\textsubscript{2} under irradiation of visible light. The order of rates of oxidation was determined to be as follows: benzoic acid (5.2 µmol h\textsuperscript{-1}) > benzyl alcohol (1.4 µmol h\textsuperscript{-1}) > benzaldehyde (0.24 µmol h\textsuperscript{-1}). These results indicate that benzaldehyde was least oxidized among the three compounds under the present conditions. Therefore, the lower rate of benzaldehyde oxidation than that of benzyl alcohol oxidation is attributed to the high benzaldehyde selectivity in the oxidation of benzyl alcohol over Rh\textsuperscript{3+}/TiO\textsubscript{2}. No detection of benzoic acid after the photocatalytic reaction shown in Fig. 2 is explained by the largest rate of oxidation and the smallest rate of formation of benzoic acid, i.e., immediate oxidation of a small amount of benzoic acid to CO\textsubscript{2} under the present conditions.

The amount of each compound adsorbed on photocatalysts in the dark was determined under the same conditions as those for the photocatalytic reaction. The adsorption amount decreased in the following order: benzoic acid (8.4 µmol) > benzyl alcohol (2.5 µmol) > benzaldehyde (0.46 µmol). The large amount of benzoic acid adsorbed was probably due to the formation of a chemical bond between the hydroxyl group on the surface of TiO\textsubscript{2} and the carboxylic group of benzoic acid, similar to the system of dye-sensitized TiO\textsubscript{2}.\textsuperscript{24,25} On the other hand, benzaldehyde was least adsorbed on photocatalysts among the three compounds under the present conditions.\textsuperscript{13} Therefore, the smallest adsorption amount of benzaldehyde is attributed to the smallest rate of benzaldehyde oxidation (consumption) over Rh\textsuperscript{3+}/TiO\textsubscript{2}, resulting in the accumulation of benzaldehyde in the reaction system. In this reaction system, the high selectivity of benzaldehyde formation explained by kinetics controlled by adsorption properties requires no extra modification of the photocatalyst, which generally consumes some modification materials and decreases the reaction rate itself. From these results, it can be concluded that the selective oxidation of benzyl alcohol to
benzaldehyde with O₂ over Rh³⁺/TiO₂ is a simple and environmentally friendly system.

Which compound was easily oxidized over Rh³⁺/TiO₂ under irradiation of visible light? Fig. 6 shows plots of the rates of oxidation of benzyl alcohol, benzaldehyde and benzoic acid against their adsorption amounts of in the dark. A linear correlation between each of them was observed and the line went through the origin. This result indicates that the rates of oxidation of the three compounds were decided only by the amounts of the compounds adsorbed on the photocatalyst and that the three compounds were equally oxidized under the present conditions.

3.4. Selective oxidation of benzyl alcohol derivatives and reaction mechanism of selective oxidation in an aqueous suspension of Rh³⁺/TiO₂

Selective oxidation of p-substituted benzyl alcohol derivatives over Rh³⁺/TiO₂ was examined. Table 3 shows results of photocatalytic selective oxidation of benzyl alcohol derivatives substituted by electron-donating groups (-OMe and -Me) and electron-withdrawing groups (-Cl and -NO₂) in aqueous suspensions of 1.2 wt% Rh³⁺/F-6 under irradiation of visible light. All of the derivatives were converted to the corresponding aldehydes with high selectivity. Fig. 7 shows the rates of formation of p-substituted benzyl alcohol derivatives against the Hammett constants. The rate linearly decreased in the order of -OMe > -Me > -H > -Cl > -NO₂, and a Hammett ρ value of -0.70 was obtained. This order indicates that the rate of p-substituted benzaldehyde formation is accelerated by electron-donating substituents, i.e., the intermediates formed in the reaction were cationic and the formation of the intermediates was the rate-determining step. Based on the above-described results, a possible reaction mechanism for the photocatalytic oxidation of benzyl alcohol to corresponding aldehydes over Rh³⁺/TiO₂ under visible light irradiation is shown in Scheme 1. This scheme is partially derived from the mechanism for electrochemical
oxidation of benzyl alcohols to aldehydes.\textsuperscript{26}

The working mechanism of \( \text{Rh}^{3+}/\text{TiO}_2 \) in oxidation of VOC in gas phase under irradiation of visible light\textsuperscript{21} can be mostly applied for the selective oxidation of benzyl alcohols to benzaldehydes. Charge transfer from \( \text{Rh}^{3+} \) to the conduction band of \( \text{TiO}_2 \) occurred under irradiation of visible light and \( \text{Rh}^{3+} \) changed to a higher oxidation state. The \( \text{Rh} \) species having a higher oxidation state oxidized benzyl alcohols adsorbed on \( \text{TiO}_2 \) and returned to the initial and stable oxidation state, \( \text{Rh}^{3+} \). As also shown in Fig. 2, \( \text{CO}_2 \) was not observed in the early stage of the reaction, indicating that the rate of direct oxidation of benzyl alcohol to \( \text{CO}_2 \) was very small. The small or negligible rate of direct oxidation may be explained by the oxidation power of \( \text{Rh} \) species milder than that of positive holes formed by the band-gap excitation of \( \text{TiO}_2 \) under irradiation of UV light. As shown in Scheme 1, conversion of benzyl alcohols to benzaldehydes requires two-step oxidation. In the first-step, there is no doubt that benzyl alcohols are oxidized by \( \text{Rh} \) species having a higher oxidation state, while some possibilities can be considered in the second-step oxidation, i.e., 1) subsequent oxidation by the \( \text{Rh} \) species having a higher oxidation state, 2) electron injection by benzyl alcohol radical intermediates to the conduction band of \( \text{TiO}_2 \) (current doubling effect), and 3) thermal oxidation of the benzyl alcohol radical intermediates by \( \text{O}_2 \). At this point, we have no experimental evidence explaining which process is predominant. From the results shown in section 3.3, most of the formed benzaldehydes were eliminated from the surface of the photocatalyst, avoiding further oxidation to benzoic acid and \( \text{CO}_2 \), and another benzyl alcohol molecule was adsorbed on the surface of the photocatalyst, resulting in continuous selective oxidation of benzyl alcohols to benzaldehydes. Electrons injected to the conduction band transferred to \( \text{O}_2 \) molecules through one or two-electron reduction, and active oxygen species, \( \text{O}_2^- \) or \( \text{H}_2\text{O}_2 \), were formed. Active oxygen species generally induce oxidation of various organic and inorganic
compounds. However, this was not the case as shown and discussed here as well as in several reaction systems such as Au/CeO$_2$.\textsuperscript{27} If the active oxygen species are further reduced to H$_2$O and H$_2$O$_2$ is decomposed to H$_2$O and O$_2$ under visible light irradiation or in the dark, i.e., thermally, there would be no possibility of oxidation of benzaldehydes. Investigation of the behavior of active oxygen species in the presence of Rh$^{3+}$/TiO$_2$ in the visible light irradiation and in the dark is now in progress.

4. Conclusions

Photocatalytic oxidation of benzyl alcohols in aqueous suspensions of an Rh$^{3+}$/TiO$_2$ photocatalyst in the presence of O$_2$ under irradiation of visible light was investigated. Benzaldehyde was obtained in a high yield (97%) at >99% conversion of benzyl alcohol, and a high carbon balance (>99%) was preserved during the reaction. The rate of benzaldehyde formation increased with increase in the surface area of the Rh$^{3+}$/TiO$_2$ photocatalyst, indicating that the surface area was a decisive factor controlling the reaction rate. The rates of oxidation of compounds were decided only by the amounts of the compounds adsorbed on the photocatalyst, and the smaller adsorption amount of benzaldehyde than that of benzyl alcohol is attributed to the smaller rate of benzaldehyde oxidation (consumption) than that of benzyl alcohol over Rh$^{3+}$/TiO$_2$, resulting in high benzaldehyde selectivity in the reaction system.

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REFERENCES


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Fig. captions

Table 1  Results of blank experiments under various conditions for 20 h
Table 2  The physical properties of TiO$_2$ used
Table 3  Results of selective oxidation of benzyl alcohols to benzaldehydes in an aqueous suspension of 1.2 wt% Rh$^{3+}$/F-6 for 20 h under irradiation of visible light

Fig. 1  UV-vis diffuse reflection spectra of unmodified and 0.5 wt% Rh$^{3+}$-modified F-6 samples and emission spectrum of visible light from a blue LED.

Fig. 2  Time courses of the amounts of benzyl alcohol (open circles), benzaldehyde (closed circles), $1/7$ CO$_2$ (triangles) and benzoic acid (open squares) and carbon balance (closed squares).

Fig. 3  Reaction rate of the selective oxidation of benzyl alcohol to benzaldehyde using the Rh$^{3+}$/TiO$_2$ sample in repeated experiments.

Fig. 4  Diffuse reflection spectra of unmodified TiO$_2$ (A) and Rh$^{3+}$-modified TiO$_2$ (B) samples.

Fig. 5  Formation rate of benzaldehyde in aqueous suspensions of Rh$^{3+}$/TiO$_2$ samples against the specific surface area of TiO$_2$ under irradiation of visible light.

Fig. 6  Rates of substance oxidation (black: benzyl alcohol, blue benzaldehyde, red: benzoic acid) under irradiation of visible light against the amount adsorbed in the dark.

Fig. 7  Hammett correlation study from oxidation of $p$-substituted benzyl alcohols in aqueous suspension of 1.2 wt% Rh$^{3+}$/F-6 under irradiation of visible light.
Scheme 1  Assumed reaction mechanism for oxidation of benzyl alcohols over Rh\textsuperscript{3+}/TiO\textsubscript{2}
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<td>Rh(^{3+})/F-6</td>
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Table 2  
Physical properties of TiO$_2$ used

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Fig. 6 Rates of substance oxidation (black: benzyl alcohol, blue benzaldehyde, red: benzoic acid) under irradiation of visible light against the amount adsorbed in the dark.
Table 3  Results of selective oxidation of benzyl alcohols to benzaldehydes in an aqueous suspension of 1.2 wt% Rh$^{3+}$/F-6 for 20 h under irradiation of visible light.

\[
\begin{array}{cccc}
\text{Entry} & \text{R} & \text{Conv. / %} & \text{Sel. / %} \\
1 & \text{OMe} & 93 & 91 \\
2 & \text{Me} & 92 & 92 \\
3 & \text{Cl} & 81 & 88 \\
4 & \text{NO}_2 & 70 & 97 \\
\end{array}
\]
Fig. 7 Hammett correlation study from oxidation of $p$-substituted benzyl alcohols in aqueous suspension of 1.2 wt% Rh$^{3+}$/F-6 under irradiation of visible light.
Scheme 1  Assumed reaction mechanism for oxidation of benzyl alcohols over Rh$^{3+}$/TiO$_2$