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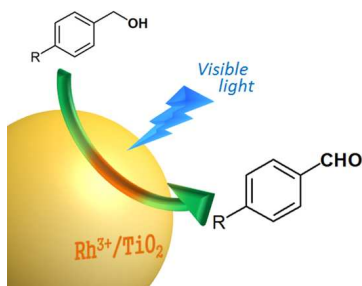
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Benzyl alcohol was converted to benzaldehyde with 97% yield in aqueous suspension of $\text{Rh}^{3+}/\text{TiO}_2$ photocatalysts under visible light irradiation.



Selective oxidation of alcohols in aqueous suspensions of rhodium ion-modified TiO₂ photocatalyst under irradiation of visible light

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ABSTRACT

Photocatalytic oxidation of benzyl alcohols in aqueous suspensions of rhodium ion-modified titanium(IV) oxide (Rh³⁺/TiO₂) in the presence of O₂ 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. Rh³⁺/TiO₂ photocatalysts having various physical properties were prepared using commercially available TiO₂ powders as supporting material for Rh³⁺ to investigate the effect(s) of physical properties of TiO₂ on photocatalytic activities of Rh³⁺/TiO₂ for selective oxidation. Adsorption properties of benzyl alcohol, benzaldehyde and benzoic acid on TiO₂ were also investigated to understand the high benzaldehyde selectivity over the Rh³⁺/TiO₂ 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 KMnO_4 and CrO_3 . 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 (O_2) instead of oxygen donor agents has attracted attention.^{1,2}

Titanium(IV) oxide (TiO_2) is known as an excellent photocatalyst.³⁻⁵ Under irradiation of UV light, TiO_2 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 TiO_2 photocatalyst has been widely used for oxidative degradation of pollutants, i.e., purification of the atmosphere and water. The TiO_2 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 TiO_2 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 O_2 . Photocatalytic selective oxidation over TiO_2 is an environmentally friendly reaction since only harmless substances, i.e., water, O_2 and TiO_2 , are used, and solar light can be utilized as an energy source. However, selectivity in the photocatalytic

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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 ($\text{Rh}^{3+}/\text{TiO}_2$), 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 $\text{Rh}^{3+}/\text{TiO}_2$ were enhanced by precise control of the physical properties of TiO_2 . In addition, we found that the $\text{Rh}^{3+}/\text{TiO}_2$ photocatalyst produced acetone with relatively high selectivity in oxidation of gaseous 2-propanol.^{17,18} Based on these results, we speculated that the $\text{Rh}^{3+}/\text{TiO}_2$ 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 $\text{Rh}^{3+}/\text{TiO}_2$ under irradiation of visible light and found that the $\text{Rh}^{3+}/\text{TiO}_2$ 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 TiO₂ powders was synthesized by the HyCOM (Hydrothermal Crystallization in Organic Media) method at 300°C as reported previously.²⁰ HyCOM-TiO₂ was calcined at 550°C in a box furnace for 1 h. Hereafter, the HyCOM-TiO₂ sample is denoted as HyCOM550. Various TiO₂ powders (ST-01, Ishihara Sangyo; MT-150A, TAYCA; F-6, Showa Titanium; P 25, Degussa; HyCOM550) were modified with Rh³⁺ by using the equilibrium adsorption method.¹⁷⁻¹⁹ Each of the TiO₂ powders was suspended in an aqueous solution of rhodium(III) chloride, RhCl₃, and stirred and then heated in a water bath at *ca.* 90°C for 1 h. The suspension was filtered and washed repeatedly. The residue was dried *in vacuo* at room temperature. The Rh³⁺-modified TiO₂ samples are designated as Rh³⁺/TiO₂; for example, the Rh³⁺-modified F-6 TiO₂ sample is designated as Rh³⁺/F-6. The amounts of Rh³⁺ on TiO₂ 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 α radiation by a Rigaku MultiFlex equipped with a carbon monochromator. Specific surface area (S_{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.

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2.3. Photocatalytic reaction

Each of the samples (50 mg) was suspended in distilled water (5 cm³) in a test tube (35 cm³), bubbled with O₂ 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 / cm², Hayashi Watch Works, Tokyo). The amount of carbon dioxide (CO₂) in gas phase (30 cm³) and the amounts of substrates and products in the reaction system were measured by using a Shimadzu GC-8A gas chromatograph with a Porapak 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 cm³) was added to a diethyl ether/water mixture (2:1 v/v, 3 cm³). 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 O₂ was not measured during the reaction since the amount of O₂ (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 Rh³⁺/F-6 under irradiation of visible light

Fig. 1 shows diffuse reflection spectra of unmodified and 0.5 wt% Rh³⁺-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 Rh³⁺/F-6 sample showed photoabsorption in the visible light region, which originated from the charge transfer from Rh³⁺ to the conduction band of TiO₂, as

reported previously.²¹

Fig. 2 shows the time courses of oxidation of benzyl alcohol in an aqueous suspension of 0.5 wt% Rh³⁺/F-6 in the presence of O₂ under irradiation of visible light from a blue LED. The amount of CO₂ evolved in the gas phase is also shown in Fig. 2. Since seven CO₂ molecules are formed from a benzyl alcohol molecule in the complete mineralization, one-seventh of the amount of CO₂ 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 CO₂ dissolved in the suspension was negligible. These results indicate that the Rh³⁺/F-6 photocatalyst possessed excellent performance for selective conversion of benzyl alcohol to benzaldehyde in water in the presence of O₂. In addition, no Rh³⁺ 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 μmol dm⁻³ for Rh³⁺. Since the concentration for 100% leaching of Rh³⁺ from TiO₂ corresponds to 490 μmol dm⁻³, the maximum leaching ratio was calculated to be 0.058%, indicating that Rh³⁺ 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 TiO₂ in an acetonitrile suspension.¹³⁻¹⁶ The result (Entry 2) indicates that oxidation of benzyl alcohol does not occur in water. Free

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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 $\text{Rh}^{3+}/\text{F-6}$ 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 $\text{Rh}^{3+}/\text{TiO}_2$ (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 $\text{Rh}^{3+}/\text{TiO}_2$ sample in repeated experiments. A decrease in reaction rate was not observed in the second use and third use of the $\text{Rh}^{3+}/\text{TiO}_2$ sample, suggesting that the $\text{Rh}^{3+}/\text{TiO}_2$ 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 ($\text{Cu}^{2+}/\text{TiO}_2$ and $\text{Fe}^{3+}/\text{TiO}_2$), which exhibited photocatalytic activities for decomposition of VOC in gas phase,^{22,23} 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 $\text{Cu}^{2+}/\text{TiO}_2$ and $\text{Fe}^{3+}/\text{TiO}_2$, 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 $\text{Rh}^{3+}/\text{TiO}_2$ 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 $\text{Rh}^{3+}/\text{TiO}_2$

under irradiation of visible light

Various kinds of TiO_2 powders were used as supporting material for Rh^{3+} to investigate the effects of physical properties of TiO_2 on photocatalytic activities of $\text{Rh}^{3+}/\text{TiO}_2$ for selective oxidation of benzyl alcohol. TiO_2 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 TiO_2 samples (A) and Rh^{3+} -modified TiO_2 samples (B). Photoabsorption in the visible light region was observed for all of the Rh^{3+} -modified TiO_2 samples, and the intensity of photoabsorption depended on the kind of TiO_2 as reported previously.¹⁹ $\text{Rh}^{3+}/\text{TiO}_2$ 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 $\text{Rh}^{3+}/\text{TiO}_2$ samples. The rate increased with increase in the surface area, indicating that the surface area of TiO_2 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 TiO_2 affected the activities, and balance of them was important for higher activities.¹⁷⁻¹⁹ Therefore, the most contributory physical properties of TiO_2 were dependent on the type of reaction, and the photocatalytic performance of $\text{Rh}^{3+}/\text{TiO}_2$ can be controlled by selecting appropriate TiO_2 .

3.3. Correlations between amounts of adsorbed and reaction rates of benzyl alcohol, benzaldehyde and benzoic acid over TiO_2

Each photocatalytic oxidation of benzaldehyde and benzoic acid on $\text{Rh}^{3+}/\text{F-6}$ was also examined (not competitive oxidation of benzyl alcohol, benzaldehyde and

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benzoic acid) under the same conditions to clarify the high benzaldehyde selectivity in the oxidation of benzyl alcohol over $\text{Rh}^{3+}/\text{TiO}_2$ under irradiation of visible light. The order of rates of oxidation was determined to be as follows: benzoic acid ($5.2 \mu\text{mol h}^{-1}$) > benzyl alcohol ($1.4 \mu\text{mol h}^{-1}$) > benzaldehyde ($0.24 \mu\text{mol h}^{-1}$). 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 $\text{Rh}^{3+}/\text{TiO}_2$. 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_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 ($8.4 \mu\text{mol}$) > benzyl alcohol ($2.5 \mu\text{mol}$) > benzaldehyde ($0.46 \mu\text{mol}$). 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_2 and the carboxylic group of benzoic acid, similar to the system of dye-sensitized TiO_2 .^{24,25} On the other hand, benzaldehyde was least adsorbed on photocatalysts among the three compounds under the present conditions.¹³ Therefore, the smallest adsorption amount of benzaldehyde is attributed to the smallest rate of benzaldehyde oxidation (consumption) over $\text{Rh}^{3+}/\text{TiO}_2$, 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

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oxidation of benzyl alcohols to aldehydes.²⁶

The working mechanism of Rh³⁺/TiO₂ in oxidation of VOC in gas phase under irradiation of visible light²¹ can be mostly applied for the selective oxidation of benzyl alcohols to benzaldehydes. Charge transfer from Rh³⁺ to the conduction band of TiO₂ occurred under irradiation of visible light and Rh³⁺ changed to a higher oxidation state. The Rh species having a higher oxidation state oxidized benzyl alcohols adsorbed on TiO₂ and returned to the initial and stable oxidation state, Rh³⁺. As also shown in Fig. 2, CO₂ was not observed in the early stage of the reaction, indicating that the rate of direct oxidation of benzyl alcohol to CO₂ was very small. The small or negligible rate of direct oxidation may be explained by the oxidation power of Rh species milder than that of positive holes formed by the band-gap excitation of TiO₂ 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 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 Rh species having a higher oxidation state, 2) electron injection by benzyl alcohol radical intermediates to the conduction band of TiO₂ (current doubling effect), and 3) thermal oxidation of the benzyl alcohol radical intermediates by O₂. 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 CO₂, 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 O₂ molecules through one or two-electron reduction, and active oxygen species, O₂^{•-} or H₂O₂, 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/CeO₂²⁷ and photosensitized benzyl alcohol-TiO₂.¹³⁻¹⁶ If the active oxygen species are further reduced to H₂O and H₂O₂ is decomposed to H₂O and O₂ 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 Rh³⁺/TiO₂ 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 Rh³⁺/TiO₂ photocatalyst in the presence of O₂ 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 Rh³⁺/TiO₂ 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 Rh³⁺/TiO₂, resulting in high benzaldehyde selectivity in the reaction system.

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Fig. captions

- Table 1** Results of blank experiments under various conditions for 20 h
- Table 2** The physical properties of TiO₂ used
- Table 3** Results of selective oxidation of benzyl alcohols to benzaldehydes in an aqueous suspension of 1.2 wt% Rh³⁺/F-6 for 20 h under irradiation of visible light
- Fig. 1** UV-vis diffuse reflection spectra of unmodified and 0.5 wt% Rh³⁺-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 CO₂ (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 Rh³⁺/TiO₂ sample in repeated experiments.
- Fig. 4** Diffuse reflection spectra of unmodified TiO₂ (A) and Rh³⁺-modified TiO₂ (B) samples.
- Fig. 5** Formation rate of benzaldehyde in aqueous suspensions of Rh³⁺/TiO₂ samples against the specific surface area of TiO₂ 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% Rh³⁺/F-6 under irradiation of visible light.

Scheme 1 Assumed reaction mechanism for oxidation of benzyl alcohols over $\text{Rh}^{3+}/\text{TiO}_2$

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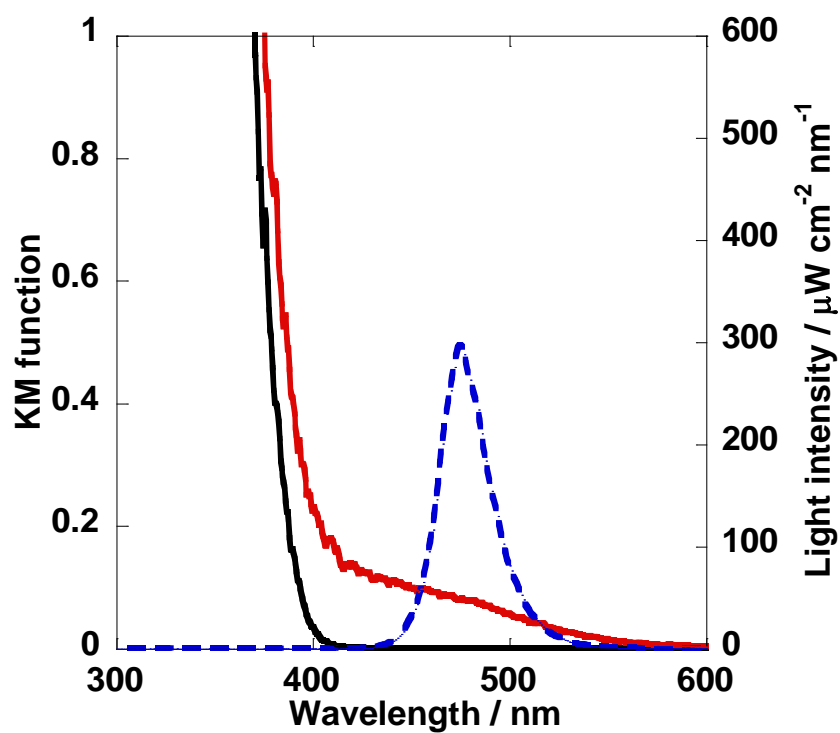


Fig. 1 UV-vis diffuse reflection spectra of unmodified and 0.5 wt% Rh³⁺-modified F-6 samples and emission spectrum of visible light from a blue LED.

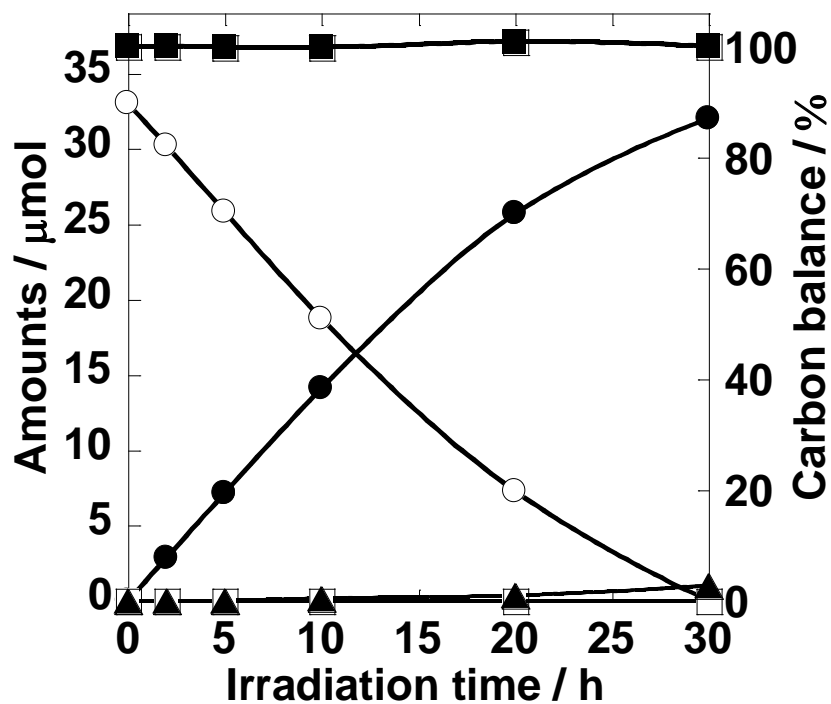


Fig. 2 Time courses of the amounts of benzyl alcohol (open circles), benzaldehyde (closed circles), $1/7 \text{ CO}_2$ (triangles) and benzoic acid (open squares) and carbon balance (closed squares).

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Table 1 Results of blank experiments under various conditions for 20 h

Entry	Sample	Light	Conv. /%	Sel. /%
1	Rh ³⁺ /F-6	on	78	>99
2	F-6	on	trace	trace
3	Rh ³⁺ (Aq. RhCl ₃)	on	trace	trace
4	Rh ³⁺ /F-6	off	trace	trace

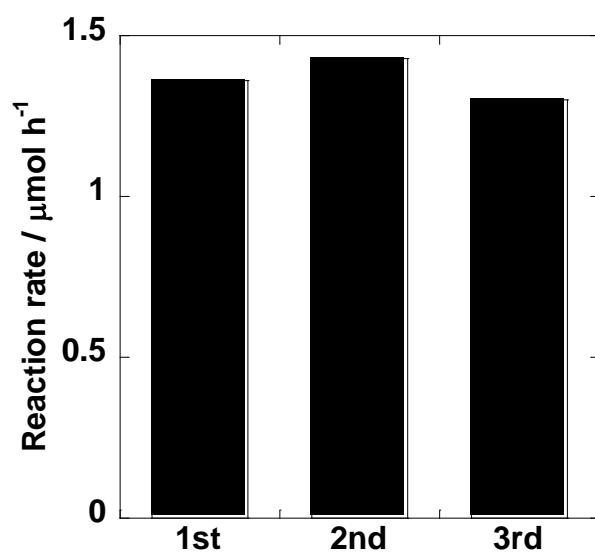


Fig. 3 Reaction rate of the selective oxidation of benzyl alcohol to benzaldehyde using the $\text{Rh}^{3+}/\text{TiO}_2$ sample in repeated experiments.

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Table 2 Physical properties of TiO₂ used

Sample	S _{BET} / m ² g ⁻¹	Phase
ST-01	260	Anatase
F-6	98	Anatase, Rutile
MT-150A	95	Rutile
HyCOM550	81	Anatase
P 25	54	Anatase, Rutile

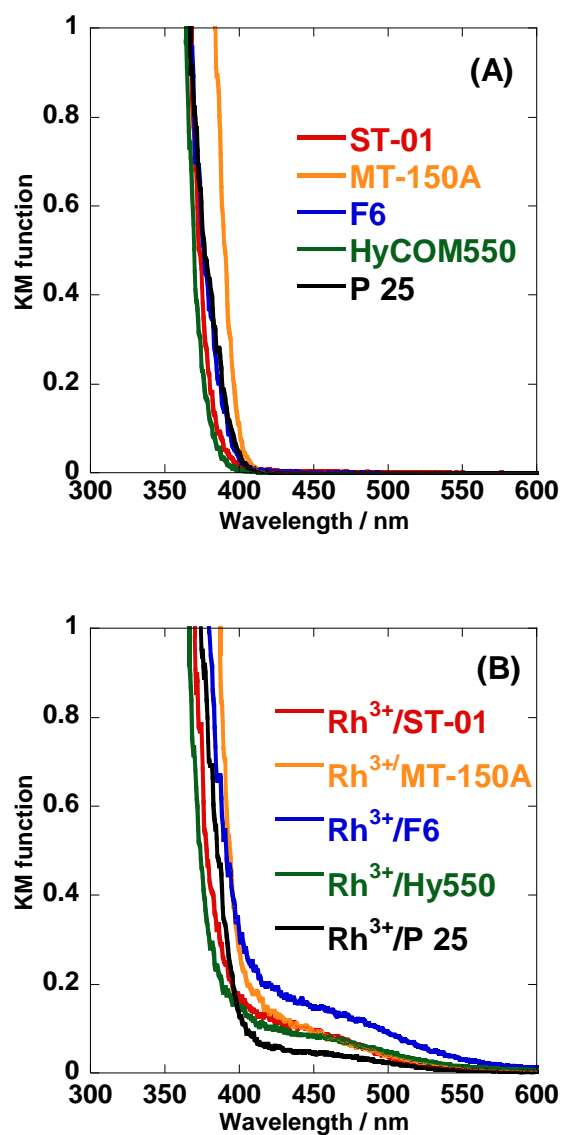


Fig. 4 Diffuse reflection spectra of unmodified TiO₂ (A) and Rh³⁺-modified TiO₂ (B) samples.

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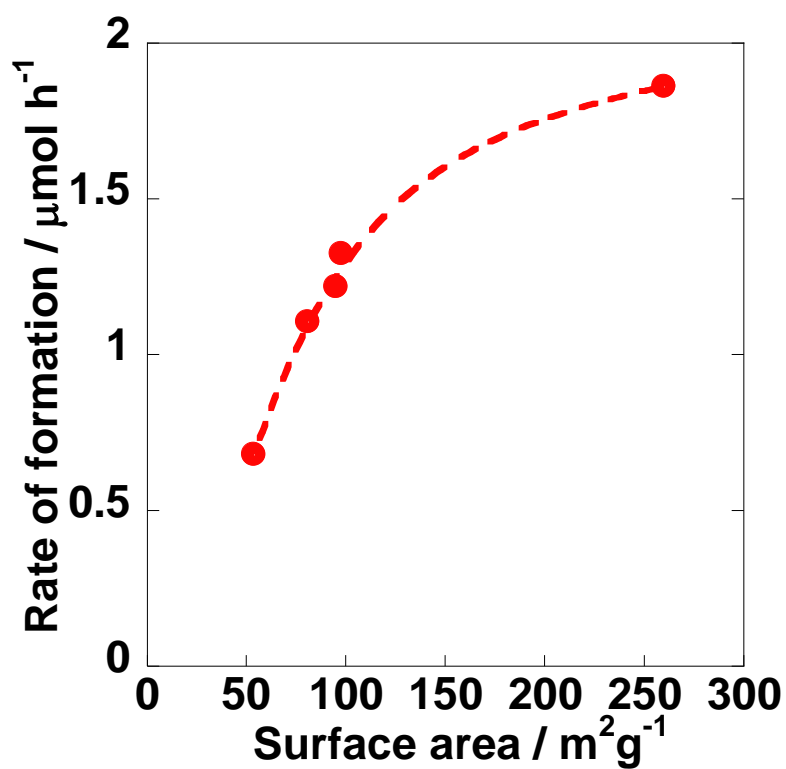


Fig. 5 Formation rate of benzaldehyde in aqueous suspensions of Rh³⁺/TiO₂ samples against the specific surface area of TiO₂ under irradiation of visible light.

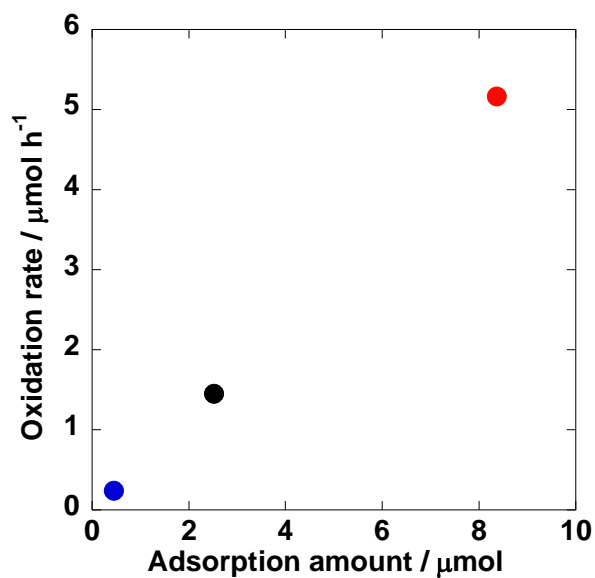
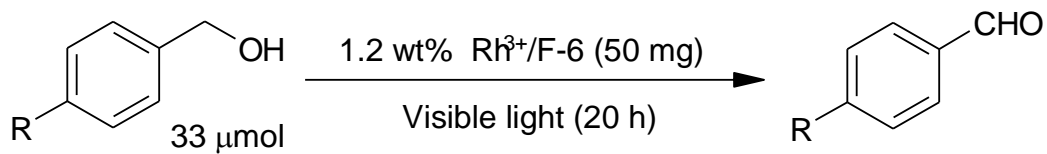


Fig. 6 Rates of substance oxidation (black: benzyl alcohol, blue benzaldehyde, red: benzoic acid) under irradiation of visible light against the amount adsorbed in the dark.

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Table 3 Results of selective oxidation of benzyl alcohols to benzaldehydes in an aqueous suspension of 1.2 wt% Rh³⁺/F-6 for 20 h under irradiation of visible light



Entry	R	Conv. / %	Sel. /%
1	OMe	93	91
2	Me	92	92
3	Cl	81	88
4	NO ₂	70	97

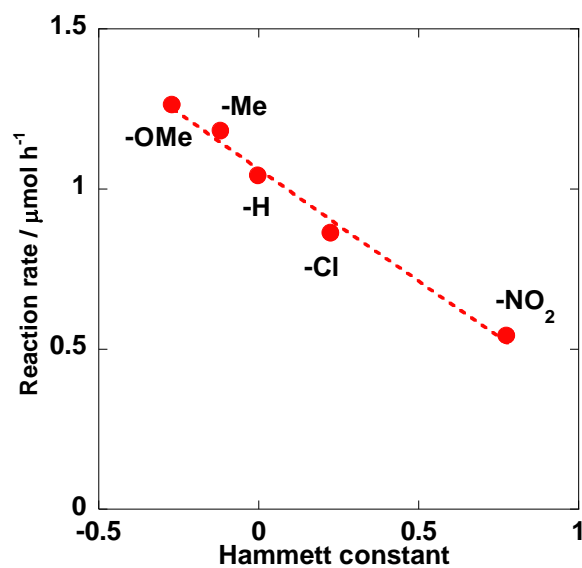
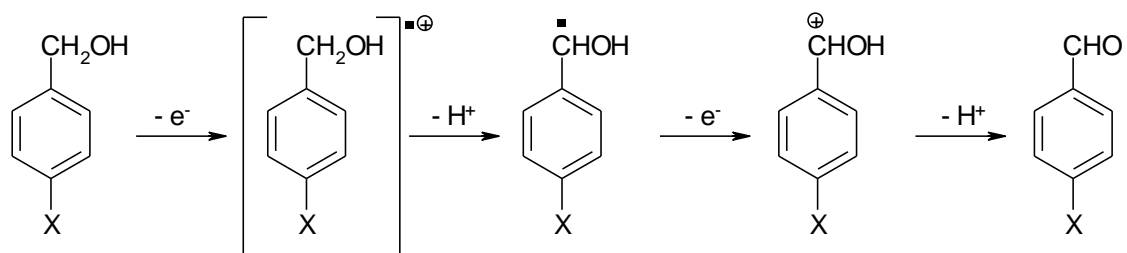


Fig. 7 Hammett correlation study from oxidation of *p*-substituted benzyl alcohols in aqueous suspension of 1.2 wt% Rh³⁺/F-6 under irradiation of visible light

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Scheme 1 Assumed reaction mechanism for oxidation of benzyl alcohols over $\text{Rh}^{3+}/\text{TiO}_2$