Selective oxidation of aldehydes on TiO$_2$ photocatalysts modified with functional groups

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Abstract

Surfaces of SiO$_2$-covered titanium dioxide (TiO$_2$) photocatalysts (SiO$_2$-TiO$_2$) were modified with alkylsilyl groups such as hydrocarbon, fluorocarbon, and phenyl groups. Oxidation of propanal, hexanal, nonanal, pentafuluorobenzaldehyde, and benzaldehyde proceeded much more efficiently on the surface-modified SiO$_2$-TiO$_2$ particles than on SiO$_2$-TiO$_2$ photocatalysts without surface modification. In the case of SiO$_2$-TiO$_2$ photocatalysts modified with hydrocarbon chains, one of the most important factors for improvement of the photocatalytic activities of surface-modified TiO$_2$ photocatalysts is the hydrophobic interaction between substrates and alkylsilyl groups introduced onto SiO$_2$-TiO$_2$ photocatalysts. SiO$_2$-TiO$_2$ modified with phenyl groups is more active in the photocatalytic oxidation of benzaldehyde than SiO$_2$-TiO$_2$-C$_6$. Furthermore, oxidation of pentafluorobenzaldehyde proceeded more favorably on SiO$_2$-TiO$_2$-C$_8$(F) chains than on SiO$_2$-TiO$_2$-C$_8$. These results indicated that the functional groups introduced onto the surface of SiO$_2$-TiO$_2$ play an important role in showing selectivity for photocatalytic oxidation of organic compounds.
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1. Introduction

Titanium dioxide (TiO$_2$)-mediated heterogeneous photocatalysis has attracted much attention recently because of its potential applications to decomposition of pollutants in water and air [1–5]. TiO$_2$ and some other semiconductor photocatalysts have also been extensively studied for the purpose of solar energy conversion [6–11]. In many applications, anatase TiO$_2$ powders consisting of particles with large surface areas are used as photocatalysts. In contrast to these compounds, oxidation of water efficiently proceeds on large rutile TiO$_2$ particles [4,5,9]. In addition to the importance of the crystal structures of TiO$_2$ powders for improving photocatalytic activity as described above, the properties of surfaces of TiO$_2$ particles are also important factors for determining their photocatalytic activity for degradation of organic compounds in aqueous media.

Under photoirradiation, the surfaces of TiO$_2$ particles show a hydrophilic property [12]. This property prevents hydrophobic organic compounds from adsorbing on the surfaces of TiO$_2$ photocatalysts in aqueous media. This condition is a great disadvantage for the degradation of organic compounds in aqueous media. Park and Choi [13], Wang et al. [14], and Li et al. [15,16] reported fluorine atoms adsorbed on the surfaces of TiO$_2$ photocatalysts, the surfaces of which are more hydrophobic than pure TiO$_2$. Hydrophobic TiO$_2$ pillard clay catalysts were also developed by Ooka et al. [17–19]. However, the surface properties of these photocatalysts are not optimized to improve selectivity and activity for oxidation of organic pollutants in aqueous media. In addition, photodegradation of a mixture of organic pollutants at an extremely low concentration in aqueous media requires very high molecular selectivity and concentration of the organic pollutant. Otherwise, the surfaces of TiO$_2$ photocatalysts are saturated with co-existing compounds with much higher concentrations.

In order to overcome these disadvantages, the surfaces of TiO$_2$ particles were modified with hydrocarbon or fluorocarbon

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chains or with other functional groups through Ti–O–Si bonds. For instance, by introducing hydrocarbon chains on the surfaces of TiO_2 particles, the surfaces of TiO_2 particles become hydrophobic. TiO_2 photocatalysts modified with hydrophobic functional groups or molecular recognition groups show higher levels of photocatalytic activity and selectivity than do pure TiO_2 photocatalysts without surface modification. Here, we report the syntheses of surface-modified TiO_2 powders and the selective oxidation of aldehydes in aqueous media on the TiO_2 powders.

2. Experimental

2.1. Materials and instruments

TiO_2 particles uniformly covered with porous silica (SiO_2-TiO_2; average pore size: 50 Å; anatase phase: 15% of SiO_2 and 85% of TiO_2; relative surface area: 170 $m^2\,g^{-1}$) were supplied by Taihei Kagaku Sangyo. Propionaldehyde, nonanal, benzaldehyde, and hexanoic acid were obtained from Sigma–Aldrich Fine Chemicals. *n*-Hexyltrichlorosilane, tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane, trichloromethylsilane, hexanal, propionic acid, nonanoic acid, benzoic acid, and 3-phenylpropionic acid were obtained from Wako Pure Chemical Industries Ltd. *n*-Decyltrichlorosilane, *n*-dodecyltrichlorosilane, *n*-octadecyltrichlorosilane, and valeraldehyde were supplied by Tokyo Kasei Kogyo Co. Ltd. *n*-Butyltrichlorosilane, *n*-octyltrichlorosilane, and phenyltrichlorosilane were obtained from Sin-Etsu Chemical Co. Ltd. Other commercial chemicals were of the highest available grade and were used without further purification. The crystal structures of TiO_2 powders were determined from X-ray diffraction (XRD) patterns measured with an X-ray diffractometer (Philips, X'Pert-MRD) with a Cu target Kα-ray ($l = 1.5405$ Å). The relative surface areas of the powders were determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300). X-ray photoelectron spectra (XPS) of the TiO_2 powders were measured using a Shimadzu ESCA1000 photoelectron spectrometer with an Al Kα source (1486.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.0 eV as an internal standard. The XPS peaks were assumed to have Gaussian line shapes and were resolved into components by a non-linear least squares procedure after proper subtraction of the baseline. Fourier transform infrared spectroscopy was carried out using a Bruker IFS66 spectrometer with a diffuse reflectance accessory.

2.2. Modification of surfaces of SiO_2-TiO_2 particles

Modifications of the surfaces of SiO_2-TiO_2 particles with alkylsilyl, fuluoroalkylsilyl, or other functional groups were carried out according to previously reported methods [20,21]. One typical procedure for modification of the surfaces of SiO_2-TiO_2 particles is as follows. SiO_2-TiO_2 (6.0 g) was suspended in toluene containing 5.0 mmol of octadecyltrichlorosilane (ODS). The solution was stirred for 10 min at room temperature, and methanol was added to the solution to stop the reaction. The precipitate was then dried at 50 °C under reduced pressure for 5 h.
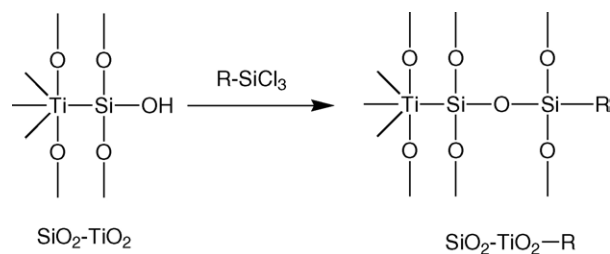
Scheme 1.

In order to change the coverage of functional groups introduced on SiO_2-TiO_2, the amount of alkyltrichlorosilan was changed. The functional groups were introduced on the surfaces of SiO_2-TiO_2 particles through R–Si–O–Si bonds by the reaction shown in Scheme 1.

The resulting powder was labeled SiO_2-TiO_2-C_{10} (10: number of hydrocarbons). Labels of other surface-modified TiO_2 powders are as follows: SiO_2-TiO_2-C_1, SiO_2-TiO_2-C_4, SiO_2-TiO_2-C_8, SiO_2-TiO_2-C_{12}, SiO_2-TiO_2-C_{18}, SiO_2-TiO_2-C_8F, and SiO_2-TiO_2-Ph. Based on weight fractions of carbon and ash components obtained by an elemental analysis, the amount ($\mu mol\,g^{-1}$: M_a) of surface organosilyl groups was determined by assuming that the remaining ash is composed of a mixture of TiO_2 and SiO_2. Using M_a, external surface area and the estimated cross-section of an organosilyl group based on atomic radii [22,23], the surface coverage of functional groups on SiO_2-TiO_2 was calculated.

2.3. Hydrophobicity and surface areas of surface-modified SiO_2-TiO_2 particles

The overall hydrophobicity–hydrophilicity of surface-modified SiO_2-TiO_2 particles such as SiO_2-TiO_2-C_{10} particles was evaluated by observing their behavior (floatability) when surface-modified powder was added to water–acetonitrile mixtures of various compositions [22]. Ten milligrams of SiO_2-TiO_2-C_{10} powder was added to 5 ml of a given concentration of aqueous acetonitrile. After shaking for 5 min, the mixture was centrifuged and the precipitate was collected. The percent fraction of floating particles was calculated as the difference between weights of added and precipitated particles. The floatability of SiO_2-TiO_2-C_n ($n = 4$ and 18), SiO_2-TiO_2-C_8F, and SiO_2-TiO_2-Ph on water–acetonitrile mixtures was also examined under the same conditions.

Surface areas of SiO_2-TiO_2 particles were also measured before and after surface modification.

2.4. Stability of functional groups introduced onto the surfaces of SiO_2-TiO_2 particles

In order to evaluate the photostabilities of SiO_2-TiO_2 modified with functional groups, the photocatalyst was photoirradiated using a 500 W Hg lamp for 5 h in pure aqueous solutions. The intensity of the incident light was 6.5 mW cm^{-2}. The FT-IR spectra of the surface-modified SiO_2-TiO_2 particles were measured before and after photoirradiation. Coverage of functional

groups introduced onto SiO_2-TiO_2 particles was also analyzed before and after photoirradiation.

2.5. Photocatalytic degradation of aldehyde compounds on SiO₂-TiO₂ particles surface-modified with functional groups

Activities of SiO_2-TiO_2-C_n ($n = 1, 4, 8, 10, 12$, and 18), SiO_2-TiO_2-C_8F, and SiO_2-TiO_2-Ph for photodegradation of aldehydes in aqueous media were evaluated as follows. Surface-modified photocatalyst particles (100 mg) were added to an aqueous solution of aldehydes (20 mM: propanal, hexanal, nonanal, benzaldehyde, and pentafluorobenzaldehyde) and H_2O (5 ml). The mixture was then stirred vigorously to form an emulsion and photoirradiated under aerated conditions. Photoirradiation was performed using a super-high-pressure mercury lamp (Wakom BMS-350S, 350 W) from the top of a cylindrical reaction vessel (transparent at >300 nm, 2.5 cm in diameter) at room temperature. The intensity of the incident light was 7.0 mW cm^{-2}. The reaction mixture was agitated vigorously with a magnetic stirrer during photoirradiation. After the reaction, photocatalyst powder was removed by centrifugation. The filtrate was injected into a gas chromatograph instrument. The reaction products were identified by co-injecting corresponding authentic samples. Decreases in the amounts of aldehydes and products generated in the aqueous solution were analyzed using a capillary gas chromatograph (Hitachi G3500, FID detector) equipped with an RTx-5 capillary column and using a Shimadzu C-R6A-FFC Chromatopac data processor.

Amounts of substrates (aldehyde compounds) adsorbed on SiO_2-TiO_2-C_n ($n = 1, 4, 8, 10, 12$, and 18), SiO_2-TiO_2-C_8F, and SiO_2-TiO_2-Ph were estimated in aqueous media as follows. Surface-modified photocatalyst particles (100 mg) were added to an aqueous solution of aldehydes (20 mM: propanal, hexanal, nonanal, benzaldehyde, and pentafluorobenzaldehyde) and H_2O (5 ml). The mixture was then stirred vigorously to make an emulsion. The reaction mixture was agitated vigorously with a magnetic stirrer during photoirradiation. After stirring for an appropriate time, acetonitrile (5 ml) was added to the solution to dissolve substrates adsorbed on photocatalysts into the solution and photocatalyst powder was removed by centrifugation. The filtrate was injected into a gas chromatograph instrument. Decreases in the amounts of aldehydes in the aqueous solution were analyzed as described above.

3. Results and discussion

3.1. Surface coverage of SiO₂-TiO₂ particles modified with functional groups

The degrees of surface coverage of SiO_2-TiO_2-C_n ($n = 1, 4, 8, 10, 12$, and 18), SiO_2-TiO_2-C_8(F), and SiO_2-TiO_2-Ph are shown in Table 1. The estimated cross-sections of linear alkyl (0.213 nm^2), phenyl (0.226 nm^2), and fluorocarbon (0.274 nm^2) groups [22,23] were used to calculate the degrees of coverage. In the case of SiO_2-TiO_2-C_n photocatalysts, surface coverage was changed in the range of 10–50%. When the coverage was higher than 30%, the activity of SiO_2-TiO_2-C_n for oxidation

of aldehydes greatly decreased because an excessive amount of alkylsilyl groups prevents a reactant from adsorbing on the surfaces of photocatalysts due to steric hindrance. The enhancement of activity of SiO_2-TiO_2-C_n with surface coverage of less than 10% was smaller than the enhancement of activity of SiO_2-TiO_2-C_n with about 20% surface coverage because of lower hydrophobicity. For instance, the data for oxidation of nonanal on SiO_2-TiO_2-C_{10} with various degrees of surface coverage are as follows (coverage: %, amount of nonanal decreased: mM, amount of nonanoic acid: mM): (10.5, 6.5, 5.6), (17.8, 7.8, 5.8), (29.6, 7.0, 5.4), (40.8, 6.1, 4.8), and (49.5, 4.9, 3.8). The surface-modified SiO_2-TiO_2 photocatalysts showed a similar tendency for all of the organic aldehydes used in this study.

We also investigated the optimum coverage of SiO_2-TiO_2-C_8(F) and SiO_2-TiO_2-Ph photocatalysts. The optimum coverage of SiO_2-TiO_2-C_8F was found to be 62.9%, which is larger than that in the case of SiO_2-TiO_2-C_n. In addition to the hydrophobic interaction between the functional groups on SiO_2-TiO_2 and the substrates, the interaction of fluorine atoms between the substrate and the functional group introduced on SiO_2-TiO_2 particles is an important factor for selectivity of the reaction. Therefore, an increase in coverage of the surface-modified photocatalysts improves the selectivity as will be discussed in Section 3.5. In the case of SiO_2-TiO_2-Ph, the optimum coverage was found to be 55.9%. This value is also larger than that in the case of SiO_2-TiO_2-C_n. The target compounds that are thought to be decomposed by the surface-modified SiO_2-TiO_2 photocatalysts affect these optimum values. These tendencies will be discussed in Section 3.5.

3.2. Surface areas of SiO₂-TiO₂ particles modified with functional groups

By introducing functional groups on the surfaces of SiO_2-TiO_2 particles, their surface area decreased as shown in Table 1. The amount of functional groups introduced onto SiO_2-TiO_2 particles increased with decrease in surface area. These results indicate that the functional groups are introduced not only onto the outer surfaces of SiO_2-TiO_2 particles but also onto the pore surfaces of SiO_2-TiO_2 particles. Therefore, some pores mainly located on the surfaces of SiO_2-TiO_2 particles disappear with formation Si–O–Si bonds as a result of the reaction between

Table 1
Surface area and coverage of the surface-modified TiO_2 particles

TiO_2 powders	Surface area (m^2 g^{-1})	Coverage (%)
SiO_2-TiO_2	135.5	0
SiO_2-TiO_2-C_1	93.6	31.2
SiO_2-TiO_2-C_4	104.1	28.3
SiO_2-TiO_2-C_6	77.5	24.8
SiO_2-TiO_2-C_8	99.8	20.9
SiO_2-TiO_2-C_{10}	96.7	17.8
SiO_2-TiO_2-C_{12}	94.7	15.9
SiO_2-TiO_2-C_{18}	84.6	19.2
SiO_2-TiO_2-phenyl	81.4	55.9
SiO_2-TiO_2-C_8(F)	61.1	62.9

the alkyl–silane coupling reagent and the surfaces of SiO_2-TiO_2 particles.

3.3. Hydrophobicity of SiO_2-TiO_2 particles modified with functional groups

Fig. 1 shows the floatability of SiO_2-TiO_2-C_4 (coverage: 28.3%), SiO_2-TiO_2-C_6 (coverage: 24.8%), SiO_2-TiO_2-C_{10} (coverage: 17.8%), and SiO_2-TiO_2-C_{18} (coverage: 19.2%) particles as a function of the volume fraction of acetonitrile in water. In the case of SiO_2-TiO_2-C_{10}, almost all of the surface-modified particles (SiO_2-TiO_2-C_{10}) floated, i.e., without any appreciable precipitation, when the volume fraction of acetonitrile was less than 20%, indicating that the particle surfaces were hydrophobic. With increase in the acetonitrile fraction from 30 to 40%, some of the SiO_2-TiO_2-C_{10} particles settled, and complete sedimentation of both samples was observed when the acetonitrile fraction became greater than 45%. The amount of floating SiO_2-TiO_2 particles modified with hydrocarbon chains increased with increase in the number of hydrocarbon chains introduced on SiO_2-TiO_2 particles. These results indicate that the hydrophobicity is dependent on the number of hydrocarbons introduced on the surfaces of SiO_2-TiO_2 particles.

The floatability of SiO_2-TiO_2-C_8(F) particles (coverage: 42.9%) was also investigated in a mixture of acetonitrile and water as shown in Fig. 1. When the volume fraction of acetonitrile was less than 40%, almost all of the SiO_2-TiO_2-C_8(F) particles floated. This result indicates that the surface of the modified sample (SiO_2-TiO_2-C_8(F)) was more hydrophobic than that of SiO_2-TiO_2-C_{10} particles. With increase in the acetonitrile fraction from 45 to 60%, some of the SiO_2-TiO_2-C_8(F) particles settled, and complete sedimentation of both samples was observed when the acetonitrile fraction became greater than 70%.

Fig. 1 also shows the floatability of SiO_2-TiO_2-Ph particles (coverage: 42.9%) as a function of the volume fraction of acetonitrile in water. Almost all of the surface-modified particles (SiO_2-TiO_2-C_8(F)) floated when the volume fraction of acetonitrile was less than 15%, indicating that the surface of the modified sample (SiO_2-TiO_2-Ph) was less hydrophobic than

that of SiO_2-TiO_2-C_{10} particles. With increase in the acetonitrile fraction from 20 to 40%, some of the SiO_2-TiO_2-Ph particles settled, and complete sedimentation of both samples was observed when the acetonitrile fraction became greater than 50%.

3.4. Stability of functional groups introduced onto the surfaces of SiO_2-TiO_2 particles

The floatability of the surface-modified SiO_2-TiO_2 particles was investigated before and after photoirradiation in order to estimate the stability of functional groups introduced onto the surfaces of SiO_2-TiO_2 particles. After photoirradiation, a few particles settled. The settled particles were collected and dried under reduced pressure at 60 °C for 12 h. The collected particles floated again when the powder was put into water. Under photoirradiation, the surfaces of TiO_2 particles become hydrophilic. Therefore, the hydrophobicity of the functional groups and hydrophilicity of the surfaces of SiO_2-TiO_2 particles are balanced under photoirradiation. As a result, some particles settle. In order to determine the amounts of functional groups on the surfaces of SiO_2-TiO_2 particles before and after photoirradiation, XPS spectra and FT-IR spectra of surface-modified SiO_2-TiO_2 particles were examined.

Fig. 2 shows the FT-IR spectra of SiO_2-TiO_2 particles modified with functional groups before and after photoirradiation. In the case of fluorocarbon chains introduced onto SiO_2-TiO_2 particles, peaks assigned to C–F stretching vibrations of the fluorocarbon chains were observed at around 1315 and 1365 cm^{-1}. The intensities of the peaks were not changed after photoirradiation for 5 h as shown in Fig. 2.

The peak at around 2920 cm^{-1} assigned to C–H stretching vibrations on SiO_2-TiO_2-C_n was not changed either after photoirradiation as shown in Fig. 3. FT-IR peaks assigned to CH_2 stretching were observed at 2926 and 2853 cm^{-1} in the case of SiO_2-TiO_2-C_n. Peaks assigned to CH_3 stretching were also observed at 2962 and 2872 cm^{-1}. There was little change in these after photoirradiation for 5 h. Fig. 4 shows XPS peaks assigned
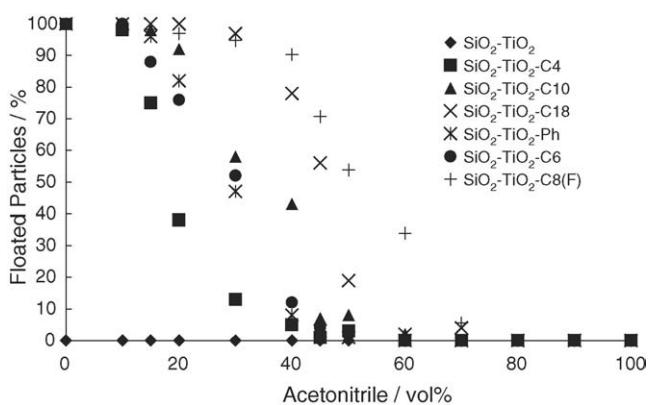

Fig. 1. Dependence of amount of floating particles of surface-modified TiO_2 particles as well as SiO_2-TiO_2 itself on the volume fraction of acetonitrile in water.
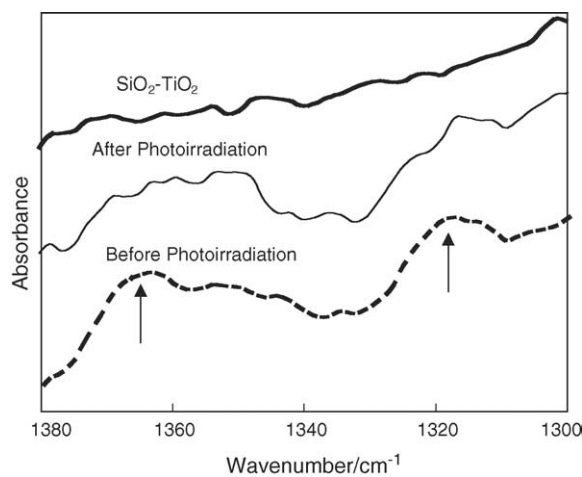

Fig. 2. FT-IR absorption spectra of SiO_2-TiO_2-C_8(F) before and after photoirradiation in water for 5 h and SiO_2-TiO_2 without surface modification. Arrows indicate the peaks assigned to C–F stretching vibrations.
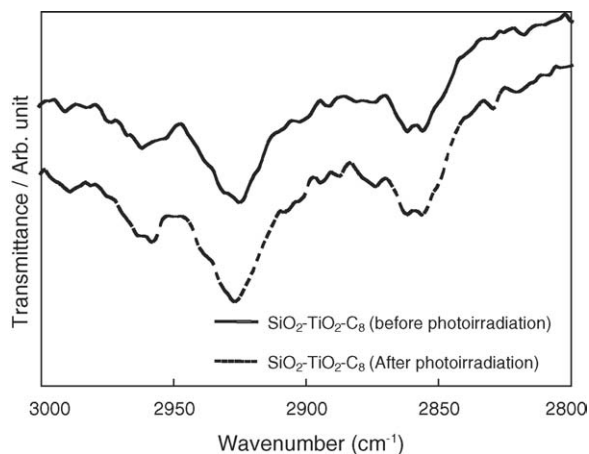
Fig. 3. FT-IR absorption spectra of SiO_2-TiO_2-C_8 before and after photoirradiation in water for 5 h.

to F atoms at around 688.4 eV. The intensities of the peaks did not change after photoirradiation for 5 h. These results indicate that the grafted fluorocarbon chains were not decomposed by photocatalysis of SiO_2-TiO_2 because grafted functional groups are thought to be mainly introduced onto the surfaces of SiO_2 moieties of SiO_2-TiO_2 particles. Functional groups such as phenyl groups introduced onto SiO_2-TiO_2 particles also show similar stability under UV light irradiation. These stabilities are supported by FT-IR measurements in addition to results of elemental analyses. These results suggest that the functional groups introduced onto the surfaces of the SiO_2-TiO_2 particles are stable under photocatalytic conditions.

3.5. Activities of surface-modified SiO_2-TiO_2 particles photocatalytic for degradation of aldehyde compounds

Figs. 5–7 show the photocatalytic activities of SiO_2-TiO_2-C_n ($n = 1, 4, 8, 10, 12,$ and 18) for oxidation of aldehydes such as propanal, hexanal, and nonanal by irradiation for 1 h at room temperature. For any kind of aldehyde, the main products were calboxylic acids (propanoic acid, hexanoic acid, or nonionic acid).
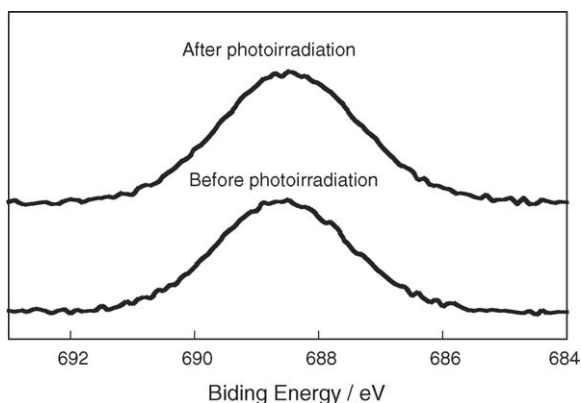

Fig. 4. X-ray photoelectron spectra of F 1s of SiO_2-TiO_2-C_8(F) particles before and after photoirradiation.

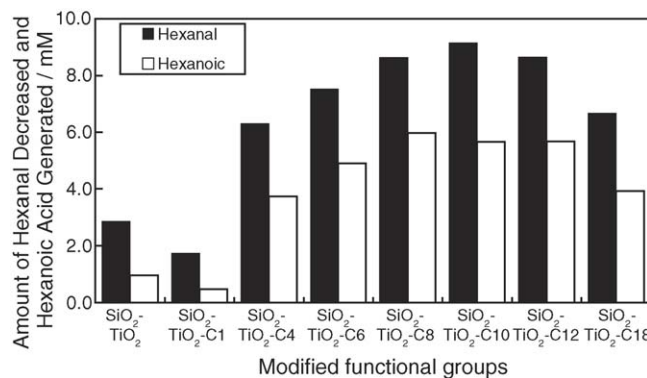Fig. 5. Photocatalytic activities for oxidation of hexanal on surface-modified TiO_2 powders (SiO_2-TiO_2-C_1, SiO_2-TiO_2-C_4, SiO_2-TiO_2-C_8, SiO_2-TiO_2-C_{12}, and SiO_2-TiO_2-C_{18}). Amounts of hexanal decreased and hexanoic acid generated are plotted.
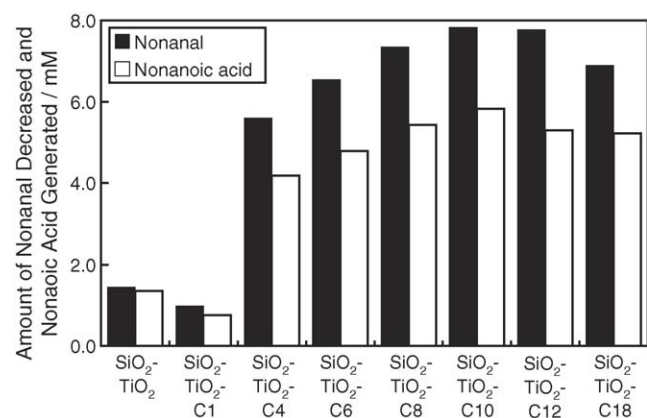

Fig. 6. Photocatalytic activities for oxidation of nonanal on surface-modified TiO_2 powders (SiO_2-TiO_2-C_1, SiO_2-TiO_2-C_4, SiO_2-TiO_2-C_8, SiO_2-TiO_2-C_{12}, and SiO_2-TiO_2-C_{18}). Amounts of nonanal decreased and nonanoic acid generated are plotted.

When hexanal was used as a substrate, photooxidation proceeded on SiO_2-TiO_2 photocatalysts with a fairly high yield as shown in Fig. 5. Photocatalytic activities increased with increase in the number of hydrocarbon chains introduced on SiO_2-TiO_2

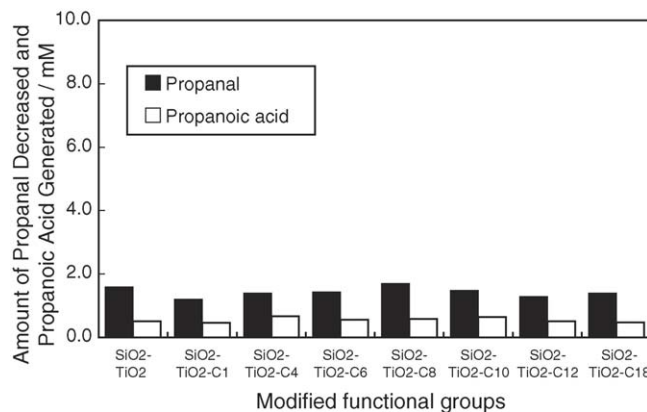Fig. 7. Photocatalytic activities for oxidation of propanal on surface-modified TiO_2 powders (SiO_2-TiO_2-C_1, SiO_2-TiO_2-C_4, SiO_2-TiO_2-C_8, SiO_2-TiO_2-C_{12}, and SiO_2-TiO_2-C_{18}). Amounts of propanal decreased and propanoic acid generated are plotted.

particles except methylsilyl groups. The highest level of activity was observed when SiO_2-TiO_2-C_{10} was used as a photocatalyst. The photocatalytic activity level of SiO_2-TiO_2-C_{10} was about three times as high as that of SiO_2-TiO_2 without surface modification. In addition, the photocatalytic activities of SiO_2-TiO_2-C_{12} and SiO_2-TiO_2-C_{18} were lower than that of SiO_2-TiO_2-C_{10} because of steric hindrance between these functional groups and the substrate. When nonanal was used as a substrate, similar enhancement of photocatalytic activity was observed (data not shown). The enhancement by introducing functional groups on SiO_2-TiO_2 was larger in the case of hexanal because hydrophobicity of nonanal is higher than that of hexanal. As a result, the hydrophobic interaction between hexanal and alkylsilyl groups on the surfaces of TiO_2 particles is thought to be the most important factor for improving their reactivity. Enhancement of photocatalytic activity for oxidation of nonanal on surface-modified SiO_2-TiO_2 photocatalysts was similar to that for oxidation of hexanal as shown in Fig. 6. The activity for oxidation of nonanal is more enhanced than that for oxidation of hexanal because of hydrophobicity of the substrate.

On the other hand, enhancement of the photocatalytic activity of SiO_2-TiO_2-C_n ($n = 1, 4, 8, 10, 12$, and 18) was not observed in the case of oxidation of propanal as shown in Fig. 7. These results suggest that the hydrophobic interaction between propanal and alkylsilyl groups on SiO_2-TiO_2 is very weak because propanal is less hydrophobic than hexanal. These results were supported by the difference in adsorbtivities of propanal, hexanal, and nonanal on SiO_2-TiO_2-C_n ($n = 1, 4, 8, 10, 12$, and 18). The adsorbtivities of hexanal on SiO_2-TiO_2-C_n ($n = 4, 8, 10$, and 18) and SiO_2-TiO_2 were about 1.79, 2.71, 2.99, 2.93, and 0.93 mmol dm^{-3}/(100 mg), respectively. Similar tendencies of adsorbtivity for nonanal on SiO_2-TiO_2-C_n ($n = 4, 8, 10$, and 18) and SiO_2-TiO_2 were also observed. On the other hand, no difference was found between the adsorbtivities of propanal on surface-modified SiO_2-TiO_2 {SiO_2-TiO_2-C_n ($n = 4, 8, 10$, and 18)} and SiO_2-TiO_2, the values being 0.41, 0.35, 0.40, 0.36, and 0.38 mmol dm^{-3}/(100 mg), respectively.

Figs. 8 and 9 show the photocatalytic activities of SiO_2-TiO_2 powders with or without surface modification for oxidation of pentafluorobenzaldehyde and benzaldehyde under photoirradiation for 1 h at room temperature. Photooxidation of pentafluorobenzaldehyde and benzaldehyde proceeded on SiO_2-TiO_2 photocatalysts with a relatively high yield. In the case of pentafluorobenzaldehyde as a substrate, marked acceleration was observed when SiO_2-TiO_2-C_8(F) was used as a photocatalyst. When the coverage was 62.9%, the activity level of SiO_2-TiO_2-C_8(F) was maximum as shown in Fig. 8. The photocatalytic activity level of SiO_2-TiO_2-C_8(F) with 62.9% coverage was about three times as high as that of SiO_2-TiO_2 without surface modification. The enhancement of activity of SiO_2-TiO_2-C_8(F) was decreased with decrease in the coverage because the interaction between the substrate and the surface-modified functional groups introduced onto the surfaces of SiO_2-TiO_2 particles was decreased.

In order to elucidate the effect of fluoroalkyl groups on the selectivity of the reaction, we also investigated the activities of SiO_2-TiO_2-C_8(F) for degradation of benzaldehyde, which has no fluorine atoms. The results are shown in Fig. 8. Regardless of increase in the coverage, the photocatalytic activity of SiO_2-TiO_2-C_8(F) particles was similar to that of SiO_2-TiO_2 particles without modification. On the other hand, the activity of SiO_2-TiO_2-C_8(F) for degradation of pentafluorobenzaldehyde increased remarkably with increase in the coverage as described above.

Slight enhancement of photocatalytic activity for oxidation of benzaldehyde on SiO_2-TiO_2-C_8 was observed as shown in Fig. 9. When the coverage was 18.2%, the maximum activity of SiO_2-TiO_2-C_8 was attained. The enhancement of activity of SiO_2-TiO_2-C_8 was decreased with increase in the coverage because of the steric hindrance between the substrate and hydrocarbon chain introduced on SiO_2-TiO_2. On the other hand, the photocatalytic activity level for oxidation of pentafluorobenzaldehyde on SiO_2-TiO_2-C_8 was decreased when hydrocarbon chains were introduced on SiO_2-TiO_2 photocatalysts because
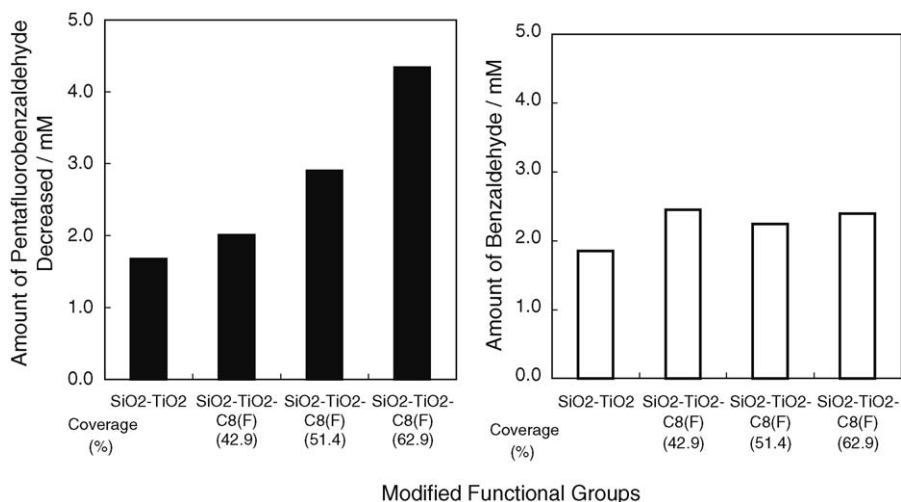

Fig. 8. Photocatalytic activities for oxidation of aldehydes on fluorocarbon chain-modified TiO_2 powders (SiO_2-TiO_2-C_8(F)) with different degrees of coverage.
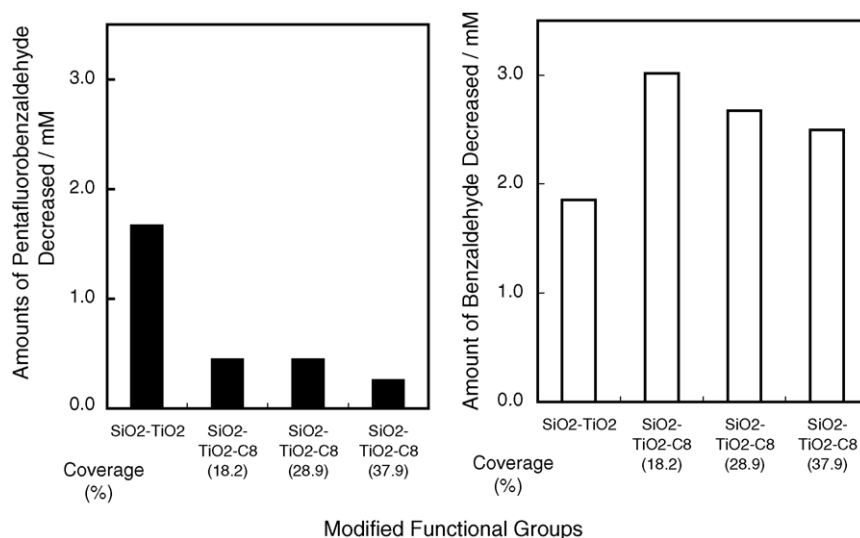
Fig. 9. Photocatalytic activities for oxidation of aldehydes on hydrocarbon-chain modified TiO$_2$ powders (SiO$_2$-TiO$_2$-C$_8$) with different degrees of coverage.

of weaker interaction between pentafluorobenzaldehyde and hydrocarbon chain on SiO$_2$-TiO$_2$.

These results indicate that the interaction between F atoms of the substrate and fluorocarbon chains introduced onto SiO$_2$-TiO$_2$ particles is more important than hydrophobic interaction for exhibiting selectivity [24,25]. These results were supported by the difference in adsorbtivities of aldehydes between SiO$_2$-TiO$_2$-C$_8$(F) and SiO$_2$-TiO$_2$ particles. The adsorbtivities of pentafluorobenzaldehyde on SiO$_2$-TiO$_2$-C$_8$(F) (coverage: 62.9%) and SiO$_2$-TiO$_2$ particles were about 1.31 and 0.65 mmol dm^{-3}/(100 mg), respectively. On the other hand, no difference was found in the adsorbtivities of benzaldehyde between SiO$_2$-TiO$_2$-C$_8$(F) (coverage: 62.9%) and SiO$_2$-TiO$_2$ particles, the values being 0.81 and 0.67 mmol dm^{-3}/(100 mg), respectively.

The selectivity of SiO$_2$-TiO$_2$ modified with phenyl and hydrocarbon (C$_6$) groups for oxidation of aldehyde compounds was also investigated, and the results are shown in Fig. 10.

When benzaldehyde was used as a substrate, SiO$_2$-TiO$_2$-Ph photocatalysts showed higher activity than SiO$_2$-TiO$_2$-C$_6$ powder. Furthermore, the activity of SiO$_2$-TiO$_2$-C$_6$ powder for oxidation of heptanal was higher than that of SiO$_2$-TiO$_2$-Ph powder. These results suggest that π–π interaction between phenyl groups is a more important factor than hydrophobic interaction for exhibiting selectivity for oxidation of benzaldehyde. In addition, an important factor for selective oxidation of heptanal is thought to be hydrophobic interaction between the functional group introduced on surface-modified SiO$_2$-TiO$_2$ photocatalysts and the substrates. These results are also supported by adsorbtivities of these substrates on SiO$_2$-TiO$_2$, SiO$_2$-TiO$_2$-C$_6$, and SiO$_2$-TiO$_2$-phyenyl particles. The adsorbtivities of benzaldehyde on the surfaces of SiO$_2$-TiO$_2$, SiO$_2$-TiO$_2$-C$_6$, and SiO$_2$-TiO$_2$-Ph particles are 0.25, 0.47, and 1.08 mmol dm^{-3}/(100 mg), respectively. The amounts of adsorbed heptanal on the surfaces of SiO$_2$-TiO$_2$, SiO$_2$-TiO$_2$-C$_6$, and SiO$_2$-TiO$_2$-Ph particles are 0.29, 1.13, and 0.97 mmol dm^{-3}/(100 mg), respectively.
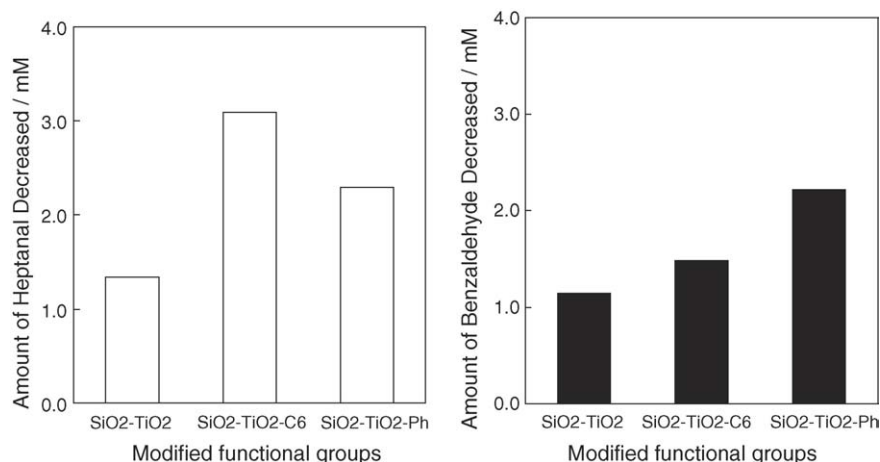

Fig. 10. Photocatalytic activities for oxidation of benzaldehyde and heptanal on surface-modified TiO$_2$ powders (–C$_6$, SiO$_2$-TiO$_2$-Ph) as well as SiO$_2$-TiO$_2$ without surface modification. Amounts of benzaldehyde and heptanal are plotted.

4. Conclusions

Oxidation of aldehyde compounds proceeded more efficiently on surface-modified TiO_2 photocatalysts (SiO_2-TiO_2-C_1, SiO_2-TiO_2-C_4, SiO_2-TiO_2-C_8, SiO_2-TiO_2-C_{12}, SiO_2-TiO_2-C_{18}, SiO_2-TiO_2-C_8F, and SiO_2-TiO_2-Ph) than on TiO_2 particles without surface modification (SiO_2-TiO_2). By introducing several kinds of functional groups on the surfaces of SiO_2-TiO_2 particles, the selectivity for oxidation of aldehyde was achieved. The difference in photocatalytic activities is due to the hydrophobic interaction, π–π interaction, and interaction of F atoms between functional groups introduced on SiO_2-TiO_2 photocatalysts and substrates. Further improvements to surface-modified TiO_2 photocatalysts, such as introduction of functional groups having positive or negative charges, are currently being investigated.

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