Catalysis Letters Vol. 102, Nos. 3–4, August 2005 (© 2005)
DOI: 10.1007/s10562-005-5857-3

Selective oxidation of benzaldehyde derivatives on TiO_2 photocatalysts modified with fluorocarbon group

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Received 27 January 2005; accepted 13 April 2005

Fluorocarbon groups were introduced onto surfaces of SiO_2-covered TiO_2 particles (SiO_2–TiO_2). Oxidation of pentafuluorobenzaldehyde on the surface modified TiO_2 powders proceeded much efficiently than that on SiO_2-covered TiO_2 particles without surface modification. In addition, no enhancement of activity level of surface-modified SiO_2–TiO_2 for oxidation of benzaldehyde was observed. The enhancement of the surface-modified SiO_2–TiO_2 is due to the interaction of F atoms between the substrate and fluorocarbon groups introduced on SiO_2–TiO_2.

KEY WORDS: photocatalysts; titanium dioxide; surface modification; SiO_2–TiO_2; fluorocarbon; interaction of F atom; selective oxidation.

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 [1–3]. In many applications, anatase TiO_2 powders consisting of particles with large surface areas are used as photocatalysts. 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 [4]. This property prevents hydrophobic organic compounds from being adsorbed on the surfaces of TiO_2 photocatalysts in aqueous media. This condition is a great disadvantage for degradation of organic compounds in aqueous media. We have reported that the surfaces of TiO_2 particles were modified with hydrocarbon chains through Ti–O–Si bonds. The levels of photocatalytic activity of surface-modified TiO_2 particles is higher than that of TiO_2 particles without surface modification because the surfaces of TiO_2 particles become hydrophobic [5]. By taking these methods, we developed surface-modified TiO_2 powders having fluorocarbon chains and photocatalytic activities for oxidation of aldehydes (pentafluorobenzaldehyde and benzaldehyde) in aqueous media.

2. Experimental

2.1. Materials and instruments

TiO_2 particles uniformity 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. Tridecafluoro-1, 1, 2, 2-tetrahydrooctyltrichlorosilane, benzaldehyde, and pentafluorobenzaldehyde ware obtained from Wako pure chemical Industries 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 Ka-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 Ka source (1486.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1 s 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 measured using a Bruker IFS66 with a diffuse reflectance accessory.

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2.2. Modification of surfaces of SiO_2–TiO_2 particles

Modifications of the surfaces of SiO_2–TiO_2 particles with fuluorocarbon was carried out according to previously reported methods [5–7]. One of typical preparation procedure of modification of SiO_2–TiO_2 is as follows. SiO_2–TiO_2 (6.0 g) was suspended in toluene containing 5.0 mmol of tridecafluoro-1, 1, 2, 2-tetrahydrooctyltrichlorosilane. 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. The resulting powder was labeled SiO_2–TiO_2–C_8(F) (8: number of carbons). Based on weight fractions of carbon and ash components obtained by elemental analysis, the amount of surface fluorocarbon chains was determined by assuming that the remaining ash is composed of a mixture of TiO_2 and SiO_2. The amount of fluorocarbon groups attached to the photocatalysts was estimated to be 389 μmol g^{-1} (coverage; 42.9%), 466 μmol g^{-1} (coverage; 51.4%), and 571 μmol g^{-1} (coverage; 62.9%) μmol g^{-1} (M_a), respectively. These data were confirmed by XPS analysis. Using M_a, external surface area and the estimated cross-sectional area of an fluoroalkylsilyl group (0.274 nm^2) [8], the surface coverage of SiO_2–TiO_2–C_8(F) was calculated.

2.3. Physical properties of SiO_2–TiO_2–C_8(F) particles

The overall hydrophobicity–hydrophilicity of SiO_2–TiO_2–C_8(F) particles was evaluated by observing their behavior (floatability) when surface-modified powder was added to water-acetonitrile mixtures of various compositions[7]. About 10 mg of SiO_2–TiO_2–C_8(F) 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.

2.4. Stability of functional groups introduced onto the surface of SiO_2–TiO_2 particles

In order to evaluate the photostabilities of surface-modified TiO_2 (SiO_2–TiO_2–C_8(F)), the photocatalyst was photoirradiated using a 500 W Hg lamp (6.6 mW cm^{-2}) for 5.5 h in aqueous solutions. FT-IR analyses and elemental analyses of the powder were performed before and after photoirradiation. The powder before and after photoirradiation was analyzed by means of XPS spectroscopy.

2.5. Photocatalytic degradation of aldehyde compounds on SiO_2–TiO_2 modified with functional groups

Activities of SiO_2–TiO_2–C_8(F) were estimated by photo-degradation of aldehydes in aqueous media as follows. SiO_2–TiO_2–C_8(F) (50 mg) was added to an aqueous solution of aldehydes (20 mM: pentafluorobenzaldehyde or benzaldehyde) and H_2O (5 mL). Then the mixture was stirred vigorously to make an emulsion, and it was 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 6.7 mW cm^{-2}. The reaction mixture was agitated vigorously with a magnetic stirrer during photoirradiation. Decrease of aldehydes in the aqueous solution was analyzed using a capillary gas chromatograph equipped with an RTx-5 capillary column.

3. Results and discussion

3.1. Physical properties of SiO_2–TiO_2–C_8(F)

The surface coverage of SiO_2–TiO_2–C_8(F) was changed in range the of 43.9–62.9% in order to determine the relationship between coverage and photocatalytic activity.

Figure 1 shows the floatability of SiO_2–TiO_2–C_8(F) particles (coverage: 42.9%) as a function of the weight fraction of acetonitrile in water. Almost all surface-modified sample (SiO_2–TiO_2–C_8(F)) floated, i.e., without any appreciable precipitation, when the weight fraction of acetonitrile was less than 40%, indicating that the particle surfaces had a hydrophobic property. 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%.

3.2. Stabilities of SiO_2–TiO_2–C_8(F)

The stability of the surface modified TiO_2 particles waw estimated by photoirradiation of SiO_2–TiO_2–C_8(F)

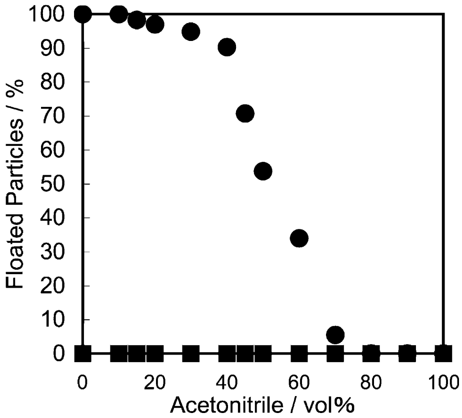

Figure 1. Dependence of amount of floating particles on the volume fraction of acetonitrile in water. Closed circles, SiO_2–TiO_2–C_8(F); Closed squares, SiO_2–TiO_2.

particles in aqueous media. After photoirradiation of SiO_2–TiO_2–C_8(F) particles, no sedimentation of the particles was observed. It was confirmed from elemental analysis of the resulting TiO_2 photocatalysts that degradation of fluoroalkylsilyl groups hardly proceeds after photoirradiation. The coverage of the photocatalysts before irradiation is 42.9%. This value hardly changed after photoirradiation. The coverage of SiO_2–TiO_2–C_8(F) particles after irradiation for 3 and 5 h are 42.3% and 41.8%, respectively. We also observed FT-IR spectra of the photocatalysts before and after photoirradiation in order to elucidate the stability of functional groups introduced onto the surface of the SiO_2–TiO_2–C_8(F) particles. The intensities of IR peaks at around 1320–1370 cm^{-1}, which were attributed to vibrations of C–F bonds, hardly change after photoirradiation as shown in figure 2. We also observed XPS spectra of SiO_2–TiO_2–C_8(F) particles before and after photoirradiation. Figure 3 shows F1s spectra. The intensity of a peak assigned to F1s did not change before and after photoirradiation as shown in figure 3. The coverage of fluorocarbon chain introduced onto SiO_2–TiO_2 particles ware also analyzed before and after photoirradiation. The coverage of fluoroalkylsilyl groups before photoirradiation is 42.9%, 51.5%, and 62.9%, respectively. After photoirradiation, the data are 42.2%, 51.6%, and 62.3%, respectively. These results suggested that the fluoroalkylsilyl groups introduced onto the surfaces of SiO_2–TiO_2 particles are stable under photocatalytic conditions.

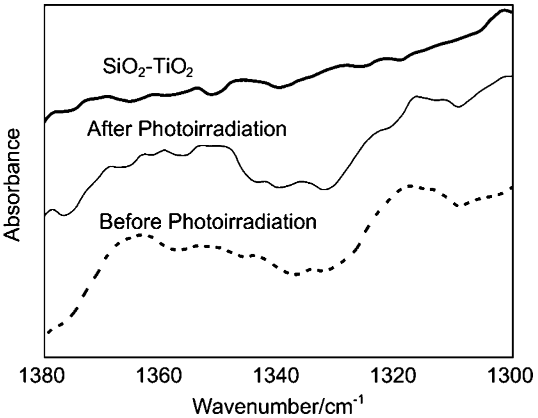

Figure 2. FT-IR absorption spectra SiO_2–TiO_2–C_8(F) before and after photoirradiation in water for 5 h and SiO_2–TiO_2 without surface modification.

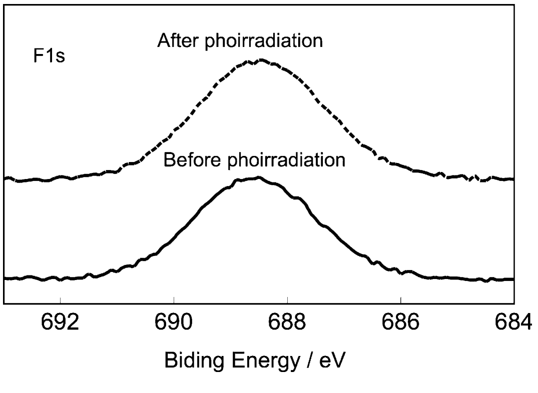

Figure 3. X-ray photoelectron spectra of F1s of SiO_2–TiO_2–C_8(F) particles before and after photoirradiation.

3.3. *Photocatalytic activities of SiO_2–TiO_2–C_8(F)*

Figure 4 shows the photocatalytic activities of TiO_2 powders for oxidation of aldehydes by irradiation for 1 h at room temperature. When pentafluorobenzaldehyde was used as a substrate, photooxidation proceeded on SiO_2–TiO_2 photocatalysts with a relatively high yield. 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 figure 4. The photocatalytic activity level of SiO_2–TiO_2–C_8(F) with 62.9% coverage was about three-times higher than that of SiO_2–TiO_2 without surface modification. The enhancement of activity of SiO_2–TiO_2–C_8(F) with surface coverage of less than 62.9% was less because of a weak interaction between the substrate and the surface-modified functional groups introduced onto the surfaces of SiO_2–TiO_2 particles. The hydrophobic interaction or F atom ineraction between pentafluorobanzaldehyde and fluoroalkylsilyl groups on the surfaces of TiO_2 particles is thought to be an important factor for improving their reactivity. These results were supported by the difference in adsorbtivities of aldehydes on 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 3.1 and 1.2 mmol dm^{-3}/100 mg, respectively. On the other hand, no difference was found between the adsorbtivities of benzaldehyde on SiO_2–TiO_2–C_8(F) (Coverage; 62.9%) and SiO_2–TiO_2 particles, the values being 1.2 and 1.1 mmol dm^{-3}/100 mg, respectively.

In order to elucidate the efficiency of fluoroalkyl groups for selectivity of the reaction, we also investigated the activities of SiO_2–TiO_2–C_8(F) for degradation of benzaldehyde. Regardless of 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 enhancement of SiO_2–TiO_2–C_8(F) for degradation of pentafluorobenzaldehyde increased remarkably with increase in the coverage as shown in figure 4. These results indicated that the interaction of F atoms between the substrate and fluorocarbon chain introduced onto SiO_2–TiO_2 particles is more important than hydrophobic interaction to exhibit selectivity [9,10].

4. Summary

It is notable that oxidation of pentafluorobenzaldehyde proceeded more efficiently on the surface-modified

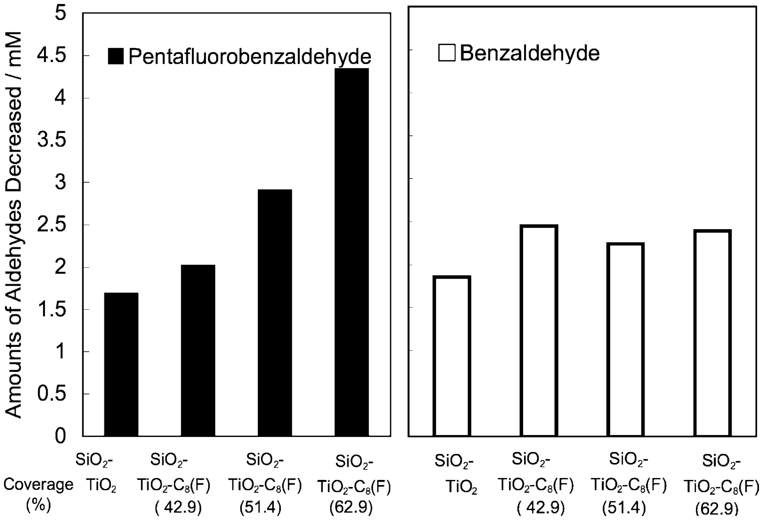

Figure 4. Photocatalytic activities for oxidation of aldehydes on the surface modified TiO_2 powders with different coverage.

TiO_2 photocatalyst (SiO_2–TiO_2–C_8(F)) than on TiO_2 particles without surface modification (SiO_2–TiO_2). On the other hand, enhancement of photocatalytic activity for oxidation of benzaldehyde was not observed by surface modification of SiO_2–TiO_2 particles. The difference in photocatalytic activities is mainly due to the interactions of F atoms between fluoroalkylsily groups on SiO_2–TiO_2 particles and pentafluorobenzaldehyde. Further improvements in TiO_2 photocatalysts surface-modified with various functional groups are currently being investigated.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Science, and Technology (MEXT), Japan.

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