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Oxidation of Aldehydes on TiO_2 Photocatalysts Modified with Alkylsilyl Group

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Surfaces of SiO_2-covered TiO_2 photocatalysts were modified with alkylsilyl groups. Oxidation of hexanal on surface-modified TiO_2 proceeded more efficiently than that on photocatalysts without surface modification. The improvement of the photocatalytic activities of surface-modified TiO_2 photocatalysts is due to the hydrophobic interaction between hexanal and alkylsilyl groups modified on TiO_2 photocatalysts.

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. In order to overcome this disadvantage, the surfaces of TiO_2 particles were modified with hydrocarbon chains through Ti–O–Si bonds. By introducing hydrocarbon chains on the surfaces of TiO_2 particles, the surfaces of TiO_2 particles become hydrophobic. Here, we report the syntheses of surface-modified TiO_2 powders and the photocatalytic activities of the TiO_2 powders for oxidation of aldehydes (propanal, hexanal) in aqueous media.

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. Other commercial chemicals were of the highest available grade and were used without further purification.

Modification of the surfaces of SiO_2–TiO_2 particles with alkylsilyl groups was carried out according to previously reported methods.[13,14] 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. The resulting powder is labeled SiO_2–TiO_2–C_{10} (10: number of hydrocarbons). On the basis of weight fractions of carbon and ash components obtained by an elemental analysis, the amount of surface alkylsilyl groups was determined by assuming that the remaining ash is composed of a mixture of TiO_2 and SiO_2. The amount of alkylsilyl groups attached to the photocatalysts was estimated to be $191\,\mu mol\,g^{-1}$ (M_a). Using M_a, external surface area, and the estimated cross section of an alkylsilyl group ($0.226\,nm^2$),[15] the surface coverage of SiO_2–TiO_2–C_{10} was calculated to be ca. 19.2%. We changed surface coverage of SiO_2–TiO_2–C_{10} in range of 10 to 80%. When the coverage was more than 20%, the activity of SiO_2–TiO_2–C_{10} for oxidation of aldehydes greatly decreased because an excessive amount of alkylsilyl groups prevent a reactant from adsorbing on the surfaces of photocatalysts due to steric hindrance. The enhancement of activity of SiO_2–TiO_2–C_{10} with surface coverage of less than 10% was less than the enhancement of activity of SiO_2–TiO_2–C_{10} with 20% surface coverage because of less hydrophobicity.

The overall hydrophobicity–hydrophilicity of 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.[16] 10 mg 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. Figure 1 shows the floatability of SiO_2–TiO_2–C_{10} particles as a function of the weight fraction of acetonile in water. Almost all surface-modified sample (SiO_2–TiO_2–C_{10}) floated, i.e., without any appreciable precipitation, when the weight fraction of acetonitrile was less than 20%, indicating that the particle surfaces had a hydrophobic property. 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%.

In order to evaluate the photostabilities of surface-modified TiO_2 (SiO_2–TiO_2–C_{10}), the photocatalyst was photoirradiated using a 500-W Hg lamp for 24 h in aqueous solutions. After photoirradiation, no sedimentation of particles was observed. It was also confirmed from elemental analysis of the resulting TiO_2 photocatalysts that degradation of alkylsilyl groups did not proceed after photoirradiation for 24 h. These results suggested that the alkylsilyl groups introduced onto the surfaces of the SiO_2–TiO_2 particles are stable under photocatalytic conditions.

Activities of SiO_2–TiO_2–C_{10} were estimated by photodegradation of aldehydes in aqueous media as follows. SiO_2–TiO_2–C_{10} (50 mg) was added to an aqueous solution of aldehydes (20 mM: propanal or hexanal) and H2O (5 mL). Then the mixture was stirred vigorously to make an emulsion, and it was pho-

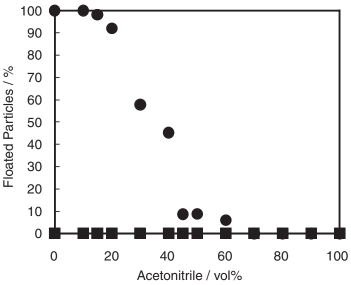

Figure 1. Dependence of amount of floating particles on the volume fraction of acetonitrile in water. Closed circles, SiO_2–TiO_2–C_{10}; Closed squares, SiO_2–TiO_2.

toirradiated 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. Decrease of aldehydes and calboxylic acids generated in the aqueous solution were analyzed using a capillary gas chromatograph equipped with an RTx-5 capillary column.

Figure 2 shows the photocatalytic activities of TiO_2 powders for oxidation of aldehydes by irradiation for 1 h at room temperature. Using any kind of aldehyde, the main products are calboxylic acids (propanoic acid or hexanoic acid). When hexanal was used as a substrate, photooxidation proceeded on SiO_2–TiO_2 photocatalysts with a fairly high yield. Marked acceleration 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 higher than that of SiO_2–TiO_2. 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. On the other hand, enhancement of the activity of SiO_2–TiO_2–C_{10} was not observed in the case of propanal. The hydrophobic interaction between propanal and alkylsilyl groups is very weak because propanal is less hydrophobic than is hexanal. These results were supported by the difference in adsorbtivities of aldehydes on SiO_2–TiO_2–C_{10} and SiO_2–TiO_2. The adsorbtivities of hexanal on SiO_2–TiO_2–C_{10} and SiO_2–TiO_2 were about 9.1 and 3.2 mmol dm^{-3}/100 mg, respectively. On the other hand, no difference was found in the adsorbtivities of propanal between on SiO_2–TiO_2–C_{10} and SiO_2–TiO_2, the values being 2.6 and 2.4 mmol dm^{-3}/100 mg, respectively.

It is notable that oxidation of hexanal proceeded more efficiently on the surface-modified TiO_2 photocatalyst (SiO_2–TiO_2–C_{10}) than that it did on TiO_2 particles without surface modification (SiO_2–TiO_2). The difference in photocatalytic activities is due to the hydrophobic interaction between alkylsily groups and hexanal. Further improvements to surface-modified TiO_2 photocatalysts (SiO_2–TiO_2–C_{10}), such as length of alkylsilyl groups, are currently being investigated.

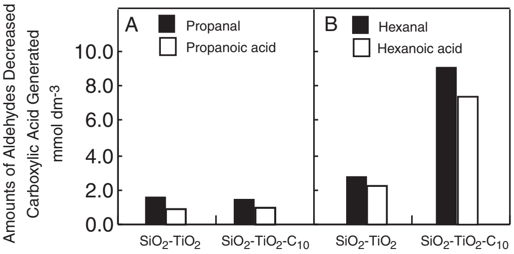

Figure 2. Photocatalytic activities for oxidation of aldehydes on TiO_2 poweders. A: Oxidation of propanal, B: Oxidation of hexanal. SiO_2–TiO_2–C_{10}: surface modified TiO_2, SiO_2–TiO_2: porous silica covered pure TiO_2.

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