Photoinduced Transformation of Silicone-modified TiO_2

Akira Nakabayashi,[†,††] Junko N. Kondo,[††] Michikazu Hara,[††] and Kazunari Domen*,[†††]
[†]Performance Materials R&D Center, Asahi Kasei Chemicals Co., Ltd., Kawasaki-ku, Kawasaki 210-0863
[††]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503
[†††]Department of Chemical System Engineering, School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656

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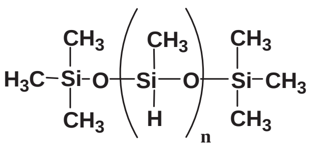
Silicone-modified titanium dioxide (TiO_2) was prepared by solid–liquid reaction between TiO_2 powder and H-siloxane. The surface energy of the synthesized powder was found to increase upon irradiation, an effect that was determined through electron spin resonance and ^{29}Si nuclear magnetic resonance studies to be due to photocatalytic oxidation of the silicone present on the TiO_2.

Titanium dioxide has excellent potential as a photocatalyst for the decomposition of various undesirable substances in the environment.[1–4] In essence, the photocatalytic performance of TiO_2 is based on the strong redox power of the photogenerated electron–hole pairs in its structure. The oxidation power of the holes is sufficient to completely oxidize a wide range of organic substances to inorganic compounds.

Recently, a number of studies have examined means of controlling the photocatalytic activity of TiO_2 by modifying its surface.[5–11] For example, TiO_2 powder treated with octadecyltrichlorosilane has been reported to exhibit high activity and selectivity for the photocatalytic oxidation of benzene to phenol in water.[6] Thus, control of the surface properties of the photocatalyst can be regarded as a viable strategy for the improvement of photocatalytic performance. In the present work, the irradiation-induced changes in surface energy and structure of a silicone-modified TiO_2 obtained by liquid-phase reaction between TiO_2 and H-siloxane are examined.

Titanium dioxide (ST-01, Ishihara Sangyo Kaisha Co.) and H-siloxane (KF99, Shin-Etsu Chemical Co.; $SiH = 15.8$ $mmol{\cdot}g^{-1}$, $M_n = 2900$, structural formula shown in Figure 1) were purchased and used without further purification. TiO_2 powder (9.0 g) was reacted with H-siloxane (1.0 g) in toluene (40.0 g) at 323 K for 8 h. A total of 306 mL of H_2 gas was evolved over this reaction period. The unreacted H-siloxane and toluene were then removed by filtration, and the silicone-modified TiO_2 powder was dried in air overnight at 323 K.



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O\left(\overset{CH_3}{\underset{H}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Figure 1. Structural formula of KF99. (n (average) = 47)

Infrared (IR) spectra of TiO_2 and the silicone-modified TiO_2 were measured by Fourier transform IR (FT-IR) spectroscopy (FT/IR-5300, Japan Spectroscopic Co.) The IR spectrum (not shown) of the silicone-modified TiO_2 exhibited several bands assignable to H-siloxane: the antisymmetric (2972 cm^{-1}) and symmetric (2912 cm^{-1}) stretching vibrations of CH_3 groups, the stretching vibration of Si–H groups (2166 cm^{-1}), and the symmetric deformation of CH_3 groups (1271 cm^{-1}).[12] The band representative of O–H stretching vibration in the Ti–OH groups (3635 cm^{-1}) was not apparent following the reaction between TiO_2 powder and H-siloxane.

The degree of surface modification of the silicone-modified TiO_2 was examined by X-ray photoelectron spectroscopy (XPS; ESCA 3200, Shimadzu Co.) The surface atomic ratio of Si/Ti (Ti2P3/2; 459.6 eV, Si2P; 102.5 eV) was estimated to be 0.26.

The silicone-modified TiO_2 powder was pressed into a disk (diameter: 1 cm) for water contact angle measurements, taken before and after irradiation under a black light blue (BLB) light (FL20S-BLB, Toshiba Lighting and Technology Co.). The intensity of the BLB light was adjusted to 1 $mW{\cdot}cm^{-2}$, as measured using an ultraviolet radiometer (UVR-2, Topcon; with UD-36 detector). A drop of deionized water was placed on the surface of the disk and allowed to stand for 1 min at 293 K. The water contact angle was then measured using a contact angle meter (CA-X150, Kyowa Interface Science Co.)

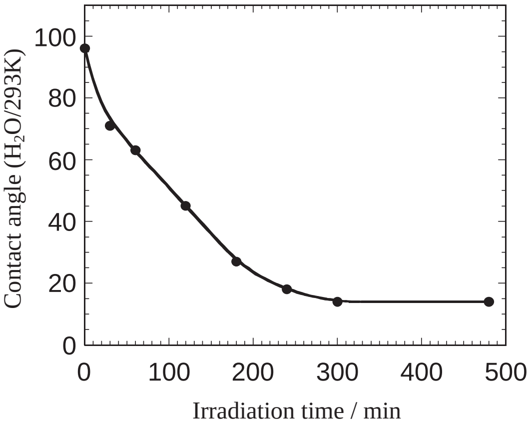


Figure 2. Changes in water contact angle of silicone-modified TiO_2 disk upon irradiation.

As shown in Figure 2, the silicone-modified TiO_2 disk was initially hydrophobic (water contact angle: 98°), but became highly hydrophilic (water contact angle: 17°) after irradiation for more than 300 min. The surface tension of the silicone-modified TiO_2 was estimated from the contact angle using Sell and Neumann's empirical formula,[13] as given by

$$\cos\theta = \frac{(0.015\gamma_s - 2) \times \sqrt{\gamma_s \times \gamma_l} + \gamma_l}{\gamma_l \times (0.015 \times \sqrt{\gamma_s \times \gamma_l} - 1}$$

where γ_s represents the surface tension ($mN{\cdot}m^{-1}$) of the silicone-modified TiO_2, and γ_l represents the surface energy of water, i.e., 72.8 $mN{\cdot}m^{-1}$ (293 K). The calculated surface tension was 25 $mN{\cdot}m^{-1}$ before irradiation and 68 $mN{\cdot}m^{-1}$ after irradiation. Thus, the surface energy of the silicone-modified TiO_2 increased upon irradiation.

The photoinduced change in surface tension was further examined by electron spin resonance (ESR) analysis of the silicone-modified TiO_2 powder under irradiation using an Xe lamp (KXL-500F, Wacom; with V40-filter, Kenko Co.). Analysis was performed using an ESR spectrometer (EMX10/15, Bruker) under evacuation at 77 K. The intensity of the Xe lamp was adjusted to 1 $mW{\cdot}cm^{-2}$.

Figure 3 shows the resultant ESR spectrum. The spectrum indicates the formation of a methyl radical (quartet signal; $g = 1.984$, 1.998, 2.011, and 2.025) during irradiation, in addition to Ti^{3+} ($g = 1.961$ and 1.991) and an OH radical ($g = 2.003$ and 2.015).[14] Based on this result, it is considered that irradiation induced the formation of Ti^{3+} species and positive holes in TiO_2. The positive holes would then have reacted with water to form OH radicals, which would then have attacked the silicone species on the surface of the TiO_2, generating Si–OH groups and methyl radicals. The TiO_2 surface is thus considered to become hydrophilic as a consequence of the irradiation-induced reactions. Under irradiation, TiO_2 oxidizes a fraction of the silicone present on the TiO_2 surface, yielding hydrophilic silica.

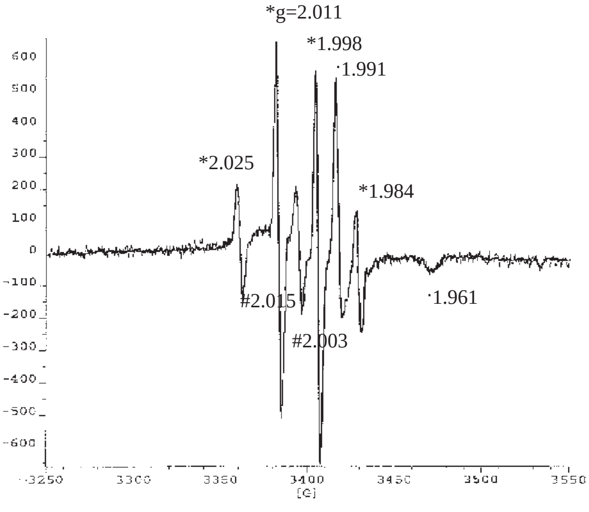


Figure 3. ESR spectrum of silicone-modified TiO_2 under irradiation (77 K). Bands due to Ti^{3+} (·), methyl radicals (∗), and OH radicals (#), are indicated.

This mechanism was confirmed through ^{29}Si nuclear magnetic resonance (NMR) analysis using a JNM-LA400 spectrometer (JOEL Co.) The ^{29}Si NMR spectra taken before and after irradiation of the silicone-modified TiO_2 powder under a BLB light (1 $mW{\cdot}cm^{-2}$) for 1 week are shown in Figure 4. The spectra show that a fraction of the silicone present on the surface of the TiO_2 is transformed from the T-unit structure to a Q-unit structure by irradiation (representing the degree of functionality of the silicone atom, see inset of Figure 4). This result clearly supports the mechanism mentioned above.

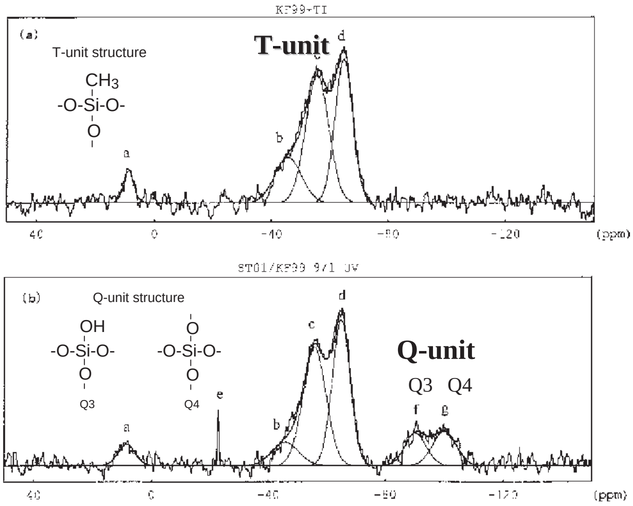


Figure 4. ^{29}Si NMR spectra of silicone-modified TiO_2 (a) before and (b) after irradiation.

In conclusion, silicone-modified TiO_2 powder obtained by liquid-phase reaction between TiO_2 powder and H-siloxane was found to be transformed under ultraviolet irradiation from hydrophobic to hydrophilic. It was confirmed that this change in surface property is attributable to the formation of Si–OH species.

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