Kinetic Study of Dehydrogenation between H–Siloxane and Ti–OH on TiO_2

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The kinetics of the solid–liquid reaction between titanium dioxide (TiO_2) and H–siloxane was investigated. The solid–liquid reaction involved two dehydrogenation condensations; one between free Ti–OH groups and Si–H groups, and another between hydrated Ti–OH groups and Si–H groups. The reactivity of the Ti–OH group is considered to be restricted by hydrogen bonding with a molecule containing an OH group, such as water or alcohol.

Titanium dioxide, TiO_2, is the most widely used photocatalyst for the decomposition of various undesirable substances in the environment.[1–3] The photocatalytic performance of TiO_2 is based on the high redox potential of the photogenerated electron-hole pairs, and the oxidative power of the holes is sufficient to completely oxidize a wide range of organic substances into inorganic compounds.

Recently, a number of studies have focused on achieving control of the photocatalytic activity of TiO_2 through surface modification.[4–9] For example, silicone-modified TiO_2 prepared by solid–vapor reaction between TiO_2 powder and H–siloxane followed by calcination in air at 773 K has been shown to exhibit strong Lewis acidity and excellent photocatalytic activity.[8] Thus, control of the surface properties of the photocatalyst can be regarded as one of the strategies for improving photocatalytic performance.

The surface-modification reaction between TiO_2 and H–siloxane is an excellent method for obtaining silicone-modified TiO_2 because of the high selectivity of the reaction.[9] The solid–vapor reaction between TiO_2 and H–siloxane is considered to involve dehydrogenation condensation between Ti–OH groups on the TiO_2 surface and Si–H groups of H–siloxane. However, the details of the reaction have yet to be confirmed due to the difficulty of analysis for solid–vapor reactions. This paper reports the kinetic analysis of the solid–liquid reaction between TiO_2 powder and H–siloxane for the purpose of developing a better understanding of the formation of silicone-modified TiO_2.

The reaction system was simplified by using bis(trimethylsiloxy)methylsilane (BTMS), which contains only one Si–H group per molecule, as the H–siloxane. TiO_2 powder (ST-01, Ishihara Sangyo Kaisha) and BTMS (Gelest; 99.5%) were purchased and used without further purification.

TiO_2 powder (3.2 g) was reacted with BTMS (1.6 g) in toluene (19.2 g) at a fixed temperature, and the rate of H_2 evolution was measured using a gas burette. The reactant was then separated into a liquid phase and the silicone-modified TiO_2 powder by filtration, and the powder was dried in air overnight at 323 K. Analysis of the liquid phase by gas chromatograph (GC-14B, Shimadzu) using a G-100 (Chemicals Evaluation and Research Institute) column revealed the consumption of BTMS without the formation of any by-products. The infrared (IR) spectrum of the TiO_2 powder was measured using a Fourier transform IR (FT-IR) spectrometer (FT/IR-5300, Japan Spectroscopic Co.). In the IR spectrum of the TiO_2 powder (not shown), several bands due to BTMS were observed at 2972, 2912, and 1271 cm^{-1}, assigned to antisymmetric and symmetric stretching vibrations and symmetric deformation of CH_3 groups, respectively.[10] The band corresponding to O–H stretching vibration in the Ti–OH groups (3635 cm^{-1}) disappeared completely upon reaction between the TiO_2 powder and BTMS (not shown).

Figure 1 shows the time courses of H_2 evolution at various temperatures. From the amount of H_2 evolved at saturation, the concentration of Ti–OH groups on the TiO_2 surface available for reaction with BTMS is $0.68\ \text{mmol} \times \text{g}^{-1}$ TiO_2. When there is a large excess of Si–H groups in relation to Ti–OH groups throughout the solid–liquid reaction, the kinetic equation is as follows.

$$a\frac{dx}{dt} = ka(1-x)(A-ax)$$

$$A \gg ax$$

$$\frac{dx}{dt} = kA(1-x) = k_{\text{app}}(1-x)$$

$$\int \frac{1}{1-x}dx = k_{\text{app}}\int dt \qquad \ln\frac{1}{1-x} = k_{\text{app}}t$$

where A, a, k, x, and t represent the initial concentration of Si–H groups, the initial concentration of Ti–OH groups, the rate constant, conversion, and time, respectively. A straight line can be obtained by plotting $\ln(1/(1-x))$ against t, the slope of which represents the apparent rate constant (k_{app}).

TiO_2 powder (3.2 g, Ti–OH = 2.2 mmol) was then reacted

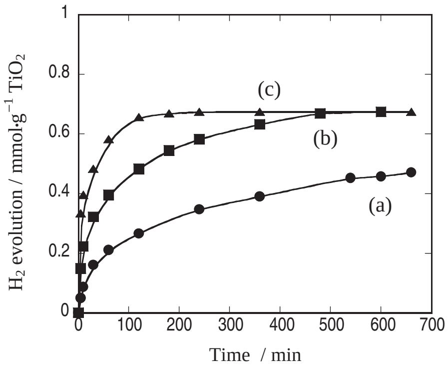


Figure 1. Rate of H_2 evolution in solid–liquid reaction between TiO_2 and BTMS at (a) 323, (b) 343, and (c) 363 K.

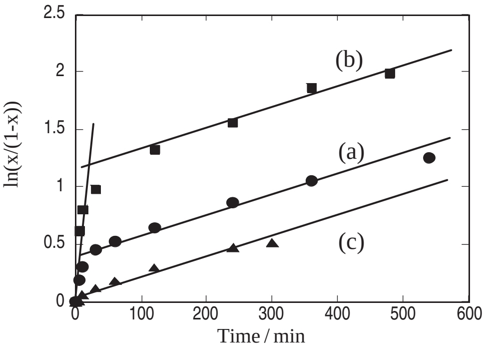
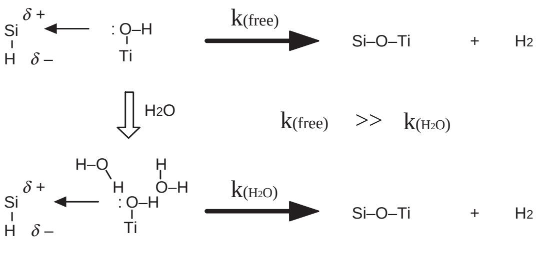


Figure 2. Plots of $\ln(1/(1-x))$ against reaction time at 323 K for (a) 10 wt % water-containing TiO_2 without pretreatment, (b) 2 wt % water-containing TiO_2 preheated at 393 K for 12 h, and (c) 10 wt % water-containing TiO_2 in solvent with added water.

with BTMS (5.0 g, Si–H = 22.5 mmol) in toluene (16.8 g) at 323 K. The plot of $\ln(1/(1-x))$ against time for this reaction (Figure 2a) indicates the existence of two distinct reaction regions; an initial reaction region with relatively high reaction rate, and a subsequent slow reaction region.

Thermogravimetric/differential thermal analysis (TG-DTA; DTG-60A/60AH, Shimadzu) of the TiO_2 powder revealed that the powder contained about 10 wt % physically adsorbed water. The influence of this physically adsorbed water on the reactivity of the TiO_2 powder with BTMS was therefore examined using preheated TiO_2 powder[11] containing about 2 wt % physically adsorbed water. It was observed that use of the preheated TiO_2 powder clearly increased the rate of reaction in the fast initial reaction region (Figure 2b). In contrast, the rate of reaction in the fast initial reaction region was substantially suppressed when water (0.1 g) was simply added before mixing the TiO_2 powder with toluene and BTMS (Figure 2c), presumablly resulting from the increased proportion of hydrated TiOH groups.

A tentative reaction mechanism between TiO_2 and BTMS including this water suppression effect is postulated as shown in Scheme 1. In this mechanism, the dehydrogenation condensation between the Ti–OH group and the Si–H group is assumed to be a nucleophilic substitution reaction. In the presence of water, the nucleophilicity of the Ti–OH group is reduced due to the formation of hydrogen bonds with water, lowering the reaction rate. This implies that there may be two types of Ti–OH groups, that is, free Ti–OH groups that react with Si–H groups at a rate constant of $k_{(\text{free})}$ (fast initial reaction region), and hydrogen-bonded Ti–OH groups that react with Si–H groups with a rate constant of $k_{(H_2O)}$ (slow following reaction region). The ratio of the number of free Ti–OH and hydrogen-bonded Ti–OH on the surface of 10 wt % water-containing TiO_2 was estimated to be 0.5 from Figure 2a. From the slopes in the fast and slow reaction regions shown in Figure 2, values of $k_{(\text{free})} = 133.3\ \text{g·mol}^{-1}\text{·min}^{-1}$ and $k_{(H_2O)} = 1.8\ \text{g·mol}^{-1}\text{·min}^{-1}$ are obtained at 323 K. Thus, $k_{(\text{free})}$ is two orders of magnitude larger than $k_{(H_2O)}$.



Scheme 1. Proposed mechanism of the solid–liquid reaction between TiO_2 and BTMS.

Table 1. Rate constants of reaction between Ti–OH groups and Si–H groups in the presence of molecules containing an OH group at 323 K

Molecule containing an OH group	Water	2-Butoxyethyl alcohol	Propyl alcohol	Isopropyl alcohol	*t*-Butyl alcohol
$k_{app} \times 10^2/\text{min}^{-1}$	0.16	0.25	0.34	0.8	0.83
$k/\text{g·mol}^{-1}\text{·min}^{-1}$	1.8	2.7	3.8	8.9	9.2
pK_{SH}	14.0		19.4	20.3	

k_{app}: Apparent rate constant of reaction in the presence of alcohol, obtained from the slope of the plot of $\ln(1/(1-x))$ against time.
k: Rate constant of reaction, calculated by dividing k_{app} by the initial concentration of Si–H groups.
K_{SH}: Self dissociation constant.[12]

This reaction mechanism was further investigated by examining the effect of alcohol, which also contains OH, on the reaction rate. Various alcohols were used as solvents in place of toluene. From the plot of $\ln(1/(1-x))$ against time (not shown), the rate constants of the reaction between alcohol-solvated Ti–OH groups and Si–H groups were obtained, as listed in Table 1. The rate constants are in agreement with the acid strengths (electrophilicity) of alcohol. Strong solvation of the Ti–OH groups by alcohol results in a substantial decrease in the nucleophilicity of the Ti–OH groups and a corresponding suppression of the reaction rate. This effect is considered to be due to restriction of the reactivity of Ti–OH groups as a result of hydrogen bonding with the alcohol.

In conclusion, kinetic study of the solid–liquid reaction between TiO_2 and H–siloxane revealed that the dehydrogenation condensation between Ti–OH groups and Si–H groups involves two dehydrogenation condensations; one between free Ti–OH groups and Si–H groups, and another between hydrated Ti–OH groups and Si–H groups. The reaction was found to be strongly inhibited by the presence of molecules containing OH, with the degree of inhibition dependent on the acid strength of the molecule, that is, the strength of the hydrogen bond with the Ti–OH group.

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