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## Photocatalytic Reaction Sites at the TiO<sub>2</sub> Surface as Studied by Solid-State <sup>1</sup>H NMR Spectroscopy

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The adsorption and photodecomposition of ethanol that was employed as a model substrate of organic pollutants were investigated in the presence of adsorbed water with TiO<sub>2</sub> by solid-state <sup>1</sup>H NMR spectroscopy in order to obtain information about the actual photocatalytic reaction sites of organic pollutants on TiO<sub>2</sub> photocatalysts. Consequently it was revealed that ethanol molecules in practical conditions as contaminants were firmly captured in mobile physisorbed water layers to be photodecomposed to CO<sub>2</sub> and water after photoillumination, suggesting that actual photocatalytic reactions should proceed in physisorbed water layers.

Because of its stability and nontoxicity, TiO<sub>2</sub> has been extensively investigated for the photocatalytic degradation of a variety of environmentally harmful organic compounds.<sup>1,2</sup> Most investigations have been performed for the chemical species directly adsorbed on the surface after the evacuation of adsorbed water<sup>3–10</sup> on the assumption that the photoinduced reactions take place on the solid surface region. However, photocatalysis can occur also in adsorbed water layers. More attention should be paid to photocatalytic reaction sites for the development of effective applications of TiO<sub>2</sub> photocatalysts. We employed ethanol as a model substrate of organic pollutants and investigated the adsorption and photodecomposition in the presence of adsorbed water with TiO<sub>2</sub> by solid-state <sup>1</sup>H NMR spectroscopy.

The TiO<sub>2</sub> powder used was Degussa P25 (Japan Aerosil). Ethanol used was of guaranteed reagent grade. For UV illumination, the sample was spread on the glass plate and UV-illuminated outside the NMR probe. The light source was a handy type UV lamp (365 nm, Funakoshi UVL21, 4 W). <sup>1</sup>H NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz with a solid echo sequence consisting of two 3-μs 90° pulses with a 50-μs delay in between and a 5-s relaxation delay. TiO<sub>2</sub> powder was packed into 4 mm o.d. ZrO<sub>2</sub> NMR sample tubes in contact with air through a small hole, and the samples were rotated at the magic angle at the rate of 12.6 kHz unless otherwise stated. To eliminate the

background signal of the NMR probe, the spectrum measured with an empty NMR sample tube was subtracted from all the spectra. Chemical shifts were measured relative to DSS (2,2 dimethyl-2-silapentane-5-sulfonate) as an external reference.

As shown in Figure 1a, the <sup>1</sup>H NMR spectrum of TiO<sub>2</sub> (Degussa P25) in powder form measured with magic angle spinning (MAS) presents a single signal (5.43 ppm) with the line width of 680 Hz at a half peak height at 295 K, which was ascribed to the relatively mobile physisorbed water.<sup>11</sup> With increasing temperature, the intensity decreased gradually along with the vaporization of water. Although the temperature could not be raised above 358 K because of the instrumental limitation, the line width became rather broader (780 Hz) at 358 K and the peak area became 40% of that at 295 K (Figure 1b). On decreasing temperature back to 295 K, the peak became 3 times broader (2065 Hz, Figure 1c) than that before the temperature increase. This broad signal can be ascribed to very rigid water molecules with restricted mobility near the solid surface region of TiO<sub>2</sub> since it disappeared completely at the temperature where surface OH groups are still present on TiO<sub>2</sub>.<sup>11</sup> This indicates that sharp and broad water signals could not be discriminated at 295 K before temperature increase due to the signal overlap. On increase of temperature, with the vaporization of the mobile water the rigid water components remaining in the system would become dominant to contribute to the broader signal. When the sample was kept at 295 K, water in the air readsorbed gradually on the surface of the photocatalyst to form mobile water layers and in about 20 h the water signal recovered completely to that before temperature increase (Figure 1d). The details on the structure of water on the surface of TiO<sub>2</sub> have not been elucidated well. The present results suggest that the physisorbed water region of the photocatalysts consists of complex layers where water molecules take different structures and mobility.

On load of a small quantity of ethanol (170 nmol) onto the top of the NMR sample tube containing 25 mg of TiO<sub>2</sub> powder at 295 K, ethanol molecules rapidly diffused in 30 min in the powder to give a small peak at 0.99 ppm with the line width of 750 Hz ascribed to methyl (–CH<sub>3</sub>) protons

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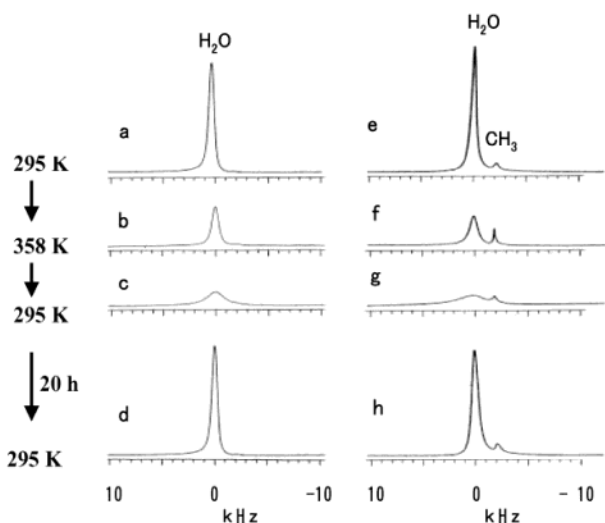
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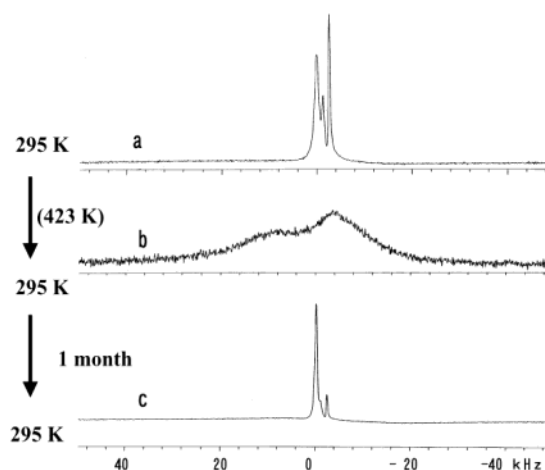
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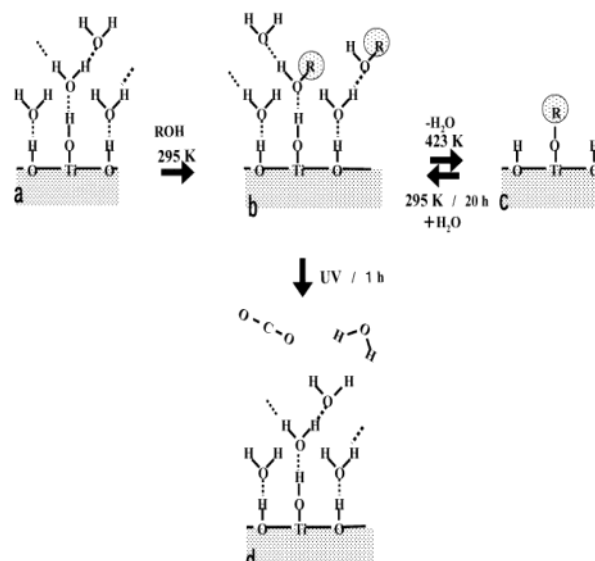
**Figure 1.**  $^1\text{H}$  MAS NMR spectra of  $\text{TiO}_2$  powder (Degussa P25) (a–d) and those on addition of ethanol (170 nmol) (e–h) measured at 295 K (a,e), 358 K (b,f), 295 K (c,g) (just after the temperature was decreased back to 295 K), and 295 K (d,h) (after the sample was kept at room temperature for 20 h and 1 month).

of ethanol as shown in Figure 1e. Methylene ( $-\text{CH}_2$ ) and OH signals of ethanol were not observed due to the overlap with the water signal. With increasing temperature up to 358 K, the ethanol peak became sharper (line width, 240 Hz at 358 K) most probably due to the gained mobility, but the peak area and chemical shift barely changed within the temperature range studied. On the other hand, the water peak showed a similar temperature dependence to that in the absence of ethanol and the intensity became 40% of that at 295 K as shown in Figure 1f. On decrease of temperature back to 295 K, the ethanol peak presented the same line width and intensity as those before the temperature increase. These observations indicate that the ethanol molecules incorporated into the photocatalytic system do not vaporize even at 385 K but are firmly captured in the physisorbed water region although a substantial amount of the adsorbed water molecules vaporize. The water signal recovered completely in 20 h to give the same spectral feature as that before temperature increase. And it was confirmed that at room temperature ethanol was still in the same state even after 1 month (Figure 1h), suggesting that ethanol molecules exist in a highly stabilized state in the mobile physisorbed water region.

Next we packed the  $\text{TiO}_2$  sample, which was saturated with ethanol molecules and vacuum-dried, in a 4-mm glass NMR sample tube and heated it in an electric furnace at 423 K for an hour. Although the NMR spectrum was measured without rotation, sharp and intensified water and the methylene ( $-\text{CH}_2$ , 3.67 ppm) and methyl ( $-\text{CH}_3$ , 1.0 ppm) signals of ethanol were observed before calcination as shown in Figure 2a, indicating that ethanol stays in a fairly mobile state. The OH signal of ethanol overlapped with the water signal. After calcination at 423 K, very broad two peaks were observed (Figure 2b). As reported previously, in the absence of ethanol the water peak disappeared completely at 423 K.<sup>11</sup> Therefore, these broad peaks can be ascribed to  $\text{CH}_2$  and  $\text{CH}_3$  originating from the ethanol molecule by taking account of the relative signal intensity of 2–3. When the sample was kept at room temperature in atmospheric conditions for more than several hours, with the recovery of the signal from physisorbed water that was readsorbed from the air, relatively sharp ethanol signals gradually appeared. As



**Figure 2.**  $^1\text{H}$  NMR spectra of  $\text{TiO}_2$  Degussa P25 with ethanol measured at 295 K. P25 was suspended in ethanol solution and vacuum-dried at room temperature. The sample was packed in a 4-mm glass tube and measured without rotation (a) before calcination, (b) after calcination at 423 K for 1 h in an electric furnace, and (c) after sample b was kept at room temperature for 1 month.



**Figure 3.** Schematic illustration of the photocatalytic  $\text{TiO}_2$  surface. (a)  $\text{TiO}_2$  surface with water. (b) Ethanol molecules loaded preferably stay in the mobile physisorbed water layers. (c) On increasing temperature up to 423 K, water molecules in the inner phase would be replaced successively by ethanol and the ethanol molecules reaching the solid surface react with titanols to form ethoxide. At room temperature, the powder gradually readsorbs water molecules in the air and the ethoxide is hydrolyzed to ethanol, which returns to state b. (d) Photocatalytic reactions of ethanol under atmospheric conditions take place in this state of the reactant, which decomposes to  $\text{CO}_2$  and water via several intermediate species.

shown in Figure 2c, even after 1 month it does remain in the photocatalytic system although the intensity was reduced significantly. From the sharp peaks, it is obvious that ethanol molecules exist in a mobile state. The results indicate that at 423 K physisorbed water molecules vaporized completely. On the other hand, the ethanol molecules that reached the surface region reacted with the surface titanols to form ethoxide, resulting in remarkable line broadening due to the restricted mobility. The ethanol molecules that could not form ethoxide vaporized since the amount of surface titanols is about 50

times smaller than that of physisorbed water.<sup>12</sup> With the recovery of the water layers, the ethoxide would be hydrolyzed to form ethanol molecules that migrate back to the physisorbed water layer and give sharp NMR signals with reduced intensity. This fact indicates that a small amount of ethanol would stay more preferably in the physisorbed water layers with high water content rather than near the solid surface region of the TiO<sub>2</sub> photocatalyst at room temperature in atmospheric conditions.

After 1 h of UV illumination, only a water peak was observed, indicating that a small amount of ethanol in P25 TiO<sub>2</sub> powder was completely photodecomposed into water and CO<sub>2</sub>.

The above observation was summarized in Figure 3. At room temperature, the loaded ethanol molecules preferably stay in the mobile physisorbed water layers to form hydrogen bonds with water molecules, where both ethanol and water molecules are fairly mobile. The ethanol molecules in this state would be oxidized photocatalytically to water and CO<sub>2</sub> under atmospheric conditions.

The concentration of the chemical species incorporated into the photocatalyst as a pollutant would be quite low.

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Industrial gas emissions often contain contaminants in low concentrations (<100 ppm) and flow at high rates, and under these conditions ethanol can be oxidized photocatalytically mainly in the mobile physisorbed water layers. Since the physisorbed water region consists of layers where water molecules take different structures and mobility, the mechanism of the interaction of ethanol with water molecules in each layer must be complicated. However, the elucidated adsorption behaviors of ethanol suggest the possibility to place organic compounds in the desired region of photocatalytic systems by regulating the amount of adsorbed water and/or temperature. A proper understanding of the role of the water layers interacting with organic chemicals must lead to novel developments of efficient photocatalytic systems specific to particular chemical species.

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