Photoinduced Changes of Surface and Adsorbed Water in TiO_2 Photocatalytic Systems as Studied by Solid State ^{1}H-NMR Spectroscopy

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(Received December 21, 2001; CL-011281)

^{1}H-NMR spectra of TiO_2 photocatalysts consist of two peaks with line widths of 500 Hz and 18 kHz. The sharp peak was attributed to physisorbed water, while the broader one is considered to correspond to the less mobile bound water or surface OH group. On UV illumination both peaks disappeared. The admission of air leads to the recovery of both peaks to some extent but in a different spectral feature for the broad peak, reflecting the surface structural change on TiO_2 by photo illumination.

TiO_2 photocatalyst has been extensively investigated because of their practical functions such as strong oxidation power, chemical inertness, and detoxicification.[1,2] Besides, the UV illumination of TiO_2 produces a highly hydrophilic surface.[3–6] These functions are mostly caused by the exertion of the active species produced through the reactions of photogenerated electrons and holes with adsorbed water or titanol on TiO_2. To understand the various functions of TiO_2 the importance to investigate the structures and behaviors of adsorbed water has been acknowledged.[7–10] ^{1}H-NMR spectroscopy has been utilized as one of the most effective techniques to investigate adsorbed water. However, to our knowledge there has been no report so far about the adsorbed water on TiO_2 studied by proton NMR spectroscopy. Hence, as a first step we tried to measure ^{1}H-NMR of several TiO_2 photocatalysts of different properties in powder and film forms and study the effect of UV illumination on the spectra.

Six different TiO_2 powders, Degussa P25 (Japan Aerosil), Hombikat UV-100 (Sachtleben Chemie), ST-01 (Ishihara Techno), F4 (Showa Titanium), and AMT-100 and AMT-600 (Tayca) were packed into 4-mm glass NMR tubes. ^{1}H-NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz at room temperature with a solid echo sequence consisted of two 3-μs 90° pulses with a 50-μs delay in-between and a 5-s relaxation delay. For all the powder samples a relatively sharp peak (I) and a broad peak (II) with a half line width of about 500 Hz and 18 kHz, respectively, were observed as shown in Figure 1. The relative peak intensities of peak I are summarized in Table 1. Unfortunately, the precise intensities of the broad peak(II) could not be obtained because of the overlap of the peak with the background signal arising from the NMR probe.

The intensities of peak I for six different TiO_2 powders are well correlated with their primary particle size and the surface area of the particles as shown in Table 1. The intensities increase with the decrease of the primary particle size and the increase of the surface area.[11] Both peaks were found to disappear at 423 K and recover within a day. Taking account of these facts and the narrow line width, peak I could be attributed to the physisorbed water peak with relatively high mobility. On the other hand, the broad signal (peak II) would correspond to the less mobile water such as very rigid structured water or/and OH group directly bound to TiO_2.

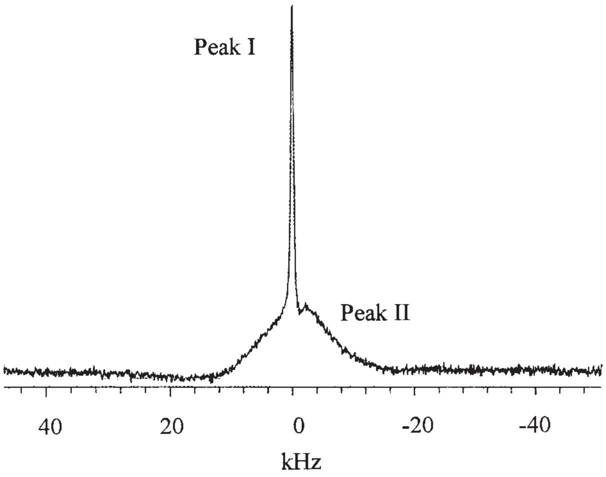

Figure 1. ^{1}H-NMR spectrum of TiO_2 powder (P25).

Table 1. The relative intensities of ^{1}H-NMR signals (Peak I) and physical properties of TiO_2 photocatalysts[11]

TiO_2	NMR intensity	Anatase component /%	Primary particle /nm	BET surface area /m^2g^{-1}
P25	1.0	80	32	49
F4	1.1	90	28	56
AMT-600	1.5	100	30	50
ST-01	11.9	100	7	320
AMT-100	13.5	100	6	260
UV-100	21.4	100	10	270

Although TiO_2 powder was illuminated with UV light for about an hour through the NMR sample tube outside the NMR probe, no significant change in the NMR spectrum was detected. The light source for UV illumination was a handy type UV lamp (Funakoshi UVL21, 365 nm, 4 W). Because the powder sample was packed in a sample tube, the light might not penetrate sufficiently deep into the inside for the detection of the effect.

Then we prepared a TiO_2 film as follows. A soda lime glass substrate coated with a silicon dioxide layer was dipped ten times into ethanol solution of tetra-*iso*-propoxy titanate containing polyethylenglycol and then calcinated in an electric furnace at 973 K under air atmosphere for 1 h. This procedure was repeated four times. Thus 0.2-μm thick TiO_2 film of 81% anatase was prepared. This TiO_2 coated glass was cut in piece in a rectangular form (about 2 mm to 3 mm) and placed in a 4 mm glass NMR sample tube and it was simply capped without evacuation. UV was illuminated as described above.

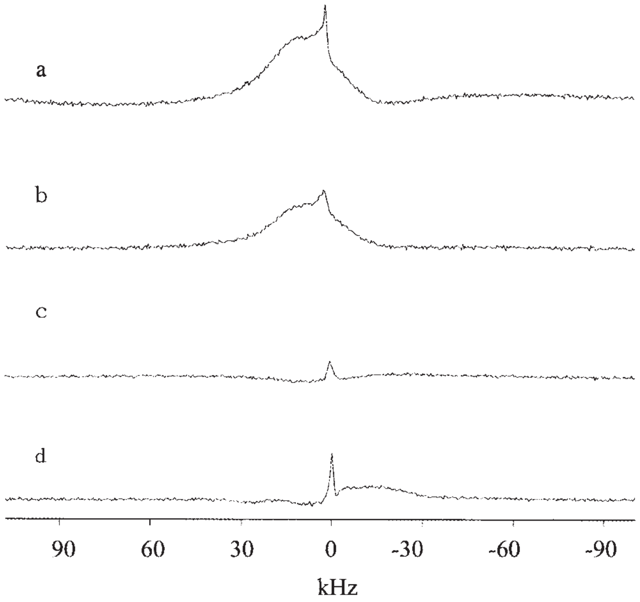

Figure 2. ^{1}H-NMR spectra of TiO_2 film. (a) Before UV illumination, (b) illumination for 10 min, (c) for 60 min, and (d) after admission of air to (c).

The spectrum before UV illumination was similar to that for powders, i.e., two peaks, sharp and broad peaks with line widths of about 500 Hz and 18 kHz, respectively, were observed (Figure 2a) although the intensity of the sharp peak decreased. After 10-min illumination, the intensities of both signals decreased slightly (Figure 2b). On further illumination for 60 min, the broad peak disappeared completely and only small amount of the sharp peak remained (Figure 2c). At this stage we opened the cap of the sample tube and introduced air. Then both peaks recovered slightly (Figure 2d). Although the sharp peak appeared at the same chemical shift, the broad peak appeared at slightly higher field as compared with that measured before photo illumination (Figure 2a). This means that the chemical environment around rigid structured water molecules or/and the OH groups adsorbed on TiO_2 surface changed before and after photo illumination. This fact is consistent with the report that the photo generation of the highly hydrophilic surface of titanium dioxide is attributed to a structural change on the TiO_2 surface that arises from surface oxygen vacancies.[3–6]

After 2-h photo illumination, both peaks disappeared completely but it was confirmed that they recovered gradually and reached to the same spectral appearance as Figure 2a within a week. However, without administration of air the signals did not recover probably because the water molecules in the sample tube were photo-decomposed completely.

Disappearance of water signal on UV illumination can be explained by the broadening of the signals by the interaction with stable paramagnetic species generated by photo illumination such as Ti^{3+} or the disruption of adsorbed water molecules. The former possibility, however, would be eliminated because the introduction of air or O_2 into the sample tube did not cause the prompt complete recovery of the signals.

It was revealed that the photo-induced hydrophilic surface was not uniform but composed of water molecular layer domains that extended corresponding to the specific crystal direction of rutile surface based on the observation of the surface of rutile single crystal after UV illumination by AFM.[3]

In order to elucidate more detailed features on the properties and structures of the adsorbed water on the surface of TiO_2, measurements of temperature dependence and relaxation times with NMR spectroscopy are now in progress in our laboratory.

This work was supported in part by a Grant-in-Aid for the Priority Area Research on "Photo Functional Interfaces" from the Ministry of Education, Culture, Science and Technology.

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