

Water Properties in TiO₂ Photocatalytic Systems as Studied by Solid-State ¹H-NMR Spectroscopy

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For the better understanding of the various functions of TiO₂ photocatalysts, it is important to investigate the structures and properties of the adsorbed water since most of the functions are caused by the exertion of the active species produced through the reactions of photogenerated electrons and holes with adsorbed water or titanol on TiO₂. In this study we measured the temperature dependence of ¹H-NMR signals of water for TiO₂ photocatalysts of different properties in powder form, *i.e.* Degussa P25 (Japan Aerosil: rutile 20% and anatase 80%) and ST-01 (Ishihara Techno: anatase 100%) and tried to characterize the adsorbed water.

¹H-NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz. TiO₂ powder was packed into the NMR sample tube in contact with air through a small hole and the samples were rotated at magic angle at the rate of 12.6 kHz. 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-sulphonate) as an external reference.

As shown in Fig.1 (a) ¹H-NMR spectrum of TiO₂ in powder form presents a single signal with the line width of several hundred Hz at a half peak height at 295 K, which was ascribed to the relatively mobile physisorbed water¹

With increasing temperature the intensity decreased gradually along with the vaporization of water and the line width became broader. When the sample was kept at 358K, the peak shifted gradually to the down field with the increase of the line width and after 2 h the peak area became 40 % of that before the temperature increase for ST-01 as shown in Fig.2, while the peak area of P25 decreased more rapidly to 40% (30 minutes). On decreasing temperature back to 295 K the peak became remarkably broad (several kHz, Fig. 1(c)) as compared with 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 TiO₂ since it disappeared completely at the temperature where surface OH groups are still present on TiO₂¹. 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 remained in the system would become dominant to contribute to the broader signal. When the sample was kept at 295 K, water in the air re-adsorbed gradually on the surface of the photocatalyst to form mobile water layers. The water signal completely recovered in about 20 h for P25 but not for ST-01 although it recovered after 1 month (Fig1. (d) and (e)). The differences in the behaviors of the adsorbed water signal on temperature increase observed for P25 and ST01 may be attributed to their difference in the primary particle size, the surface area of the particles¹ and the crystal structures. The details on the structure of water on the surface of TiO₂ have not been elucidated well. The present results suggest that physisorbed water region of the photocatalysts consists of complex layers where water molecules take different structures and mobility. The primary particle size and the ratio of rutile component may affect the formation of the layers and the variety of the water structures.

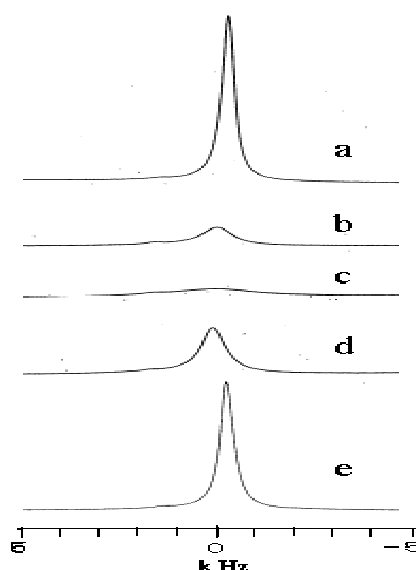


Figure 1. ¹H MAS-NMR spectra of TiO₂ powder (ST-01) measured at 295 K (a), 358 K (4.5 h after temperature was increased to 358 K) (b), 295 K (c) (just after temperature was decreased back to 295 K), and 295 K (d) and (e) (after the sample was kept at room temperature for 20 h and 1 month).

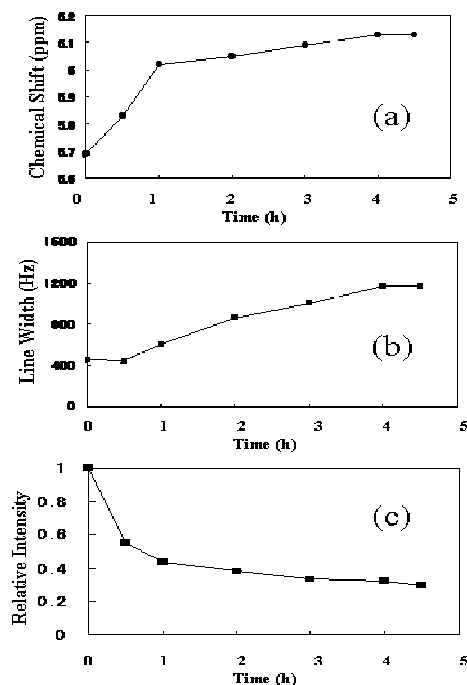


Figure 2. The change of chemical shift (a), line width at half peak height (b), and the relative peak intensity (peak area) (c) of the water signal of ST-01 with time at 358 K.

Reference

1. A.Y. Nosaka, T. Fujiwara, H. Yagi, H. Akutsu, and Y. Nosaka, *Chem. Lett.* **31**,420 (2002)