

BEHAVIOR OF ADSORBED WATER OF TiO₂ PHOTOCATALYSTS ON THERMAL TREATMENTS

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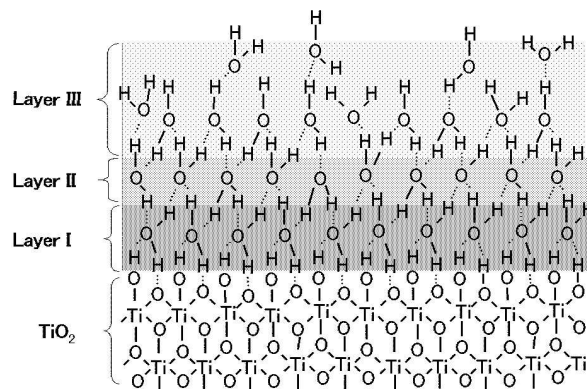
The water molecules adsorbed on TiO₂ photocatalytic systems must play important roles in photocatalytic reactions since most of the functions are caused by the exertion of the active species produced through the reactions of photogenerated electrons and holes with the adsorbed water or titanol on TiO₂. We have been investigating the properties of water adsorbed on various TiO₂ photocatalysts in powder and film forms mainly by ¹H-NMR spectroscopy (1-4). In the present study we investigated the change of the ¹H-NMR signals on temperature increase up to 358 K for 6 kinds of commercially available TiO₂ photocatalysts of different properties in powder form, *i.e.*, Degussa P25 (Japan Aerosil), Hombikat UV-100 (Sachtleben Chemie), ST-01 (Ishihara Techno), F4 (Showa Titanium), AMT-100 and AMT-600 (Tayca). ¹H-NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz.

¹H-NMR of the six TiO₂ photocatalysts presented a single signal with line width of several hundred Hz, at a half peak height at 295 K. For all the six TiO₂ photocatalysts the signal intensity decreased rapidly along with the vaporization of water when the temperature was increased up to 358 K. The peak shifted with the increase of the line width and within 10 min the peak area became 50-40 % of that before the temperature increase when the temperature was kept at 358K. In the following 2 h the signals continued to decrease gradually and thereafter barely decreased. On decreasing temperature back to 295 K the peak became remarkably broad (several kHz) 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 TiO₂. These results indicate that the 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. The difference in the chemical shifts of the broad water signals among six different photocatalysts became significantly large as compared with that of the sharp water signals before temperature increase. These results suggest that the water structures and their chemical environments near the solid surface

region should be quite different reflecting the characteristics and crystal structures of the individual TiO₂ photocatalysts. Thus the apparent single water peak observed at 295 K before temperature increase was found to comprise of the signals with different line widths and chemical shifts, which correspond to those of the water molecules with different structures and mobility.

The time profiles of the intensities, line widths and chemical shifts of ¹H-NMR signals of adsorbed water at 358 K were examined in detail. In consequence, as illustrated in Figure, the adsorbed water region observed with NMR was found to be characterized by three layers; (I) the innermost layer with rigid water molecules with highly restricted mobility and/or hydroxyl groups on the solid surface, (II) the intermediate layer with relatively mobile water molecules, (III) the outermost layer with highly mobile water molecules. The thickness of the water layer is almost the same for six photocatalysts. The ratio of the amount of the water molecules contained in each layer could be roughly estimated to be 3 (I) : 2 (II) : 5 (III). The surface properties of the individual photocatalyst are reflected in the water molecules distinctly in layer I but not those in the layer III

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