Mechanistic Investigation of TiO_2 Photocatalysis by Spin Probing Method

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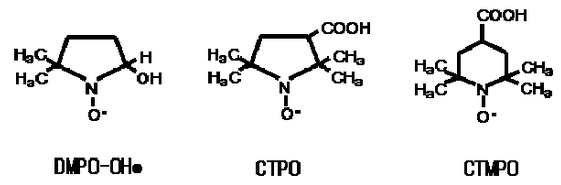
We applied stable nitroxide radicals to detect photocatalytic reaction in TiO_2 aqueous suspension by means of electron spin resonance (ESR) spectroscopy, and found that direct oxidation plays an important role in photocatalytic decomposition of materials as well as the oxidation with. •OH radical.

Photocatalytic reactions by using TiO_2 powder have attracted much attention because of its practical applications to the clean-up of building materials and the mineralization of waste water. One of the important issues in the photocatalytic reactions is the initial process of the oxidation of organic molecules. Since TiO_2 is surrounded by adsorbed water in the air or it is used in aqueous suspension, water molecules are likely oxidized first to hydroxyl radicals (•OH) by photogenerated positive holes and then they react with organic compounds to form oxidized species or decomposed products. However, the organic compound could be oxidized directly in place of the oxidation of water.[1] Then, in the present study, we tried to evaluate the difference of photocatalysis by means of spin trapping and the associated methods. The experimental observations suggest that these methods are not definitely specific for •OH radicals.

The TiO_2 powders used in the present experiment, which are supplied as photocatalysts, were Degussa P-25 (Japan Aerosil), Hombikat UV-100 (Sachtleben Chemie), ST-01 (Ishihara Techno), F4 (Showa Titanium), AMT-100, and AMT-600 (TAYCA). All TiO_2 powders are generous gifts from the corresponding manufacturers. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), 3-carboxy -2,2,5,5-tetramethyl-1-pyrrolidine-1-oxyl (CTPO), 4-carboxy-2,2,6,6–tetramethyl-piperidine-1-oxyl (CTMPO), and 4-hydroxy-2,2,6,6-tetramethylpiperidine- 1-oxyl (TEMPOL) were purchased and used as received. In ESR experiments, TiO_2 powder was dispersed in 2.5 mL of aqueous solution of 0.8 mM of spin probe reagents (CTPO, CTMPO and TEMPOL), or 2mM of DMPO by an ultrasonic vibrator and then the suspension was introduced into a thin flat ESR cell (inside size of 0.2 x 5 x 40 mm^3). The ESR measurements were carried out at room temperature with a JEOL ES–RE2X ESR spectrometer under the photoirradiation with a 500 W mercury lamp through a band-pass filter (HOYA, U-350) and a mesh filter to attenuate the light intensity. The irradiation intensity was about 20 mW.

The formation of •OH adducts of DMPO for ST-01 and UV-100 TiO_2 is smaller than that in the absence of TiO_2 powder, although the increase of the adducts with P25 TiO_2 was observed as reported in literature. The observation of smaller signal for ST-01 and UV-100 is explained by the photocatalytic decomposition of the produced OH radical adduct DMPO-OH•, because whose oxidation seems to occur much easier than that of water.

Then we investigated the photocatalytic reaction of nitroxide radicals in details. Figure 1 shows the relative decrease of the nitroxide radicals, CTPO and CTMPO, by UV irradiation. Schwarz et al. reported that the decrease of CTPO is originated from a selective reaction with •OH radical.[2] Our experimental result show CTMPO is more sensitive than CTPO. Figure 2 shows the effect of additives on the relative decrease of CTPO radical. When 2-propanol was added, the decrease was accelerated, indicating that CTPO reacts with the alcohol radical. Although 2-propanol is usually served as a •OH radical scavenger, the oxidation of alcohol becomes dominant in photocatalytic system. Cl^- and ClO_4^- caused almost similar effect, indicating that only the ionic strength affects the photocatalytic decay of CTPO radical. Since •OH radical is very reactive to Cl^-, it is not likely that CTPO decays by the selective reaction with •OH radical.



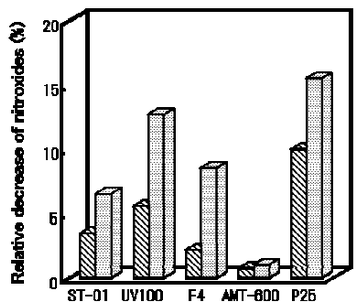


Figure 1. Relative decrease of CTPO (left) and CTMPO (right) radicals by UV irradiation of 5 s for the aqueous suspension of various TiO_2 photocatalysts.

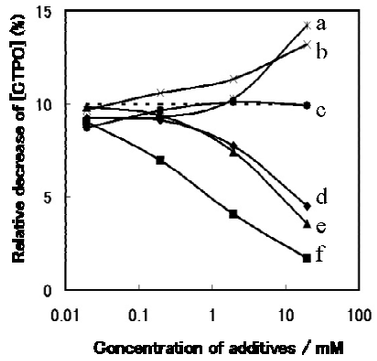


Figure 2.Relative decrease of CTPO radicals by 5-s irradiation for P25 TiO_2 aqueous suspension containing various additives is plotted as a function of the concentration. a: 2-propanol, b: methanol, c: acetic acid, d: sodium perchlorate, e: sodium chloride, f: sodium iodide.

1 T. Hirakawa and Y. Nosaka, *Langmuir*, **18,** 3247 (2002)
2. P.F. Schwarz, N.J. Turro, S.H. Bossmann, A.M. Braun, A. A. Abdel Wahab, and H. Duerr. *J. Phys. Chem. B*, **101,** 7127 (1997) .