In Situ FTIR study of photocatalytic reduction of O_2 on Particulate TiO_2 film in contact with Aqueous Solutions

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Photocatalytic reaction on TiO_2 powder or particulate films have been attracting much attention in view of their possible application to solar energy conversion (water splitting) as well as decomposition of waste materials and harmful organic compounds. Intensive work has been done on reaction products, yields, and mechanisms to increase the efficiencies and clarify the optimized conditions, but the details of reaction mechanisms are still unclear probably because of a shortage of *in-situ* direct spectroscopic detection of unstable reaction intermediates.

In this paper, we have applied multiple internal reflection infrared (MIR-IR) spectroscopy for *in-situ* IR studies of photocatalytic process at TiO_2-aqueous solution interfaces. The main focus has been placed on clarifying the molecular mechanisms of photocatalytic reduction of O_2. The process is of particular interest because it gives active oxygen species crucially important for photocatalytic oxidation of organic compounds.[1]

In our multiple internal reflection infrared (MIR-IR) measurements, a particulate TiO_2 film was applied on one face of the internal reflection element (IRE) by a dip-coating method. The IRE was dipped in a 0.01 M TiO_2 (JRC-TIO-2, JRC-TIO-5) aqueous suspension and dried in air, followed by wiping of the rear face of the IRE with a soft cloth. This procedure was repeated five times. The TiO_2 coated IRE thus obtained was set in the spectral cell made by Diflon.

Figure shows the MIR-IR spectra in the 1550-750 cm^{-1} region during the UV irradiation of TiO_2 (TIO-5) films in contact with O_2-saturated aqueous solutions of pH 4.5, 7.0, and 11.8. For a neutral solution of pH 7 (Figure b), two bands appeared at 1023 and 943 cm^{-1}, together with a broad band in the 1250-1120 cm^{-1} region. The spectral change in an acidic solution of pH 4.5 (Figure a) was rather similar to that in the neutral solution, though a band at 1023 cm^{-1} became week and a new band appeared at 887 cm^{-1} and, in addition, the 1250-1120 cm^{-1} band became stronger in the acidic solution. The spectral change in an alkaline solution of pH 11.8 (Figure c) is, on the other hand, significantly different from those for the neutral and acidic solutions. Only the sharp band at 943 cm^{-1} appeared in the alkaline solution. From these results, it is apparent that at least two individual species are photo-produced at the TiO_2 surface; One giving the 943 cm^{-1} band and the other giving the 1250-1120 cm^{-1} band.

Detailed analysis of the spectra gives the assignments of the 943-cm^{-1} band to the O-O stretching mode of a surface peroxo species, $Ti(O_2)$, and the 1250-1120 cm^{-1} for the OOH bending mode of a surface hydroperoxo species, TiOOH. It was proved that a surface peroxo species, $Ti(O_2)$, is a key intermediate for the production of TiOOH via protonation (SCHEME). The TiOOH are photodecomposed to yield the surface hydroxyls, Ti-OH, (3693 and 3645 cm^{-1}). In-situ MIR-IR measurement also found that the progress of photoreduction of O_2 results in increases in pH at the interfaces.

There are several reports of formation of surface peroxo as well as hydroperoxo species and their participation in the photocatalytic processes on TiO_2 surfaces. The present work gives the first direct *in-situ* spectroscopic evidence for the formation of such intermediate species on TiO_2 in contact with aqueous solutions. These observations open up a new level of mechanistic studies of photocatalytic reactions on TiO_2 in aqueous solution.

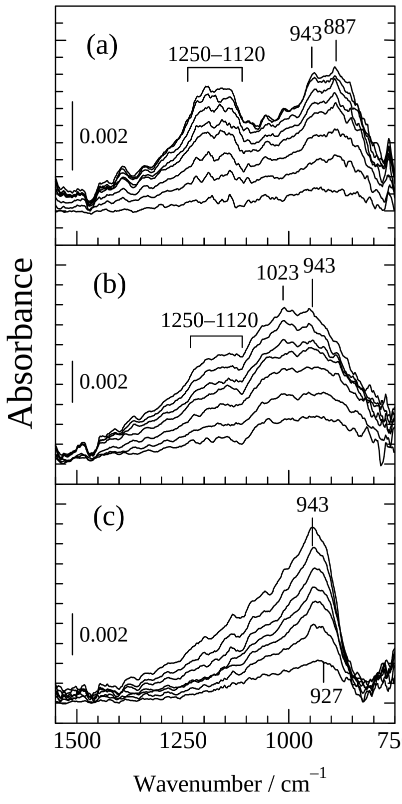
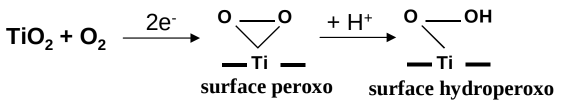


Figure Time course of MIR-IR spectra for TiO_2 (TIO-5) films in O_2-saturated aqueous solutions of pH (a) 4.5, (b) 7.0, and (c) 11.8. Spectra were recorded in times of 3, 6, 9, 12, 15, 18, and 21 min after the UV start of the irradiation.



SCHEME

1, Nakamura, R.; Sato. S. *J. Phys. Chem. B* **2002**, *106,* 5893.