In-situ MIR-IR Observation of Peroxo Species on Anatase TiO₂ Particle during Oxygen Photoevolution Reaction

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The peroxo species on ST-01 anatase TiO₂ particles in contact with FeCl₃ aqueous solution during oxygen photoevolution were investigated by in-situ MIR-IR absorption spectroscopy. The peaks assigned to the peroxo species (TiOOH and bridging O-O) were generated by UV-irradiation, though observed vibrational energy of bridging O-O species was largely shifted from that of rutile TiO₂ particles (TiO₂-3). The observed difference between both particles was mainly attributable to the difference in the local surface structure of TiO₂. The existence of unknown reaction paths to consume bridging O-O species without reacting with photogenerated holes was suggested from the observation of sequential change of absorption intensity.

Key Words : TiO₂, Peroxo Species, In-Situ MIR-IR, Oxygen Photoevolution

1 Introduction

TiO₂ has been widely studied from points of view of the solar energy conversion system of water.\(^1\) However, the details of photoinduced water splitting reaction mechanism remain unsettled. Thus, up to now, many research groups have investigated about the intermediates for oxygen photoevolution reaction on TiO₂. We recently suggested that the oxygen photoevolution reaction at a rutile TiO₂ surface in aqueous solution was initiated by a nucleophilic attack of a H₂O molecule to a surface-trapped hole, generating peroxo species such as TiOOH and TiO₂Ti on the surface (Scheme 1).\(^2\) Besides, many other groups also reported that the most plausible intermediate species was “peroxo (or peroxy) species”, though there is a difference in the detailed structure of them between the research groups. Assuming that the stability of such peroxo species is strongly affected by the local surface structure of TiO₂ surface, it is quite possible that the local structure strongly affects the photocatalytic activity (i.e. oxygen evolution efficiency). However, there were few studies in which the effect of the local surface structure on the structural and/or chemical properties of peroxide species were investigated.

It is well known that the vibration frequency of O-O stretching mode is very sensitive for the local structure of peroxo species.\(^3\) This indicates that we can obtain the structural information of peroxo species by FTIR measurements. We should also note that no researcher has shown the direct experimental evidence that such peroxo species are intermediates for oxygen photoevolution (Although some researchers experimentally revealed the existence of such species, no one investigated the reaction kinetics of them.). To investigate the reaction kinetics of such intermediates, in-situ observation of the intermediates during the photooxidation reaction is needed. In this report, we investigated the peroxo species on anatase TiO₂ during oxygen photoevolution by using in-situ multiple internal reflection infrared (MIR-IR) absorption spectroscopy under UV irradiation. The observed spectra were compared with those of rutile TiO₂ which was reported in the previous papers\(^4\) for the purpose of evaluation of the structural difference of intermediates which was induced by the difference in the local surface structure of both types of TiO₂ particles. The reaction behaviors of the peroxide species were also investigated.

2 Experimental

Anatase TiO₂ powder, ST-01 (300 m²/g) purchased from Ishihara Sangyo was used. The surface of the TiO₂ particles was cleaned by heating at 600°C in air for 5 h, followed by UV irradiation in oxygen saturated water for 1 h and sonication for 30 min. Thus cleaned particles were dried under vacuum condition (<1×10⁻³ Torr). We confirmed that the crystallinity and surface area of the particles did not change after the cleaning procedure by XRD and Raman spectroscopy.

The IR spectra of the TiO₂ particles were obtained by using a cell for the MIR-IR measurement, which was reported in a previous paper (schematic illustration of the cell is shown in Fig. 1).\(^5\) An aqueous TiO₂ slurry (10 mg/mL, 5 μL) was spread on the diamond disk with a plastic pipet and dried in air for 90 min. A 10 mM FeCl₃
(70 µL) aqueous solution (electron scavenger) deoxygenated by nitrogen bubbling for 30 min was dropped on the TiO₂ film. The IR light reflects 9 times at the diamond/TiO₂ solution interface. The cell was placed in the sample chamber of an FTIR spectrometer (Bio-Rad FTS 575C) with an MCT (HgCdTe/mercury cadmium telluride) detector. Before the measurements, the chamber was purged with N₂ and the cell was kept in the dark for 120 min. UV irradiation of the TiO₂ film was carried out by a 365 nm band selected from a 200 W Hg-Xe lamp (Hypercure 200 UV, Yamashita Denso) by use of a bandpass filter (Asahi Techno Glass UV-D36A). The incident UV light intensity at the position of the sample surface measured with a thermopile (Eppley Laboratory) was approximately 11 mW cm⁻².

3 Results and Discussion

Figure 2 shows MIR-IR spectra of ST-01 film in contact with FeCl₃ aqueous solution responding to UV irradiation. The spectrum measured just before the UV irradiation was used as the reference spectrum f₀. Three peaks appeared at 835, 860 and 912 cm⁻¹ by UV irradiation. Absorption peaks at 839 and 837 cm⁻¹ were reported on H₂O₂-absorbed TiO₂ and Ti-silicate (TS-1) and were assigned to O-O stretching mode of TiOOH.⁵⁻¹¹ Thus, the peak at 835 cm⁻¹ can be assigned to O-O stretching mode of TiOOH. The peak at 912 cm⁻¹ is probably assigned to O-O stretching mode of TiO₂.⁵⁻¹²⁻¹³ Those two kinds of peroxide species were also observed on rutile TiO₂ particles.⁵⁻⁷⁻¹³

The assignment of the peak at 860 cm⁻¹ is a little hard because the vibrational peak of well known typical peroxide species does not appear in such an energy region. The most plausible assignment is the lattice bridging O-O species (i.e. each oxygen atom of O-O is bound to different lattice Ti atoms by chemical bonds). It must be noted that Ti-O-O-Ti (at 812 cm⁻¹) which is one of bridging O-O species was also observed on rutile TiO₂ particles (TiO₂).⁵⁻³ However, the energy position of ST-01 is blue-shifted by 48 cm⁻¹ comparing with that of TiO₂. This may be due to the difference in the local surface structure of both samples, because the vibrational mode of lattice bridging O-O species is strongly affected by the local structure of TiO₂ (Note that vibrational energy of TiOOH and Ti(O₂) is hardly affected by the local surface structure because they are formed on a single Ti atom). In fact, the vibrational energies of those species observed on rutile TiO₂ particles⁹ were almost the same with those observed on ST-01. This consideration is also supported by a calculation.⁹ Li et al. carried out a DFT calculation to investigate the detailed structure of peroxo species as intermediates of oxygen photoevolution at thermodynamically stable anatase (101) and rutile (110) surfaces. There was a large difference in the structure of the peroxo species on both surfaces, and the calculated vibrational frequency of the O-O stretching mode of the peroxo species on anatase (101) surface was blue-shifted by 72 cm⁻¹ from that on rutile (110) surface.⁶⁻⁷ The reported local structures were more complex than those we speculated in this report, however, the peak shift may originate from the different local structures.

The intensity around 950 cm⁻¹ decreased as a negative peak with UV irradiation time and increased (recovered) after stopping UV irradiation (Fig. 2). This suggests that some pre-formed surface species (generated only by immersing the sample in FeCl₃ aqueous solution under dark condition) decreased by UV irradiation and was generated again after stopping UV irradiation. However, we cannot assign this peak to the specific chemical species at present.

As the bridging O-O species play a crucial role as an
intermediates for oxygen photoevolution reaction, it is important subject to investigate the reaction kinetics of such species. The peak areas of the bridging O-O species and TiOOH, which were obtained by peak fitting analyses assuming the superposition of the peaks at 835 and 860 cm⁻¹ (see Fig. 2), were plotted as a function of time in Fig. 3. The TiOOH species showed almost the same behavior with bridging O-O. It indicates that the two species were not formed independently but were closely correlated with each other. Peak intensities of the two peroxy species increased for a saturation with increasing of irradiation time. This suggests time-dependent oxygen evolution rate but we do not have direct evidence for that at present due to some experimental difficulties. It was unexpected from Scheme 1 that both species gradually decreased after stopping UV irradiation. This indicates the existence of other reaction paths which reduce the amount of the peroxy species without reacting with photogenerated holes (not shown in Scheme 1). There has been no claim of such reaction paths in literature, however, desorption or disproportionation reaction of the peroxy species are included in the possibilities. If the non-hole-consuming reactions occur under UV irradiation, the reaction kinetics of oxygen evolution should be revised.

The similar behaviour of the peroxy species was also observed in the case of rutile TiO₂-3 particles (not shown). However, the increasing and decreasing rates of peroxy species were different from those of ST-01. This indicates that the reaction kinetics depends on the local structure of TiO₂ and peroxy species. It is still difficult to discuss about the correlation between such a local structure and reaction kinetics at present. We need direct observation of the change of oxygen gas generation rate over UV irradiation time, to make a further consideration about reaction kinetics.

4 Conclusion

The peroxy species on ST-01 anatase TiO₂ particles in contact with FeCl₃ aqueous solution during oxygen photoevolution were investigated by in-situ MIR-IR absorption spectroscopy. The peaks assigned to the peroxy species (TiOOH and bridging O-O) were generated by UV-irradiation. The large frequency shift of O-O stretching mode of the bridging O-O species between ST-01 and TiO₂-3(rutile) were attributed to the difference in the local surface structure. The bridging O-O species were gradually decreased after stopping UV irradiation, indicating the existence of reaction paths to consume peroxy species without reacting with photogenerated holes.

References