Pressure dependence of electron- and hole-consuming reactions in photocatalytic water splitting on Pt/TiO₂ studied by time-resolved IR absorption spectroscopy

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ABSTRACT. The decay kinetics of photogenerated electrons in the water splitting reaction on a Pt/TiO₂ photocatalyst was studied by time-resolved IR absorption spectroscopy. The decay of the photogenerated electrons within 2 μ s was decelerated when the catalyst was exposed to water vapor. The holes were consumed by the reaction with water instead of by the recombination with the electrons. On the other hand, the decay at 10–900 μ s was accelerated by the exposure. The electrons were consumed by the reaction with water. The rate of the hole-consuming reaction was independent of the pressure of water vapor, whereas that of the electron-consuming reaction increased with the pressure from 1 to 10 Torr. The different pressure dependences indicate different reactants involved in the oxidative and reductive reactions.

1. INTRODUCTION

Photocatalysts based on TiO₂ have been intensively studied in recent years because of their potential applications toward the water splitting reaction [1], degradation of pollutants [2], solar energy conversion [3], and so on. However, many questions remain to be answered in relation to reaction mechanisms. For understanding the mechanism of photocatalytic reactions, surface reactions triggered by band gap excitation should be traced in a time-resolved manner. We built a time-resolved IR spectrometer to observe the kinetic phenomena related to the photoexcitation of TiO₂. By using the AC-coupled amplification of an IR signal, a transient absorbance change as small as 10^{−6} was detectable over a wide range of wavenumbers (4000–900 cm^{−1}) and also a wide range of delay times (50 ns–1 s).

We have reported that the photogenerated electrons in the conduction band cause a structureless IR absorption at 4000–900 cm^{−1} [4]. By tracing the absorption intensity, the decay kinetics of the electrons due to the desired reaction and the undesired recombination can be examined [5]. In the present paper, the photogenerated holes and electrons consumed in the oxidative and reductive steps of the water splitting reaction were traced on a Pt/TiO₂ catalyst. The pressure dependence of the elementary steps was examined.

2. EXPERIMENTAL SECTION

Transient IR absorption was observed with a home-built spectrometer [4]. IR light transmitted through the sample was monochromatized with a 32 cm^{−1} resolution in a grating monochromator (JASCO, CT50TF). The output IR intensity was measured with a photovoltaic MCT

detector (Kolmar). The signal at a fixed wavenumber was amplified with AC-coupled amplifiers and accumulated in a digital sampling oscilloscope as a function of delay time. The time-resolution of the spectrometer was limited by the response of the MCT detector to be 50 ns. The steady-state IR absorption spectra were obtained using a FT-IR spectrometer (JASCO, FT/IR-610) equipped with a MCT detector. The spectral resolution was set at a 4 cm^{−1} and typically 300 scans were averaged.

The Pt/TiO₂ catalyst was prepared with TiO₄ (P-25), a standard TiO₂ catalyst supplied by the Catalysis Society of Japan [6]. Platinum was deposited at 1 wt% by photodeposition from a H₂PtCl₆ aqueous solution. The catalyst was fixed on a CaF₂ plate in a density of 2 mg/cm². The catalyst on the plate was photoexcited by 355 nm light from the third harmonic generation of a Q-switched Nd : YAG laser (Spectron, SL401). The pulse energy was 7 mJ with a 10 ns width. A transient response in absorbance as small as 10^{−6} was detected by signal averaging of 300 flashes at 1–0.5 Hz.

3. RESULTS AND DISCUSSION

Figure 1 shows the decay of the transient IR absorption observed at 2000 cm^{−1} in the absence and presence of H₂O molecules in the gas phase. This IR absorption is assigned to the electrons photogenerated by 355 nm UV pulse irradiation [4]. The behavior of the electrons can be examined by tracing the temporal decay of the IR absorption. As seen in Figure 1(a), the decay at 0–2 μ s was slowed by the exposure to water vapor. The decay of electrons obtained in the vacuum reflects the rate of the recombination with holes. The decelerated decay is thus ascribed to the quenching of the holes. The holes

Figure 1. Temporal profiles of the transient IR absorption of Pt/TiO₂ irradiated by the 355 nm pump pulse at time = 0. The decay curves were measured at 2000 cm⁻¹ in the absence and presence of water atmosphere at 1, 5, and 10 Torr.

photogenerated in the valence band have a potential to oxidize water [2, 3, 7, 8]. This hole-consuming reaction competes with the recombination, and the decay of the electrons is decelerated. This hole quenching reaction corresponds to the oxidation of water. On the contrary, the decay observed at 10–900 μs was accelerated by the introduction of water (Figure 1(b)). On Pt/TiO₂, the electrons photogenerated in the conduction band have a potential to reduce water [2, 3, 7, 8]. The accelerated decay is ascribed to the electron-consuming reaction by water. These results show that both the holes and electrons are consumed by the complementary reactions with water. We observed that these reactions are completed in different time domains, i.e., the holes quickly oxidize water within 2 μs, while the electrons gradually reduce water at 10–900 μs. The hole-consuming reaction proceeds much faster than the electron-consuming reaction.

The hole-consuming reaction showed no pressure dependence of water vapor (Figure 1(a)). The decay curves obtained at 1, 5, and 10 Torr of water vapor were identical. The electron-consuming reaction exhibited a positive dependence on water pressure as shown in Figure 1(b). The increased water pressure enhanced the acceleration of the electron decay. The different

Figure 2. The FT-IR spectra of the surface hydroxyl groups on Pt/TiO₂ recorded in the vacuum and the subtracted spectra in the presence of H₂O gas at 1, 2, 5, 8, 10, and 15 Torr. The inset shows the integrated peak intensities of the bands at 3330 cm⁻¹ (○) and 1640 cm⁻¹ (□) as a function of the water pressure.

pressure dependences of the decay kinetics indicate different species at the catalyst involved in the hole-consuming and electron-consuming reactions.

The steady-state IR absorption of Pt/TiO₂ catalyst exposed to water vapor was observed for identifying the adsorbates responsible for the two reactions. Figure 2 shows the steady-state spectra. By exposing the catalyst to water vapor, the bands at 3730 and 3677 cm⁻¹ observed in the vacuum decreased in intensity and new bands appeared at 3330 and 1640 cm⁻¹. The bands at 3730 and 3677 cm⁻¹ have been assigned to the O–H stretch ($\nu(\text{OH})$) of the surface hydroxyl groups on TiO₂ [9–11]. The decrement of these band intensities is attributed to the wavenumber shift or broadening due to the formation of the hydrogen bond with additionally adsorbed water [9, 10]. The new bands at 3330 and 1640 cm⁻¹ were assigned to the $\nu(\text{OH})$ mode and the H–O–H bending of the adsorbed water, respectively [10]. The integrated peak intensities of these two bands increased in the same manner as a function of the pressure of H₂O. This result suggests that the main part of the band at 3330 cm⁻¹ is due to the $\nu(\text{OH})$ of the undissociated water. The additionally

adsorbed water can be partly dissociated on the TiO₂ surface as,

where O(L) is a lattice oxygen atom and OH(a) is an adsorbed hydroxyl group, respectively. The $\nu(\text{OH})$ of the hydroxyls falls in a range at 3700–3400 cm⁻¹ [9, 10], superimposing the broad peak of the undissociated water. The contribution of the hydroxyls could not be identified in the spectra in Figure 2, unfortunately.

The identical electron decay rates at 0–2 μs in the presence of 1–10 Torr of water suggest that the coverage of the hole scavenger is saturated even at 1 Torr. This is consistent with the accepted proposal that surface hydroxyls act as the hole consumer at the initial step of the water splitting reaction [2, 3, 7, 8]. The dissociation of water is a structure-sensitive reaction on TiO₂ and thought to require an oxygen vacancy at the surface [12, 13]. On the other hand, the electron-consuming reaction displayed a positive order to water pressure. We thus propose that the undissociated water or some species equilibrated with it is responsible for the electron-consuming reaction.

4. CONCLUSION

The ability of time-resolved IR absorption spectroscopy to trace the kinetics of the photocatalytic splitting reaction of water was demonstrated on the Pt/TiO₂ catalyst. We found that the photogenerated holes are consumed within 2 μs during the oxidative elementary step and that the photogenerated electrons are utilized to reduce the water at 10 μs or later. These two reactions showed different dependences on the pressure of water vapor. The oxidation step (hole-consumption) was not affected whereas the reduction (electron-consumption)

was accelerated by increasing the water pressure from 1 to 10 Torr.

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