Electron- and Hole-Capture Reactions on Pt/TiO₂ Photocatalyst Exposed to Methanol Vapor Studied with Time-Resolved Infrared Absorption Spectroscopy

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The decay kinetics of photogenerated electrons in a Pt/TiO₂ catalyst has been studied by time-resolved infrared absorption (TR-IR) spectroscopy. The electron decay was drastically affected by exposure to methanol vapor, and the electron−hole pair recombination was prevented. A certain fraction of the electrons remained beyond 1 s and slowly decayed from ∼1−9 s. The prevented recombination was interpreted with the effective capture of the holes. The extent of the hole capture was insensitive to the pressure of methanol vapor. An irreversibly adsorbed methoxy groups was proposed to capture the holes on the basis of the steady-state FT-IR spectra of the catalyst exposed to methanol vapor of different pressures. However, the slow decay of the electrons exhibited a positive-order response to the methanol pressure. Undissociated methanol physisorbed and equilibrated with the gas phase, which was identified in the steady-state spectra, should play a key role in the electron capture process. Possible mechanisms of the process are discussed.

1. Introduction

The potential use of wide band gap semiconductors is of continuing interest because of their photoactive nature in the oxidation of a wide variety of organic and inorganic substrates.[1-3] TiO₂ is an excellent candidate for a photocatalyst because it is not expensive and is chemically quite stable under the conditions in which surface redox reactions take place.[4,5] Its band-edge positions and gap width are compatible with a large number of desirable redox reactions. The photocatalytic reactions are induced by the charge carriers generated by the band-gap photoexcitation. The reaction efficiency is determined by the competition between the recombination and the charge-transfer reaction. Therefore, it is necessary to know both the recombination process in the particle and the charge-transfer process from the particle to the reactants to understand the reaction mechanisms fully.

Time-resolved infrared absorption (TR-IR) spectroscopy is a powerful tool with which to observe charge-carrier dynamics.[6-12] UV-irradiated TiO₂ particles have strong IR absorption in a wide wavenumber region from 4000 to 900 cm⁻¹. We assigned the absorption with a featureless spectrum to the photoexcited electrons[10,11] on the basis of a theory of optical transitions in semiconductors.[13] By observing the IR absorption at a fixed wavenumber, the decay of photogenerated electrons due to recombination and carrier consuming reactions can be traced. In a study of a water-splitting reaction on a Pt/TiO₂ catalyst, we demonstrated the ability of TR-IR spectroscopy to identify a hole-capture reaction completed within 2 μs following band-gap excitation, whereas the electron-capture reaction took place from 10 to 200 μs.[11]

Time-resolved microwave conductivity[14-16] and transient UV−vis[17,18] measurements are alternative methods for the detection of photogenerated charge carriers. The kinetics of conductivity decay was observed at a delay time from 10⁻⁸ to 10⁻² s with high sensitivity.[14-16] It is, however, difficult to identify the contribution of different carriers (electrons or holes) with comparable mobilities, whereas the transient IR spectrum contains information about the underlying optical transitions. In the transient UV−vis measurement, Bahnemann et al. have proposed that photogenerated electrons and holes induce the transient absorptions centered at 650 and 450 nm, respectively.[17,18] Transient absorbance change down to 10⁻⁴ was traced on a nanosized TiO₂ colloid. When transient UV−vis is applied to the catalyst powders (<1 μm), a strong scattering of probe light and photoluminescence from the radiative recombination make further sensitive detection difficult. Our TR-IR spectrometer can detect absorbance change as small as 10⁻⁶ because the instrument is free from the interference of scattering and luminescence. TR-IR offers a unique opportunity to obtain further information about molecular kinetics because intramolecular vibrations are sensitive to geometrical and electronic structures of molecules. The changes of C−O,[6] C−N,[8] and O−H[19] vibrations related to the charge carrier dynamics were reported.

In the present study, the photocatalytic reaction of methanol on the Pt/TiO₂ catalyst is studied. The photocatalytic reaction including methanol oxidation is one of the most efficient reactions available, and thus methanol is often used as a sacrificial reagent to produce hydrogen gas in the photocatalytic water-splitting reaction over various photocatalysts.[20] In addition, methanol injects an electron into the catalyst during the course of the oxidation, known as the "current doubling effect," which was found in photocurrent[21] and ESR[22] measurements. The charge-carrier dynamics of Pt/TiO₂ in the presence of methanol vapor is therefore an interesting subject worth examining.

2. Experimental Procedures

Transient IR absorption was observed with a home-built TR-IR spectrometer described previously.[10] Briefly, the IR emission from the MoSi₂ source was focused on the sample, and the transmitted light was guided to a dispersive spectrometer

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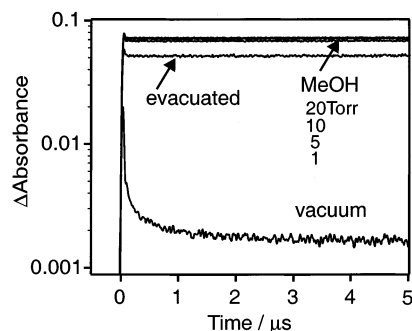
Figure 1. Time profiles of the transient IR absorption of the Pt/TiO$_2$ catalyst triggered by the pump irradiation of the 355-nm laser pulse of 10-ns duration. The absorbance at 2000 cm^{-1} is shown as a function of delay time, $\sim$0$-$5 μs. The curves were obtained at 323 K by accumulating 50 traces repeated at 0.01 Hz in a vacuum and in the presence of methanol vapor of 1, 5, 10, and 20 Torr. The curve labeled "evacuated" was observed on the catalyst exposed to 20-Torr methanol and then evacuated.
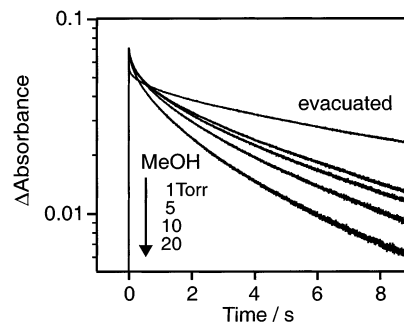

Figure 2. Time profiles of the transient IR absorption of the Pt/TiO$_2$ catalyst triggered by the pump irradiation of the 355-nm laser pulse of 10-ns duration. The absorbance at 2000 cm^{-1} is shown as a function of delay time, $\sim$0$-$9 s. The curves were obtained at 323 K by accumulating 50 traces repeated at 0.01 Hz in the presence of methanol vapor of 1, 5, 10, and 20 Torr. The curve labeled "evacuated" was observed on the catalyst exposed to 20-Torr methanol and then evacuated.

(JASCO; CT50TF). The monochromatized output was detected by a photovoltaic MCT detector (Kolmar). The transient response of the IR signal intensity triggered by a UV pump pulse was observed at a fixed wavenumber and stored in a digital oscilloscope (Lecroy; LT342L). The time resolution of this apparatus was determined by the response of the MCT detector (50 ns). Steady-state IR absorption was observed via an FT-IR spectrometer (JASCO; FT/IR 610) with an MCT detector. In the FT-IR measurements, the spectral resolution was set at 4 cm^{-1}, and 300 scans were averaged.

The Pt/TiO$_2$ sample was prepared with TIO4 (P-25), a standard catalyst supplied by the Catalyst Society of Japan. It includes a mixture of anatase (80%) and rutile (20%) powder of 20-nm diameter and a surface area of 50 m^2 g^{-1}.[23] Platinum was photodeposited at 1 wt % from a H$_2$PtCl$_6$ aqueous solution. This powder catalyst was fixed on a CaF$_2$ plate at $\sim$2 mg cm^{-2}. The catalyst-loaded plate was placed in an IR cell, evacuated by a turbo-molecular pump (70 L/s), with a base pressure of less than 10^{-5} Torr. To remove organic contaminants, the catalyst was calcined at 573 K in a 20-Torr (1 Torr = 133.3 Pa) O$_2$ atmosphere for several hours and then evacuated at that temperature before the IR measurements were made. The catalyst was photoexcited by a 355-nm pulse from the third-harmonic generation of a Q-switched Nd:YAG laser (Spectron; SL401). The pulse energy was 1 mJ, and the pulse duration was 10 ns. The diameter of the irradiated spot was 6 mm. The temporal profile of the transient IR absorption was obtained by accumulating 50 traces at 0.01 Hz. The transient IR absorption intensity was gradually reduced with prolonged 1-Hz laser irradiation, and the color of the catalyst darkened, which indicated the reduction of the sample. Pump pulses more intense than 8 mJ induced a significant temperature jump of the sample and caused thermal artifacts induced by the change of the refractive index and IR emission. Great care was taken to avoid these artifacts, and they were thus not observed with the 1-mJ pulse that was used to irradiate the sample 50 times at 0.01 Hz.

3. Results and Discussion

3.1. Hole-Capture Reaction Induced by Methanol. The decay kinetics of photogenerated electrons in the Pt/TiO$_2$ catalyst was examined in the presence and absence of methanol vapor. Figure 1 shows the transient IR absorption observed at 2000 cm^{-1} as a function of pump$-$probe delay time ($\sim$0$-$5 μs). The UV pulse irradiation of the TiO$_2$ particles induced a structureless, broad IR absorption ranging from 4000 to 1000 cm^{-1}.[10,11] This

absorption was assigned to the optical transitions of the photogenerated electrons.[10,13] Therefore, the temporal profiles of the transient IR absorption in Figure 1 show the decay of the photogenerated electrons. The electron decay of the catalyst placed in a vacuum is assigned to the genuine recombination. When exposure to a reactant affects the decay, the reaction-induced consumption of electrons or holes is deduced.[11]

Exposure to methanol caused two distinct features, as shown in the curves of Figure 1. The absorbance at time = 0 (i.e., the absorbance averaged over the time resolution of the spectrometer (50 ns)) was enhanced four times as much as that observed in the vacuum. The enhanced absorption did not decay at all on the time scale of the Figure, whereas the absorption observed in the vacuum showed a remarkable decay in the first microsecond. The absorbance at 1 μs was enhanced more than 20 times as a result. These enhancements in the electron population are ascribed to the effective capture of photogenerated holes by methanol-derived adsorbates. The constant absorbance at $\sim$0$-$5 μs indicates that the hole-capture reaction was completed within our time resolution of 50 ns.

The decay curve was insensitive to the pressure of the methanol atmosphere ranging from 1 to 20 Torr. Hence, irreversibly adsorbed species could capture the holes, whereas weakly adsorbed species equilibrated with the gas phase could not. Evacuation of the exposed catalyst caused a partial (ca. 30%) reduction of the absorbance. The reduction was ascribed to the depletion of the hole-capture adsorbates due to the photocatalytic decomposition. The absorbance was reduced with the accumulation of the number of UV pulses in a separate observation.

3.2. Electron-Capture Reaction Induced by Methanol. The photogenerated electrons of the enhanced population had a surprisingly long lifetime. Figure 2 shows the decay of the IR absorbance at 2000 cm^{-1} as a function of the delay time of $\sim$0$-$9 s. More than half of the electrons at time = 0 remained at 1 s on the catalyst exposed to methanol. In the vacuum, the number of electrons that survived the recombination was less than 10^{-5} (in absorbance units) at 1 s and far below the ordinate scale of Figure 2. In the methanol atmospheres, slow decays were still observed at delay times of 1 s or longer. We believe that the photoexcited holes were no longer available on this time scale because of the fast reaction with the irreversibly adsorbed species depicted in Figure 1. Instead, methanol-derived adsorbates are proposed to capture the electrons. The rate of the slow decay seen in Figure 2 is positively dependent on the methanol pressure. The positive order suggests that the adsor-
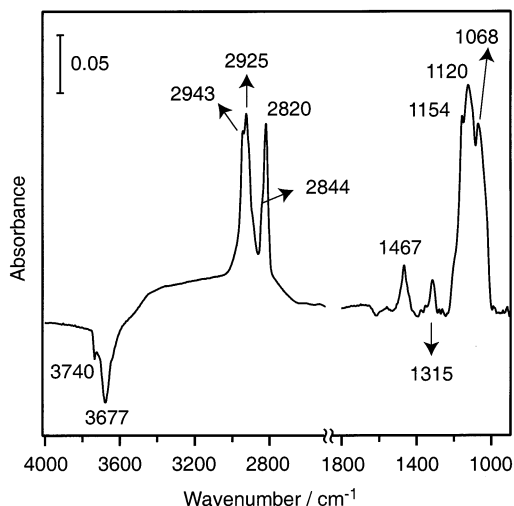
Figure 3. FT-IR spectrum of the methanol-derived species irreversibly adsorbed on the Pt/TiO$_2$ catalyst. A subtracted spectrum of the catalyst exposed to 20-Torr methanol vapor is shown.

Figure 4. FT-IR spectrum of the adsorbates on the Pt/TiO$_2$ catalyst equilibrated with methanol vapor of 1, 5, 10, and 20 Torr at 323 K. The spectrum of the irreversibly adsorbed species in Figure 3 is shown for comparison.

bates that equilibrated with the atmosphere receive the electrons from the catalyst.

The electron decay was not observed on the catalyst that was not loaded with platinum, whereas the hole-capture reaction was completed irrespective of platinum loading. The color of the catalyst in methanol vapor changed to dark blue from the UV irradiation, which indicates the reduction of the unloaded catalyst. Thus, the electrons are transferred to the adsorbates via Pt particles.

3.3. Adsorbates on the Catalyst and Possible Reaction Mechanisms. The different responses to the methanol pressure suggest that the hole-capture species proposed in section 3.1 is different from the electron-capture species proposed in section 3.2. To identify what those species are, adsorbates on the catalyst were analyzed by steady-state IR absorption. Figure 3 shows the steady-state spectrum of the adsorbates present on the catalyst exposed to a 20-Torr methanol atmosphere at 323 K and then evacuated at 323 K. On the basis of the literature,[24-26] three peaks at 2925, 2820, and 1120 cm^{-1} are assigned to the asymmetric CH$_3$ stretching, symmetric CH$_3$ stretching, and C$-$O stretching modes of methoxy groups. Negative peaks at 3740 and 3677 cm^{-1} are ascribed to the hydroxyl groups[19,27,28] replaced by the methoxy groups as[29,30]

$$OH^-(a) + CH_3OH(g) \rightarrow CH_3O^-(a) + H_2O(g) \quad (1)$$
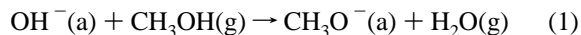
where (a) and (g) represent the adsorbate and gas-phase species, respectively. A C$-$O stretching band split at 1154 cm^{-1} suggests the existence of a variety of CH$_3$O$^-$(a) species according to the states of the OH$^-$(a) species that are replaced. Twin peaks split at 3740 and 3677 cm^{-1} reflect different environments of the hydroxyl groups.

An almost comparable amount of undissociated methanol compared to the amount of dissociated methanol was found on the evacuated surface. The peak at 1315 cm^{-1} is attributed to the H$-$O$-$C deformation mode of CH$_3$OH(a).[30,31] A broad band ($\sim$3500$-$3000 cm^{-1}) was assigned to the hydrogen-bonded O$-$H stretching mode due to the undissociated CH$_3$OH(a). The CH$_3$ and C$-$O stretching modes of the undissociated species are observed at 2943, 2844, and 1068 cm^{-1}. The band at 1467 cm^{-1} can be assigned to the CH$_3$ deformation mode of the dissociated or undissociated adsorbates.

When the catalyst was placed in methanol vapor, additional peaks appeared and strengthened with pressure. Figure 4 shows
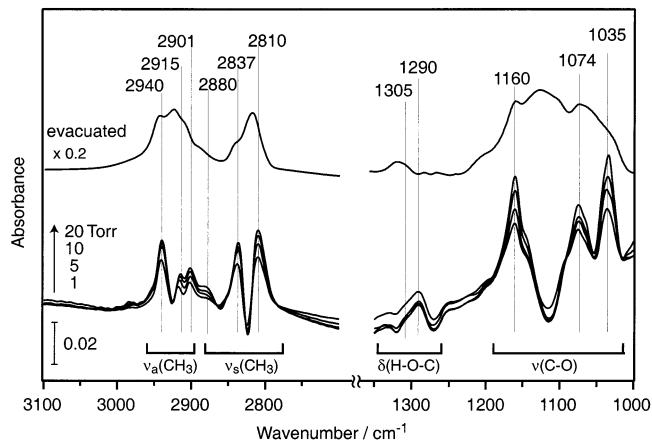
the steady-state spectra of the exposed catalyst, where the absorption of gas-phase molecules was subtracted. Vibrational bands were identified in the CH$_3$ stretching region (2940, 2915, 2901, 2880, 2837, 2810 cm^{-1}), the H$-$O$-$C deformation region (1305, 1290 cm^{-1}), and the C$-$O stretching region (1160, 1074, 1035 cm^{-1}). The multiple peaks in the H$-$O$-$C deformation and C$-$O stretching regions indicate that two or more undissociated states of adsorption are involved. The absorbance of those bands at 20 Torr is $^1/_5$ of that of the methoxy groups. Thus, we assume the methanol/methoxy ratio to be 1:5 at 20 Torr of methanol pressure as a first approximation.

The intensities of the methoxy bands at 2925, 2820, and 1120 cm^{-1} were not affected by the presence of the gas phase. The pressure-independent IR absorption indicates that the methoxy groups are saturated on the evacuated surface. We thus propose that the pressure-independent methoxy groups capture the holes:

$$CH_3O^-(a) + h^+ \rightarrow CH_3O^\bullet(a) \quad (2)$$

This reaction was completed within 50 ns, as mentioned in section 3.1. The large oxidative potential of the holes in TiO$_2$, which is represented by an over-potential of 2 eV for the methanol oxidation reaction,[32-34] favors the rapid hole-capture reaction 2.

The hole-capture species is considered to decompose as[21,33]

$$CH_3O^\bullet(a) \rightarrow CH_2O^{\bullet-}(a) + H^+ \rightarrow CH_2O(a) + H^+ + e^- \quad (3)$$
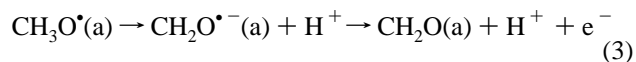
This process, in which the hole-capture species is transformed to a radical anion intermediate and then injects an electron into the conduction band of the catalyst, is known as the "current-doubling effect" in the photocatalytic decomposition of alcohols.[21,22,33] The increase of the absorption due to the injected electron, however, was not observed on our time scale from 50 ns to 9 s. The absence of the expected rise shows that the electron injection was completed within 50 ns or started at 9 s or later. The enhanced IR absorbance at time = 0 shown in Figure 1 suggests the former interpretation. Observation at a better time resolution is required to elucidate reaction 3 further.

The undissociated adsorbates found in Figure 4 are related to the electron-capture reaction in section 3.2 because the amount of the undissociated methanol and the rate of the electron-capture reaction displayed positive order dependence on the methanol gas pressure. It remains to be examined how

the CH$_3$OH(a) species receive the electrons from the catalyst. The hydrogen evolution from the preadsorbed proton produced in reaction 3,

$$H^+ + e^- \rightarrow {}^1/_2 H_2 \qquad (4)$$

is usually assumed. However, the coverage of the preadsorbed proton cannot respond to the methanol pressure. Additionally, a direct attachment

$$CH_3OH(a) + e^- \rightarrow CH_3OH^-(a) \qquad (5)$$

or solvation in condensed methanol molecules may be considered. One more possibility is related to the dissociation of a second methanol molecule:

$$CH_3OH(a) + (*) \rightarrow CH_3O^-(a) + H^+(a) \qquad (6)$$
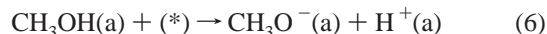
The surface site for the methoxy adsorption (*) is fully occupied by the first CH$_3$O$^-$(a) before the UV irradiation. The band-gap excitation induces a small fraction of the first CH$_3$O$^-$(a) ions to decompose via reactions 2 and 3. A second methanol molecule from the gas phase or physisorbed phase is adsorbed onto the site following the desorption of the CH$_2$O(a). The proton released in reaction 6 can receive the electron, as it does in reaction 4.

4. Conclusions

Reaction kinetics of electrons and holes photogenerated in the Pt/TiO$_2$ catalyst exposed to methanol vapor was analyzed by time-resolved and steady-state IR spectroscopy. The adsorbed methoxy groups quickly capture the holes. The capture reaction is completed within 50 ns following the band-gap excitation. The complementary electrons are slowly decayed in seconds. The molecularly adsorbed methanol equilibrated with the gas phase is related to the electron capture.

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