Effects of Water Addition on the Methanol Oxidation on Pt/TiO₂ Photocatalyst Studied by Time-Resolved Infrared Absorption Spectroscopy

Akira Yamakata, Taka-aki Ishibashi,* and Hiroshi Onishi

Surface Chemistry Laboratory, Kanagawa Academy of Science and Technology (KAST), KSP East 404, 3-2-1 Sakado, Takatsu, Kawasaki 213-0012, Japan

The reaction kinetics of electrons photoexcited in a Pt/TiO₂ catalyst were observed by time-resolved infrared absorption in the presence of methanol−water vapor mixtures. The recombinative decay of the electrons was completed in microseconds on the catalyst exposed to a vacuum. The decay was suspended in the catalyst exposed to pure methanol vapor due to an effective hole-consuming reaction by adsorbed methoxy species. The suspension was released as partial water pressure was increased, indicating that the holes reacted with the methoxy species without the aid of adsorbed water or hydroxyl species. The excess electrons remaining in the catalyst were consumed by adsorbed water in a time domain of 0.1 s. The water-induced promotion of the methanol oxidation reaction described in the literature was interpreted with these results.

1. Introduction

Photocatalytic reactions have been intensively studied in recent years because of their potential use in water splitting and pollutant degradation using solar energy.[1−5] It is of scientific interest and a technological demand to determine reaction kinetics of charge carriers photogenerated in TiO₂ and related materials. Time-resolved IR spectroscopy (TR-IR) provides a powerful means of investigating the mechanism of photocatalytic reactions.[6] It allows us simultaneous observation of charge carrier dynamics and reaction kinetics of adsorbates because photogenerated electrons give structureless broad absorption,[7,8] whereas molecules give inherent vibrational bands[9−11] in the IR region. We have already studied electron decay kinetics in pure water[12,13] and in pure methanol gases,[14] and reaction intermediate and product formation kinetics in 2-propanol oxidation has been observed by TR-IR.[15]

In the present study, we investigated the effects of water addition in methanol oxidation on a Pt/TiO₂ photocatalyst. The addition of water is known to enhance photocatalytic activity.[16,17] For example, the adsorbed methoxy species on Pt/TiO₂ stayed almost constant in a vacuum under UV light irradiation but were rapidly oxidized when the surface was exposed to water vapor.[16] Also, in the case of other organic compounds, water was a prerequisite for maintaining high activity in steady-state conditions.[18,19] Thus, it has been proposed[16,17] that the hole reacts with water first, and hydroxyl radical is produced:
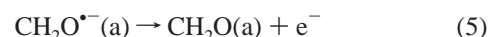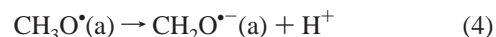
$$H_2O(a) + h^+ \rightarrow OH^\bullet(a) + H^+(a) \text{ or } OH^-(a) + h^+ \rightarrow OH^\bullet(a) \tag{1}$$
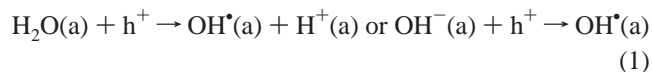
The hydroxyl radical has a high activity in hydrogen abstraction of organic molecules and, thus, may react with methoxy species:

$$CH_3O^-(a) + OH^\bullet(a) \rightarrow CH_2O^{\bullet-}(a) + H_2O(a) \tag{2}$$

Many papers have been written on this hydroxyl radical-mediated mechanism on the oxidation of organics.[1−5] However,

methanol strongly adsorbs on the TiO₂ surface as methoxy species, which can react directly with holes and decomposes as:

$$CH_3O^-(a) + h^+ \rightarrow CH_3O^\bullet(a) \tag{3}$$

$$CH_3O^\bullet(a) \rightarrow CH_2O^{\bullet-}(a) + H^+ \tag{4}$$

$$CH_2O^{\bullet-}(a) \rightarrow CH_2O(a) + e^- \tag{5}$$

This direct hole attachment in the absence of water was deduced from our TR-IR measurements, and the steps following reaction 3 were also discussed.[14] However, in the water-mixed system, a controversial issue has been whether the methanol reacts directly with the hole as reaction 3 or reacts indirectly via hydroxyl radicals as reaction 2.[20−22] Our TR-IR measurements would provide convincing evidence on the matter. To elucidate the role of water, electron- and hole-consuming processes in the water-mixed system were investigated independently.

2. Experimental Section

Transient IR absorption was observed with a home-built spectrometer.[7,23] IR light transmitted through the sample was monochromatized at a 32 cm⁻¹ resolution with a grating monochromator. The output IR intensity was measured with an MCT detector. The signal was amplified by AC-coupled amplifiers and accumulated in a digital sampling oscilloscope as a function of delay time. The time resolution of this spectrometer, which was limited by the response of the detector, was 50 ns. The steady-state IR spectra were recorded by a conventional FT-IR spectrometer (JASCO, FT/IR-610) at a 4 cm⁻¹ resolution. For each spectrum, 300 scans were averaged.

Pt/TiO₂ catalysts were prepared with TIO4 (P-25), a standard TiO₂ catalyst supplied by the Catalysis Society of Japan.[24] 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 and was irradiated by 355-nm third harmonic of a Q-switched Nd:YAG laser. The pulse energy

* To whom correspondence should be addressed. E-mail: ti@net.ksp.or.jp.
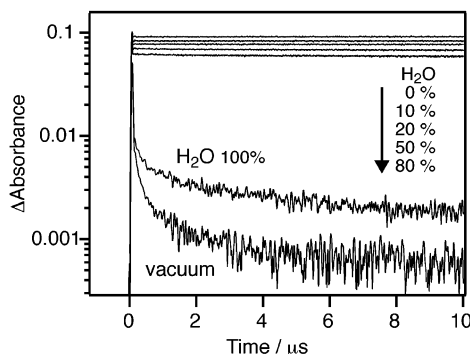
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Figure 1. Temporal profiles in a shorter time frame ($\sim$0$-$10 μs) of transient IR absorption at 2000 cm^{-1} of the Pt/TiO$_2$ catalyst. The catalyst was pumped by a 355-nm laser pulse of 10 ns duration. These curves were obtained in a vacuum and in the presence of 10 torr of methanol vapor and 10 torr of methanol$-$water-mixed gases of 10, 20, 50, 80, and 100% H$_2$O.

Figure 2. Temporal profiles in a longer time frame ($\sim$0$-$0.5 s) of transient IR absorption of the Pt/TiO$_2$ catalyst. The catalyst was pumped by a 355-nm laser pulse of 10 ns duration. These curves were obtained in the presence of 10 torr of methanol vapor and 10 torr of methanol$-$water-mixed gases of 10, 20, 50, and 80% H$_2$O.

was 1 mJ with a 10 ns pulse duration. Transient response in absorbance was obtained by signal averaging of 50 flashes at 0.01 Hz.

3. Results and Discussion

3.1. Decay Kinetics of Photogenerated Electrons in Methanol$-$Water-Mixed Gas. The decay kinetics of photogenerated electrons in methanol$-$water-mixed gas was examined. Figure 1 shows the decay profiles of transient IR absorption observed at 2000 cm^{-1} from 0 to 10 μs. As reported previously,[7,12] this transient IR absorption of the catalyst is assigned to electrons photogenerated by UV pulse irradiation. The decay of electrons in the absence of reactant molecules, in a vacuum, reflects the kinetics of recombination. The change in decay by exposure to reactants is ascribed to carrier-consuming reactions by the reactants. As seen from the figure, most electrons were recombined within 1 μs in a vacuum, whereas the electrons did not decay at all in exposure of 10 torr of pure methanol until 10 μs after irradiation. The absorption intensity immediately after irradiation ($<$50 ns) was greater than that in a vacuum. As reported previously,[14] this result suggests that the holes were exhausted by the reaction with methanol within 50 ns, and thus, recombination was prevented.

Next, the effects of water addition on the hole-consuming reaction were examined. Partial pressure of water was changed, while total pressure of ambient gas was kept at 10 torr. When 1 torr of water was added to 9 torr of methanol, the number of surviving electrons after 50 ns slightly decreased. Increments of partial water pressure further decreased the number of these surviving electrons. This result suggests that the hole-consuming reaction was prevented by the addition of water.

Then, the effects of water mixture on the electron-consuming reaction were examined. The electrons on a catalyst exposed to pure methanol decayed in a second time frame, whereas most of the electrons in vacuum and pure water decayed in microseconds. As shown in Figure 2, the addition of 10% water to the methanol gas enhanced the rate of the electron-consuming reaction. Increments of partial water pressure further enhanced the decay. Since most of the holes were exhausted within 50 ns, the decay of electrons at this later time is assumed to be caused by the electron-consuming reaction. The observed changes by the addition of water in hole- and electron-consuming reactions were probably related to the change of adsorbates.

In the methanol oxidation, regardless of the reaction path via reaction 2 or 3, the number of electrons in the catalyst should
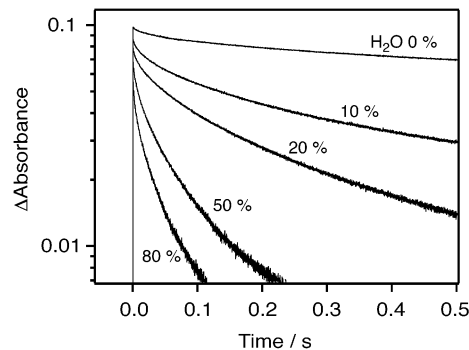
be increased via reaction 5, which is known as the current doubling effect.[21] However, the increment of electrons was not observed at any delay time between 50 ns and 1 s. We had a similar result in our previous study on the photocatalytic oxidation of pure methanol gas.[14] We assume that the increment was unobservable because the number of electrons increased within the time resolution, 50 ns, of our apparatus. To confirm the assumption, observation at a better time resolution is indispensable.

3.2. Surface Species on the Catalyst in the Methanol$-$Water-Mixed Gas. To identify the electron- and hole-consuming adsorbates in the methanol$-$water-mixed system, the adsorbates on Pt/TiO$_2$ were examined. Figure 3a is the steady-state IR spectrum measured in a vacuum after exposure to 10 torr of methanol. As reported previously,[14] the methoxy species (CH$_3$O$^-$(a)) and molecular methanol (CH$_3$OH(a)) were present on the evacuated surface. The peaks at 2925, 2820, 1154, and 1120 cm^{-1} are assigned to the bands of CH$_3$O$^-$(a), and those at 2943, 2844, 1338, 1315, 1290, 1160, 1074, and 1035 cm^{-1} are assigned to the bands of CH$_3$OH(a).[14,25] By adding 10 torr of methanol gas again, the bands of CH$_3$OH(a) increased, while those of CH$_3$O$^-$(a) did not (Figure 3b). Methoxy species strongly adsorbed on the catalyst and did not desorb by evacuation.

Next, the adsorbates under the methanol$-$water-mixed gas were examined. Figure 3c shows the spectra measured in the mixed gas. The spectrum of the evacuated surface (Figure 3a) was subtracted from each spectrum of Figure 3c. The total pressure was kept at 10 torr, and the partial water pressure was changed. When water was added to the methanol vapor, the number of adsorbed water increased; the bands of H$-$O$-$H bending at 1630 cm^{-1} and O$-$H stretchings at 3700$-$3000 cm^{-1} monotonically increased with the partial water pressure. The exposure of water-mixed methanol gas also induced a decrement of the adsorbed methanol and methoxy species. When pure water was exposed, all the methoxy species and the methanol disappeared. This is ascribed to the exchange reaction of the methoxy species with the surface OH species, namely:

$$CH_3O^-(a) + H_2O(g) \leftrightarrow OH^-(a) + CH_3OH(g) \qquad (6)$$

These results suggest that the adsorption sites for OH$^-$(a) and CH$_3$O$^-$(a) are limited in number and the adsorption ratio of these two species is dependent on their partial pressure.

3.3. Effects of Water Addition on the Reaction. In the present study of methanol$-$water-mixed system, we identified
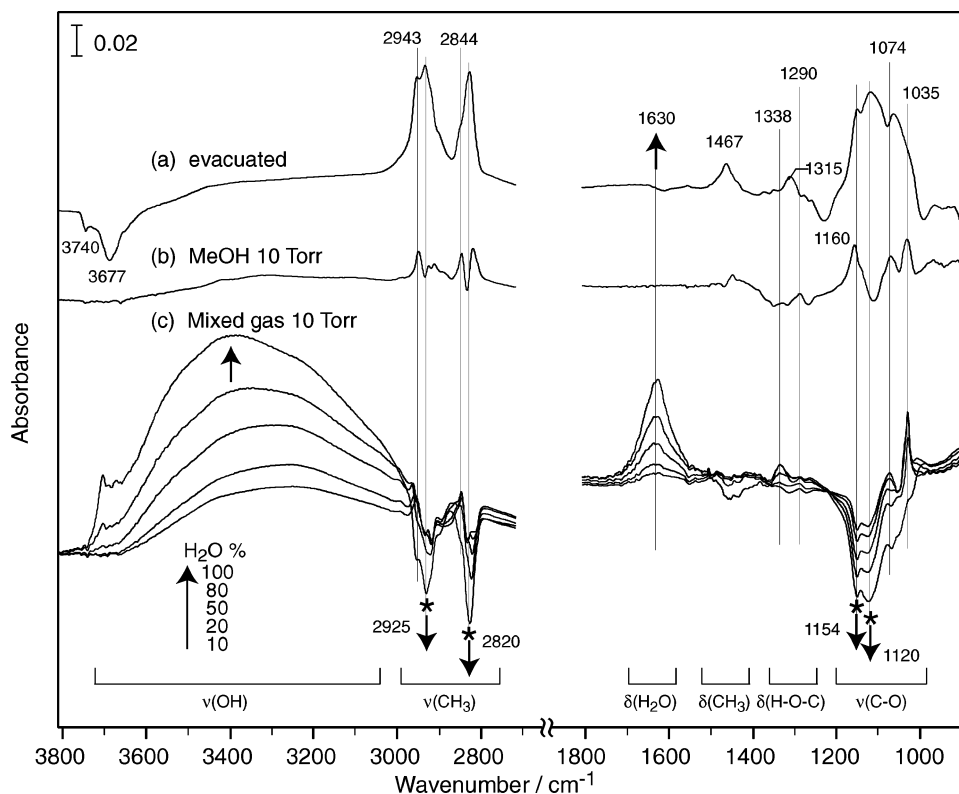
Figure 3. Steady-state IR spectra of adsorbed species on Pt/TiO$_2$ at 323 K. (a) A spectrum of the catalyst exposed to 20 torr of methanol vapor followed by the evacuation. (b) A spectrum of the adsorbates on Pt/TiO$_2$ catalyst equilibrated with 10 torr of methanol vapor. The spectrum of the evacuated surface (a) was subtracted. (c) Spectra of adsorbates on Pt/TiO$_2$ catalyst equilibrated with 10 torr of methanol−water-mixed gases of 10, 20, 50, and 80% H$_2$O. The spectrum of the evacuated surface (a) was subtracted from each spectrum. The bands of methoxy species are marked by an asterisk in the figure.

four kinds of surface species in the steady-state IR spectra: surface OH species, adsorbed water, methoxy species, and molecular methanol. These species are considered to be responsible for the electron- and hole-consuming reactions. In pure water[13] and pure methanol[14] ambient gases, dissociatively adsorbed species (OH$^-$(a) and CH$_3$O$^-$(a)) were responsible for the hole-consuming reaction, and undissociated and equilibrated adsorbates (H$_2$O(a) and CH$_3$OH(a)) were responsible for the electron-consuming reaction. In the mixed system, increments of partial water pressure deactivated the effective hole-consuming reaction. The number of methoxy species was monotonically decreased with the increment of the partial water pressure. Therefore, the methoxy species are responsible for the hole-consuming reaction. This result suggests that the hole directly reacted with the methoxy species and the hydroxyl radicals were not concerned in the photooxidation because the highest activity of the hole-consuming reaction was achieved in the absence of water and the surface hydroxyl species. On the other hand, the electron-consuming reaction was accelerated by the increment of the partial water pressure. The increments of the partial water pressure enhanced the adsorption of water. Thus, the adsorbed water would be responsible for the electron-consuming reaction.

It is reported[16,17] that water enhances the catalytic activity of photooxidation of organic molecules, and therefore it is proposed that water-derived species capture the hole (reaction 1), and then the produced hydroxyl radicals attack the methanol as reaction 2. However, our observation contradicts this mechanism. In the following, we propose an alternative mechanism that is compatible with our observations. As mentioned above, electrons have an extremely long lifetime in methanol exposure. The long-life electrons should be accumulated and increase electron density

in the catalyst when the UV light is irradiated continuously. Water consumes these accumulated electrons as

$$H^+(a) + e^- \rightarrow \frac{1}{2}H_2(g) \tag{7}$$
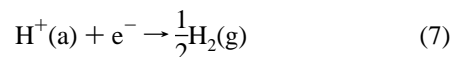
and decreases the electron density. We studied the effects of accumulated electrons on recombination kinetics and reported that undesirable recombination was accelerated when the electron density increased.[26] Thus, the water prevents electron accumulation and recombination, resulting in increments of the quantum yield of the reaction. It is also reported that Pt loading enhances oxidation.[27] Our proposed mechanism also explains this enhancement because the electron-consuming reaction by water as reaction 7 is accelerated by Pt loading.[14] Another role of water is to reoxidize the reduced TiO$_2$ (such as Ti$_2$O$_3$) as[28]

$$Ti_2O_3 + H_2O(a) \rightarrow 2TiO_2 + H_2(g) \tag{8}$$

Prolonged UV irradiation on the electron-accumulated catalyst reduces TiO$_2$ to Ti$_2$O$_3$ and makes defective sites. The added water repairs the defect as reaction 8. These functions of water would maintain the catalytic activity in steady-state conditions.

We have studied the effects of water addition on methanol oxidation on Pt/TiO$_2$ photocatalyst. By changing the mixing ratio of methanol and water gases, the amounts of surface hydroxyl species and methoxy species were monotonically changed with those partial pressures. The highest activity of the hole-consuming reaction that triggers the oxidation was performed in the absence of surface OH species; thus, it was proposed that methoxy species react directly with the hole. On the other hand, the electron-consuming reaction was accelerated by the

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increment of the water partial pressure. Water acted as an electron remover from the catalysts and prevented electron accumulation in the catalyst. It is proposed that removing electrons by water decelerates recombinative decay of holes and enhances the activity of photocatalytic methanol oxidation.

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