Oxygen Species Active for Photooxidation of *n*-Decane over TiO₂ Surfaces

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Surface-enhanced IR absorption spectroscopy (SEIRAS) was applied to in-situ observation of surface products during the photooxidation of gas-phase *n*-decane on TiO₂ films coated with an island Au film The bands assignable to C=O stretching, O−H stretching, and H−O−H bending were observed with good intensity, indicating the formation of ketone(s) and water on the surface. Ketone as well as water was produced in the dark when a Au/TiO₂ sample was illuminated in advance in O₂ and then exposed to *n*-decane. This result clearly indicates that oxygen species active for *n*-decane oxidation remain in the dark after stopping UV irradiation. The formation of ketone and water declined with increasing time lapse of *n*-decane introduction after illumination, from which the lifetime of the active oxygen species was estimated to be at least 1 min. The active oxygen species formed from O₂ on illuminated Au/TiO₂ were concluded to be O^- and O_3^-, judging from the results of ESR and oxygen-isotope tracing measurements so far reported.

1. Introduction

The photooxidation power of TiO₂ photocatalysts is so strong as to mineralize completely organic pollutants in air as well as in water.[1] Upon band-gap irradiation, active intermediate species are believed to be formed on TiO₂ surfaces,[1] and many efforts have been made to detect such species. ESR has been often used to investigate radical species formed on solid catalysts, and O_2^-, O^-, and O_3^- were found on illuminated TiO₂ powders at low temperatures as active species for photooxidation reactions.[2−6] As for a room-temperature ESR measurement, Jaeger and Bard[7] reported that a hydroxyl radical (·OH) and a perhydroxyl radical (·O₂H) produced on illuminated TiO₂ powders in an aqueous solution were detected using a spin-trapping reagent. This result, however, remained as an uncertainty because of its indirect method. Kaise et al.[8] observed directly a methyl radical (·CH₃) and a carboxymethyl radical (·CH₂COOH) formed during the photodecomposition of acetic acid in an aqueous solution at room temperature using flow-type ESR. Hirakawa et al.[9] employed, on the other hand, chemiluminescence techniques, in which luminol is used as a probe, and found two types of active species produced on illuminated TiO₂ powders in an aqueous solution with different lifetimes. They assigned the short-lived species to superoxide ion (O_2^-) and the long-lived one to hydrogen peroxide (H_2O_2). Ishibashi et al.[10] also applied chemiluminescence techniques to TiO₂ film photocatalysts in air and in water. They found that the quantum yield of superoxide ion (O_2^-) formation in water is twice as large as that in air and that the steady-state concentration of superoxide ion (O_2^-) is almost constant irrespective of light intensity. Recently, Einaga et al.[6] reported that CO oxidation occurs on Pt/TiO₂ at room temperature in the dark when Pt/TiO₂ is irradiated in advance under an atmosphere of humidified air, while bare TiO₂ is inactive. They also made ESR measurements for active oxygen species.

We have shown in previous papers[11−14] that surface-enhanced IR spectroscopy (SEIRAS) is so sensitive as to detect surface species at submonolayer quantities and capable of in-situ surface analysis during photocatalytic reactions over TiO₂ film surfaces. We found that UV irradiation of TiO₂ films in gas-phase H_2O leads to the formation of chemisorbed water, which explains well the photoinduced hydrophilicity of TiO₂ film surfaces.[13] In the present paper, we report in-situ observation of surface species during the photocatalytic oxidation of gas-phase *n*-decane over TiO₂ films using SEIRAS. The formation of intermediate ketone as well as adsorbed water was successfully detected with good sensitivity during the reaction. These intermediates were produced in the dark, when the TiO₂ film was irradiated in advance in the presence of O₂, indicative of the formation of a long-lived active oxygen species. The lifetime of active oxygen species was estimated by changing time lapse of *n*-decane introduction after irradiation.

2. Experimental Section

The details of sample preparation and experimental setup have been described in previous papers.[12−14] Briefly, a transparent TiO₂ film coated on a CaF₂ disk (30 mm in diameter) was prepared by a sol−gel method, followed by calcination at 500 °C in air. Au deposition on the TiO₂ film was made by a vacuum evaporation method. The average thickness of the Au film was ca. 6 nm. Reaction gas was introduced into an evacuable IR cell from a gas handling system equipped with a Baratron pressure gauge. SEIRAS measurements were carried out in a backside reflection mode,[12−14] in which an IR beam was reflected at the interface between the TiO₂ and Au films, and the reflected beam was collimated to an external MCT detector. This method enables us to observe surface species without the disturbance of IR absorption by gas- or liquid-phase reactants and products such as an ATR method. SEIRA spectra were recorded with the resolution of 4 cm⁻¹ and with 200 scan unless otherwise stated. *n*-Decane (99.5%) and Millipore water (H_2O) were deaerated by repeating a freeze-and-thaw cycle three times. The light source was a high-pressure Hg lamp (Ushio UIV-570) that was filtered through a band-pass filter (Toshiba

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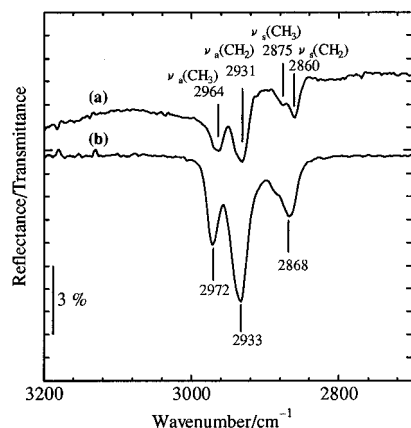
Figure 1. (a) SEIRA spectrum of *n*-decane adsorbed on Au/TiO$_2$. (b) Transmission spectrum of gas-phase *n*-decane. ν_s and ν_a denote symmetric and asymmetric stretching, respectively.

Figure 2. SEIRA spectra during the photooxidation of *n*-decane on Au/TiO$_2$. *n*-Decane pressure, 0.15 Torr; O$_2$ pressure, 3 Torr.
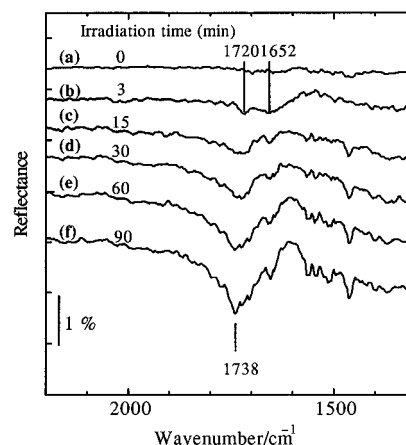
UV-D33S, 240−400 nm) and a water filter (10 cm long) to remove heat.

Photooxidation of *n*-decane was carried out by introducing a mixture of *n*-decane and O$_2$ into the SEIRAS cell, followed by illuminating Au/TiO$_2$/CaF$_2$ sample from the CaF$_2$ side. For measurements of the lifetime of active oxygen species, the sample was first irradiated in O$_2$ and, after stopping irradiation, a mixture of *n*-decane and Ar was supplemented to the cell. The use of Ar is for pressure increase of the supplement gas to overcome O$_2$ pressure, since the vapor pressure of *n*-decane is low (∼2 Torr) at room temperature.

3. Results and Discussion

Spectrum (a) in Figure 1 shows SEIRA spectra of *n*-decane adsorbed on Au/TiO$_2$. In the C−H bending region no bands due to adsorbed *n*-decane were observed, while sharp bands due to C−H stretching were observed at 2964, 2931, 2875, and 2860 cm^{-1}. The assignments of these bands are shown in the figure. This SEIRA spectrum is different from the IR transmission spectrum of gas-phase *n*-decane; the intensity of ν_a(CH$_2$) is weaker than that for gas-phase *n*-decane. This is because SEIRAS is sensitive only to vibrations in the close vicinity of Au particles and has a surface selection rule.[11,15] The spectrum disappeared promptly after evacuating the cell, indicating that *n*-decane is weakly adsorbed (physisorbed) on the surface. No spectral changes occurred when the sample was left in *n*-decane in the dark.

UV irradiation gave no changes in SEIRA spectrum when *n*-decane alone was present in the cell, but led to a significant change in the coexistence of O$_2$ as shown in Figure 2. During UV irradiation, the band centered at 1652 cm^{-1}, which is assigned to H−O−H bending of adsorbed H$_2$O, first developed, and the broad O−H stretching band was also observed at around 3385 cm^{-1} (not shown here). The band at 1720 cm^{-1}, which is assigned to the C=O stretching of carbonyl, then grew up with a band shift to 1738 cm^{-1}. The preference formation of adsorbed H$_2$O at the initial stage of reaction indicates that the photooxidation of *n*-decane is initiated by the abstraction of hydrogen from *n*-decane. The 1720 cm^{-1} band could be assigned to adsorbed ketone(s), since the ketones of linear-chain hydrocarbons exhibit the C=O stretching band at 1717−1719 cm^{-1} irrespective of their carbon numbers and the position of C=O. The formation of aldehyde would be ruled out, since aldehydes are much more easily photooxidized than ketones on illuminated TiO$_2$, and the band broadening of C=O stretching did not occur. The band shift of C=O stretching to higher frequencies after

prolonged UV irradiation would be due to the dipole−dipole coupling of C=O stretching, which increases with increasing coverage of adsorbed ketone. The blue shift of IR bands with increasing coverage of adsorbed species has often been observed for strong stretching vibrations such as C−O stretching of adsorbed CO. When ^{18}O$_2$ was used instead of ^{16}O$_2$ for photooxidation, the C=O stretching band shifted 19 cm^{-1} to lower frequencies, indicating that *n*-decane was oxidized by active oxygen species derived from gas-phase O$_2$. The C−H stretching bands of adsorbed *n*-decane decreased slightly during the reaction, indicating that adsorbed *n*-decane desorbed from the surface. Since the pressure of gas-phase *n*-decane was virtually unchanged during the reaction, the desorption of *n*-decane is ascribed to increasing coverage of intermediate species.

The photocatalytic oxidation of hydrocarbons over illuminated TiO$_2$ photocatalysts have been studied intensively. Teichner and co-workers[16,17] investigated the photooxidation of various alkanes with O$_2$ over TiO$_2$ powders. They found that main reaction products are ketones and aldehydes, which are formed by the partial oxidation of intermediates such as alcohols or olefins.[16,17] The formation of aldehydes was smaller in amount than that of ketones. Therefore, it is reasonable that the carboxyl compounds formed over illuminated Au/TiO$_2$ film is assigned to adsorbed ketone(s).

There is an issue as to whether gas-phase H$_2$O enhances photooxidation reactions over semiconductor photocatalysts. The effects of H$_2$O(g) on the adsorption of *n*-decane was first examined, and the result shows that adsorbed *n*-decane was removed to some extent by the addition of H$_2$O(g). This may arise from that H$_2$O is more strongly adsorbed on the surface than *n*-decane. For the *n*-decane photooxidation with a mixture of H$_2$O(g) and O$_2$, the increasing rate of C=O stretching band was significantly suppressed as shown in Figure 3 when compared with the reactions in the absence of H$_2$O(g). We have found that the oxygen isotopic exchange reaction between ^{18}O$_2$ and surface hydroxyl groups (Ti−^{16}OH) over illuminated TiO$_2$ powders is completely inhibited by the addition of H$_2$O(g) to the system.[18] This result indicates the inhibition effects of H$_2$O-(g) on the adsorption of O$_2$. Therefore, a decrease in the photooxidation rate in the presence of H$_2$O(g) would be due to the decrease in the amounts of adsorbed *n*-decane and O$_2$. Irradiation of *n*-decane in the presence of H$_2$O(g) alone led to no changes in the SEIRA spectrum. This result indicates that Au/TiO$_2$ has no ability to promote a photoelectrochemical reaction unlike Pt/TiO$_2$, on which a photoelectrochemical

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J. Phys. Chem. B, Vol. 106, No. 23, 2002 **5895**
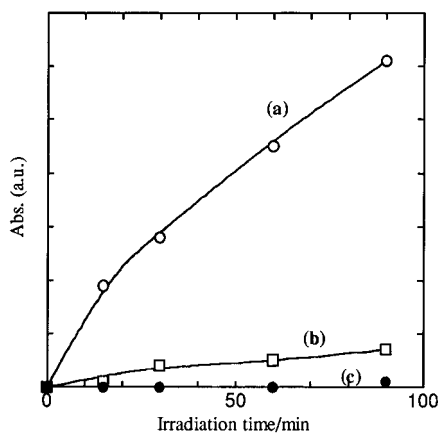
Figure 3. Time dependence of the intensity of the C=O stretching band during the reactions of *n*-decane with (a) O_2, (b) a mixture of O_2 and $H_2O(g)$, and (c) $H_2O(g)$. *n*-Decane pressure, 0.15 Torr; O_2 pressure, 3 Torr; H_2O pressure, 5 Torr.
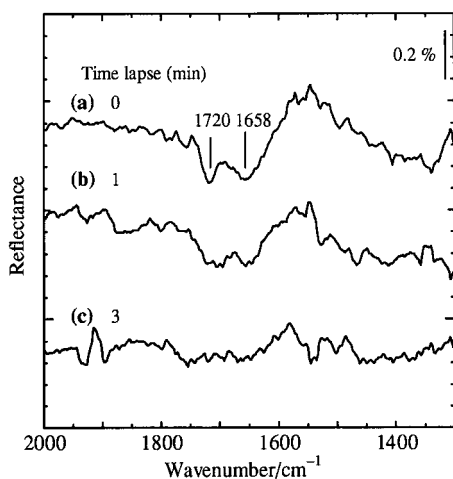
Figure 4. SEIRA spectra when Au/TiO$_2$ was irradiated for 3 h in O_2 (3 Torr) in advance and then a mixture of *n*-decane and Ar was introduced into the cell. Time lapse indicates the time of *n*-decane introduction after stopping irradiation. The number of scans was 100 times in this experiment to shorten measurement.

reaction of *n*-decane with $H_2O(g)$ takes place to produce the C=O stretching band in SEIRAS.[19]

As described earlier, using chemiluminescence techniques Ishibashi et al.[10] detected active oxygen species formed on TiO$_2$ film which was irradiated in air in advance. They concluded that superoxide ion (O_2^-) species remains on TiO$_2$ film surfaces in the dark for 50 s after stopping UV irradiation. To examine as to whether active oxygen species formed on illuminated Au/TiO$_2$ films remain in the dark, Au/TiO$_2$ sample was irradiated for 3 h in O_2, and then exposed to a mixture of *n*-decane and Ar in the dark. As shown in Figure 4, two bands assignable to adsorbed ketone and adsorbed H_2O appeared at 1720 and 1658 cm^{-1}, respectively. These two bands decreased in intensity with increasing time lapse of *n*-decane introduction after irradiation and were no longer observed after 3 min of stopping irradiation. This result demonstrates clearly that active oxygen species remain on the surface in the dark. The lifetime of active oxygen species estimated from decline of the SEIRAS bands is at least 1 min. When O_2 was pumped out from the cell after irradiation, the introduction of *n*-decane or *n*-decane/O_2 mixture immediately after pumping gave rise to no changes in the SEIRA spectrum, indicating that *n*-decane was not oxidized to ketone. The reason for this will be discussed later.

Although the present results give no tangible information about oxygen species responsible for the photooxidation of *n*-decane, it is most likely atomic oxygen, judging from the fact that a photocatalytic isotopic exchange reaction of O_2 with surface OH, $^{18}O_2 + Ti-^{16}OH = ^{16}O^{18}O + Ti-^{18}OH$, over TiO$_2$ surfaces is completely inhibited by the addition of hydrocarbon or CO,[17,20,21] because this isotopic exchange reaction requires the atomization of O_2. The formation of atomic oxygen over illuminated TiO$_2$ surfaces is also deduced from oxygen isotopic exchange, $^{16}O_2 + {}^{18}O_2 = 2^{16}O^{18}O$. The photocatalytic activities of metal oxide semiconductors for the photoinduced isotopic exchange of O_2 exhibit a good correlation with those for the photooxidation of CO,[22] suggesting that a common rate-determining step for these reactions is the photodissociation of O_2 to atomic oxygen. Superoxide ion (O_2^-) has often been assumed to be the active oxygen species for photooxidation on TiO$_2$ surfaces.[9,10] This species is often observed by ESR on metal oxide catalysts in the dark, but not necessarily active for catalytic oxidation reactions at room temperature.[2,23] In addition, O_2^- cannot be an intermediate for the oxygen isotopic exchange reactions. Atomic oxygen is, on the other hand, a very active species for any kinds of oxidation reactions on metal and metal oxide catalysts even at temperatures lower than room temperature. Therefore, atomic oxygen formed on TiO$_2$ surfaces can be much more active for oxidation reactions than O_2^-. Lattice oxygen of TiO$_2$ is sometimes suspected to play a part of photooxidation.[16,17] When a pressed pellet of TiO$_2$ powders with a large surface area is illuminated in the presence of an easily oxidizable organic compound such as alcohol, its IR transmission is markedly reduced and its color turns to blue.[18] This change in IR transmission as well as in color is almost restored upon the admission of O_2.[18] Photocolorization of powdered TiO$_2$ hardly occurs in the presence of CO.[18] Since this color change of TiO$_2$ is thought to arise from the reduction of TiO$_2$ and the formation of Ti^{3+}, lattice oxygen may be involved in the photooxidation of some organic compounds but not in CO photooxidation. The Au/TiO$_2$ sample underwent little photo-induced IR-transmission change in the presence of *n*-decane, indicating that lattice oxygen is not used for *n*-decane photo-oxidation.

Recently, Einaga et al.[6] reported interesting features of Pt/TiO$_2$ for photoinduced active oxygen species. They found that Pt/TiO$_2$ is active for CO oxidation in the dark at room temperature after UV irradiation, while bare TiO$_2$ inactive. In their experiments, Pt/TiO$_2$ was first illuminated in flowing humidified air and then exposed to flow of a mixture of CO and dry air in the dark. The consumption of CO lasted for more than 40 min, and they ascribed this result to the remaining of active oxygen species in the dark after illumination. However, the duration of CO oxidation in the dark seems extremely long even though CO was continuously supplied. The fact that Pt and $H_2O(g)$ were indispensable to their results may give an important clue to better understanding of their results. As we reported 20 years ago, the photodecomposition of $H_2O(g)$ takes place on Pt/TiO$_2$, but H_2 as well as O_2 is not detected in the gas phase because of their rapid recombination reaction on Pt sites.[24] Although no products are detected during the irradiation of Pt/TiO$_2$ in $H_2O(g)$, Pt surfaces are covered with adsorbed hydrogen, while TiO$_2$ surfaces are covered with oxygen species. When a mixture of $H_2O(g)$ and CO is exposed to illuminated Pt/TiO$_2$, O_2 (or its precursor) formed by $H_2O(g)$ photosplitting is scavenged by CO so that CO_2 and H_2 are produced.[25] If Pt/TiO$_2$ is illuminated in a mixture of O_2 and $H_2O(g)$ as done by Einaga et al.,[6] then adsorbed H formed on Pt by $H_2O(g)$

photolysis would react with O_2, and Pt would be catalytically activated by this redox reaction, a conventional method for the activation of metal catalysts. Pt is usually inactive for CO oxidation at room temperature, because CO adsorbed strongly on Pt inhibits the adsorption of O_2. Pt becomes active for CO oxidation if its surface is vacant or covered with adsorbed oxygen, but its activity declines as observed by Einaga et al.,[6] since the surface is rapidly covered with strongly adsorbed CO. Therefore, the consumption of CO after illuminating Pt/TiO$_2$ in humidified air is not due to the remaining of photoinduced active oxygen species, but arises from the catalytic activation of Pt.

For active oxygen species on metal oxide surfaces, ESR measurements have revealed that atomic oxygen presents as O^- in the absence of O_2 and as O_3^- in the presence of O_2 at low temperatures.[2–6] It should be noted here that O^- can be produced on TiO$_2$ surface not only under illumination but also in the dark.[2,23] This implies that negative charge of adsorbed oxygen species is not necessarily supplied from photoinduced electrons but from TiO$_2$ bulk. Since O^- reacts with O_2 to form O_3^- in the dark, there should be a reversible reaction,

$$O^-(a) + O_2 \rightleftarrows O_3^-(a) \qquad (1)$$
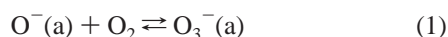
on the surfaces. Einaga et al.[6] found that the ESR signal of O_3^- produced on Pt/TiO$_2$ disappears after room-temperature evacuation of O_2 without the appearance of an O^- signal. The introduction of CO after O_2 removal, however, led to the appearance of a CO_2^- signal. They ascribed the formation of CO_2^- to the reaction,

$$O^-(a) + CO \rightarrow CO_2^-(a) \qquad (2)$$
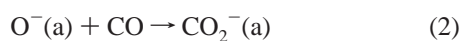
under the assumption that $O^-(a)$ remains after O_2 removal although its ESR signal cannot be detected. It should be noted here that atomic oxygen must be formed on Pt sites during their pretreatment of Pt/TiO$_2$ and can remain after O_2 removal. Upon CO introduction, atomic oxygen adsorbed on Pt would react with CO to form CO_2, which then migrates to TiO$_2$ surface to produce CO_2^-, viz.,

$$O(a)/Pt + CO \rightarrow CO_2(a)/Pt \qquad (3)$$

$$CO_2(a)/Pt \rightarrow CO_2^-(a)/TiO_2 \qquad (4)$$
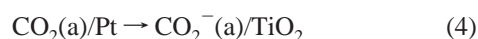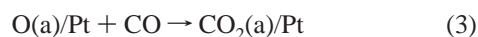
Negative charge of $CO_2^-(a)/TiO_2$ has no significant meaning in this case since CO_2 as well as oxygen species are usually negatively charged when adsorbed on metal oxides as described above.[2,23] We assume that $O^-(a)$ disappeared by the removal of O_2 in their experiment, since $O^-(a)$ would migrate on TiO$_2$ surface at room temperature and undergo recombination as

$$2O^-(a) \rightarrow O_2 \qquad (5)$$

On the other hand, O_3^- would be relatively stable in the presence of O_2 since O_3^- needs to pass through reactions 1 and 5 to desorb from the surface. In the present experiments, active oxygen species formed on illuminated Au/TiO$_2$ from O_2 remains in the dark when O_2 was present, but not when O_2 was removed. Therefore, in the presence of O_2, active oxygen species may exist as $O_3^-(a)$, which would be relatively stable at room temperature as evidenced by Einaga et al.[6] and desorb from the surface upon evacuating O_2.

In summary, O_2 would be photodissociated on TiO$_2$ surfaces to $O^-(a)$, which reacts spontaneously with O_2 to form $O_3^-(a)$. In the presence of O_2, $O_3^-(a)$ remains in the dark with a lifetime of more than 1 min and can oxidize n-decane, at least, to ketone. In the absence of O_2, active oxygen species disappears from TiO$_2$ surfaces probably due to its desorption. Superoxide ion (O_2^-), if present, would be much less active for oxidation reactions than O_3^-. Lattice oxygen of TiO$_2$ is not involved in n-decane photooxidation on TiO$_2$ films.

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