

Photocatalytic Oxidation of Ethylene to CO₂ and H₂O on Ultrafine Powdered TiO₂ Photocatalysts: Effect of the Presence of O₂ and H₂O and the Addition of Pt

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Abstract—The complete photocatalytic oxidation of C₂H₄ with O₂ into CO₂ and H₂O has been achieved on ultrafine powdered TiO₂ photocatalysts and the addition of H₂O was found to enhance the reaction. The photocatalytic reaction has been studied by IR, ESR, and analysis of the reaction products. UV irradiation of the photocatalysts at 275 K led to the photocatalytic oxidation of C₂H₄ with O₂ into CO₂, CO, and H₂O. The large surface area of the photocatalyst is one of the most important factors in achieving a high efficiency in the photocatalytic oxidation of C₂H₄. The photo-formed OH species as well as O₂⁻ and O₂^{•-} anion radicals play a significant role as a key active species in the complete photocatalytic oxidation of C₂H₄ with O₂ into CO₂ and H₂O. Interestingly, small amount of Pt addition to the TiO₂ photocatalyst increased the amount of selective formation of CO₂ which was the oxidation product of C₂H₄ and O₂.

Key words: Photocatalyst, Oxidation, Ethylene, TiO₂

INTRODUCTION

Photocatalysis of titanium oxide semiconductors has recently received considerable attention in relation to a variety of applications for environmental issues such as the purification of polluted air and water [Anpo, 1997; Kamat, 1993; Ollis and Al-Ekabi, 1993; Lee and Lee, 1998; Chai, 2000]. Especially, the efficient photocatalytic degradation of hazardous wastes is one of the most desirable and challenging goals in the research of the development of environmentally friendly catalysts. As one of the most popular photoactive catalysts, TiO₂ photocatalysts have long been investigated in their different forms as bulk materials, colloidal suspension, and dispersed into SiO₂ matrices and on porous supports such as zeolites and porous vycor glass [Fox and Dulay, 1993; Yamashita, 1998; Anpo and Yamashita, 1997]. Although the utilization of extremely small powdered TiO₂ particles has attracted a great deal of attention as photocatalysts due to their high photocatalytic reactivities, the actual factors controlling the photocatalytic activity of TiO₂ particles are still unknown, except for a few important factors such as the magnitude of the band gap, surface area, and crystallinity [Anpo, 1989; Kubokawa et al., 1981; Yamashita et al., 1996]. Such difficulties mainly arise because the photocatalytic effectiveness of the fine particles varies greatly with their chemical and physical properties as well as their chemical and physical molecular environments.

On the other hand, because C₂H₄ is harmful to plants, in order to keep enough food fresh in the CELSS (Controlled Ecological Life Support Systems), it is necessary to remove ethylene, which is re-

leased from plants. In this regard, photocatalysts can be considered as they are generally referred to as an advanced oxidation process.

We investigated the photocatalytic oxidation of C₂H₄ with O₂ into CO₂ and H₂O on ultrafine powdered TiO₂ photocatalysts. Special attention was focused on the effects of the particle size on the reaction and the effects of the addition of H₂O on the reaction rates by means of *in situ* ESR and FT-IR measurements. Analyses of the reaction products as functions of the UV irradiation time were also carried out. Although the detailed mechanisms of the photocatalytic oxidation of the olefins with O₂ on the well-evacuated dried TiO₂ photocatalysts were investigated in the past [Kubokawa et al., 1981], the effect of H₂O vapor on the photocatalytic oxidation has not been explored yet.

In the present paper, we report that ethylene can be completely oxidized into CO₂ on the powdered titanium oxide photocatalysts, the rate depending on the nature of the catalysts, and that the photocatalytic oxidation of C₂H₄ can be enhanced by adding H₂O vapor in the reaction system.

EXPERIMENTAL

Five different types of ultrafine powdered TiO₂ catalysts, which were supplied by the Catalysis Society of Japan as reference TiO₂ catalysts (JRC-TIO-1,2,3,4,5), were used as photocatalysts (grain size, 0.02-1 mm). Pt-loaded TiO₂ catalysts were prepared by impregnation with an aqueous solution of H₂PtCl₆. Three type of photocatalysts referred to as F-2, F-4, and F-6 were supplied by Shyowa Denko Company. Photocatalytic reactions were carried out in a quartz cell (volume: 100 cm³) with a flat bottom connected to a conventional vacuum system (10⁻⁶ Torr range). The catalysts were degassed

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at 723 K for 2 h and calcined in O₂ at 723 K for 3 h. Prior to the photoreaction, the catalysts were degassed at 473 K for 2 h until 10⁻⁶ Torr. The pretreated catalysts were spread out on the flat bottom of the quartz cell, and then ethylene and oxygen were introduced onto the catalyst at 275 K. The catalyst was irradiated from the flat bottom side. UV irradiation of the catalysts in the presence of ethylene and oxygen was carried out by using a Toshiba SHL 100 W high-pressure lamp ($\lambda > 280$ nm) at 275 K. The reaction time is 2 h. The reaction products were analyzed by gas chromatography. The ESR spectra were recorded with a JES-RE-2X (X-band) spectrometer at 77 K and the IR spectra were recorded on a Shimadzu IR-460 spectrometer at 295 K. Experimental details can be found in previous literature [Anpo, 1989; Kubokawa et al., 1981].

RESULTS AND DISCUSSION

The typical physical properties of these TIO-1~5 catalysts are shown in Table 1. The relative OH concentration was calculated from the intensities of the IR peak of the samples assigned to the surface OH group on TiO₂. The acid concentration was calculated from the peak intensities observed in the temperature-programmed desorption (TPD) patterns of preadsorbed NH₃. The surface area of the titanium oxide powders, F-2, F-4, F-6, are 27, 54, and 102 m²/g, respectively. It was observed that the surface area of F-6 is the largest in all of the catalysts.

UV irradiation of several standard TiO₂ catalysts in the presence

Table 1. Physical properties of TiO₂ powdered photocatalysts

Catalysts (JRC-TIO-)	Surface area (m ² /g)	Relative OH conc.	Band gap (eV)
1. Anatase	73	1.3	3.54
2. Anatase	16	1.0	3.47
3. Rutile	51	1.6	3.32
4. Anatase	49	3.0	3.50
5. Rutile	3	3.1	3.09

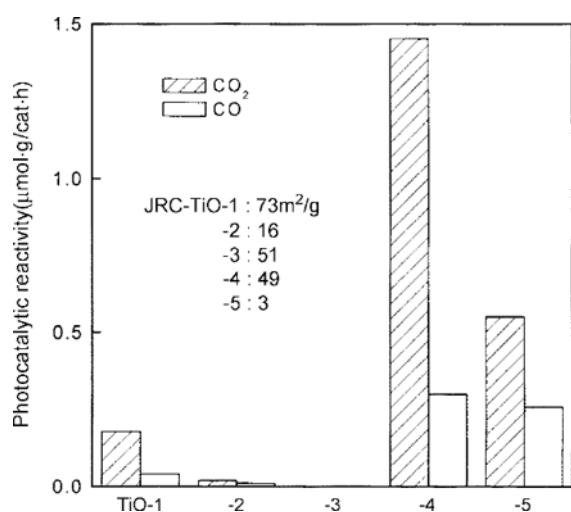


Fig. 1. Product distribution of the photocatalytic oxidation of ethylene on TiO₂ photocatalysts: JRC-TIO-1, TIO-2, TIO-3, TIO-4, TIO-5.

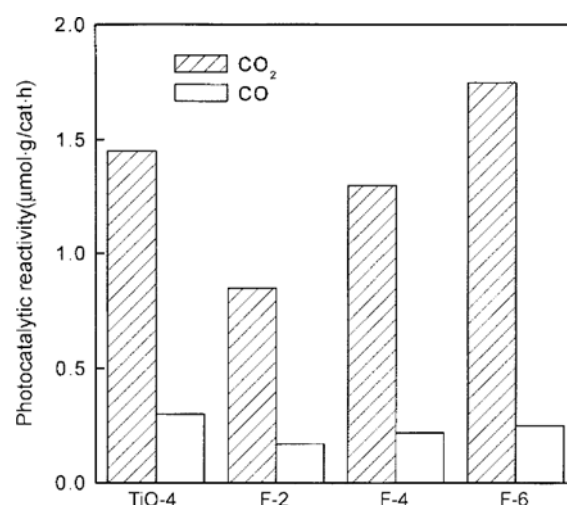


Fig. 2. Product distribution of the photocatalytic oxidation of ethylene on TiO₂ photocatalysts: JRC-TIO-4, F-2, F-4, F-6.

of C₂H₄ and O₂ led to the oxidation of C₂H₄ to produce CO₂, CO, and H₂O as the main products, but with relative reactivity and selectivity, depending on the specific properties of the catalysts. Figs. 1, 2 show the products distribution in the photocatalytic oxidation of ethylene on various TiO₂ catalysts.

The observed photocatalytic reactivities were in the order of JRC-TIO-4 > -5 > -1 > -2 > -3. So, these results are in good agreement with those of the reactions investigated, i.e., the hydrogenolysis of methyl acetylene with H₂O, the isomerization of 2-butene, and the reduction of CO₂ with H₂O [Yamashita et al., 1996]. From Table 1 and Fig. 1, it can be seen that anatase TiO₂ with a large surface area, large band gap, and numerous OH group is more efficient for the oxidation of ethylene. Especially, for the TiO₂ photocatalyst, F-6, having a large surface area, shows the highest photocatalytic reac-

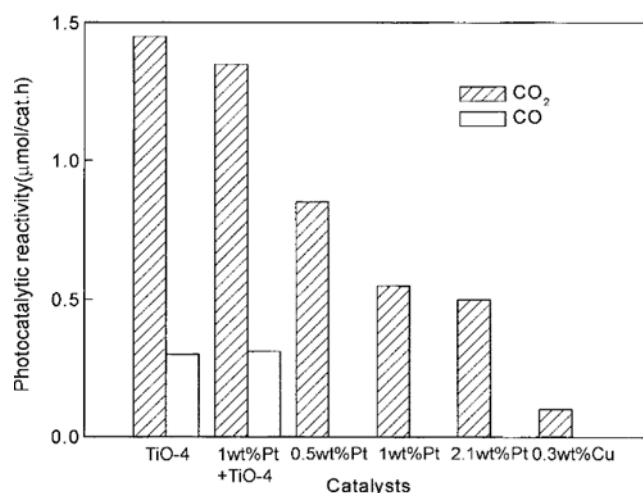


Fig. 3. Product distribution of the photocatalytic oxidation of ethylene on TiO₂ photocatalysts and metal loaded TiO₂ catalysts: JRC-TIO-4 (a), TIO-4 (1 wt% of Pt, mixing) (b), Pt-loaded (0.5 wt%) TiO-4 (c), Pt-loaded (1.0 wt%) TiO-4 (d), Pt-loaded (2.0 wt%) TiO-4 (e), and Cu-loaded (0.3 wt%) TIO-4(f).

tivity. From these results, anatase TiO_2 , with a large surface area, a large band, and numerous OH groups, is preferable for efficient photocatalytic reaction to proceed. The increased band gap is accompanied by a shift in the conduction band edge to higher energies. This moves the reductive potential to more negative values and enhances the photocatalytic reactivity. It is also often suggested that the surface OH group and/or physisorbed H_2O plays a significant role in the photocatalytic reactions through the formation of OH radicals [Anpo, 1989].

Fig. 3 shows the products distribution in the photocatalytic oxidation of ethylene on Pt-loaded TiO_2 catalysts. Interestingly, small amount of Pt addition to the TiO_2 photocatalyst increased the selective formation of CO_2 , which was the oxidation product of C_2H_4 and O_2 . Anpo [1989] suggested that the photohydrogenolysis reactions on TiO_2 proceed *via* the interaction of alkyne (or alkene) with the active species of (electron-hole) pairs formed on TiO_2 . While with Pt/TiO_2 , hydrogenation reactions proceed on the Pt particles and the oxidation reactions in which OH radicals play a significant role proceed on the surface of TiO_2 . Accordingly, it is considered that the photo-formed OH radicals and the holes on Pt/TiO_2 lead the formation of CO_2 without CO. The total reactivity to the formation of CO_2 and CO was lowered in the case of Pt/TiO_2 . This is explained as that the surface area of Pt/TiO_2 was decreased during the preparation procedure by impregnation of Pt compared with that of pure TiO_2 .

Fig. 4 shows the product distribution of the photocatalytic oxidation of C_2H_4 with different amounts of oxygen on the anatase TiO_2 powder (F-6). The yield of CO_2 increases with the amount of added oxygen; however, the yield of CO decreases with the amount of added oxygen. So, the oxygen added is responsible for the product distribution of CO and CO_2 . Only when there is excessive oxygen in the reaction system, it is possible that ethylene is oxidized completely to CO_2 and does not produce CO. It is suggested that initially ethylene is oxidized to produce CO and then CO continues to oxidize to CO_2 by the excessive oxygen. The mechanism of the reaction can be expressed as follows:

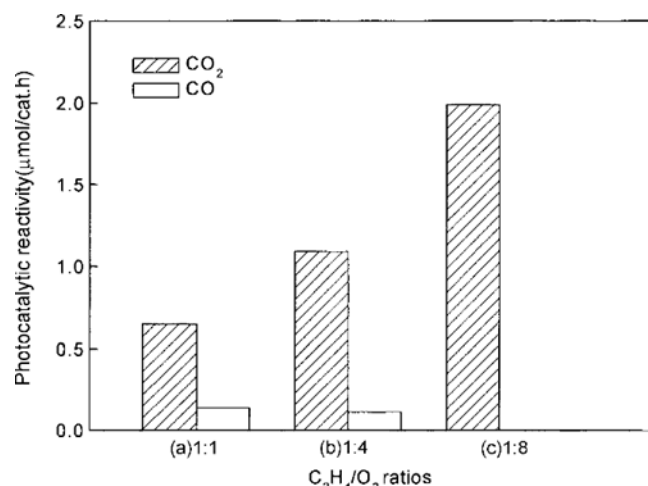


Fig. 4. Product distribution of the photocatalytic oxidation of ethylene with oxygen on the anatase TiO_2 powder (F-6), (ethylene 7 μmol , oxygen 7 μmol) (a), (ethylene 3 μmol , oxygen 12 μmol) (b), and (ethylene 3 μmol , oxygen 24 μmol) (c).

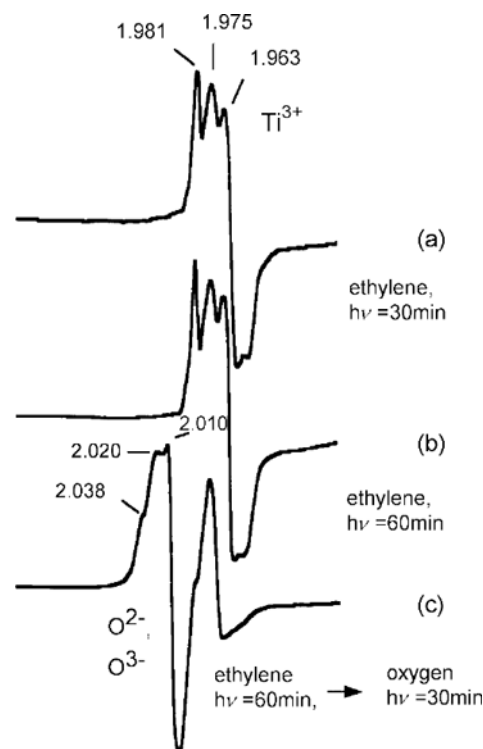


Fig. 5. ESR spectra obtained by UV irradiation of the JRC-TiO-4 catalysts in the presence of ethylene and oxygen at 77 K (recorded at 77 K).

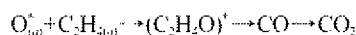


Fig. 5a and 5b show the ESR signals obtained under UV irradiation of anatase TiO_2 (JRC-TiO-4) in the presence of ethylene. These signals are attributed to the characteristic photogenerated Ti^{3+} ions ($g_1 = 1.975$ and $g_2 = 1.963$) and the signal of $g = 2.198$ and $g = 1.856$ were assigned to the H radicals. When the powdered TiO_2 photocatalysts were irradiated, e^-h^+ pairs were formed. In the absence of the electron and hole scavengers, most of them recombined with each other within a few nanoseconds. If the scavengers or surface defects are present to trap the electron or hole, an e^-h^+ recombinations can be prevented and the subsequent reactions caused by the electrons and holes may be dramatically enhanced. In this case, ethylene absorbed on the surface plays significant role in the reaction with holes. The surface OH groups may also play an important role in the trapping of the holes. The contribution of hole trapping by C_2H_4 or surface OH^- strongly depends on their surface concentration. On the other hand, the electron can be trapped by Ti^{3+} to give an isolated Ti^{3+} ion. Details on the chemical nature of such electrons and holes have been noted in previous paper [Kubokawa et al., 1981; Anpo et al., 1991].

In the presence of O_2 , the Ti^{3+} sites easily react with O_2 leading to the formation of $\text{O}_2^{\bullet-}$, as shown in state (c), while the hole trapping center (O_2^+) reacts with O_2 to form $\text{O}_3^{\bullet-}$ anion radicals. Therefore, such $\text{O}_2^{\bullet-}$ and $\text{O}_3^{\bullet-}$ and also OH radicals may play an important role in the oxidation of C_2H_4 . Investigations on the detailed mechanisms are now in progress.

In order to understand the effect of H_2O adsorption on the catalysts on the product yields in the photocatalytic oxidation of C_2H_4 ,

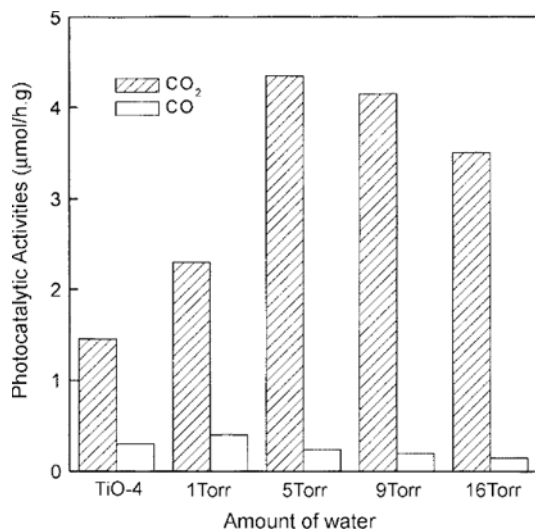


Fig. 6. The effect of the addition of H_2O on the yields of photoproducts in the photocatalytic oxidation of ethylene on JRC-TiO-4 catalyst.

different amounts of water vapor were added into the well-evacuated catalysts, and their results are shown in Fig. 6. From Fig. 6, it was found that oxidation reactions producing CO_2 are promoted by adding 1 Torr water vapor, and when 5 Torr water vapor was added, the oxidation reactivity was the highest. As the water vapor was added onto the well-evacuated catalysts, the amount of CO was not changed, while the amount of CO_2 increased greatly. This indicates that the addition of water vapor onto the catalysts is of benefit in realizing efficient photoreactions for the complete oxidation of C_2H_4 . The adsorbing water is activated on the irradiated TiO_2 surface to form OH species as precursors of radicals. The OH radicals are reactive for the complete oxidation of C_2H_4 [Meagher and Heicklen, 1976].

From Fig. 6, it can be seen that the photocatalytic activities are

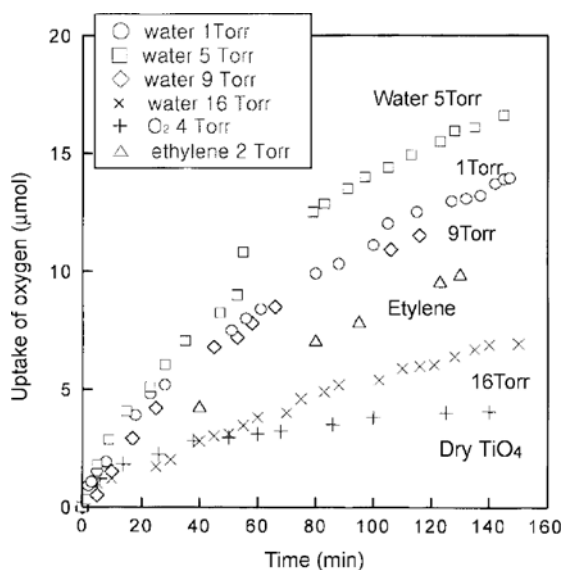


Fig. 7. The effect of the addition of water vapor on the photo-induced uptake of oxygen at 275 K.

high with an increase in the amount of water initially added, while when the amount of water vapor introduced is more than 5 Torr, the photocatalytic activity gradually decreases. To clarify the mechanism of this reaction further, the effect of the addition of water vapor on the photo-induced uptake of oxygen was investigated. The results are shown in Fig. 7. The addition of water vapor onto the photocatalyst leads to an enhancement of the photo-induced uptake of oxygen. But, when the amount of water vapor introduced exceeds 5 Torr, the uptake of oxygen decreases. These results clearly indicate that when a small amount of water vapor was introduced onto the photocatalyst, water and oxygen were adsorbed on the surface of the photocatalyst and produced reactive OH radicals under irradiation. This was shown to enhance the oxidation reaction of ethylene and the uptake of oxygen, while when water vapor was introduced in excess the effective adsorption sites were occupied completely by water molecules. This decreases the photo-induced uptake of oxygen, and the OH radicals decrease, also.

A comparative study of Fig. 6 and Fig. 7 shows that the photocatalytic reactivity of JRC-TiO-4 at 5, 9, and 16 Torr of water is almost similar, and in the case of 1 Torr (Fig. 6), it is higher, but the photoreactivity for oxygen uptake is remarkably different among these systems (Fig. 7). It is known that the adsorption of water on the TiO_2 surface causes a decrease in the upward bending of the band [Anpo et al., 1991], resulting in the efficient recombination of the photo-generated electrons and holes. On the other hand, the adsorption of H_2O results in the formation of surface OH groups by the reaction of H_2O with the bridging-oxygen atoms. These two factors may play an important role in determining the photocatalytic reactivity of TiO_2 , and the contribution of these factors strongly depends on the amount of H_2O added. When 1 Torr of water was introduced, the oxygen uptake increased; however, the OH radicals formed were still insufficient for any significant photocatalytic reactions to occur. It can, therefore, be seen that the photocatalytic activity in the presence of 1 Torr of water is lower.

In order to confirm whether the OH species as precursors of OH

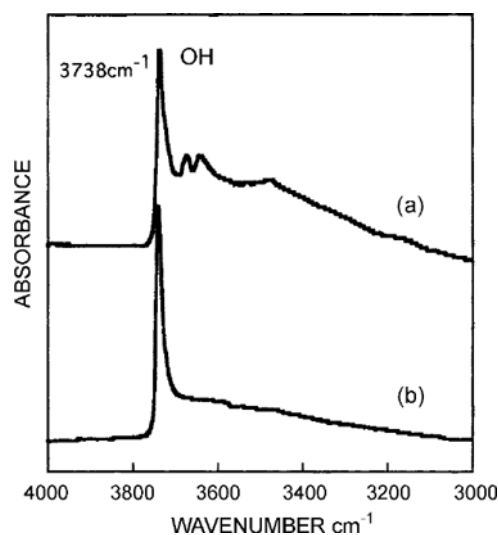


Fig. 8. Infrared spectra of the TiO_2 photocatalyst at 295 K: (a) after pretreatment at 450°C in O_2 and the introduction of C_2H_4 onto the catalysts, (b) after UV irradiation of the catalyst (a) for 30 min.

radicals are produced when water is introduced onto the photocatalysts under UV irradiation, IR spectrum measurements were employed. The results are shown in Fig. 8. Fig. 8a shows the IR spectrum after pretreatment at 450°C in O₂ and the introduction of C₂H₄ onto the catalyst. The peak at 3,640-3,680 cm⁻¹ was attributed to H₂O. Fig. 8b shows the IR spectrum after UV irradiation of the catalysts. From Fig. 8, it can be seen that the peak at 3,738 cm⁻¹ attributed to the absorbed OH species increases in intensity with increasing irradiation time, while the peak of the water decreases in intensity with increasing irradiation time. These results clearly suggest that adsorbing water on the surface of TiO₂ does indeed produce OH species as well as OH radicals via the OH species under UV irradiation.

CONCLUSIONS

Evidently, the presence of C₂H₄ and oxygen makes it possible to produce CO₂ and CO when TiO₂ photocatalysts are irradiated by UV light ($\lambda > 280$ nm). It has been clarified that ethylene can be completely oxidized to produce only CO₂ if titanium oxide catalysts of large surface area are used and oxygen is introduced onto photocatalysts in excess. The addition of a constant amount of water vapor leads to an increase in the yield of CO₂, while it has no effect on the yield of CO. It was confirmed that the adsorbed H₂O and O₂ on the photocatalyst activate to generate OH radicals and O₂⁻ and O₃⁻, respectively, when the photocatalysts are irradiated. It can be seen that the OH radicals and O₂⁻ and O₃⁻ play significant roles as the key active species in the complete photocatalytic oxidation of ethylene.

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