Photocatalytic Oxidation of Ethylene to CO_2 and H_2O on Ultrafine Powdered TiO_2 Photocatalysts in the Presence of O_2 and H_2O

Dal-Rung Park,† Jinlong Zhang,[1] Keita Ikeue, Hiromi Yamashita, and Masakazu Anpo[2]

Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka 599-8531, Japan; and †Division of Gas Utilization, KOGAS R&Center, Ansan City, Kyunggi-Do 425-150, Korea

The complete photocatalytic oxidation of C_2H_4 with O_2 into CO_2 and H_2O has been achieved on ultrafine powdered TiO_2 photocatalysts and the addition of H_2O was found to enhance the reaction. The details of the photocatalytic reaction have 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 C_2H_4 with O_2 into CO_2, CO, and H_2O. The large surface area of the photocatalyst is one of the most important factors in achieving a high efficiency in the photocatalytic oxidation of C_2H_4. The photo-formed OH species as well as O_2^- and O_3^- anion radicals play a significant role as a key active species in the complete photocatalytic oxidation of C_2H_4 with O_2 into CO_2 and H_2O. © 1999 Academic Press

Key Words: photocatalyst; oxidation; ethylene.

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 (1–3). 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, TiO_2 photocatalysts have long been investigated in their different forms as bulk materials, colloidal suspensions, and dispersed into SiO_2 matrices and on porous supports such as zeolites and porous vycor glass (4, 5). Although the utilization of extremely small powdered TiO_2 particles has attracted a great deal of attention as photocatalysts due to their high photocatalytic reactivities, the actual factors controlling the photocatalytic activity of TiO_2 particles are still unknown, except for a few important factors such as the magnitude of the band gap, surface area, and crystallinity (6–9). Such difficulties mainly arise because the photocata-

lytic 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 C_2H_4 is harmful to all like forms, in order to keep enough food fresh in the CELSS (Controlled Ecological Life Support Systems), it is necessary to remove ethylene, which is released from plants. In this regard, photocatalysts can be considered as they are generally referred to as an advanced oxidation process.

Along these lines, in the present paper, we investigated the photocatalytic oxidation of C_2H_4 with O_2 into CO_2 and H_2O on ultrafine powdered TiO_2 photocatalysts. Special attention is focused on the effects of the particle size on the reaction and the effects of the addition of H_2O 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 we investigated the detailed mechanisms of the photocatalytic oxidation of the olefins with O_2 on the well-evacuated dried TiO_2 photocatalysts in the past (8), the effect of the coexistence of H_2O on the photocatalytic oxidation has not been explored until now.

In the present paper, we report that ethylene can be completely oxidized into CO_2 on the powdered titanium oxide photocatalysts, the rate depending on the nature of the catalysts, and that the photocatalytic oxidation of C_2H_4 can be enhanced by the coexistence of H_2O vapor in the reaction system.

EXPERIMENTAL

Five different types of ultrafine powdered TiO_2 catalysts which were supplied by the Catalysis Society of Japan as reference TiO_2 catalysts (JRC-TIO-1, 2, 3, 4, 5) were used as photocatalysts (grain size, 0.02∼1 mm). Detailed information on these reference TiO_2 catalysts is available from the Catalysis Society of Japan. Three types 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
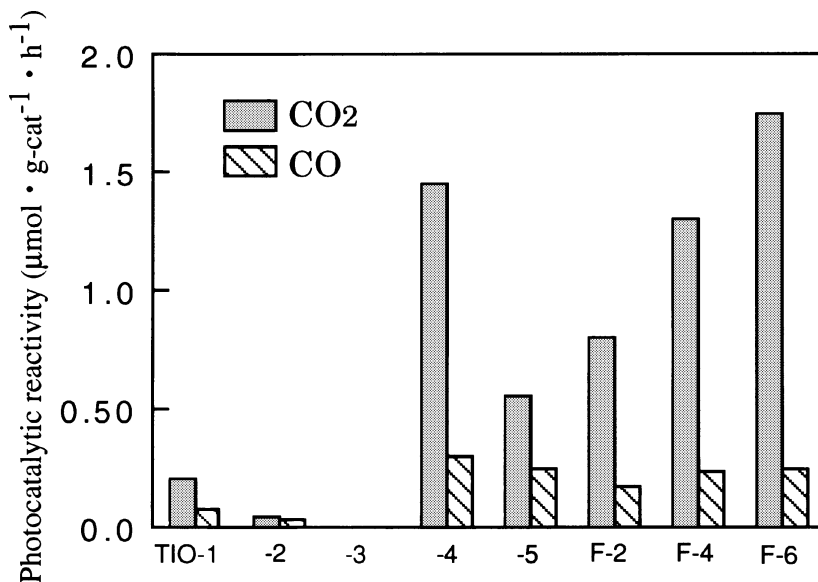

FIG. 1. Product distribution of the photocatalytic oxidation of ethylene on TiO₂ photocatalysts: JRC-TIO-1, -TIO-2, -TIO-3, -TIO-4, -TIO-5, F-2, F-4, and F-6.

connected to a conventional vacuum system (10^{-6} Torr range). The catalysts were degassed at 723 K for 2 h and calcined in O_2 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 using a Toshiba SHL 100 W high-pressure Hg 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 (6, 8).

RESULTS AND DISCUSSION

The typical physical properties of these TIO-1 ~ 5 catalysts are shown in Table 1. The relative OH concentration

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

was calculated from the intensities of the IR peak of the samples assigned to the surface OH group on TiO_2. The acid concentration was calculated from the peak intensities observed in the temperature-programmed desorption (TPD) patterns of preadsorbed NH_3. The surface area of the titanium oxide powders, F-2, F-4, F-6, are 27, 54, and 102 m^2/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 TiO_2 catalysts in the presence of C_2H_4 and O_2 led to the oxidation of C_2H_4 to produce CO_2, CO, and H_2O as the main products, but with relative reactivity and selectivity, depending on the specific properties of the catalysts. Figure 1 shows the product distribution in the photocatalytic oxidation of ethylene on various TiO_2 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 H_2O, the isomerization of 2-butene, and the reduction of CO_2 with H_2O (9). From Table 1 and Fig. 1, it can be seen that anatase TiO_2 with a large surface area, large band gap, and numerous OH groups is more efficient for the oxidation of ethylene. Especially, for the TiO_2 photocatalyst, F-6, having a large surface area, shows the highest photocatalytic reactivity. From these results, anatase TiO_2, with a large surface area, a large band, and numerous OH groups, is preferable for efficient photocatalytic reactions 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 groups and/or physisorbed H_2O plays a
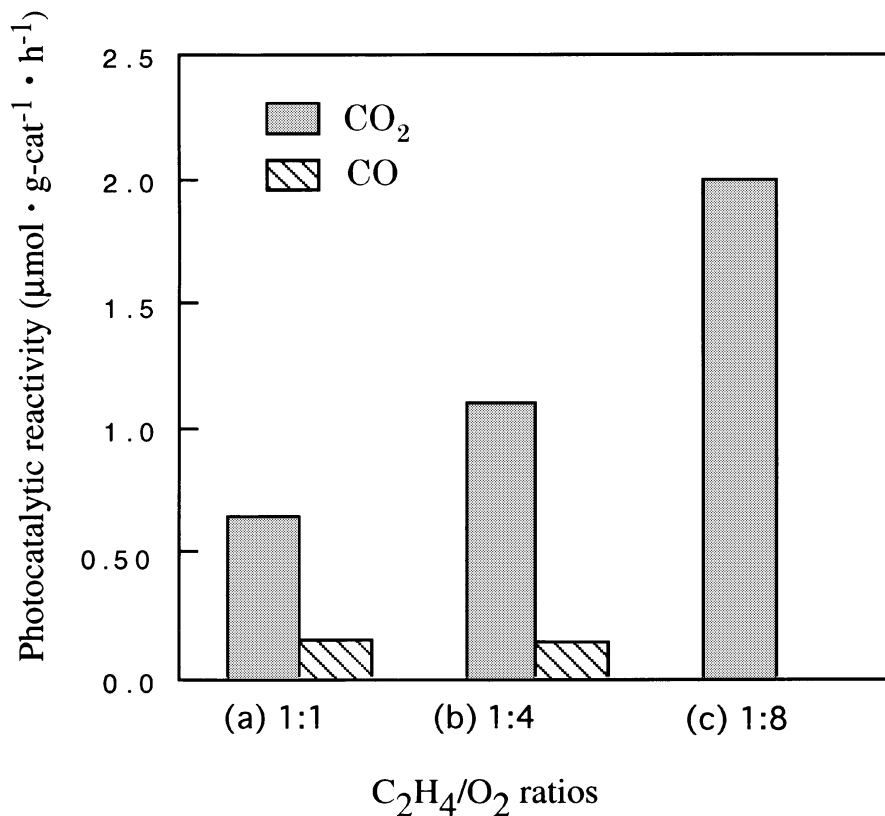
FIG. 2. Product distribution of the photocatalytic oxidation of ethylene with oxygen TiO_2 powder (F-6), (ethylene 7 μmol, oxygen 7 μmol) (a), (ethylene 3 μmol, oxygen 12 μmol) (b), and (ethylene 3 μmol, oxygen 24 μmol) (c).

significant role in the photocatalytic reactions through the formation of OH radicals (6).

Figure 2 shows the product distiribution 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:

$$O_{(a)}^* + C_2H_{4(a)} \rightarrow (C_2H_4O)^* \rightarrow CO \rightarrow CO_2.$$
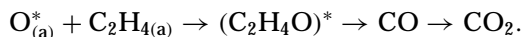
Figures 3a and 3b show the ESR signals obtained under UV irradiation of anatase TiO_2 (JRC-TIO-4) in the presence of ethylene. These signals are attributed to the characteristic photogenerated Ti^{3+} ions ($g_\perp = 1.975$ and $g_\parallel = 1.963$) and the signals of $g = 2.198$ and $g = 1.856$ were 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 adsorbed on the surface plays a 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 $Ti_{(l)}^{4+}$ to give an isolated Ti^{3+} ion. Details on the chemical nature of such electrons and holes have been noted in previous papers (8, 12).

In the presence of O_2, the Ti^{3+} sites easily react with O_2 leading to the formation of O_2^-, as shown in stage (c), while the hole trapping center (O_1^-) reacts with O_2 to form O_3^- anion radicals. Therefore, such O_2^- and O_3^- 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
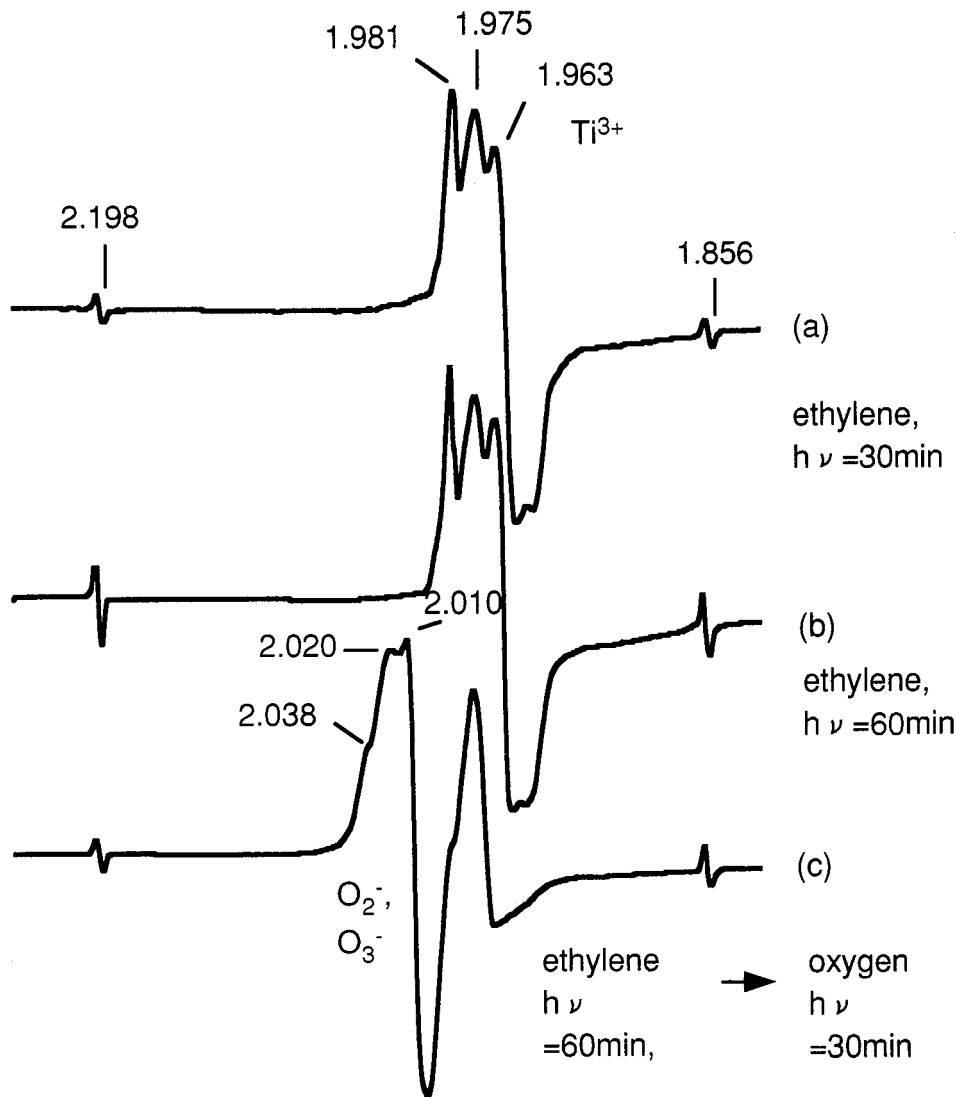
FIG. 3. ESR spectra obtained by UV irradiation of the JRC-TIO-4 catalysts in the presence of ethylene and oxygen at 77 K (recorded at 77 K).

oxidation of C_2H_4, different amounts of water vapor were added into the well-evacuated catalysts, and their results are shown in Fig. 4. From Fig. 4, 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. As reported previously (11), the OH radicals are reactive for the complete oxidation of C_2H_4.

From Fig. 4, it can be seen that the photocatalytic activities are high with an increase in the amount of water initially added, while when the amount of the water vapor introduced is more than 5 Torr, the photcatalytic 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. 5. 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
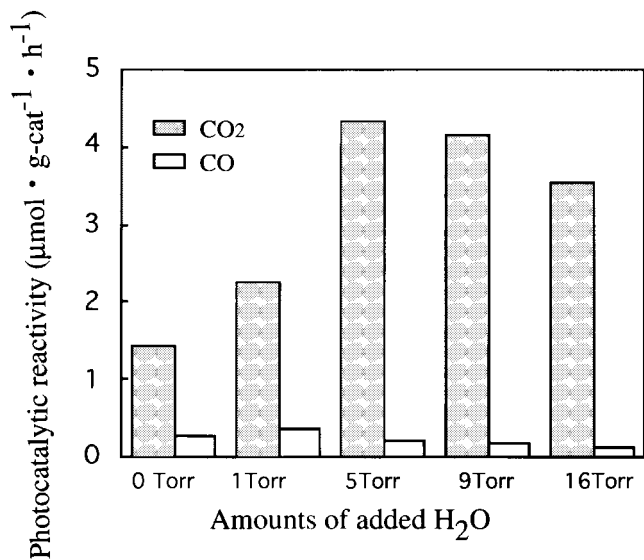
FIG. 4. The effect of the addition of H_2O on the yields of photoproducts in the photocatalytic oxidation of ethylene on JRC-TIO-4 catalysts.

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. 4 and Fig. 5 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. 4), it is higher, but the photoreactivity for oxygen uptake is remarkably different among these systems (Fig. 5). It is known that the adsorption of water on the TiO_2 surface causes a decrease in the upward bending of the band (12), 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 (13). 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
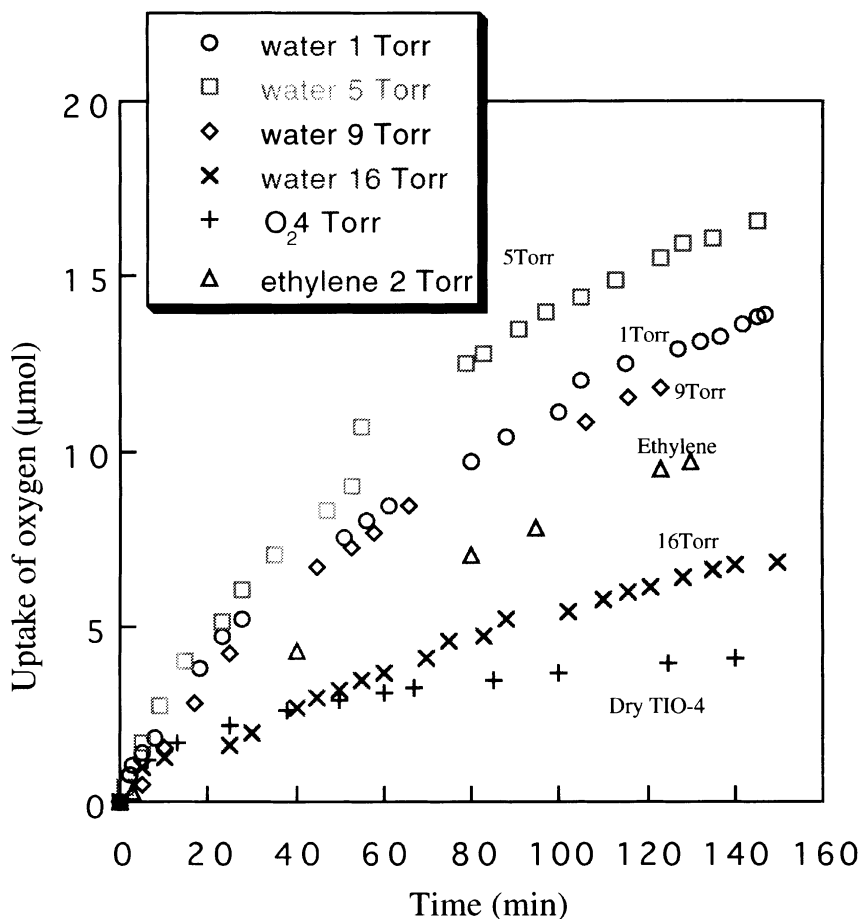

FIG. 5. The effect of the addition of water vapor on the photo-induced uptake of oxygen at 275 K. (After 4 Torr of oxygen was introduced, 2 Torr of ethylene was added, and then varying amounts of water were added.)
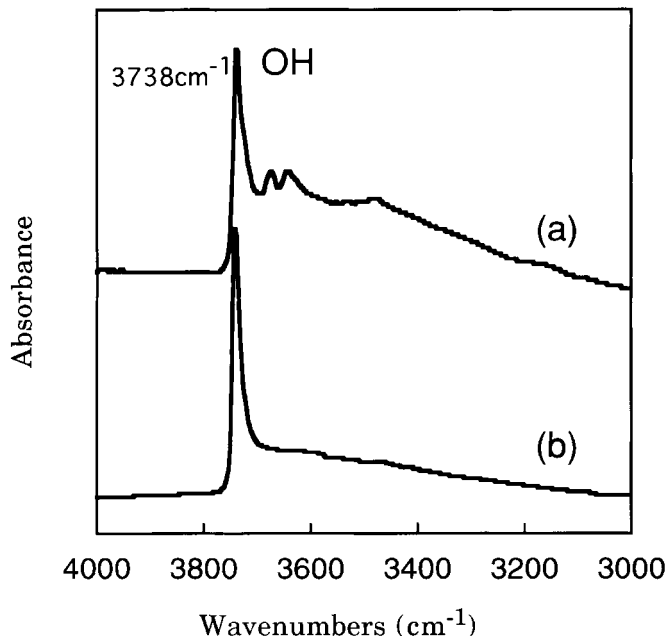
FIG. 6. Infrared spectra of the TiO_2 photocatalyst at 295 K: (a) after pretreatment at 450°C in O_2 and introduction of C_2H_4 onto the catalyst, (b) after UV irradiation of the catalyst (a) for 30 min.

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 radicals are produced when water is introduced onto the photocatalysts under UV irradiation, IR spectrum measurements were employed. The results are shown in Fig. 6. Figure 6a shows the IR spectrum after pretreament at 450°C in O_2 and the introduction of C_2H_4 onto the catalyst. The peak at $3640 \sim 3680$ cm^{-1} was attributed to H_2O. Figure 6b shows the IR spectrum after UV irradiation of the catalysts. From Fig. 6, it can be seen that the peak at 3738 cm^{-1} attributed to the adsorbed OH species increases in intensity with increasing irradiation time, while the peak of water decreases in intensity with increasing irradiation

time. These results clearly suggest that adsorbing water on the surface of TiO_2 does indeed produce OH species as well as OH radicals via the OH species under UV irradiation.

CONCLUSIONS

Evidently, the presence of C_2H_4 and oxygen makes it possible to produce CO_2 and CO when the TiO_2 photocatalysts are irradiated by UV light ($\lambda > 280$ nm). It has been clarified that ethylene can be completely oxidized to produce only CO_2 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 CO_2, while it has no effect on the yield of CO. It was confirmed that the adsorbed H_2O and O_2 on the photocatalyst activate to generate OH radicals and O_2^- and O_3^-, respectively, when the photocatalysts are irradiated. It can be seen that the OH radicals and O_2^- and O_3^- play significant roles as the key active species in the complete photocatalytic oxidation of ethylene.

REFERENCES

1. Anpo, M., *Catal. Surv. Jpn.* **1**, 169 (1997).
2. Kamat, P. V., *Chem. Rev.* **93**, 267 (1993).
3. Ollis, D. F., and Al-Ekabi, H., "Photocatalytic Purification and Treatment of Water and Air." Elsevier, Amsterdam, 1993.
4. Fox, M. A., and Dulay, M. T., *Chem. Rev.* **93**, 341 (1993).
5. Anpo, M., and Yamashita, H., *in* "Heterogeneous Photocatalysis" (M. Schiavelo, Ed.), p. 133, Wiley, Chichester, 1997.
6. Anpo, M., *Res. Chem. Intermed.* **9**, 67 (1989).
7. Anpo, M., Yamashita, H., Ichihashi, Y., Fujii, Y., and Honda, M., *J. Phys. Chem.* **101**, 2632 (1997).
8. Kubokawa, Y., Anpo, M., and Yun, C., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," Part B, p. 1170. Elsevier, Amsterdam, 1981.
9. Yamashita, H., Ichihashi, Y., Harada, M., Stewart, G., Fox, M. A., and Anpo, M., *J. Catal.* **158**, 97 (1996).
10. Graf, J. C., "Photocatalytic Oxidation of Volatile Organic Contaminants." 5th ICES SAE 951660, 1995.
11. Izumi, I., Dunn, W. W., Wilbourn, K. O., Fan, F. R., and Bard, A. J., *J. Phys. Chem.* **84**, 3207 (1980).
12. Anpo, M., Chiba, K., Tomonari, M., Coluccia, S., Che, M., and Fox, M. A., *Bull. Chem. Soc. Jpn.* **64**, 543 (1991).
13. Kurtz, R. L., Stockbauer, R., Madey, T. E., Roman, E., and de Segovia, J. L., *Surf. Sci.* **218**, 178 (1989).