

## Photocatalytic Oxidation of Ethylene to $\text{CO}_2$ and $\text{H}_2\text{O}$ on Ultrafine Powdered $\text{TiO}_2$ Photocatalysts: Effect of the Presence of $\text{O}_2$ and $\text{H}_2\text{O}$ and the Addition of Pt

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**Abstract**—The complete photocatalytic oxidation of  $\text{C}_2\text{H}_4$  with  $\text{O}_2$  into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  has been achieved on ultrafine powdered  $\text{TiO}_2$  photocatalysts and the addition of  $\text{H}_2\text{O}$  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  $\text{C}_2\text{H}_4$  with  $\text{O}_2$  into  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$ . The large surface area of the photocatalyst is one of the most important factors in achieving a high efficiency in the photocatalytic oxidation of  $\text{C}_2\text{H}_4$ . The photo-formed OH species as well as  $\text{O}_3$  and  $\text{O}_3^-$  anion radicals play a significant role as a key active species in the complete photocatalytic oxidation of  $\text{C}_2\text{H}_4$  with  $\text{O}_2$  into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Interestingly, small amount of Pt addition to the  $\text{TiO}_2$  photocatalyst increased the amount of selective formation of  $\text{CO}_2$  which was the oxidation product of  $\text{C}_2\text{H}_4$  and  $\text{O}_2$ .

Key words: Photocatalyst, Oxidation, Ethylene,  $\text{TiO}_2$

### 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,  $\text{TiO}_2$  photocatalysts have long been investigated in their different forms as bulk materials, colloidal suspension, and dispersed into  $\text{SiO}_2$  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  $\text{TiO}_2$  particles has attracted a great deal of attention as photocatalysts due to their high photocatalytic reactivities, the actual factors controlling the photocatalytic activity of  $\text{TiO}_2$  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  $\text{C}_2\text{H}_4$  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  $\text{C}_2\text{H}_4$  with  $\text{O}_2$  into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on ultrafine powdered  $\text{TiO}_2$  photocatalysts. Special attention was focused on the effects of the particle size on the reaction and the effects of the addition of  $\text{H}_2\text{O}$  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  $\text{O}_2$  on the well-evacuated dried  $\text{TiO}_2$  photocatalysts were investigated in the past [Kubokawa et al., 1981], the effect of  $\text{H}_2\text{O}$  vapor on the photocatalytic oxidation has not been explored yet.

In the present paper, we report that ethylene can be completely oxidized into  $\text{CO}_2$  on the powdered titanium oxide photocatalysts, the rate depending on the nature of the catalysts, and that the photocatalytic oxidation of  $\text{C}_2\text{H}_4$  can be enhanced by adding  $\text{H}_2\text{O}$  vapor in the reaction system.

### EXPERIMENTAL

Five different types of ultrafine powdered  $\text{TiO}_2$  catalysts, which were supplied by the Catalysis Society of Japan as reference  $\text{TiO}_2$  catalysts (JRC-TIO-1,2,3,4,5), were used as photocatalysts (grain size, 0.02-1 mm). Pt-loaded  $\text{TiO}_2$  catalysts were prepared by impregnation with an aqueous solution of  $\text{H}_2\text{PtCl}_6$ . 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  $\text{cm}^3$ ) 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  $\text{O}_2$  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 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].

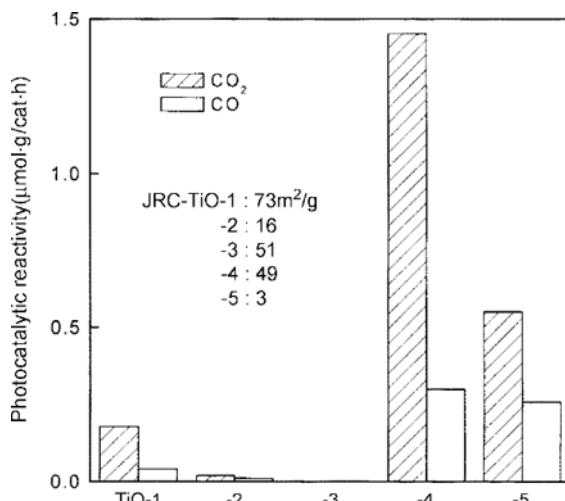
## RESULTS AND DISCUSSION

The typical physical properties of these  $\text{TiO}_{1\sim 5}$  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  $\text{TiO}_2$ . The acid concentration was calculated from the peak intensities observed in the temperature-programmed desorption (TPD) patterns of preadsorbed  $\text{NH}_3$ . The surface area of the titanium oxide powders, F-2, F-4, F-6, are 27, 54, and 102  $\text{m}^2/\text{g}$ , respectively. It was observed that the surface area of F-6 is the largest in all of the catalysts.

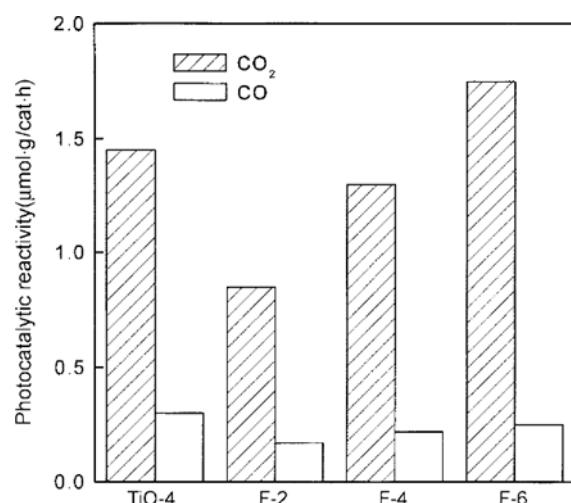
UV irradiation of several standard  $\text{TiO}_2$  catalysts in the presence

**Table 1. Physical properties of  $\text{TiO}_2$  powdered photocatalysts**

Catalysts (JRC-TiO- <i>i</i> )	Surface area ( $\text{m}^2/\text{g}$ )	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



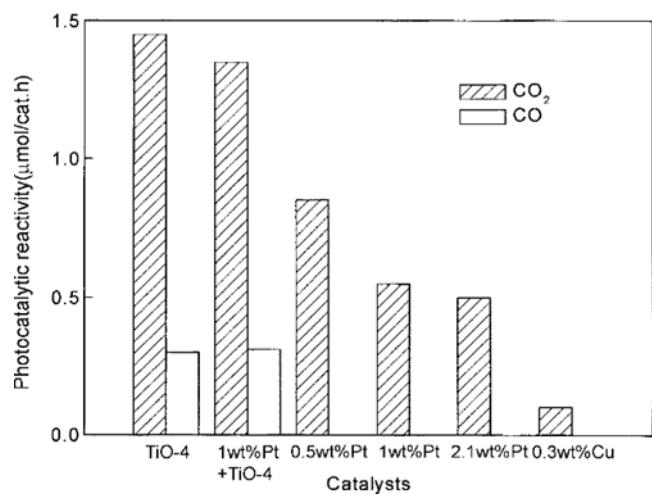
**Fig. 1. Product distribution of the photocatalytic oxidation of ethylene on  $\text{TiO}_2$  photocatalysts: JRC-TiO-1, TiO-2, TiO-3, TiO-4, TiO-5.**



**Fig. 2. Product distribution of the photocatalytic oxidation of ethylene on  $\text{TiO}_2$  photocatalysts: JRC-TiO-4, F-2, F-4, F-6.**

of  $\text{C}_2\text{H}_4$  and  $\text{O}_2$  led to the oxidation of  $\text{C}_2\text{H}_4$  to produce  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  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  $\text{TiO}_2$  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  $\text{H}_2\text{O}$  [Yamashita et al., 1996]. From Table 1 and Fig. 1, it can be seen that anatase  $\text{TiO}_2$  with a large surface area, large band gap, and numerous OH group is more efficient for the oxidation of ethylene. Especially, for the  $\text{TiO}_2$  photocatalyst, F-6, having a large surface area, shows the highest photocatalytic reac-



**Fig. 3. Product distribution of the photocatalytic oxidation of ethylene on  $\text{TiO}_2$  photocatalysts and metal loaded  $\text{TiO}_2$  catalysts: JRC-TiO-4 (a), TiO-4 (1 wt% of Pt, mixing) (b), Pt-loaded (0.5 wt%)  $\text{TiO}_2$  (c), Pt-loaded (1.0 wt%)  $\text{TiO}_2$  (d), Pt-loaded (2.0 wt%)  $\text{TiO}_2$  (e), and Cu-loaded (0.3 wt%)  $\text{TiO}_2$  (f).**

tivity. From these results, anatase  $\text{TiO}_2$ , 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  $\text{H}_2\text{O}$  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  $\text{TiO}_2$  catalysts. Interestingly, small amount of Pt addition to the  $\text{TiO}_2$  photocatalyst increased the selective formation of  $\text{CO}_2$  which was the oxidation product of  $\text{C}_2\text{H}_4$  and  $\text{O}_2$ . Anpo [1989] suggested that the photohydrogenolysis reactions on  $\text{TiO}_2$  proceed via the interaction of alkyne (or alkene) with the active species of (electron-hole) pairs formed on  $\text{TiO}_2$ . While with  $\text{Pt}/\text{TiO}_2$ , hydrogenation reactions proceed on the Pt particles and the oxidation reactions in which OH radicals play a significant role proceed on the surface of  $\text{TiO}_2$ . Accordingly, it is considered that the photo-formed OH radicals and the holes on  $\text{Pt}/\text{TiO}_2$  lead the formation of  $\text{CO}_2$  without CO. The total reactivity to the formation of  $\text{CO}_2$  and CO was lowered in the case of  $\text{Pt}/\text{TiO}_2$ . This is explained as that the surface area of  $\text{Pt}/\text{TiO}_2$  was decreased during the preparation procedure by impregnation of Pt compared with that of pure  $\text{TiO}_2$ .

Fig. 4 shows the product distribution of the photocatalytic oxidation of  $\text{C}_2\text{H}_4$  with different amounts of oxygen on the anatase  $\text{TiO}_2$  powder (F-6). The yield of  $\text{CO}_2$  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  $\text{CO}_2$ . Only when there is excessive oxygen in the reaction system, it is possible that ethylene is oxidized completely to  $\text{CO}_2$  and does not produce CO. It is suggested that initially ethylene is oxidized to produce CO and then CO continues to oxidize to  $\text{CO}_2$  by the excessive oxygen. The mechanism of the reaction can be expressed as follows:

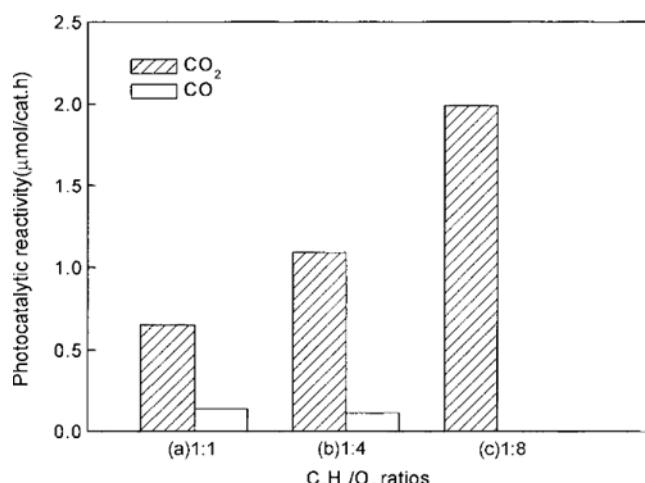


Fig. 4. Product distribution of the photocatalytic oxidation of ethylene with oxygen on the anatase  $\text{TiO}_2$  powder (F-6), (ethylene 7  $\mu\text{mol}$ , oxygen 7  $\mu\text{mol}$ ) (a), (ethylene 3  $\mu\text{mol}$ , oxygen 12  $\mu\text{mol}$ ) (b), and (ethylene 3  $\mu\text{mol}$ , oxygen 24  $\mu\text{mol}$ ) (d).

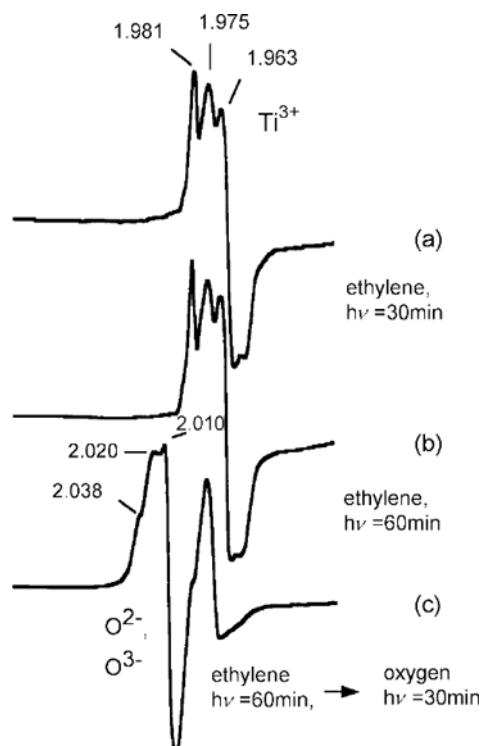


Fig. 5. ESR spectra obtained by UV irradiation of the JRC-TiO-4 catalysts in the presence of ethylene and oxygen at 77 K (recorded at 77 K).

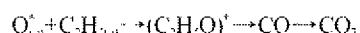


Fig. 5a and 5b show the ESR signals obtained under UV irradiation of anatase  $\text{TiO}_2$  (JRC-TiO-4) in the presence of ethylene. These signals are attributed to the characteristic photogenerated  $\text{Ti}^{3+}$  ions ( $g_s = 1.975$  and  $g = 1.963$ ) and the signal of  $g = 2.198$  and  $g = 1.856$  were assigned to the H radicals. When the powdered  $\text{TiO}_2$  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  $\text{C}_2\text{H}_4$  or surface OH strongly depends on their surface concentration. On the other hand, the electron can be trapped by  $\text{Ti}^{3+}$  to give an isolated  $\text{Ti}^{3+}$  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  $\text{O}_2$ , the  $\text{Ti}^{3+}$  sites easily react with  $\text{O}_2$  leading to the formation of  $\text{O}_2^-$ , as shown in state (c), while the hole trapping center ( $\text{O}_2^+$ ) reacts with  $\text{O}_2$  to form  $\text{O}_3^-$  anion radicals. Therefore, such  $\text{O}_2^-$  and  $\text{O}_3^-$  and also OH radicals may play an important role in the oxidation of  $\text{C}_2\text{H}_4$ . Investigations on the detailed mechanisms are now in progress.

In order to understand the effect of  $\text{H}_2\text{O}$  adsorption on the catalysts on the product yields in the photocatalytic oxidation of  $\text{C}_2\text{H}_4$ ,

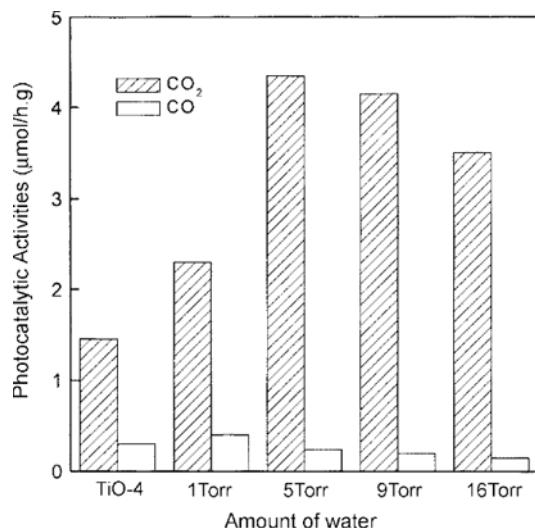


Fig. 6. The effect of the addition of  $\text{H}_2\text{O}$  on the yields of photoproducts in the photocatalytic oxidation of ethylene on JRC-TIO-4 catalyst.

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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{C}_2\text{H}_4$ . The adsorbing water is activated on the irradiated  $\text{TiO}_2$  surface to form OH species as precursors of radicals. The OH radicals are reactive for the complete oxidation of  $\text{C}_2\text{H}_4$  [Meagher and Heicklen, 1976].

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

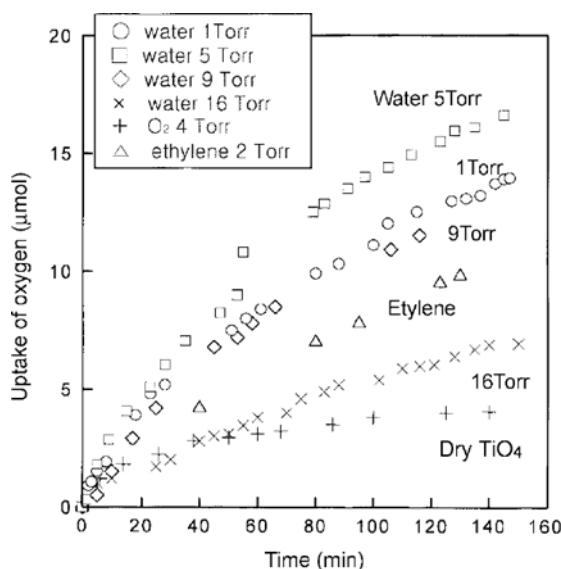


Fig. 7. The effect of the addition of water vapor on the photo-induced uptake of oxygen at 275 K.

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  $\text{TiO}_2$  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  $\text{H}_2\text{O}$  results in the formation of surface OH groups by the reaction of  $\text{H}_2\text{O}$  with the bridging-oxygen atoms. These two factors may play an important role in determining the photocatalytic reactivity of  $\text{TiO}_2$ , and the contribution of these factors strongly depends on the amount of  $\text{H}_2\text{O}$  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

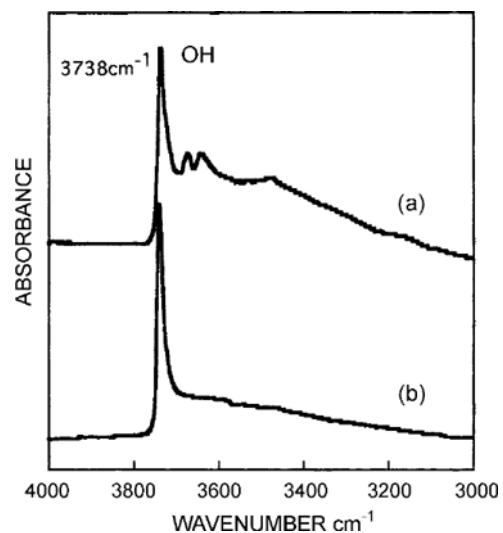


Fig. 8. Infrared spectra of the  $\text{TiO}_2$  photocatalyst at 295 K: (a) after pretreatment at 450 °C in  $\text{O}_2$  and the introduction of  $\text{C}_2\text{H}_4$  onto the catalysts, (b) after UV irradiation of the catalyst (a) for 30 min.

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 shown the IR spectrum after pretreatment at 450°C in O<sub>2</sub> and the introduction of C<sub>2</sub>H<sub>4</sub> onto the catalyst. The peak at 3,640-3,680 cm<sup>-1</sup> was attributed to H<sub>2</sub>O. 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<sup>-1</sup> 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 TiO<sub>2</sub> does indeed produce OH species as well as OH radicals via the OH species under UV irradiation.

## CONCLUSIONS

Evidently, the presence of C<sub>2</sub>H<sub>4</sub> and oxygen makes it possible to produce CO<sub>2</sub> and CO when TiO<sub>2</sub> photocatalysts are irradiated by UV light ( $\lambda > 280$  nm). It has been clarified that ethylene can be completely oxidized to produce only CO<sub>2</sub> 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<sub>2</sub>, while it has no effect on the yield of CO. It was confirmed that the adsorbed H<sub>2</sub>O and O<sub>2</sub> on the photocatalyst activate to generate OH radicals and O<sub>2</sub><sup>·</sup> and O<sub>3</sub><sup>·</sup>, respectively, when the photocatalysts are irradiated. It can be seen that the OH radicals and O<sub>2</sub><sup>·</sup> and O<sub>3</sub><sup>·</sup> play significant roles as the key active species in the complete photocatalytic oxidation of ethylene.

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