



Removal of Ethylene and Secondary Organic Aerosols Using UV-C_{254 + 185 nm} with TiO₂ Catalyst

Ken-Lin Chang¹, Kazuhiko Sekiguchi^{2,3*}, Qingyue Wang^{2,3}, Feng Zhao¹

¹ Key Laboratory of Urban Environment and Health, Institute of Urban and Environment, Chinese Academy of Sciences, Xiamen 361021, China

² Graduate School of Science and Engineering, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan

³ Institute for Environmental Science and Technology, Saitama University, 255 Shimo-Okubo, Sakura, Saitama 338-8570, Japan

ABSTRACT

In this investigation we evaluated the feasibility and effectiveness of ozone-producing UV (254 + 185 nm) irradiation and a TiO₂ photocatalyst for degradation of ethylene, which is strongly hydrophobic and does not decompose easily in a humid environment. Tests were performed in a photoreactor (V = 0.55 L) under UV irradiation at various wavelengths (365, 254 and 254 + 185 nm), relative humidities (RH < 1% and RH > 86%), atmospheres (pure N₂ and air), residence times (11–33 sec), initial ethylene concentrations in the range of 25–105 ppmv and TiO₂ contact areas (86.4–259 cm²) with presumably ambient pressure and temperature.

The experimental results demonstrated that the use of TiO₂ under 254 + 185 nm UV irradiation significantly enhanced the photodegradation of ethylene compared to the case of UV irradiation alone, due to the synergistic effect of photochemical oxidation in the gas phase and photocatalytic oxidation on the TiO₂ surface. Photodegradation induced with 254 + 185 nm UV irradiation was compared with photodegradation induced with UV irradiation at wavelengths of 365 and 254 nm. The highest conversion and mineralization levels were obtained with 254 + 185 nm UV irradiation among the three tested UV sources. Moreover, irradiating with 254 + 185 nm light generated secondary organic aerosols (SOA) via gas-to-particle conversion of organic compounds in the air stream. The results indicate that the concentration of generated SOAs decreased in the presence of the TiO₂ catalyst, and thus that TiO₂ may be used to effectively control the emissions of undesirable SOAs.

In an application test, for photocatalytic oxidation with 254 + 185 nm UV irradiation, corresponding to a flow rate of 0.5 L/min, and an initial concentration of 34 ppmv, over 90% of the inlet ethylene could be degraded.

Keywords: Ethylene; Photochemical oxidation; Photocatalytic oxidation; Ozone-producing UV lamp; Secondary organic aerosols.

INTRODUCTION

Ethylene (C₂H₄) is a naturally produced and is also created by man-made sources, simple gaseous plant growth hormone containing two carbon atoms. The presence of high levels of ethylene in the atmosphere in which fruit, vegetables, plants and flowers are has been shown to have certain detrimental effects, including inhibition of growth, premature ripening, accelerated senescence, excessive softening of fruits, early sprouting of potatoes, stimulated abscission of leaves and flowers, and discoloration (e.g., browning), and accelerated toughening of vegetables, potentially reducing

fruit and vegetable productivity (Saltveit, 1999; Villavicencio *et al.*, 2001; Hogan *et al.*, 2006). Bower *et al.* (2003) reported that the concentration of ethylene in the storage environment can be directly related to the rate of quality loss. Therefore, the presence of ethylene is usually undesirable in stored fruits and vegetables. Economical and effective degradation of ethylene can delay ripening of fruits and vegetables in storage and prolong the storage life of certain commodities. Thus, ethylene removal has great significance in the fruit, vegetable and flower industry.

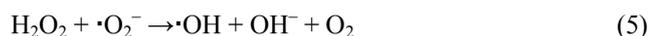
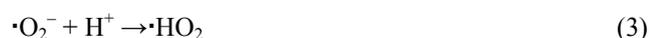
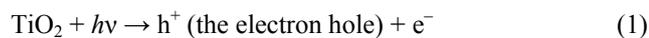
Recent studies have suggested some processes for treating ethylene-containing air, including photocatalytic oxidation (Fu *et al.*, 1996; Krishnankutty *et al.*, 1996; Obee and Hay, 1997; Sirisuk *et al.*, 1999; Yamazaki *et al.*, 1999; Zorn *et al.*, 2000; Rojluechai *et al.*, 2007), biofiltration (Kim, 2003), adsorption (Chen *et al.*, 1999), and cyclic adsorption-catalytic degradation processes (Kim *et al.*, 2005). However, the degradation of ethylene using a TiO₂ photocatalyst in an

* Corresponding author. Tel.: +81-48-858-9192;
Fax: +81-48-858-9542
E-mail address: kseki@mail.saitama-u.ac.jp

actual environment with humidity is difficult because the degradation rate decreases with increasing relative humidity (Obee and Hay, 1997) due to the strong hydrophobicity of ethylene (Henry's law constant for solubility in water = 0.0048 mol/kg/bar at 298.15 K) (NIST Chemistry Web Book, 2012). Although an ozone-producing UV lamp is effective for hydroxyl (OH) radical and ozone (O₃) generation under the condition of high humidity, to our knowledge, photocatalytic degradation of ethylene with an ozone-producing UV lamp has not yet been investigated.

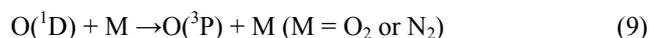
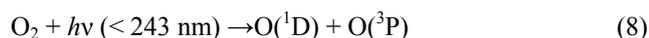
Deactivation of photocatalysts after a period of use has been reported (Luo and Ollis, 1996; Cao *et al.*, 2000). To avoid deactivation of photocatalysts and increase the efficiency of mineralization of contaminants, addition of ozone has been the focus of much recent research (Kim *et al.*, 2003; Kasprzyk-Hordern *et al.*, 2003; Pengyi *et al.*, 2003; Einaga and Futamura, 2004; Zhang and Liu, 2004; Giri *et al.*, 2007). In photocatalyst ozonization, the photocatalytic oxidation rate greatly increases due to synergistic photocatalytic and photochemical effects in the combined systems (Jeong *et al.*, 2004; Jeong *et al.*, 2005; Jeong *et al.*, 2006).

When the TiO₂ catalyst is subjected to UV₃₆₅ or UV₂₅₄ irradiation, only photocatalytic oxidation is of importance in the decomposition of pollutants (Kasprzyk-Hordern *et al.*, 2003; Pengyi *et al.*, 2003):



254 nm UV irradiation is significantly more effective in decomposing ethylene than 365 nm UV irradiation owing to the direct photolysis of decomposition intermediates from 254 nm UV irradiation. Furthermore, labile species were not consumed in the destruction of intermediates and could be used for ethylene decomposition.

In the UV₂₅₄₊₁₈₅ system, ozone was formed via the following reaction (Jeong *et al.*, 2005; Jeong *et al.*, 2006):

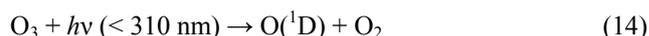


The produced ozone molecule can accept a photo-generated electron and generated OH radicals according to the following equations (Pengyi *et al.*, 2003; Zhang and

Liu, 2004):



OH radicals were also generated as follows under humid conditions (Jeong *et al.*, 2004; Jeong *et al.*, 2005):



Additionally, water molecules exhibit a continuous UV absorption spectrum between wavelengths of 175 and 195 nm and in this wavelength range much $\cdot\text{OH}$ can be generated by direct decomposition of moisture in the gas phase (Wang and Ray, 2000; Jeong *et al.*, 2004; Chou *et al.*, 2005; Jeong *et al.*, 2005). Consequently, in the 185 nm UV irradiation process, $\cdot\text{OH}$ was generated via Eqs. (6), (7), (13), (15) and the following reaction:



With UV₂₅₄₊₁₈₅ irradiation, photochemical oxidation in the gas phase and photocatalytic oxidation on the TiO₂ surface are available simultaneously for photodegradation of ethylene.

In this study, a photoreactor equipped with TiO₂ and a UV lamp was used to investigate the effects of UV wavelength, formation of labile species, reaction atmosphere, relative humidity (RH), flow rate, initial concentration and TiO₂ contact area on ethylene conversion. An application experiment was also conducted to evaluate the feasibility of the developed ozone-producing UV lamp/TiO₂ process for ethylene degradation.

METHODS

Equipment

Fig. 1 shows the experimental system employed in this investigation. The 0.55 L photoreactor consisted of a Pyrex glass cylinder with five inner cylinders. The three innermost cylinders were coated with the TiO₂ catalyst, and a UV lamp was inserted along the axial line of the reactor to serve as a UV source. The photoreactor was of an annular design with a wire net disposed at the inlet. Such a design enables production of a stable reaction by creating a laminar flow in the reactor. Each time, irradiation was carried out with one of three UV lamps: a black-light blue lamp (UV₃₆₅) with a maximum light intensity output at a wavelength of 365 nm (Sankyo Denki Co. Ltd.), a GL4 germicidal lamp (UV₂₅₄) with a maximum light intensity output at a wavelength of 254 nm (Sankyo Denki Co. Ltd.), and a GLZ4 ozone-producing lamp (UV₂₅₄₊₁₈₅) with a maximum light intensity output at a wavelength of 254 nm and a smaller (< 5%) output at a wavelength of 185 nm (Sankyo

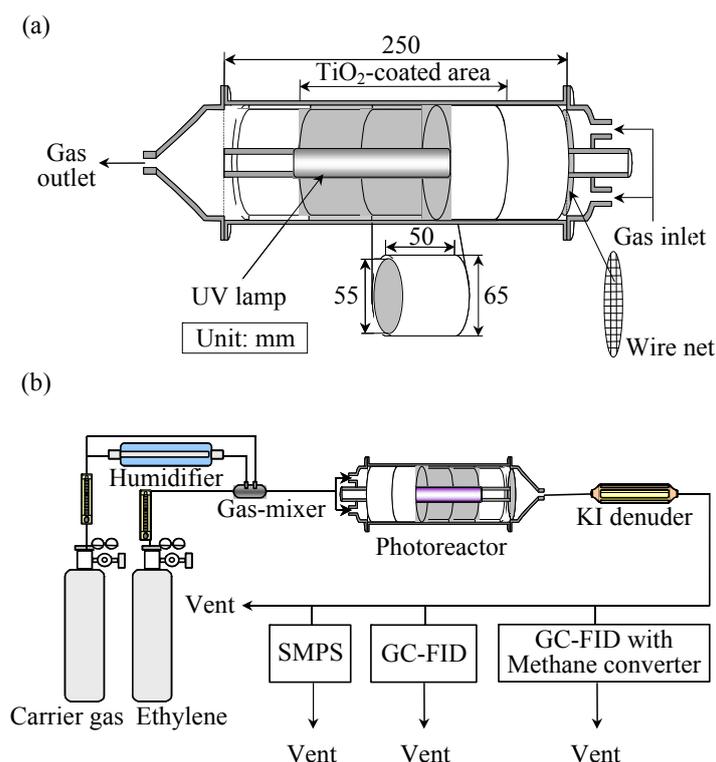


Fig. 1. (a) Cylindrical photoreactor. (b) Schematic diagram of experimental apparatus.

Denki Co. Ltd.). The electric power consumption of all three UV lamps was identical (4 W).

Catalyst Preparation

The catalyst used was Degussa P25 TiO₂ (75% anatase/25% rutile; Nippon Aerosil Co. Ltd.) with a Brunauer–Emmett–Teller (BET) surface area of 50 m²/g. A sonicated mixture of 5 g of TiO₂ in 300 mL of deionized water was dip-coated onto the innermost three cylinders of the photoreactor, and the cylinders were dried at 150°C for 2 h in an oven. The dipping procedure was repeated four times, and then the cylinders were dried at 150°C for 24 h. After the dipping procedure, approximately 40 mg of TiO₂ was coated on the inside of the cylinders (ca. 0.15 mg/cm²).

Experimental Operations and Methods

The ethylene concentration was adjusted to the desired value (the model VOC) by mixing ethylene standard gas with one of the desired atmospheres, i.e., dried high-purity air (N₂:O₂ = 8:2; RH < 1%, Suzuki Shokan Co. Ltd) or dried high-purity nitrogen gas (purity > 99.999%, RH < 1%, Suzuki Shokan Co. Ltd). The desired RH was obtained by passing dried air through a porous polytetrafluoroethylene tube containing deionized water at room temperature. The TiO₂ contact area was varied by the different number of the cylinders covered with TiO₂ photocatalyst. The reaction temperature was maintained at room temperature (298 ± 1 K). Before the gas stream containing ethylene and water was introduced into the photoreactor, clean air was allowed to flow through the illuminated photoreactor for 1 h to pretreat the catalyst. The UV irradiation experiments were

started once the inlet and outlet ethylene concentrations were equal (1 h).

The tested initial concentration of ethylene was in the range of 25.4–105 ppmv, and the RH in most experiments was < 1% (the RH was > 86% in high-humidity experiments). Most experiments were performed for a relatively long residence time (33 s), to achieve a laminar flow and stable photodegradation.

The conversion of ethylene was calculated from the following equations:

$$\text{Conversion of ethylene (\%)} = \frac{\{[\text{ethylene}]_{\text{in}} - [\text{ethylene}]_{\text{out}}\}}{[\text{ethylene}]_{\text{in}}} \times 100 \quad (17)$$

Meanwhile, in this study, a mineralization ratio is defined as the sum of product yield of inorganic CO₂ and CO to the decomposed ethylene amount.

Analysis

Syringe samples were periodically taken for analysis of the ethylene, CO and CO₂ concentrations during the test period. The ethylene concentrations in the effluent gas were measured by a gas chromatograph (GC 14B, Shimadzu Co. Ltd.) equipped with a flame ionization detector (FID). CO and CO₂ in the effluent gas were analyzed with a gas chromatograph (GC 15A, Shimadzu Co. Ltd.) equipped with a methane converter (MT-221, GL Science Co. Ltd.) and an FID. Calibration curves were prepared for quantitative determinations. In the 254 + 185 nm UV irradiation experiments, a KI (potassium iodide)-coated annular denuder was used to selectively remove the ozone,

since effluent gas with a high ozone content can seriously damage the GC column (Williams and Grosjean, 1990).

Size distributions of secondary organic aerosols (SOA), which were generated from photochemical oxidation of ethylene, were measured by using a scanning mobility particle sizer (SMPS 3934, TSI Co. Ltd.). The equipment was composed of a differential mobility analyzer (DMA: 3071A) and a condensation particle counter (CPC 3022). The flow rates of the aerosols and sheath air were set at 0.6 L/min and 6 L/min, respectively.

RESULTS AND DISCUSSION

In this study we tested the effects of UV wavelength (365, 254 and 254 + 185 nm), formation of labile species (OH radicals and O₃), reaction atmosphere (pure N₂ and air), relative humidity (RH < 1% and RH > 86%), residence time (11–33 s), initial concentration (25.4–105 ppmv) and TiO₂ contact area (86.4–259 cm²) on the decomposition of ethylene.

Comparison of Different UV Sources

Fig. 2 illustrates the effects of UV source on ethylene conversion and amount of CO + CO₂. The amount of ethylene converted under UV₂₅₄₊₁₈₅ irradiation was much higher than that converted under UV₃₆₅ or UV₂₅₄ irradiation. For UV₂₅₄₊₁₈₅ irradiation, conversion percentages of 45.1% were obtained with TiO₂, whereas conversion percentages of no more than 5.14% and 12.1% were obtained for UV₃₆₅ and UV₂₅₄ irradiation, respectively. In addition, the amounts of CO and CO₂, which are expressed in terms of mineralization, were enhanced.

As Eqs. (15) and (16) described, the relative humidity could significantly affect generation of •OH. Therefore the effects of relative humidity on the conversion of ethylene were examined with TiO₂ using the three UV sources (UV₃₆₅, UV₂₅₄, and UV₂₅₄₊₁₈₅), and the results are shown in Fig. 3. In the UV₃₆₅ and UV₂₅₄ irradiation systems, the amount of ethylene converted decreased with increasing

relative humidity. This phenomenon can be explained by water molecules impeding contact between ethylene and the catalyst, and competitive adsorption of water with ethylene on the catalyst surface. However, in UV₂₅₄₊₁₈₅ irradiation system, the conversion increased with increasing humidity. This can be easily explained by examining Eqs. (15) and (16), which explicitly indicate that a higher moisture content promoted the formation of reactive OH radicals. The generated OH radicals thus further promoted ethylene conversion.

Photochemical and Photocatalytic Degradation of Gaseous Ethylene by 254 + 185 nm UV Irradiation

In pure nitrogen with low relative humidity (RH < 1%) and without TiO₂, because nitrogen does not absorb photons with wavelengths exceeding 125 nm (Wang and Ray, 2000; Jeong et al., 2004), the irradiated UV photons (185 nm) are absorbed only by ethylene molecules. Therefore, it can be postulated that some ethylene degradation resulted from the direct photolysis reaction:



The conversion of ethylene by 254 + 185 nm UV irradiation alone was less than approximately 7%. Thus, the contribution to the decomposition of ethylene by 254 + 185 nm UV irradiation was minor. To characterize the photochemical and photocatalytic reaction, we examined photodegradation of gaseous ethylene in the presence or absence of TiO₂ under 254 + 185 nm UV irradiation, and the experiments were carried out in an air stream with two different values of RH, as shown in Table 1. Effective decomposition of ethylene without TiO₂ catalyst was due to photochemical degradation by abundant reactive species in the gas phase. However, reaction in the absence of TiO₂ is not ideal, because complete oxidation to CO₂ (only 3.16 ppmv) is not achieved. This can be explained by the fact that part of the conversion was caused by photolysis or ozone oxidation, which were weaker than OH radicals.

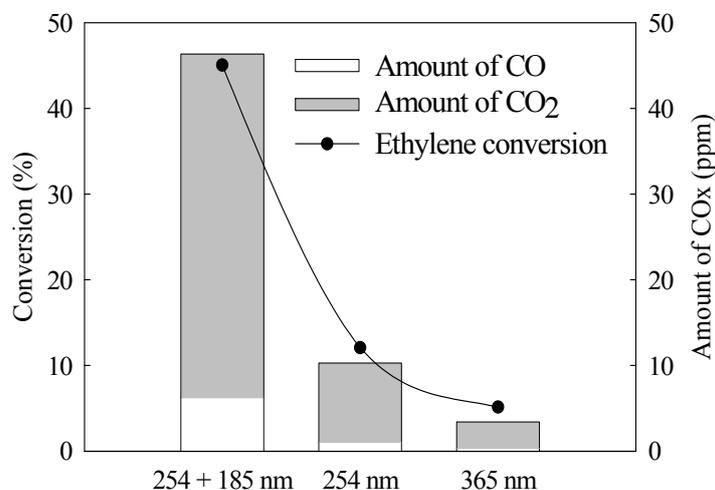


Fig. 2. Effect of UV source on ethylene conversion and amount of CO + CO₂. [C₂H₄]₀: 100 ppmv; retention time: 33 s; RH: > 86%.

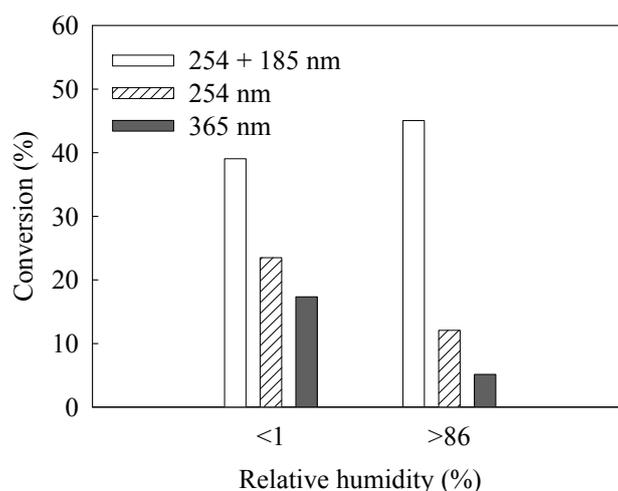


Fig. 3. Effect of RH on conversion of ethylene for UV irradiation using each of the three sources in the presence of TiO_2 catalyst. $[\text{C}_2\text{H}_4]_0$: 100 ppmv; retention time: 33 s.

Table 1. Conversion percentage and amount of $\text{CO} + \text{CO}_2$ in decomposition of ethylene in presence or absence of TiO_2 under $\text{UV}_{254+185}$ irradiation^a.

TiO_2	Relative humidity (%)	Conversion (%)	Amount of $\text{CO} + \text{CO}_2$ (ppmv)	
			CO	CO_2
Without	<math><1</math>	22.4	8.09	0.19
	>math>>86</math>	41.9	12.6	3.16
With	<math><1</math>	39.1	4.80	37.1
	>math>>86</math>	45.1	6.25	40.1

^a $[\text{C}_2\text{H}_4]_0$: 100 ppmv; retention time: 33.3 s.

Therefore, the use of a TiO_2 catalyst under 254 + 185 nm UV irradiation could increase the conversion of ethylene. We attributed the increased conversion of ethylene with the use of TiO_2 under 254 + 185 nm UV irradiation to a combined effect of photochemical oxidation in the gas phase and photocatalytic oxidation over the TiO_2 catalyst. From these results, the complete oxidation of ethylene could be accomplished with the appropriate arrangement of TiO_2 catalyst under 254 + 185 nm UV irradiation.

Influence of Parameters for Ethylene Degradation by 254 + 185 nm UV Irradiation

Effect of Residence Time

Fig. 4 shows the effects of residence time on the decomposition of ethylene under $\text{UV}_{254+185}$ irradiation. The conversion percentage decreased gradually as residence time decreased from 33 to 11 s, which corresponds to an increase in flow rate from 1 to 3 L/min. We attributed the gradual reduction to the decreased time of contact (contact time) between the reactants and hydroxyl radicals in the gas phase or on the catalyst surface. The results suggest that the photodegradation of VOCs can be improved by increasing the contact time between the reactants and hydroxyl radicals.

Effect of Initial Concentration

Fig. 5 shows that conversion decreased with increasing initial concentration of ethylene by 254 + 185 nm UV irradiation. Under high-concentration ethylene, ethylene

molecules were too much and reactants were not enough to decompose them. However, the availability of reactants in the low-concentration ethylene was sufficient. Therefore, higher conversions of ethylene were observed at a low initial concentration.

Effect of TiO_2 Contact Area

Fig. 6 shows the conversion of ethylene for various TiO_2 contact areas. The conversion of ethylene with TiO_2 contact areas of 83.4 and 173 cm^2 were 22.4 and 25.7%, respectively. It is of great significance that the conversion of ethylene was increased up to 39% with TiO_2 contact areas of 259 cm^2 . The increased conversion was due to the higher surface area. Consequently, the TiO_2 contact area is also a key factor for controlling ethylene decomposition.

Secondary Organic Aerosols

It has been reported (Jeong et al., 2004) that 254 + 185 nm UV irradiation of gaseous toluene generates secondary organic aerosols (SOAs) via gas-to-particle conversion of organic compounds in an air stream. Generally, SOAs are produced only when the oxidation of organic molecules to lead to products that have vapor pressures sufficiently low to allow them to condense into the aerosol phase. No SOAs were detected in photocatalysis using 365 or 254 nm UV irradiation, whereas it was found that with use of 254 + 185 nm UV irradiation, trace amounts of SOAs were formed, depending on the variation of RH.

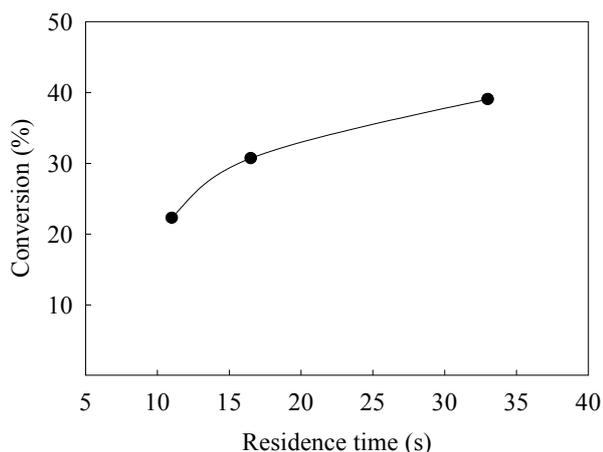


Fig. 4. Effect of residence time on decomposition of ethylene under $UV_{254+185}$ irradiation. $[C_2H_4]_0$: 100 ppmv; RH: < 1%.

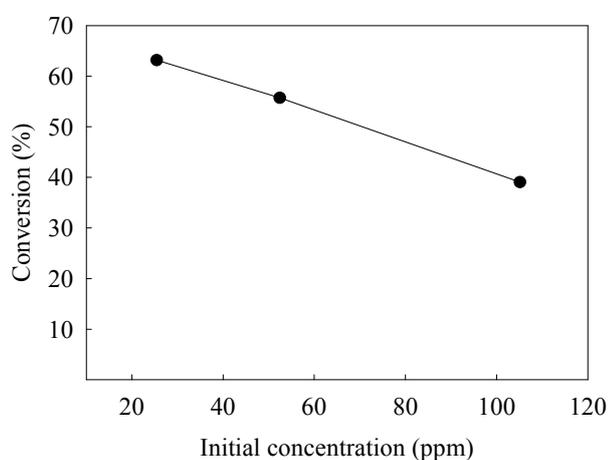


Fig. 5. Effect of initial concentration on conversion for decomposition of ethylene under $UV_{254+185}$ irradiation. Retention time: 33 s.; RH: < 1%.

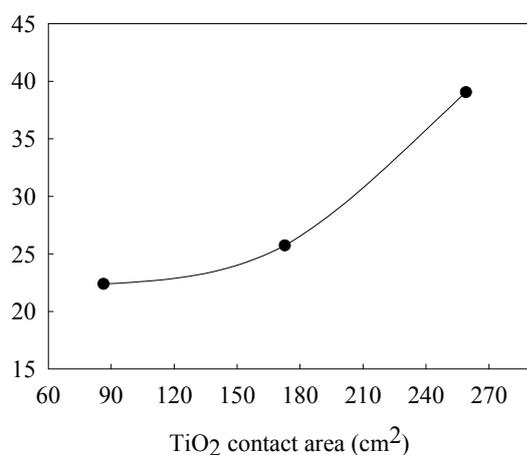


Fig. 6. Effect of TiO_2 contact area on conversion of ethylene under $UV_{254+185}$ irradiation. $[C_2H_4]_0$: 100 ppmv; retention time: 33 s; RH: < 1%.

Fig. 7 shows the number distributions of SOAs generated

from photodegradation of ethylene with low or high RH under $UV_{254+185}$ irradiation in the absence and presence of TiO_2 . As described in Fig. 7(a), an SOA was formed in the absence of TiO_2 , but not in the presence of TiO_2 . As shown in Fig. 7(b), it is apparent that reaction at high RH yielded many more SOAs than reactions at low RH. We consider that the SOAs formed from ethylene were low-molecular-weight dicarboxylic acids such as oxalic acid. Such low-molecular-weight acids have high hydroscopicity and need sufficient moisture to grow into particles, as was observed in the present study. Therefore, under the low RH condition, SOAs generation was not confirmed due to a decrease in not only the formation of the particle component but also a decrease in particle growth by water condensation. Under the high RH condition, the removal of SOAs was approximately 30%. The concentrations of components that could change into SOAs were decreased by TiO_2 and formation of a greater concentration of SOA was significantly inhibited. These results indicate that the concentration of generated SOAs decreased in presence of the TiO_2 catalyst and prove that TiO_2 may be used to effectively control the emission of undesirable SOAs. In addition, SOA can easily be removed rather than gaseous intermediates by using an existing method, such as particle charging using UV irradiation (UV/photoelectron method) (Sekiguchi *et al.*, 1998), an air filter, or a wet scrubber (Peukert and Wadenpohl, 2001).

Suggestion of Actual Application

On the basis of the experimental results, we suggest two systems for ethylene degradation using $UV_{254+185}$ irradiation with TiO_2 . The characteristics of the two systems are shown in Table 2. In the application, we decreased the flow rate and initial concentration of ethylene to 0.5 L/min and 34 ppmv, respectively. Table 3 lists the conversion and mineralization ratios for ethylene decomposition for various values of RH. Experimental results demonstrated that with photocatalytic oxidation under 254 + 185 nm UV irradiation at a flow rate of 0.5 L/min and an initial concentration of 34 ppmv, over 90% of the inlet ethylene can be degraded. In the plant ethylene emission, airborne ethylene may reach 20 ppb on annual averages and 1 ppm at hourly maximum concentrations as a result of industrial activity in polluted areas (Cape, 2003). In our application test, the ethylene concentration was much higher than industrial polluted areas. Therefore the system should be practical.

CONCLUSIONS

The feasibility of using $UV_{254+185}$ light for illumination of TiO_2 in the photodegradation of gaseous ethylene was evaluated. From the obtained results, it was clear that the conversion of ethylene under $UV_{254+185}$ irradiation was much higher than that obtained by irradiation with conventional UV sources (UV_{365} and UV_{254} irradiation), owing to the synergistic effect of photochemical degradation in the gas phase and photocatalytic degradation of TiO_2 . Given the obtained experimental data regarding the decomposition of gaseous ethylene in a photoreactor, the following conclusions can be drawn:

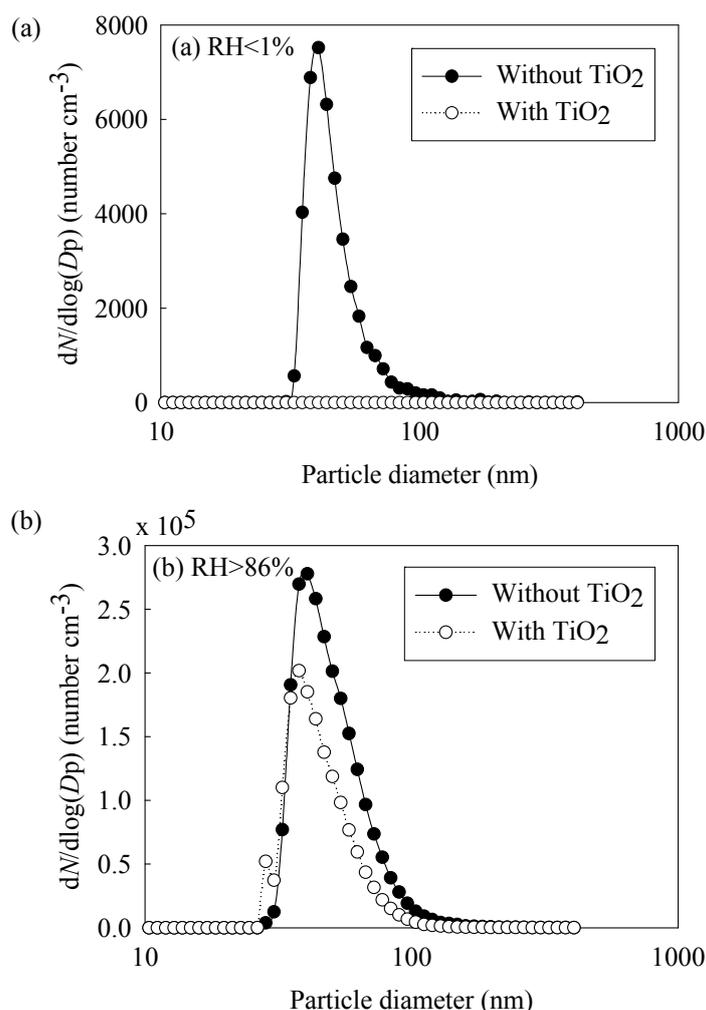


Fig. 7. Number distribution of SOAs generated in the presence or absence of TiO₂ under UV₂₅₄₊₁₈₅ light irradiation. (a) [C₂H₄]₀: 100 ppmv; retention time: 33 s; RH: < 1%; (b) [C₂H₄]₀: 100 ppmv; retention time: 33 s; RH: > 86%.

Table 2. Characteristics of two systems used for ethylene degradation with UV₂₅₄₊₁₈₅ irradiation with TiO₂.

Pre-treatment dry condition	High humidity condition
• Need pre-treatment for drying	• No pre-treatment
• Low removal ratio	• High removal ratio
• Low mineralization ratio	• High mineralization ratio
• High rate of O ₃ generation	• Low rate of O ₃ generation
• No generation of particles	• High rate of particle generation
• Need post-treatment for gas	• Need post-treatment for gas and particles

Table 3. Conversion and mineralization ratios for ethylene decomposition with UV₂₅₄₊₈₅ irradiation for various values of RH^a.

Relative humidity (%)	Conversion (%)	Mineralization ratio (%)
< 1	91.7	97.8
> 86	95.7	91.9

^a [C₂H₄]₀: 34 ppmv; flow rate: 0.5 L/min.

1. Use of TiO₂ with UV₂₅₄₊₁₈₅ irradiation significantly enhanced the photodegradation of ethylene compared with conventional UV sources (UV₃₆₅ light and UV₂₅₄ light) under most of the tested reaction conditions.
2. Generated SOAs may be comprised of hygroscopic

low-molecular-weight dicarboxylic acids and the concentration of the SOAs was somewhat reduced with the presence of TiO₂, because the concentrations of components (intermediates from ethylene), which are constituents of the SOAs, were decreased by TiO₂.

3. We propose that the combination of a dry apparatus and UV₂₅₄₊₁₈₅/TiO₂ treatment or UV₂₅₄₊₁₈₅/TiO₂ treatment and use of an existing method (photoelectron method, air filtration or wet scrubbing) are useful processes for effectively removing gaseous pollutants from the air, particularly those with high reactivity to OH radicals and ozone.
4. By means of photocatalytic oxidation with 254 + 185 nm UV irradiation at flow rate of 0.5 L/min and an initial concentration of 34 ppmv, over 90% of the inlet ethylene could be degraded and the main gaseous products obtained from ethylene were mineralized CO and CO₂.

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