J. Phys. Chem. A **2004,** *108,* 5183−5188

Reaction Mechanism of Photocatalytic Degradation of Chlorinated Ethylenes on Porous TiO_2 Pellets: Cl Radical-Initiated Mechanism

Suzuko Yamazaki,* Toshifumi Tanimura, and Atsushi Yoshida

Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan

Kenzi Hori

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Yamaguchi University, Ube 755-8611, Japan

Received: September 30, 2003; In Final Form: February 17, 2004

The photoassisted catalytic degradation of chloroethylene was studied in a tubular photoreactor packed with TiO_2 pellets prepared by a sol−gel method. The experiments were performed in a noncirculating mode. Kinetic data and the reaction products were compared with those for the photodegradation of ethylene, trichloroethylene, and tetrachloroethylene. The theoretical calculations at the MP4/6-31G**//B3LYP/6-31G** level indicated that the addition of OH radicals to chlorinated ethylenes is more exothermic than that of Cl radicals by 14.6−29.5 kcal mol^{-1}. Examination of Cl mass balance indicated that the concentration of Cl^- collected from the TiO_2 surface was higher than that from the product gas stream. When the photodegradation of ethylene was performed on the TiO_2 pellets which had been used for that of TCE or which were pretreated with HCl, the formation of chloroacetaldehyde was confirmed by the GC/MS. We proposed that during the photodegradation of the chlorinated ethylenes, the Cl^-, as one of the reaction products, accumulated and was oxidized to Cl radical on the TiO_2 surface, which might be due to the oxidation by OH radical. Then, the Cl radical reacted with chlorinated ethylenes, leading to the formation of undesirable chlorinated byproducts.

Introduction

Volatile chlorinated organic compounds (VCOCs) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) have been widely used as industrial solvents for degreasing metals and for dry cleaning.[1] Many soils and groundwater supplies have become contaminated as a result of leaking underground storage tanks and improper disposal practices. This contamination is a major issue because these chemicals are toxic, carcinogenic, and extremely persistent in the environment.

The use of TiO_2 photocatalysts for environmental cleanup has been of great interest since TiO_2 is stable, harmless, inexpensive, and potentially can be activated by solar energy.[2] The combination of a soil vapor extraction (SVE) unit and a gas-phase reactor with TiO_2 can be applied to the practical decontamination of VCOCs in the environment. Annular photoreactors packed with the TiO_2 pellets were field tested for 5 days at the Savannah River Site in Aiken, SC.[3] When the reactor was used to treat 222−1100 ppmv TCE and 1900−7000 ppmv PCE contained in the effluents from an SVE unit, no appreciable TCE and PCE were observed in the outlet gas stream, i.e., 100% conversion was achieved. However, carbon tetrachloride (40−100 ppmv) and chloroform (ca. 10 ppmv) were detected as the minor byproducts. These chemicals are suspected of being toxic and carcinogenic, and much effort has been expended in developing methods to degrade them and to detect them at trace levels.[4] Carbon tetrachloride is one of the chemicals difficult to degrade by TiO_2-mediated photocatalytic oxidation. Therefore, for the practical use of this technology, it is necessary to find operating conditions which do not produce such undesirable byproducts. This prompted us to clarify the reaction mechanism for the degradation of VCOCs on the TiO_2 pellets.

Some research groups have investigated the photooxidation of TCE in the gas phase.[5,6] Phosgene, dichloroacetyl chloride, and chloroform have been identified as byproducts.[7,8] Regarding the reaction mechanism, the roles of O_2^-, OH, and Cl radicals are still under consideration. Fan and Yates reported that the O_2^- radicals served as the major oxidizing agent of TCE and ruled out the involvement of the OH radicals.[6] Hwang et al. described that Cl radicals play an important role in the TCE photodegradation.[7] Murabayashi and co-workers suggested the involvement of Cl since phosgene was found to enhance the overall oxidation of TCE. [9,10] Previously, we have reported the formation of di- and trichloroacetates from the degradation of TCE[11,12] and PCE,[13,14] respectively, on the porous TiO_2 pellets and noted that reaction temperature and space time are key factors for the mineralization. We proposed that TCE and PCE were degraded by the Cl radical-initiated reaction to account for the detected byproducts.[14] In this paper, we describe kinetic data on the photodegradation of chloroethylene (CE) with a comparison of those for ethylene, TCE, and PCE and show new data indicating that an accumulation of Cl on the TiO_2 surface promotes a Cl radical-initiated reaction for the photodegradation of chlorinated ethylenes.

Experimental Section

Reagents and Apparatus. Chloroethylene (500 ppmv, balance nitrogen, Sumitomo Seika Chemicals Co.), nitrogen (99.999%), oxygen (99.999%), and synthesized air (oxygen 20.0−21.5%) were used as received from compressed gas

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* Corresponding author. Tel. & Fax.: +81-83-933-5763. E-mail: yamazaki@ yamaguchi-u.ac.jp.

10.1021/jp0311310 CCC: \$27.50

cylinders. Humidified air was prepared by bubbling gas through a glass saturator containing deionized water. Water content was fixed as a result of controlling temperature and the flowrate of the gas stream passing through the saturator. Porous TiO_2 pellets were prepared by sol−gel techniques and fired at 200 °C. Such a low firing temperature was chosen because more chloroform was produced with the pellets fired at higher temperature.[15] The specific surface area and porosity of these materials were 154 $m^2\ g^{-1}$ and 50%, respectively, as obtained by the BET analysis.

The photodegradation experiments were carried out in a packed bed tubular photoreactor (Pyrex, 11.5 cm long, 0.24 cm i.d., and 0.32 cm o.d.) in a noncirculating mode. Four 4 W fluorescent black light bulbs (Toshiba, FL 4BLB) surrounded the tubular reactor. Experiments at 32 °C were performed by passing cooling air through the photoreactor, and those at higher temperatures were carried out using heating tapes. The temperature of the gas stream was measured with a K-thermocouple placed in the center of the catalyst bed.

Analyses. The concentrations of CE and CO_2 as a product in the gas stream were analyzed by gas chromatography (Hewlett-Packard 5890 Series II equipped with a Porapak R column using flame ionization and thermal conductivity detectors).

The product gas streams were analyzed by GC/MS (HP 5890/HP 5970B) operating in the electron impact mode using a 60 m × 0.25 mm × 1.0 μm film thickness Aquatic column. Temperature-programming consisted of 35 °C hold for 10 min, ramping at 20 °C min^{-1} to 180 °C, and a 2 min hold at this temperature. The sample gas of 4 mL was introduced to the GC on line through a thermal desorption cold trap injector (Chrompack). The temperature for desorption or that at the injector port was 150 °C.

The identification of the carboxylates accumulated on the catalyst surface was performed by NMR (Bruker, Avance 400S) analysis. After the photodegradation experiments were carried out under the conditions where 100% CE was degraded, the carboxylates on the TiO_2 pellets (0.3 g) were extracted with six 20 mL portions of ether and then the ether was evaporated. The residue was dissolved in $CDCl_3$ for measurements.

Ion-chromatography (Yokogawa, IC 7000) was used to detect Cl^- ions which were formed by passing the product gas stream through water or by immersing the TiO_2 pellets into water after the photodegradation experiments.

Results and Discussion

Effect of "Space Time". We define "space time" as amount of catalyst employed divided by the molar flow rate of CE in the inlet gas stream.[16] Figure 1 shows effects of space times on conversions (defined as the CE molar flowrate degraded divided by the inlet CE molar flowrate) and on stoichiometric ratio of molar flowrate of CO_2 to that of CE degraded ($[CO_2]_{formed}/[CE]_{degraded}$) in the outlet gas. For comparison, the results for the degradation of ethylene, TCE, and PCE were also depicted. The behavior of CE was similar to that of TCE and PCE, i.e., CE was more efficiently photodegraded than ethylene and the stoichiometric ratio was less than 1. Most chlorinated ethylenes were not degraded to CO_2, although 95% of ethylene was mineralized. These results suggest that degradation behavior of CE is different from that of ethylene but similar to that of TCE or PCE although CE contained only one Cl atom.

Factors Affecting the Reaction Rate. The reaction rates with respect to CE disappearance were estimated under experimental conditions where the CE conversion was less than 10%. Under these conditions, the effect of intermediates or byproducts accumulated on the catalyst surface is negligible. Figure 1 suggested that the conversion less than 10% for CE corresponded to space time less than 2.6 × 10^6 g s mol^{-1}. We have already reported that the degradation rate of ethylene[17] and PCE[13] increased linearly with number of lamps irradiated. Therefore, the reaction rates for chlorinated ethylenes were obtained at the space time of 2.36 × 10^6 g s mol^{-1} with an irradiation of 1 lamp in order to secure the conversion less than 10%.

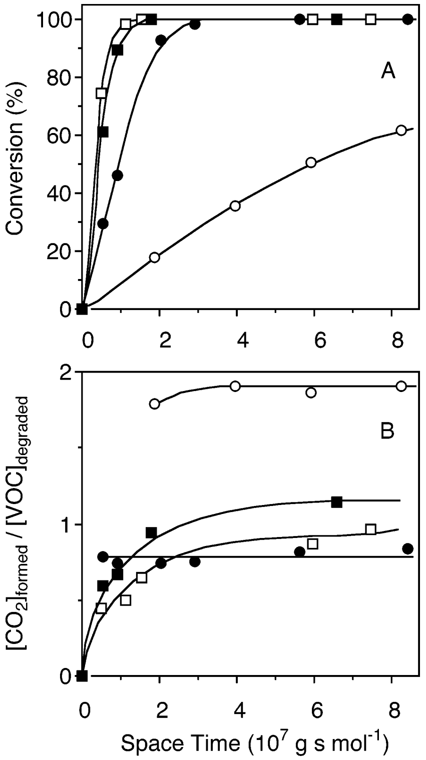


Figure 1. Effect of space time on conversion (A) and stoichiometric ratio (B). The mole fractions of VOC, oxygen, and water vapor were 1.76 × 10^{-4}, 0.203 and 1.61 × 10^{-3}, respectively. Four lamps were illuminated. VOC: ethylene (○), CE (●), TCE (□), PCE (■).

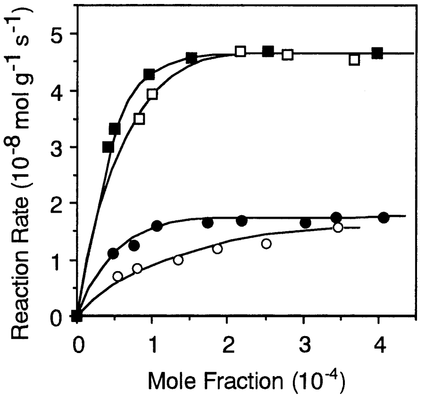


Figure 2. Dependence of reaction rate on VOC mole fraction. The mole fractions of oxygen and water vapor were 0.212 and 2.19 × 10^{-3}, respectively. One lamp for CE (●), TCE (□) or PCE (■) and four lamps for ethylene (○) were illuminated and 0.0522 g of TiO_2 was used.

The dependence of the reaction rates on the mole fractions of CE or oxygen is depicted in Figure 2 or Figure 3, respectively. Reaction rates increased with an increase in their mole fractions and reached a limiting value. These behaviors indicate that the reaction follows the Langmuir−Hinshelwood kinetic model where adsorption of the gas stream is assumed prior to reaction.[16]

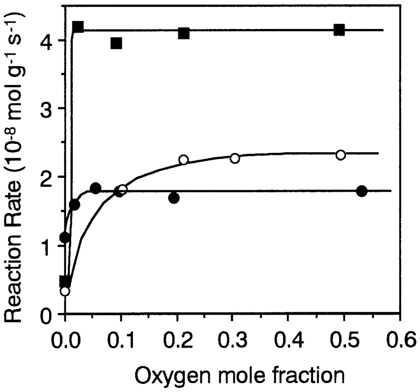


Figure 3. Dependence of reaction rate on oxygen mole fraction. The mole fraction of VOC and water vapor were 2.59×10^{-4} and 2.23×10^{-3}, respectively. Space time was 2.36×10^{6} g s mol^{-1} and 0.0419 g of TiO_2 was used. One lamp for CE (●) or PCE (■) and four lamps for ethylene (○) were illuminated.

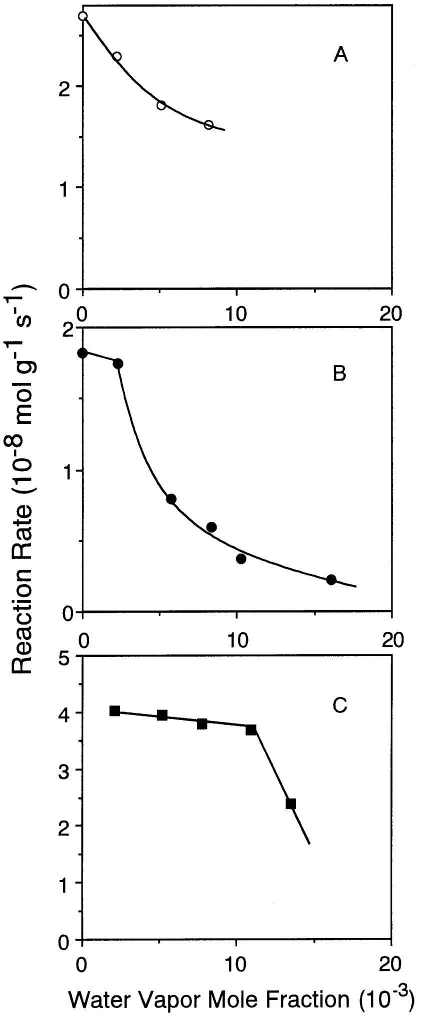


Figure 4. Effect of water vapor mole fraction on the degradation rate of ethylene (A), CE (B), and PCE (C). The mole fractions of VOC and oxygen were 2.55×10^{-4} and 0.206, respectively. Four lamps for ethylene and one lamp for CE or PCE were illuminated and 0.0423 g of TiO_2 was used.

TABLE 1: Reaction Products Detected from the Photodegradation of Ethylene, CE, TCE, and PCE

	products	
reactants	(in gas phase)	(on TiO_2 pellets)
ethylene	CO_2	
CE	CO_2, HCl	$CH_2ClCOOH$
TCE	CO_2, HCl, $CHCl_3$, $COCl_2$	$CHCl_2COOH$
PCE	CO_2, HCl, CCl_4, $COCl_2$	CCl_3COOH

Figure 4 illustrated an influence of water vapor on the reaction rate. When the experiments were performed in a feed gas stream containing 255 ppmv CE, the reaction rate with 2.23×10^{3} ppmv H_2O was almost the same as that without H_2O and then decreased greatly with an increase in the H_2O mole fraction (Figure 4 B). Such a region where reaction rate was independent of water vapor was also observed in the photodegradation of PCE, but the region extended up to 1.09×10^{4} ppmv H_2O (Figure 4C). On the contrary, such an independent region was not observed in the degradation rate of ethylene (Figure 4A). This difference is attributable to the H_2O amount adsorbed on the catalyst surface.

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \qquad (1)$$

$$C_2H_3Cl + {}^{5}\!/_{2}O_2 \rightarrow 2CO_2 + HCl + H_2O \qquad (2)$$

$$C_2Cl_4 + 2H_2O + O_2 \rightarrow 2CO_2 + 4HCl \qquad (3)$$

The degradation of ethylene and CE formed water as a product, while no H_2O was yielded from the PCE degradation. We used the single-pass reactor, and reaction rates were calculated after reaching a steady state. The abscissa in Figure 4 indicated water vapor mole fractions in the feed gas stream, but the H_2O amounts adsorbed on the TiO_2 surface at the steady state must be varied for the degradation of ethylene, CE, and PCE. Equations 1−3 suggested, even in the absence of water in the feed gas stream, more adsorbed H_2O existed on the TiO_2 surface in the following order: ethylene > CE > PCE. This is the reason that the independent region of H_2O was not observed for ethylene and was shorter for CE than PCE. The decrease in the reaction rate observed with high water vapor contents is due to the inhibitory effect of water on the adsorption of ethylenes on the TiO_2 surface.

We have reported that the degradation rate of TCE or PCE was independent of reaction temperature but the stoichiometric ratio increased with temperature.[13] Similar behavior was observed in the degradation of CE; the ratio was estimated to be 1.23 at 90 °C, indicating that 61.5% of CE was mineralized.

Reaction Products. The GC/MS measurements were conducted with product gas streams under the reaction temperature of 32 or 93 °C, but no gaseous product except CO_2 was detected from the photodegradation of CE. The ^1H NMR measurements for determination of the intermediate accumulated on the TiO_2 pellets showed a peak at a chemical shift of 4.2 ppm which was coincident with that for the authentic sample of $CH_2ClCOOH$. Table 1 summarized products from the degradation of ethylene, CE, TCE,[14] and PCE.[14] The quantitative analysis of the GC/MS indicated that formation of $CHCl_3$ as much as 1−2 ppmv was observed from the degradation of 170 ppmv TCE. The formation of all these products was explained in terms of a Cl radical-initiated mechanism as shown in Scheme 1.

Reaction Mechanism. In the photodegradation of organic compounds on the TiO_2 photocatalyst, it has been often postulated that the photogenerated holes react with adsorbed water molecules to form OH radicals which oxidize organic compounds. The addition of OH radicals to the C=C double bond in CE was followed by Cl elimination. Figure 5 indicated by theoretical calculations at MP4/6-31G**//B3LYP/6-31G** level that the addition of a Cl radical to carbon at the CH_2 side was calculated to be more exothermic by 5.6 kcal mol^{-1} than that at the CHCl. The obtained carbon-centered radicals,

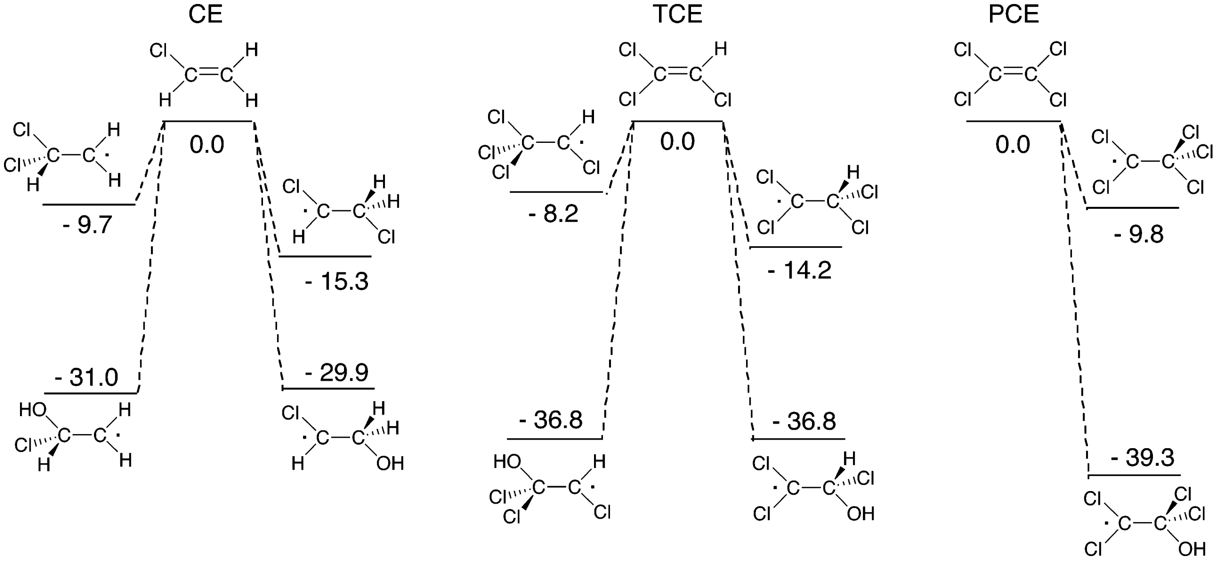
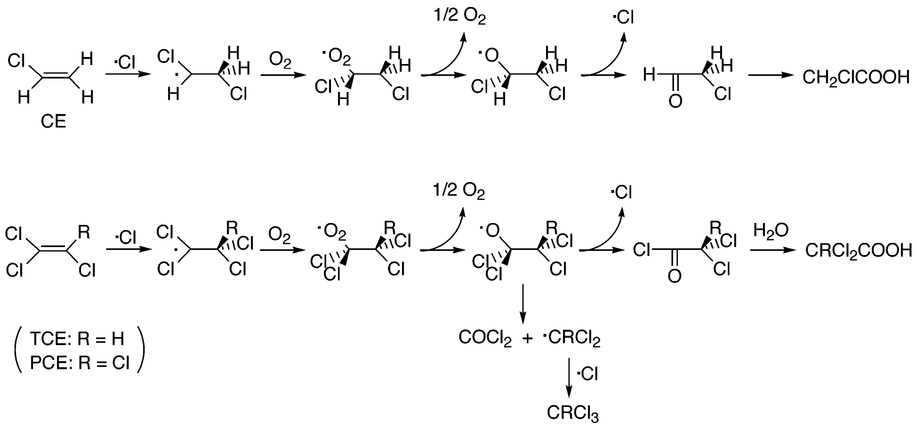


Figure 5. Energy-level diagram of the degradation of CE, TCE, and PCE with OH or Cl radical. Energies (kcal mol^{-1}) were calculated with MP4/6-31G**//B3LYP/6-31G** calculations.

SCHEME 1



CHClCH$_2$Cl, subsequently react with oxygen to form peroxy radicals as shown in Scheme 1. These species are converted to chloroethoxy radicals by reaction with a second peroxy radical. The elimination of Cl radicals from the chlorinated ethoxy radicals leads to the formation of chloroacetaldehyde. Acetaldehyde and chloroacetaldehyde have been reported to be oxidized to acetic acid and chloroacetic acids, respectively, on the TiO$_2$ surface.[18,19] In the case of TCE or PCE, similar reactions gave di- or trichloroacetyl chlorides which are converted to di- or trichloroacetic acids by hydrolysis.[20,21] The formation of phosgene and CHCl$_3$ or CCl$_4$ was explained in terms of C−C bond scission of the chlorinated ethoxy radicals followed by the addition of Cl radicals. Thus, the Cl radical-initiated mechanism can explain all the intermediates and products which were formed from the photodegradation of chlorinated ethylenes. However, theoretical calculations in Figure 5 also indicated that the addition of OH radicals to chlorinated ethylenes is more exothermic than that of Cl radicals by 14.6−29.5 kcal mol^{-1}. Thus, it is unlikely that the addition of a Cl radical to the chlorinated ethylenes proceeds more predominantly than that of an OH radical. Higher concentrations of Cl radicals than OH on the surface are required to promote the Cl radical-initiated reaction which is less favorable thermodynamically. Thus, we examined the mass balance of Cl$^-$ as a reaction product.

TABLE 2: Stoichiometric Ratio of $[\mathrm{Cl}^-]_{\mathrm{formed}}/[\mathrm{VOC}]_{\mathrm{degraded}}$

VOC	$[\mathrm{Cl}^-]_{\mathrm{formed}}$ [a] (in gas phase) / $[\mathrm{VOC}]_{\mathrm{degraded}}$	$[\mathrm{Cl}^-]_{\mathrm{formed}}$ (on TiO$_2$) / $[\mathrm{VOC}]_{\mathrm{degraded}}$
CE	0.033	0.341
TCE	0.994	1.44
PCE	1.21	1.95

[a] Total concentration of Cl$^-$ detected in four traps.

Cl Mass Balance. After 100% conversion was achieved with a feed gas stream containing 128−178 ppmv chlorinated ethylenes, 2.30×10^5 ppmv O$_2$, and 2.06×10^3 ppmv H$_2$O, the product gas stream was successively passed through four water traps for 6 h, each of which contained 250 mL of water at pH 11.4. The conversion was maintained to be 100% during conducting the effluent gas to these traps. The total amount of Cl$^-$ was determined, and the stoichiometric ratio of $[\mathrm{Cl}^-]_{\mathrm{formed}}/[\mathrm{VOC}]_{\mathrm{degraded}}$ was listed in Table 2. The Cl$^-$ amounts adsorbed on the TiO$_2$ surface were determined by immersing the TiO$_2$ pellets into water after the photodegradation experiments. Table 2 shows that the Cl$^-$ dissolved from the pellets was more than that from the product gas stream. This means that Cl accumulates on the TiO$_2$ surface, although it is unclear whether it exists as Cl$^-$, Cl$_2$, or HCl. For the degradation of CE, these ratios were totally calculated to be 0.374 for $[\mathrm{Cl}^-]_{\mathrm{formed}}/[\mathrm{CE}]_{\mathrm{degraded}}$, suggesting that 37.4% of CE was mineralized to HCl and CO$_2$. This value is in good agreement with the mineralization of 38.8% which was estimated from the ratio of $[\mathrm{CO}_2]_{\mathrm{formed}}/[\mathrm{CE}]_{\mathrm{degraded}}$ of 0.776. Therefore, 61−63% of CE was

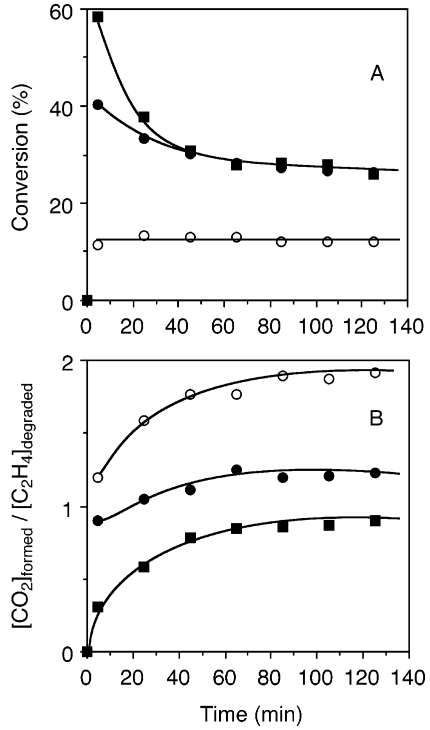


Figure 6. Effect of irradiation time on conversion (A) and stoichiometric ratio (B) for the photodegradation of ethylene on fresh TiO_2 pellets (○), TiO_2 pellets after TCE photodegradation (●), or TiO_2 pellets pretreated with HCl (■). The mole fractions of ethylene, oxygen, and water vapor were 1.60×10^{-4}, 0.210 and 2.30×10^{-3}, respectively. Four lamps were illuminated, and space time was 1.81×10^7 g s mol^{-1}.

converted to chloroacetate. On the other hand, for TCE or PCE, the mineralization percent derived from the determination of Cl^- was higher than that from CO_2. This is due to the formation of Cl^- from the decomposition of phosgene in water.[14]

Degradation of Ethylene on the TiO_2 Which Had Been Used for TCE Degradation. Figure 6 depicted time-course of conversion or stoichiometric ratio for the photodegradation of ethylene with various TiO_2 pellets. With fresh TiO_2, the conversion for the ethylene degradation remained constant at 12.4 ± 0.5% during the irradiation for 125 min, while the stoichiometric ratio increased with an irradiation time and reached a steady state of 1.9. On the other hand, when the experiments were performed with the TiO_2 which had been used for the TCE photodegradation for 4 h (hereafter, denoted as the TiO_2/TCE pellets), the conversion decreased from 40.2 to 26.4% and the stoichiometric ratio reached 1.22. The degradation rate of ethylene was accelerated by a factor of 2.1−3.2 than that with fresh TiO_2. Such an increase in the conversion and a decrease in the stoichiometric ratio were similar to the behavior of the chlorinated ethylenes compared with that of ethylene as shown in Figure 1. The GC/MS analysis of the product gas stream gave three peaks whose mass spectra were identical with those of CO_2, phosgene, and chloroacetaldehyde in the mass spectral library. It is noted that CO_2 and phosgene were also formed upon irradiation when a humid air containing no ethylene was passed through the TiO_2/TCE pellets. This means that dichloroacetates which accumulated on the TiO_2 surface during the TCE photodegradation were photodegraded to CO_2 and phosgene in the humid air stream. The peak area for phosgene which was calculated from the m/z 63 fragment was 5 times higher than that detected in the product gas stream during the ethylene degradation on the TiO_2/TCE pellets. This indicates that in the latter case, the photodegradation of ethylene competed with that of dichloroacetates accumulated on the TiO_2 surface. The photodegradation of dichloroacetates may affect the formation of chloroacetaldehyde. Thus, we performed the ethylene degradation with the TiO_2 pretreated with HCl. Such TiO_2 pellets were prepared by immersing into 6 mol dm^{-3} HCl for 1 day followed by filtration for drying. The conversion was obtained to be 58.4% and decreased to 26.1% at the irradiation for 125 min while the stoichiometric ratio reached 0.90, suggesting that only 45% of ethylene was mineralized. The formation of chloroacetaldehyde was confirmed by the GC/MS measurements. Therefore, the accumulation of the Cl^- on the catalyst surface is responsible for the formation of chloroacetaldehyde from the degradation of ethylene on the TiO_2/TCE pellets.

Conclusions

We proposed the photodegradation mechanism of the chlorinated ethylenes as follows: one of the reaction products, i.e., the Cl^- accumulated and was oxidized to Cl radical on the TiO_2 surface, which might be due to the oxidation by OH radical. Then, the Cl radical reacted with chlorinated ethylenes, leading to the formation of undesirable chlorinated byproducts.

In this study, we used the single-pass reactor where feed gas stream is continuously supplied and product gas stream is continually removed. Nevertheless, the Cl^- accumulated on the catalyst surface, leading to the Cl radical-initiated reaction. The formations of dichloroacetate and phosgene from the TCE photodegradation were reported by other research groups who carried out the experiments in a closed IR cell[6,22] or sealed NMR tubes.[7] Hegedus et al. detected phosgene and trichloroacetyl chloride as intermediates from the PCE photodegradation using an in situ photocatalytic reactor with FT-IR analysis in batch mode.[23] Sano et al. described the formation of chloroacetyl chloride from the CE photodegradation in a closed gas circulation system.[24,25] The Cl radical-initiated reaction occurs more easily in such reactor systems where there is no addition of reactants or removal of products.

The formation of undesirable chlorinated byproducts such as $CHCl_3$, CCl_4, phosgene, and chloroacetates should be suppressed in order to develop the remediation techniques using TiO_2 for practical application. The reaction mechanism as in Scheme 1 suggests that, if we could trap Cl radical not to react with the chlorinated ethylenes, the undesirable byproducts would not be formed. We are now trying to find reaction conditions to stop the Cl radical-initiated reaction.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government. We also thank the Sumitomo Foundation for the financial support.

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