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Photocatalytic mineralization of vinyl chloride on TiO₂

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Abstract

Vinyl chloride monomer (VCM; CH₂CHCl) was photocatalytically mineralized on TiO₂ (anatase and rutile) and ZnO at room temperature. The VCM decomposition rate was larger in the order of anatase > rutile > ZnO. VCM was decomposed into CO₂, CO, HCl and long-lived intermediates (formic acid and monochloroacetyl chloride), which were further decomposed into CO₂ and H₂O; more than 99.5% of carbon atoms in VCM were changed to CO or CO₂ by UV irradiation on TiO₂ (P25) within 360 min. Formic acid was also formed in the photocatalytic decomposition of ethylene on the TiO₂ pretreated with VCM. Cl⁻ ions adsorbed on TiO₂ participated in the decomposition of VCM or ethylene and enhanced the formation of formic acid and CO. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vinyl chloride; Photocatalyst; TiO₂; Chloride ion; Formic acid

1. Introduction

Vinyl chloride monomer (VCM) is produced on a large scale for raw material of poly(vinyl chloride) (PVC), and a part of VCM is emitted into the atmosphere. As VCM has carcinogenicity, mutagenicity and teratogenicity, the emission of VCM should be reduced for human health [1–3]. Photocatalytic decomposition of VCM is one of the candidates for its removal method. Because photocatalysts are suitable for treatment of low concentration gases and are used at room temperature with sunlight as the energy source, the photocatalytic decomposition has many advantages: concentration process is not necessary, reaction conditions are mild, and utilization of sunlight leads to energy saving [4,5].

Several authors have reported photocatalytic decomposition of ethylene and chloroethylenes includ-

ing *cis*-dichloroethylene (C₂H₂Cl₂), trichloroethylene (C₂HCl₃) and tetrachloroethylene (C₂Cl₄) [6–12], however, the decomposition of VCM on photocatalyst has not been reported. In an ideal photocatalytic mineralization of chlorinated hydrocarbon, it will be oxidized into CO₂, H₂O and HCl [9]. However, the complete mineralization is oftentimes not realized as by-products are formed by partial oxidation. In the mineralization of C₂HCl₃ and C₂Cl₄ by TiO₂ photocatalyst, the formations of CO, dichloroacetyl chloride, monochloroacetyl chloride (MCAC), dichloroacetic acid, monochloroacetic acid and phosgene (COCl₂) were reported [7–9]. These byproducts are even more toxic than the starting compounds. Since a VCM molecule contains a Cl atom and a C=C bond, the photocatalytic VCM decomposition has possibilities of producing the above by-products or other long-lived intermediates.

In the present paper, the photocatalytic mineralization of VCM on TiO₂ and ZnO was studied, concerning the formation of long-lived intermediates. The mechanism of the mineralization and the

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Table 1
Characteristics of photocatalysts used for VCM decomposition

Sample	Composition	Phase	Surface area (m ² g ⁻¹)	Band gap (eV)
ST-01	TiO ₂	Anatase	200	3.2
P25	TiO ₂	Anatase (80%) + rutile (20%)	50	3.2
TTO-55	TiO ₂	Rutile	30	3.0
Kadox 25	ZnO	Wurtzite	12	3.2

role of Cl⁻ ion adsorbed on photocatalyst were also discussed.

2. Experimental

Three types of TiO₂ (P25, Degussa; ST-01, Ishihara; and TTO-55, Ishihara) and ZnO (Kadox 25, New Jersey Zinc) were used for photocatalytic decomposition of VCM. The characteristics of the photocatalysts are listed in Table 1. A 0.3 g portion of photocatalyst powder was dispersed into 10 cm³ of distilled water, which was spread on a glass plate (100 cm²) and dried at 110°C for 12 h to fix the photocatalyst. For TTO-55, 0.5 g of photocatalyst was used to equalize its surface area with that of P25.

The glass plate with photocatalyst was placed in the reaction vessel (1.83 × 10³ cm³) with a cover window of Tempax glass (8 mm thickness, cut off wavelength 300 nm). The surface of photocatalyst was cleaned by UV irradiation in dry air for 10 h to remove organic impurities. The photocatalytic decomposition was carried out in a closed gas circulation system (total volume: 2.54 × 10³ cm³) with a multireflection gas cell (path length 3 m) for Fourier transform infrared spectroscopy (FT-IR). After the reaction vessel was evacuated, the required volume of VCM gas (5200 ppm, N₂ balance, from Takachiho Chemicals) was introduced into the vessel (VCM 0.22 kPa, 0.24 mmol), and then dry air (research grade synthetic air in a cylinder) was added until the inner pressure became the atmospheric pressure. The initial pressure of O₂ was 59 kPa. In the study of the effect of water vapor, distilled water was introduced into the reaction vessel by a micro syringe to be vaporized.

In the photocatalytic decomposition of VCM, the photocatalyst was irradiated with UV light from black light lamps (Toshiba FL10BL, 10 W) through the Tempax glass window. The UV irradiance at

the sample surface was controlled between 0.24 and 0.63 mW cm⁻² by changing the number of black light lamps. All the photocatalytic reactions were carried out at room temperature (298 K). Gasses in the reaction vessel were analyzed using an FT-IR spectrometer (JASCO, FT-IR 610) with a long path gas cell. The partial pressures of gasses were calculated from the absorbance areas, which had been calibrated with standard gasses. The solid phases were analyzed by powder X-ray diffractometry (XRD) with Cu K α radiation (Rigaku, model RU-300). The specific surface areas of photocatalysts were determined by BET method with N₂ adsorption at 77 K with a Quantachrome AS-1. The amount of Cl⁻ ion adsorbed on TiO₂ was determined by washing the photocatalyst with purified water (Millipore, Milli-Q system) and analyzing the washings by an ion chromatograph (Shimadzu, HIC-6A with CDD-6A).

3. Results and discussion

3.1. Photocatalytic activities of TiO₂ and ZnO for VCM decomposition

Fig. 1 shows the profiles for photochemical reaction of VCM over TiO₂ (ST-01, P25 and TTO-55) and ZnO (Kadox 25) under dry condition. The partial pressure of VCM in the reaction vessel decreased in the presence of each metal oxide under UV irradiation. The VCM introduced into the reactor (240 mmol) was completely removed in 30 min by ST-01 and in 60 min by P25. When the metal oxides were not irradiated by UV light, VCM was not removed. In the VCM removal, no change in the TiO₂ crystal was observed by XRD. These results suggest that VCM was photocatalytically decomposed by TiO₂. Since the VCM partial pressure was decreased linearly with time, the VCM decomposition rate was not dependent on VCM partial

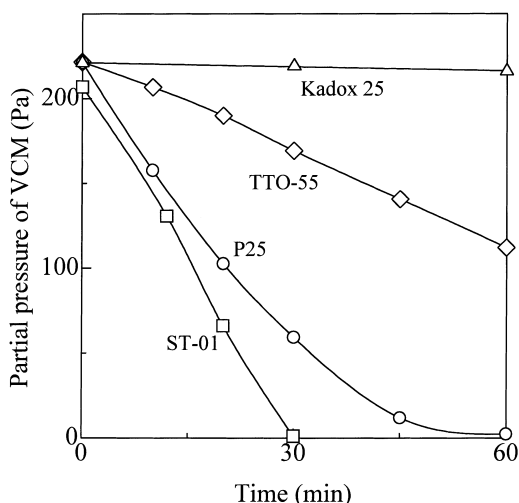


Fig. 1. Decomposition of VCM by TiO₂ (ST-01 (□), P25 (○), TTO-55 (◇)) and ZnO (Kadox 25 (△)). Photocatalyst: 0.3 g, initial VCM pressure: 0.22 kPa, UV-A irradiance at the photocatalyst: 0.63 mW cm⁻².

pressure and VCM adsorption rate. This suggests that the rate-determining step of the photocatalytic VCM decomposition is the formation of active species on TiO₂ surface, which will decompose adsorbed VCM, under the experimental conditions in the present study.

The VCM decomposition rate increased in the order of Kadox 25 (ZnO) \ll TTO-55 (TiO₂, rutile) < P25 (TiO₂, anatase 80% and rutile 20%) < ST-01 (TiO₂, anatase). Although the surface area of P25 was about four times as large as that of Kadox 25 (Table 1), the decomposition rate by P25 was 100 times larger than that of Kadox 25. This suggests that TiO₂ is more active for VCM decomposition than ZnO under the present experimental conditions. In the photocatalytic decomposition of C₂HCl₃, TiO₂ showed higher activity than ZnO, which was attributed to higher absorption ability of TiO₂ [9]. Since the structure of VCM molecule is similar to C₂HCl₃ molecule, the higher VCM decomposition activity of TiO₂ may be also attributed to the adsorption ability. The higher activity of P25 than TTO-55 suggests that anatase phase is more active for VCM decomposition than rutile phase. This may be due to the larger band gap or the higher electron mobility of anatase than rutile, or the difference in concentrations of OH groups on their surface [9,13]. In the present data, we could not clarify the dominant factors. ST-01 shows the highest decomposition rate

among the photocatalysts examined. This may be attributed to both the larger specific surface area and the higher content of anatase phase.

3.2. Analysis of VCM mineralization process

The VCM mineralization process was analyzed by gas-phase FT-IR spectroscopy. Fig. 2a–d denotes the spectra taken at different stages in the mineralization by P25. Before UV irradiation (Fig. 2a), only the absorption peaks of VCM were observed. After UV irradiation for 20 min (Fig. 2b), the peaks of VCM became smaller, and the peaks of CO₂, CO, H₂O, HCl, formic acid (FMAC; HCOOH) and monochloroacetyl chloride (MCAC; CH₂ClCOCl) appeared. The formation of FMAC was a unique reaction among the photocatalytic decomposition of ethylene and other chloroethylenes. HCOCl, CHCl₃, and CCl₄ were not detected although these molecules were formed in the

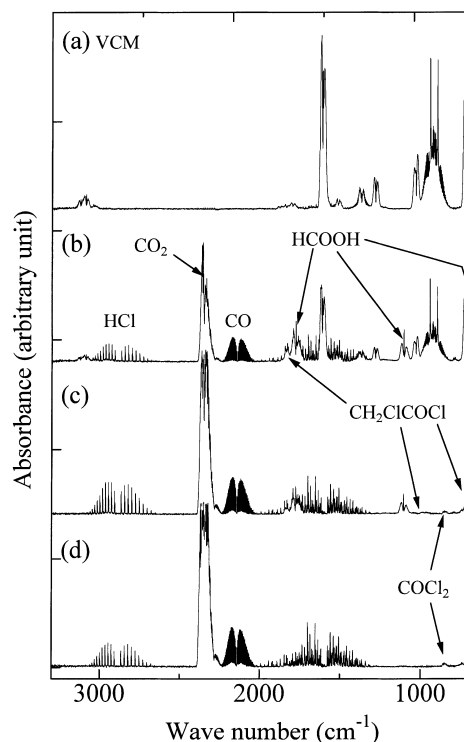


Fig. 2. Gas-phase FT-IR spectra taken at different stages of photocatalytic VCM mineralization by P25; (a) before UV irradiation, (b) after UV irradiation for 20 min, (c) 60 min, and (d) 360 min. UV irradiance was 0.63 mW cm⁻².

photocatalytic decomposition of C_2HCl_3 or C_2Cl_4 . After UV irradiation for 60 min (Fig. 2c), the peaks of VCM disappeared and the small absorption of $COCl_2$ was observed. The partial pressures of $COCl_2$ and MCAC were 0.4 and 4.8 Pa at maximum, which corresponded to 0.2 and 2.4% of removed VCM, respectively. Since $COCl_2$ and MCAC contain two Cl atoms in each molecule, their formation suggests that VCM reacted with Cl^- ion or chlorine containing species. FMAC and MCAC were completely removed within 360 min, however, 0.4 Pa of $COCl_2$ remained (Fig. 2d). $COCl_2$ was not decomposed under dry condition, however it is hydrolyzable under humid condition [9]. In the VCM mineralization by TTO-55, HCl, FMAC, $COCl_2$ and MCAC were produced along with CO_2 , H_2O and CO similarly to the case by P25. However, the production of HCl and the organic compounds were not detected during the mineralization by ST-01.

The time courses of partial pressures of VCM and products in photocatalytic VCM mineralization were analyzed and shown in Fig. 3a and b. $C_{(ads)}$ denotes the part of carbon compounds that were not detected by FT-IR measurement and may be adsorbed on TiO_2 and the reactor wall. The amount of $C_{(ads)}$ was determined from the mass balance of removed VCM, formed CO_2 , CO and FMAC, and is plotted by converting to partial pressure. After UV irradiation on P25 for 360 min (Fig. 3a), the amount of $C_{(ads)}$ became approximately zero. This indicates that the adsorbed carbon compounds ($C_{(ads)}$) were finally decomposed into CO and CO_2 . Therefore, they were regarded as long-lived intermediates.

The VCM mineralization by P25 is composed of three stages (Fig. 3a). The first stage is decomposition of VCM with the formation of CO, CO_2 , HCl and long-lived intermediates (FMAC and $C_{(ads)}$) (0–45 min). The second stage is decomposition of FMAC and the intermediates adsorbed on TiO_2 (45–120 min). The last stage is slow decomposition of the intermediates with low reactivities (120–360 min). In the first stage, the VCM partial pressure decreased linearly with irradiation time, and the partial pressures of CO_2 and CO increased linearly. The CO_2 formation rate was approximately same as that of CO (CO_2/CO ratio was 1). The partial pressure of FMAC increased during the first 30 min of UV irradiation (17 Pa at maximum), and then decreased. While the VCM was present in the gas phase, the amount of intermediates

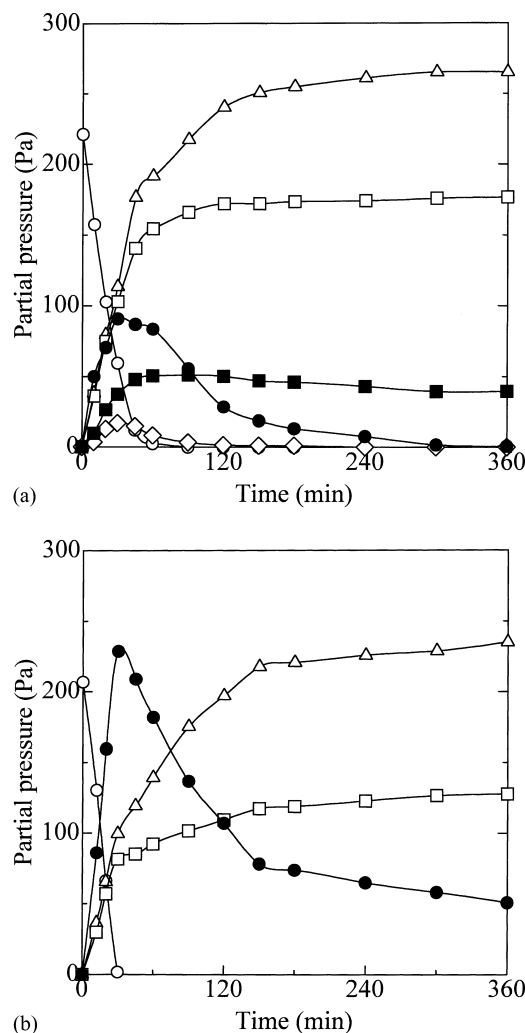
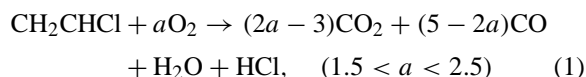


Fig. 3. Time courses of partial pressures of VCM and products in photocatalytic VCM mineralization by (a) P25 and (b) ST-01. UV irradiance was 0.63 mW cm^{-2} . (○) VCM, (△) CO_2 , (□) CO, (◇) FMAC, (■) HCl, and (●) $C_{(ads)}$.

increased. After all VCM disappeared, the amount of intermediates decreased quickly (second stage), where the formation rate of CO was smaller than that of CO_2 ; CO_2/CO ratio was 3.3. This indicates that the decomposition of intermediates produces preferably CO_2 rather than CO. The amounts of CO formed in the first and second stages were 80 and 18%, respectively, of the total amount of CO formed through the three stages. This suggests that the formation of CO is mainly due to the direct decomposition of VCM rather

than that of intermediates. In the last stage, the amount of adsorbed carbon species ($C_{(ads)}$) decreased gradually and the CO_2 partial pressure increased slightly. The CO_2 formation was quite slower than that in the first or second stage. It is speculated that organic compounds with low reactivities were formed on TiO_2 in the VCM decomposition (first stage) and that those species were gradually decomposed into CO_2 .

More than 99.5% of carbon atoms in VCM were photocatalytically changed into CO or CO_2 by P25 within 360 min. On the other hand, only 16 and 0.2% of Cl atoms in VCM were detected as HCl and $COCl_2$, respectively, in the gas phase by FT-IR. The amount of Cl^- ion adsorbed on the photocatalyst was determined to be $34 \mu\text{mol}$ (15% of decomposed VCM) by washing the photocatalyst with purified water and analyzing the washings by an ion chromatograph. Cl_2 gas was not detected by colorimetry with *o*-toluidine, although the formation of Cl_2 gas has been reported in the photocatalytic decomposition of C_2HCl_3 and C_2Cl_4 [7]. The residual Cl atoms in decomposed VCM may be adsorbed on the reactor wall as Cl^- . The total reaction is approximately represented as follows:



The VCM mineralization by ST-01 (Fig. 3b) proceeded through three stages similar to the mineralization by P25. In the first stage, the VCM decomposition rate by ST-01 was larger than that by P25, while the formation rates of CO_2 and CO by ST-01 were not so different from those by P25. As a result, a large amount of adsorbed intermediates ($C_{(ads)}$) was formed on ST-01. The amount of adsorbed intermediates (0.25 mmol at maximum) was much larger than that formed on P25 (0.099 mmol). The conversion of VCM into CO and/or CO_2 by ST-01 in 360 min-UV irradiation was 88%, which was lower than that by P25 (99.8%). This may be due to the formation of the larger amount of intermediates. Since the formation rates of CO_2 and CO by ST-01 were roughly equal to those by P25, the decomposition rate of the intermediates may not depend on the surface area and the amount of intermediates, at least under the experimental conditions in the present study.

UV irradiance onto the photocatalyst affected the decomposition rate of VCM and the formation rates

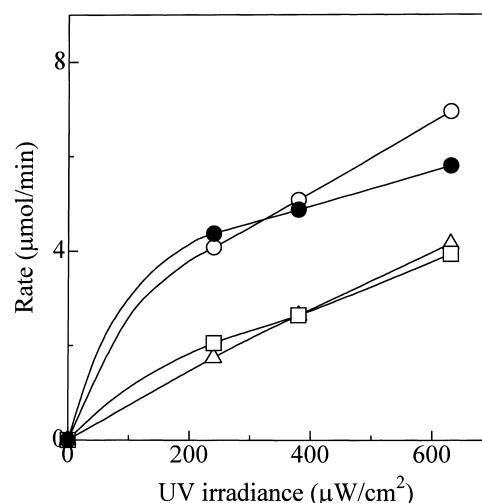


Fig. 4. Effect of UV irradiance on decomposition rate of VCM (○) and formation rate of CO_2 (△), CO (□) and $C_{(ads)}$ (●).

of CO_2 , CO and adsorbed intermediates ($C_{(ads)}$) (Fig. 4). The decomposition/formation rates were calculated from the concentration changes in the first 10 min. The VCM decomposition rate was increased with increasing UV irradiance. This suggests that the photoinduced electron and hole are the trigger of VCM decomposition. The decomposition rate was not proportional to UV irradiance; the slope of the decomposition rate became smaller at higher light intensities. This may be due to the recombination of electron and hole, which reduces the effect of electron and hole at high UV irradiance.

The VCM decomposition rate increased slightly with increasing water vapor pressure ($0 < P_{H_2O} < 3.3 \text{ kPa}$), however, the increment was not prominent. In the previous papers concerning the photocatalytic decomposition of other chloroethylenes, the decomposition rate decreased with increasing P_{H_2O} , and the following two functions of water vapor were mentioned; producing OH free radicals via surface OH group under UV irradiation, and competing with chloroethylenes on adsorption sites [7,11,14]. The former could enhance the decomposition of ethylenes and the latter could inhibit the reaction. In the VCM decomposition, the enhancement effect of OH supply may be barely larger than the suppression effect of water adsorption, resulting in the slight increase in the decomposition rate.

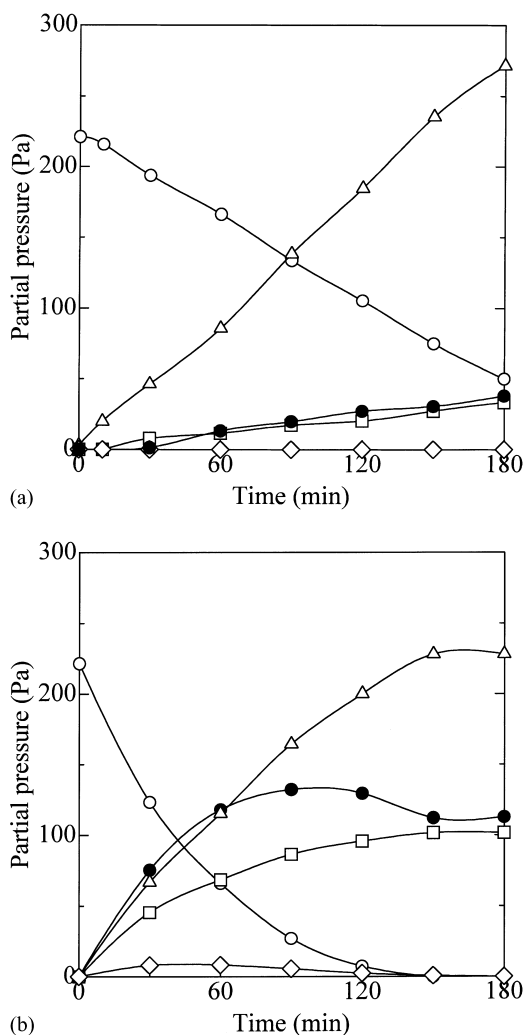


Fig. 5. Time courses of partial pressures of ethylene and products in photocatalytic mineralization of ethylene by (a) normal surface of TiO_2 and (b) chlorinated surface of TiO_2 . (○) VCM, (△) CO_2 , (□) CO, (◇) FMAC, and (●) $\text{C}_{(\text{ads})}$.

3.3. Role of Cl^- ion adsorbed on TiO_2 in photocatalytic mineralization of VCM

Photocatalytic decomposition of ethylene on chlorinated surface of TiO_2 was studied to understand the role of adsorbed Cl^- ion in the photocatalytic mineralization of VCM. At first, ethylene was photocatalytically decomposed on the normal surface of TiO_2 (P25) under dry condition. The decomposition of ethylene (Fig. 5a) was slower than that of VCM

(Fig. 3a). FMAC was not detected in the ethylene decomposition. The amount of CO formed was much smaller than that of CO_2 ; the CO_2/CO ratio was 9. As described above, in the first stage of VCM decomposition, FMAC was formed and the CO_2/CO ratio was approximately 1. These results suggest that the Cl atom in VCM molecule and/or Cl^- ion on TiO_2 surface promote the formation of FMAC and CO.

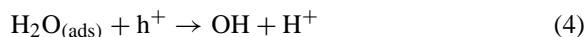
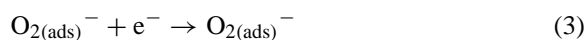
Next, ethylene was photocatalytically decomposed on the chlorinated surface of TiO_2 , which had been prepared by the VCM decomposition on TiO_2 (P25) for 360 min-UV irradiation. $34 \mu\text{mol}$ of Cl^- ion was adsorbed on 0.3 g of the chlorinated TiO_2 . Fig. 5b shows the time courses of the partial pressures of ethylene and products in the decomposition of ethylene by the chlorinated TiO_2 . FMAC was formed similarly to the VCM decomposition. The CO_2/CO ratio was approximately 2, which was much smaller than the ratio in the decomposition by normal TiO_2 . Moreover, the rate of ethylene decomposition by the chlorinated TiO_2 was larger than that by normal TiO_2 . These results suggest that the Cl^- ions on TiO_2 surface are involved in the decomposition of ethylene or VCM into FMAC and CO. Munuera and Navio [15] reported the formation of Cl and ClOO radicals on chlorinated TiO_2 surface by UV irradiation. These radicals seem to be responsible for the formation of CO and FMAC.

In the photocatalytic decomposition of C_2HCl_3 and C_2Cl_4 , FMAC was not formed, although these chloroethylenes contain Cl atoms. This indicates that vinyl group is also responsible for the formation of FMAC. It is inferred that the Cl containing radicals reacted with VCM or ethylene to form the Criegee intermediate (CH_2OO) via CH_2CHClO and then CH_2OO was transformed into FMAC. The homogeneous reaction of VCM with O_3 or $\text{O}(^3\text{P})$ was reported to form CH_2OO and FMAC [16,17], however, these active oxygen species are hardly observed on TiO_2 . CH_2OO may be possibly formed by the reaction of Cl containing radicals with VCM or ethylene on the heterogeneous photocatalyst.

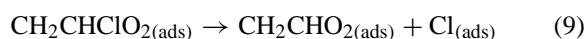
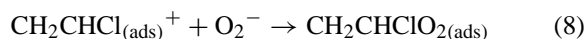
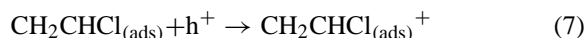
3.4. Reaction scheme of photocatalytic mineralization of VCM on TiO_2

The reaction scheme of photocatalytic VCM mineralization on TiO_2 is speculated analogously to the mineralization of other chloroethylenes and the

homogeneous photooxidation of VCM. The VCM mineralization is initiated by the formation of electron (e^-) and hole (h^+) resulting from the photon absorption by TiO_2 , since the decomposition did not proceed in the absence of either UV light or photocatalyst. The electron reduces O_2 molecule to form O_2^- radical, and the hole oxidizes H_2O or Cl^- adsorbed on TiO_2 [7,12,15].



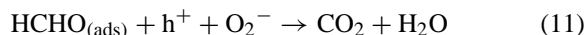
In these equations, (ads) denotes the chemical species adsorbed on the photocatalyst. Cl radicals may be also formed from VCM by attack of OH [16] or O_2^- radical [7] to C=C bond. In the humid conditions, the formation of Cl radical is possibly enhanced by the attack of OH radical.



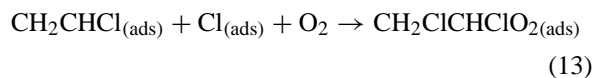
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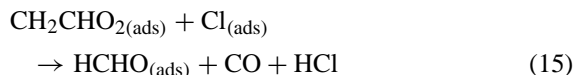
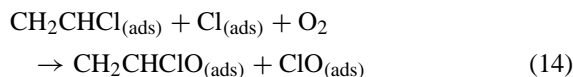
HCHO and CHClO were not detected in the present study. This suggests that they are mineralized quickly on TiO_2 as the reactions (11) and (12), or that the reaction (10) is negligible in the VCM mineralization.



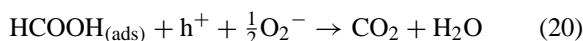
$Cl_{(ads)}$ will attack $CH_2CHCl_{(ads)}$ or $CH_2CHO_{2(ads)}$ from the side of lower chlorinated carbon because of steric exclusion [13].



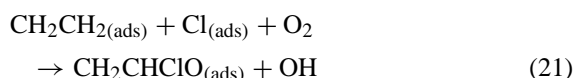
or



$CH_2ClCHClO_{2(ads)}$ may change to $CH_2ClCOCl$ (MCAC) by self decomposition. $CH_2CHClO_{(ads)}$ may be oxidized into CHClO and CH_2OO , which would either rearrange to HCOOH (FMAC) or decompose to CO and H_2O [17,18]. FMAC was finally decomposed into CO_2 and H_2O .



In the ethylene decomposition on chlorinated surface of TiO_2 , adsorbed ethylene may react with Cl radical and O_2 to form CH_2CHClO intermediate instead of reaction (14).



Formed $CH_2CHClO_{(ads)}$ may be decomposed into $CHClO_{(ads)}$ and CH_2OO as reaction (17), which are transformed into HCl, CO, and FMAC (reactions (12) and (20)). Thus, in the ethylene decomposition on chlorinated TiO_2 , CO and FMAC is produced.

4. Conclusion

More than 99.5% of carbon atoms in VCM introduced were changed into CO_2 or CO by UV irradiation on TiO_2 (P25) for 360 min. In the course of mineralization, $COCl_2$, FMAC and MCAC were formed. These long-lived intermediates were decomposed within 360 min. Cl^- ions adsorbed on TiO_2 participated in the photocatalytic decomposition of VCM and enhanced the formation of FMAC and CO. In this study, the amount of adsorbed FMAC

on photocatalyst was not determined. Therefore, the contribution of the FMAC formation on the VCM mineralization scheme was not clarified. However, since 17 Pa of FMAC (ca. 8% against VCM) was detected in the gas phase at least, the formation of FMAC and the participation of Cl containing radicals should be considered on the VCM mineralization.

References

- [1] J.N. Seiver, *Atmos. Environ.* 30 (1996) 751.
- [2] N.I. Sax, *Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold, New York, 1979, p. 1235.
- [3] Kankyo Kagaku, Busshitsu Yoran, Maruzen, Tokyo, 1988, p. 86.
- [4] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [5] K.I. Zamaraev, M.I. Khramov, V.N. Parmon, *Catal. Rev.* 35 (1994) 617.
- [6] A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735.
- [7] S. Kutsuna, Y. Ebihara, K. Nakamura, T. Ibusuki, *Atmos. Environ.* 27A (1993) 599.
- [8] J. Fan, J.T. Yates, *J. Am. Chem. Soc.* 118 (1996) 4686.
- [9] M.D. Driessen, A.L. Goodman, T.M. Miller, G.A. Zaharias, V.H. Grassian, *J. Phys. Chem. B* 102 (1998) 549.
- [10] T. Ibusuki, K. Takeuchi, *J. Mol. Catal.* 88 (1994) 93.
- [11] S. Yamazaki, S. Tanaka, H. Tsukamoto, *J. Photochem. Photobiol. A: Chem.* 121 (1999) 55.
- [12] D. Park, J. Zhang, K. Ikeue, H. Yamashita, M. Anpo, *J. Catal.* 185 (1999) 114.
- [13] M. Voinov, J. Augustynski, in: M. Schiavello (Ed.), *Heterogeneous Photocatalysis*, Wiley, New York, 1997, Chapter 1, p. 8.
- [14] K.H. Wang, Y.H. Hseh, C.H. Lin, C.Y. Chang, *Chemosphere* 39 (1999) 1371.
- [15] G. Munuera, A. Navio, *Stud. Surf. Sci. Catal.* 7 (1981) 1185.
- [16] C.J. Howard, *J. Chem. Phys.* 65 (1976) 4771.
- [17] E. Sanhueza, I.C. Hisatsune, J. Heicklen, *Chem. Rev.* 76 (1976) 801.
- [18] E. Sanhueza, J. Heicklen, *J. Phys. Chem.* 79 (1975) 677.