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Photocatalytic degradation of chloroform in the gas phase on the porous TiO_2 pellets: effect of Cl accumulated on the catalyst surface

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Abstract

The photocatalytic degradation of chloroform was studied in a tubular photoreactor packed with TiO_2 pellets prepared by sol–gel method. Concentrations of chloroform and CO_2 in the gas stream and Cl^- ion which was dissolved from the pellets into water after the photodegradation experiments were detected quantitatively. Chloroform was completely mineralized to CO_2 and HCl but the conversion decreased drastically with an increase in the irradiation time. Such a decrease in the catalytic activity was attributable to the accumulation of Cl^- on the TiO_2 surface and was recovered by washing the pellets with water. The presence of Cu and $Ca(OH)_2$ increased the concentration of Cl^- accumulated on the surface. The deterioration of the catalytic activity was suppressed with $Ca(OH)_2$ whereas no appreciable effect was observed with Cu. The TiO_2 prepared by sol–gel method exhibited a higher catalytic activity than commercially available Degussa P-25.

Keywords: Chloroform; Photocatalyst; Sol–gel method.

1. Introduction

The use of TiO_2 photocatalysts for environmental cleanup has been of great interest since TiO_2 is stable, harmless, and inexpensive and potentially can be activated by solar energy [1]. In particular, studies on the gas-phase photocatalytic degradation of trichloroethylene (TCE) have become an active field because many soils and groundwater supplies have been contaminated with TCE as a result of leaking underground storage tanks and improper disposal practices. The combination of a soil vapor extraction unit and a gas phase reactor with TiO_2 can be applied to the practical decontamination of TCE in the environment [2].

The photocatalytic degradation of TCE to CO_2 and HCl on the TiO_2 has been studied by many researchers and dichloroacetyl chloride, phosgene, and chloroform have been identified as by-products [3–13]. Dichloroacetyl chloride adsorbed strongly on the TiO_2 surface [14] and was oxidized photocatalytically to phosgene and CO_2 [4,15,16]. Phosgene was removed from the effluent gas stream by a scrubbing process which was necessary to avoid HCl from releasing to the atmosphere. In the scrubber containing water, phosgene was hydrolytically decomposed [17,18]. On the other hand, chloroform was not completely removed by scrubbing through water [17]. Chloroform has been reported to be mineralized completely in aqueous TiO_2 suspensions [19–23] and has been often selected as a model compound among chlorinated organic pollutants in water [24,25]. However, to the best our knowledge, studies on the photodegradation of chloroform in the gas phase have scarcely been performed. In this paper, the gas phase degradation of chloroform on the porous TiO_2 pellets was investigated in order to find a strategy to inhibit the formation of chloroform from the photocatalytic degradation of TCE.

2. Experimental

Chloroform (500 ppmv, balance nitrogen, Sumitomo Seika Chemicals Co.), nitrogen (99.999%), oxygen

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(99.999%) and synthesized air (oxygen 20.0–21.5%) were used as received from compressed gas cylinders. Humidified air was prepared by bubbling gas through a glass saturator containing de-ionized 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 [8]. 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 non-circulating mode. Four 4 W fluorescent black light bulbs (Toshiba, FL 4BLB) surrounded the tubular reactor. The photon flow rate (wavelength less than 400 nm) entering the reactor was determined to be 1.7×10^{-7} einstein s^{-1} using a uranyl oxalate actinometer [8]. All the experiments were conducted at room temperature and air was passed around the reactor to avoid the temperature of the pellets from rising by illumination.

The concentrations of $CHCl_3$ as reactants and CO_2 as products 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). Reactant or product gas stream was introduced to the gas-chromatograph through six-port injection valves, one of which was connected to a sample loop of 250 μl. Ion-chromatography (Shimadzu, PIA-1000) was used to determine Cl^- ions which were formed by immersing catalysts into water after the photodegradation experiments.

3. Results and discussion

In a continuous flow system with a non-circulating mode, reactant's concentrations decrease with an increase in an irradiation time and reach constant values. Conversion and stoichiometric ratio are determined after such a steady-state condition is established. However, in the photodegradation of $CHCl_3$, the $CHCl_3$ concentration in an effluent gas stream decreased instantly by irradiation but then, increased gradually with an increase in the irradiation time. This fact indicates that conversion (defined as the $CHCl_3$ molar flowrate degraded divided by the inlet $CHCl_3$ molar flowrate) decreased with the irradiation time. Fig. 1 shows dependences of the conversion and concentrations of CO_2 on the irradiation time when a reactant gas stream containing 162.6 ppmv $CHCl_3$, 1.01×10^3 ppmv H_2O and 1.99×10^5 ppmv O_2 was passed through 0.05, 0.10, 0.20, 0.30 or 0.47 g of the TiO_2 pellets at the flowrate of 61.6 ml min^{-1}. A variation of the CO_2 concentration against the irradiation time corresponded well to that of the conversion. The stoichiometric ratio of molar flowrate of CO_2 to that of $CHCl_3$ degraded in the outlet gas was estimated to be 1.04 ± 0.06 at any irradiation time, indicating that $CHCl_3$ was completely mineralized to CO_2 and HCl.

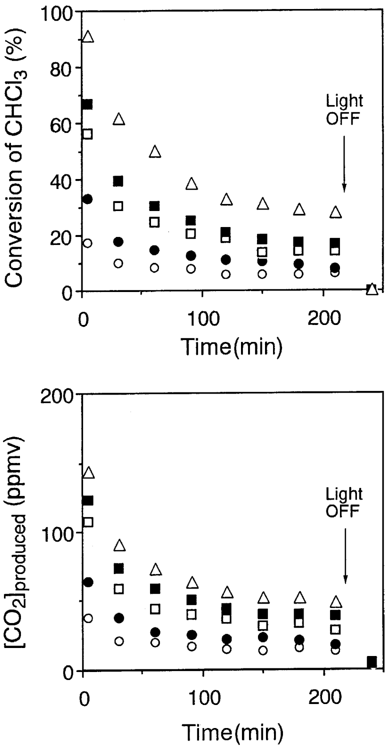

Fig. 1. Time course of conversion and the concentration of CO_2. A reactant gas stream containing 162.6 ppmv $CHCl_3$, 1.01×10^3 ppmv H_2O and 1.99×10^5 ppmv O_2 was passed through various weight of TiO_2 at the flowrate of 61.6 ml min^{-1}. TiO_2 weight: 0.05 g (○), 0.10 g (●), 0.20 g (□), 0.30 g (■), and 0.47 g (△).

Conversions calculated at the irradiation time of 5 min and 3 h were plotted in Fig. 2 as a function of the space time which defined as the weight of catalyst divided by the molar flow rate of $CHCl_3$ [26]. The conversion increased with an increase in the space time but that at 3 h decreased by a factor of 4.5 compared with that at 5 min. For a reference, the effect of space time on the TCE conversion was also depicted in Fig. 2. The decrease in the conversion as shown in Fig. 1 was not observed for the degradation of TCE and the conversion was estimated after reaching the steady state. It is noted that

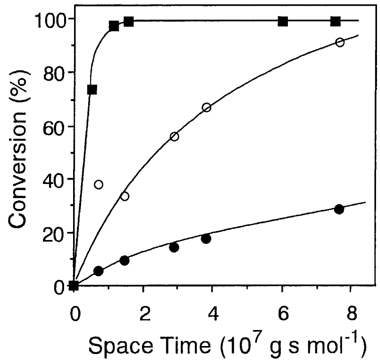

Fig. 2. Effect of space time on conversion of TCE (■) and $CHCl_3$ at the irradiation time of 5 min (○) and 3 h (●).

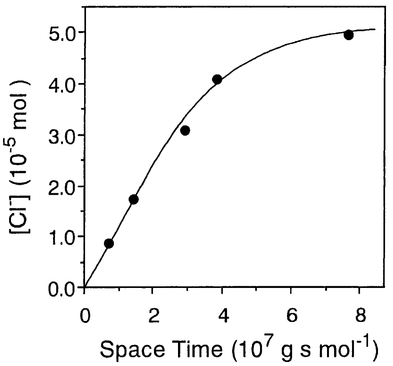

Fig. 3. Effect of space time on the Cl^- amounts dissolved into water from the TiO_2 pellets after the photodegradation of $CHCl_3$.

100% conversion of TCE was achieved at the space time of $1.6 \times 10^7\,g\,s\,mol^{-1}$ where ca. 40% of $CHCl_3$ at the most was degraded. This fact suggests that it is difficult to degrade $CHCl_3$ in the presence of TCE since the latter is degraded more easily than the former.

After the photodegradation of $CHCl_3$ for 3.5 h, the TiO_2 pellets were immersed into water and the dissolved Cl^- ions were determined. Fig. 3 showed that moles of Cl^- dissolved from the pellets increased with the space time. This is reasonable because more $CHCl_3$ was converted to HCl at higher space time as shown in Fig. 2.

Fig. 4 indicated that the $CHCl_3$ conversion decreased from 57% at the irradiation of 5 min to 20% at 3.5 h when a reactant gas stream containing 170.7 ppmv $CHCl_3$, 1.01×10^3 ppmv H_2O and 1.99×10^5 ppmv O_2 was passed through 0.40 g of the TiO_2 pellets at the flowrate of $109.0\,ml\,min^{-1}$. After the experiments, all of the TiO_2 pellets were removed from the photoreactor, washed thoroughly with water and dried in a desiccator with silica gels. The moles of Cl^- dissolved from the pellets during the washing process were estimated to be 4.08×10^{-5} mol. Then, the pellets were packed into the photoreactor and the same experiment was conducted again. The conversion at the irradiation time of 5 min was 56% and decreased similarly as the first run. This finding indicates that an activity of the TiO_2 was recovered by washing with water, suggesting that a deactivation of the photocatalyst is due to the adsorption of Cl^- on the surface. In order to verify that the adsorption of Cl^- decreased catalytic activity of the TiO_2, the photodegradation of $CHCl_3$ was performed with the TiO_2 pellets which were pre-treated with HCl. Such pellets were prepared by placing 1.0 g of the fresh TiO_2 pellets into 40 ml of $6\,mol\,dm^{-3}$ HCl for 1 day, filtering and then drying in the desiccator. The pellets of 0.40 g were used for the photodegradation of $CHCl_3$ under the same conditions as in the experiment above. These pellets were supposed to adsorb 2.07×10^{-4} mol of Cl^- by analyzing the dissolved Cl^- into water from another 0.40 g of the TiO_2 pre-treated with HCl. As shown in Fig. 4, the conversion was only 1–4% through the experiment. Therefore, it is demonstrated that the decrease in the conversion during the photodegradation of $CHCl_3$ was caused by adsorption of Cl^- on the surface.

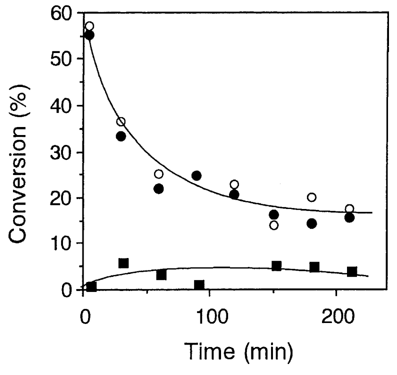

Fig. 4. Effect of washing with H_2O and pre-treatment with HCl of the TiO_2 pellets. Fresh TiO_2 pellets (○), TiO_2 pellets washed with H_2O after the photodegradation of $CHCl_3$ (●), and TiO_2 pellets pre-treated with HCl (■). A reactant gas stream containing 170.7 ppmv $CHCl_3$, 1.01×10^3 ppmv H_2O and 1.99×10^5 ppmv O_2 was passed through 0.40 g of the TiO_2 at the flowrate of $109.0\,ml\,min^{-1}$.

The effect of initial concentration of $CHCl_3$ on the conversion was examined in the range of 76.4–155.1 ppmv. Fig. 5 depicted the total moles of $CHCl_3$ degraded and the moles of Cl^- dissolved from the TiO_2 pellets after the photodegradation for 3.5 h. The former was calculated by integrating the obtained curve of the degraded $CHCl_3$ concentration versus irradiation time. The stoichiometric ratio of $[Cl^-]_{dissolved}/[CHCl_3]_{degraded}$ was obtained to be 1.10 ± 0.11, indicating that 36.7% of Cl^- produced by the mineralization of $CHCl_3$ were adsorbed on the TiO_2 surface.

We examined effects of Cu and $Ca(OH)_2$ on the photodegradation of $CHCl_3$ because these chemicals trapped Cl^- effectively and formed $CuCl_2$ and $CaCl_2$ during the photodegradation of TCE on the TiO_2 surface. The TiO_2 pellets were ground into powders with mortar and pestle and then mixed uniformly with various weights of Cu or $Ca(OH)_2$ powders. The 0.1 g of TiO_2 powders were used for the experiments and the bed length was kept at 6 cm. As shown

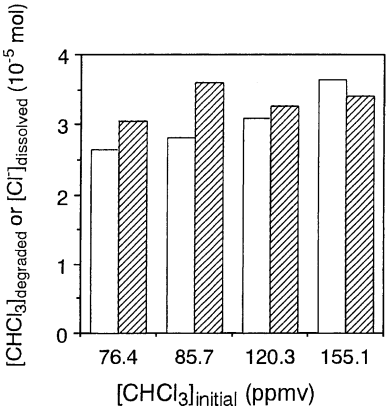

Fig. 5. Effect of $CHCl_3$ concentration on the amounts of $CHCl_3$ degraded (□) and Cl^- dissolved from the TiO_2 pellets (▨). Reaction conditions were the same as in Fig. 4 except for the mole fractions of $CHCl_3$.

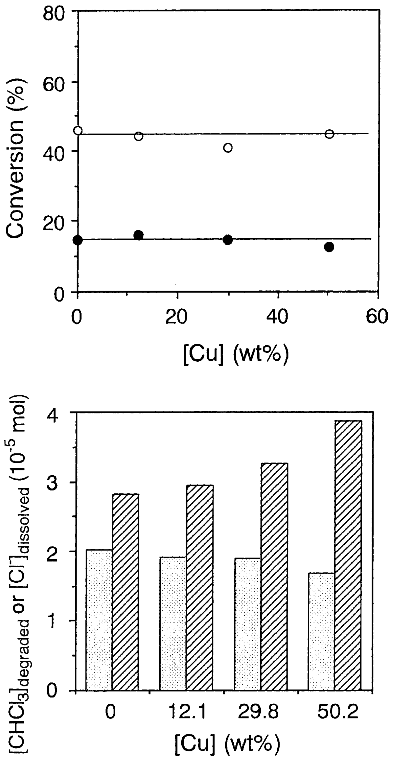

Fig. 6. Effect of Cu on conversion at the irradiation time of 5 min (○) and 3 h (●) and the amounts of $CHCl_3$ degraded (░) and Cl^- dissolved from the TiO_2 pellets (▨). Conditions were the same as in Fig. 1 except for 0.1 g of the TiO_2 powder mixed with various weight of Cu.

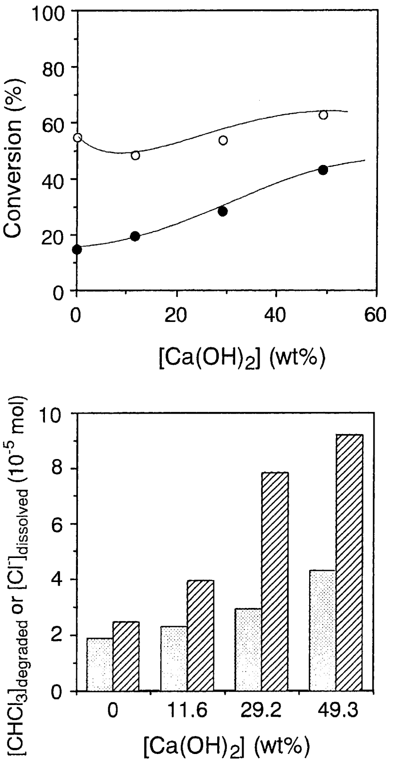

Fig. 7. Effect of $Ca(OH)_2$ on conversion at the irradiation time of 5 min (○) and 3 h (●) and the amounts of $CHCl_3$ degraded (░) and Cl^- dissolved from the TiO_2 pellets (▨). Conditions were the same as in Fig. 1 except for 0.1 g of the TiO_2 powder mixed with various weight of $Ca(OH)_2$.

in Fig. 6, the addition of Cu was no effect on the conversions which were calculated at the irradiation time of 5 min and 3 h and the stoichiometric ratio of $[CO_2]_{produced}/[CHCl_3]_{degraded}$ was estimated to be 1.00 ± 0.05. On the other hand, the Cl^- dissolved from the catalyst powders after the photodegradation experiments increased with an increase in the Cu content. The ratio of $[Cl^-]_{dissolved}/[CHCl_3]_{degraded}$ was calculated to be 1.39, 1.55, 1.73 or 2.31, respectively, with 0, 12.1, 29.8, or 50.2 wt.% of Cu. This fact suggests that the Cu trapped Cl^- which produced on the TiO_2 surface. On the other hand, when the experiments were conducted with $Ca(OH)_2$, the conversion at irradiation time of 3 h increased with the $Ca(OH)_2$ content as shown in Fig. 7. This means that the presence of $Ca(OH)_2$ inhibited the conversion from decreasing drastically. As a result, the total concentrations of $CHCl_3$ degraded increased with the increase of the $Ca(OH)_2$ content, i.e., the value of $[CHCl_3]_{degraded}$ at 49.3 wt.% became two times as high as that without $Ca(OH)_2$. The Cl^- concentration dissolved from the catalyst after the experiments increased with the $Ca(OH)_2$. The stoichiometric ratio of $[Cl^-]_{dissolved}/[CHCl_3]_{degraded}$ was calculated to be 1.31, 1.71, 2.66 or 2.14, respectively, with 0, 11.6, 29.2, or 49.3 wt.% of $Ca(OH)_2$. Since the molecular weights of $Ca(OH)_2$ and Cu are not so different, i.e., 74.1 and 63.5, respectively, the finding that the ratio at each wt.% for $Ca(OH)_2$ was similar to that for Cu indicated that both Cu and $Ca(OH)_2$ trapped the Cl^- in the same manner. However, the presence of Cu had no effect on the conversion whereas that of $Ca(OH)_2$ inhibited the decrease in the conversion. Thus, the latter effect was not attributable to the trapping of Cl^- by $Ca(OH)_2$. It might suggest a possible surface mediated hydrolysis of $CHCl_3$. Choi and Hoffmann [23] reported in TiO_2 aqueous suspensions that the degradation of $CHCl_3$ was enhanced dramatically at $pH > 11$ because of photoenhanced hydrolysis. It is noted that with 29.2 or 49.3 wt.% of $Ca(OH)_2$, the CO_2 concentration reached a maximum at the irradiation time of 25 or 60 min, respectively. That is, at the initial period before reaching the maximum, the CO_2 evolution was suppressed, which might be due to a reaction of CO_2 with $Ca(OH)_2$. After reaching the maximum, the formation of CO_2 corresponding to the complete mineralization of $CHCl_3$ was observed because the stoichiometric ratio of $[CO_2]_{produced}/[CHCl_3]_{degraded}$ was calculated to be 1.02 ± 0.04.

Fig. 8 indicated the comparison of the catalytic activity of the TiO_2 prepared by sol–gel method with commercially available Degussa P-25 in the powder form. The P-25 powders have been frequently used in the photocatalytic applications. A decrease in the conversion against the irradiation time was observed with the powder which was prepared by grinding the TiO_2 pellets. Our powders of 0.01 g were spread in the tubular photoreactor as thin as possible and then the length of the catalyst bed was 2.0 cm. On the other hand, the bed length for 0.01 g of the P-25 was 10.0 cm because the P-25 is so fine. The conversion with the P-25 decreased from

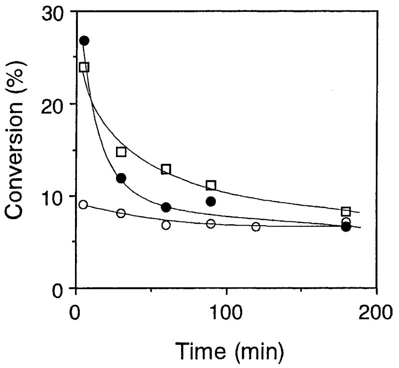

Fig. 8. Comparison of TiO_2 prepared by sol–gel method (0.01 g: □) with Degussa P-25 (0.01 g: ○, 0.015 g: ●) in the powder form. A reactant gas stream containing 168.5 ppmv $CHCl_3$, 2.11×10^5 ppmv O_2 and 1.66×10^3 ppmv H_2O was passed through the TiO_2 at the flowrate of 40.7 ml min^{-1}.

9.0 to 6.6% while that with our powders decreased from 23.9 to 8.2%. This finding suggests that the total concentration of $CHCl_3$ degraded on the TiO_2 prepared by the sol–gel method was higher than that on P-25 although the illuminated area of the former was smaller than that of the latter by a factor of 1/5. Such a higher catalytic activity of our powders is ascribed to the higher specific surface area (154 $m^2\,g^{-1}$) compared with the P-25 (ca. 50 $m^2\,g^{-1}$) and existence of only anatase phase [27]. The P-25 contains 70% of anatase and 30% of rutile. Murabayashi et al. [22] reported that rutile had no activity in the decomposition of $CHCl_3$ in water. It is worthy to note that a decrease in the conversion with P-25 during the irradiation of 3 h was smaller than that with our powders but the conversion with 0.015 g of the P-25 decreased drastically with an increase in the irradiation time. The formation of Cl^- ion was confirmed when the P-25 was immersed into water after the photodegradation experiments and the moles of Cl^- dissolved from the catalyst surface were determined to be 1.39×10^{-6} and 2.18×10^{-6} for 0.01 and 0.015 g of the P-25, respectively. This fact indicates that the remarkable decrease in the conversion with 0.015 g is also attributable to the accumulation of more Cl^- on the TiO_2. Therefore, deactivation of the catalyst by the accumulation of the Cl^- was not specific to the TiO_2 prepared by the sol–gel method.

In aqueous TiO_2 suspensions, Hoffman and his coworkers [21] proposed a detailed reaction mechanism in which the rate-determining step was the reaction of surface-bound OH radicals with adsorbed $CHCl_3$. The resulting CCl_3 radicals react with oxygen to form CCl_3OO radicals which eventually yield three Cl^- ions and CO_2 as described in the research on homogeneous radiolysis [28,29]. A similar reaction mechanism can be proposed for the photocatalytic degradation of $CHCl_3$ in the gas phase. Inhibition of the $CHCl_3$ photodegradation by Cl^- ions was also reported in TiO_2 aqueous suspensions and was attributable to the competition of Cl^- and $CHCl_3$ for OH radicals and for reactive adsorption sites on the TiO_2. Since the Cl^- is soluble well in water, the inhibitory effect due to adsorption would be more obvious in the gas phase than in water, leading to the drastic decrease in the photocatalytic activity. In the photodegradation of TCE previously reported, such a drastic deterioration of the catalytic activity was not observed although the accumulation of the produced Cl^- was observed on the TiO_2 surface [16]. Furthermore, the TiO_2 pellets pre-treated with HCl accelerated the degradation rate of TCE and ethylene [16]. These findings suggest that Cl radicals which are produced by reaction of OH radicals with the adsorbed Cl^- ions, can add to carbon–carbon double bond but can not extract a hydrogen from $CHCl_3$.

4. Conclusion

Chloroform, which is one of the undesirable by-products from the photocatalytic degradation of TCE, was completely mineralized on the porous TiO_2 pellets prepared by sol–gel method. However, the degradation rate was smaller than that of TCE and decreased drastically due to the accumulation of Cl^- on the TiO_2 surface. In this study, we used ca. 170 ppmv $CHCl_3$ for the experiments. When ca. 170 ppmv TCE was photodegraded in the bench-scale experiments, only 1–2 ppmv $CHCl_3$ was detected in the product gas stream. Even when we treated TCE as high as 222–1100 ppmv on the field demonstration, we detected ca. 10 ppmv $CHCl_3$ [2]. In the photodegradation of such a small quantity of $CHCl_3$, it is unlikely for $CHCl_3$ to be degraded before all of TCE is disappeared and the deterioration of the catalytic activity would not be pronounced as we observed in this study. Therefore, if we adopt high space time which is enough to decompose all of TCE followed by the complete mineralization of the produced $CHCl_3$, the release of $CHCl_3$ to the atmosphere would be eliminated in the practical application. Washing of the pellets with water is required to recover the catalytic activity from its deterioration due to the accumulation of Cl^- on the surface. The presence of $Ca(OH)_2$ is effective in suppressing the deterioration of the catalytic activity.

Acknowledgements

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