

Effect of Humidity on the Photocatalytic Degradation of Trichloroethylene in Gas Phase over TiO_2 Thin Films Treated by Different Conditions

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Abstract—The effect of humidity on the photocatalytic degradation reaction of trichloroethylene (TCE) in gas phase was investigated by using pretreated TiO_2 sol-gel films. It was observed that the photocatalytic activity of the TiO_2 films depended more greatly on the pretreatment conditions, for example, UV pre-illumination, than on the moisture content. When the relative humidity was over 50%, the reaction rates decreased regardless of treatment conditions of the photocatalyst. The photocatalytic decomposition rate of TCE increased with the increase of light intensity. However, the influence of humidity on the reaction rate was less significant under the increased light intensity. The intermediates and byproducts of the reaction were not changed in different humidity conditions.

Key words: Humidity, Pretreatment, Photocatalytic Activity, TiO_2 Films, Trichloroethylene

INTRODUCTION

Volatile chlorinated organic compounds such as trichloroethylene (TCE) have been used as a solvent in a wide range of industrial applications [Al-Ekabi and Serpone, 1988; Ollis et al., 1991]. A serious amount of these compounds has been discharged or leaked into the environment due to the improper management. The contamination of underground water, rivers and drinking water by chlorinated organic compounds has been an issue of social concern. In particular, some of the chlorinated organic compounds are carcinogenic and adversely affect human health [Hisanaga et al., 1990; Turuchi et al., 1990; Murabayashi et al., 1992].

Although several treatment methods are commonly used now such as adsorption on activated carbon and air bubbling, many of them simply change the state of pollutants and the harmful compounds still exist after the treatment [Liu et al., 1995; Eleazer et al., 1997]. Therefore, photocatalysis with TiO_2 has received great attention because it leads to the remarkable elimination of organic compounds, involving volatile organic compounds (VOCs) contained in air and water [Izumi et al., 1980; Tanguay et al., 1989; Dibble and Raupp, 1990; Fox and Dulay, 1993; Yamazaki-Nishida et al., 1993; Nimlos et al., 1993; Hoffmann et al., 1995; Kim et al., 1996; Hilgendorff et al., 1996; Yoon et al., 2000; Lee et al., 2000; Jeong et al., 2001; Hong et al., 2001].

Much research on the photocatalytic decomposition of TCE in water and air has been reported [Hsiao et al., 1983; Pruden and Ollis, 1983; Ollis et al., 1984; Ollis, 1985; Yoon et al., 2000]. In recent years, attention has been focused on gas-phase photocatalysis because TCE can be decomposed much faster in gas phase than in aqueous phase [Murabayashi et al., 1999]. In addition, the gas-phase photocatalytic degradation of TCE has been widely studied to elucidate its reaction mechanism [Kutsuna et al., 1993; Nimlos et al., 1993; Yamazaki-Nishida et al., 1995; Hung and Marinas, 1997; Kim et

al., 1998; Yoon et al., 2000]. Plenty of experimental results on the photocatalytic degradation of TCE in gas phase have been reported in literature. However, they are not consistent with each other so far, especially with respect to the effect of water vapor. Nimlos et al. [1993] reported a specific chain reaction mechanism of the Cl radical in the TCE photocatalytic reaction in the gas phase, while the reaction in the aqueous phase was reported [Ollis, 1985] to proceed *via* an OH radical.

It is practically quite important to clarify the effect of water vapor on the gas-phase photocatalytic reaction because most of the air polluted with organic chlorine compounds contains water vapor. In heterogeneous photocatalysis, photoinduced molecular transformations and reactions take place on the surface of photocatalyst when the reactant is adsorbed under UV illumination [Matthews, 1988]. The activity of the photocatalyst might be dependent on the surface conditions; the adsorbed species, other than reactant on the surface, may affect the reaction because they can hinder the adsorption of reactant. In particular, adsorbed water molecules on the surface of the catalyst film can participate in the reaction if their adsorption process is competitive with reactant, TCE [Kim et al., 2000].

For these reasons, we tried to find the relationship between the photocatalytic activities of the pretreated and untreated TiO_2 films with the water vapor in the gas-phase photocatalysis of TCE. Little has, however, been studied on the relation between the photocatalytic activity and humidity under different pretreatment of the photocatalyst in the previous investigations on gas-phase TCE photocatalysis. In this work, we tried to make clear the effects of humidity by using sol-gel TiO_2 films coated on glass plates (TiO_2 -GP) in the gas-phase photocatalysis of TCE when the pretreatment conditions of TiO_2 films and light intensity were changed.

EXPERIMENTAL

1. Photoreactor and Experimental Procedures

A batch reactor (125 mL) was used for the experiment [Kim et al., 1999]. It was designed for *in situ* measurements of the degrada-

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tion reaction of TCE by using Fourier Transform Infrared (FTIR) spectroscopy. The experimental procedure was as follows. (1) The TiO_2 films were prepared on glass plates ($25 \times 55 \text{ mm}^2$, two plates) by the sol-gel process; (2) the TiO_2 films were placed in the reaction chamber; (3) the atmosphere of the reaction chamber was substituted with dried air; (4) the initial concentration of TCE was adjusted by putting 4.6 mg L^{-1} into the reactor, and this concentration of TCE was used throughout the experiment. Distilled water was added into the reactor if necessary.

After the concentration of TCE had reached its equilibrium value, the degradation reaction of TCE was started. The temperature of the reaction chamber was kept at 25°C by air-cooling. The TiO_2 films were pretreated before the reaction at different conditions, and were also pretreated for repeated uses after the TCE was photocatalytically degraded to a level that was undetectable with an FTIR spectrometer.

2. Photocatalyst and Light Source

The TiO_2 -GPs ($25 \times 55 \text{ mm}^2$, BET surface area: $<0.1 \text{ m}^2 \text{ g}^{-1}$, thickness: ca. 350 nm) were prepared by a sol-gel process. The samples were finally heated at 500°C for 3.5 hours after dipping 10 times. The prepared samples, TiO_2 powder and TiO_2 -GP, were the anatase phase as shown in Fig. 1, and they were analyzed by using an X-ray diffractometer (XRD: Rigaku D/Max-RC, 12 kW) with Cu Ka radiation. A more detailed preparation method has been described in an earlier report [Kim et al., 1996].

The TiO_2 -GPs were pretreated in the following two different methods after preparation. (1) TiO_2 -GPs were washed with water and dried at 100°C for 20 min after reaction. (2) TiO_2 -GPs were then pre-illuminated for 60 min with UV lamps.

The light intensity was adjusted from 0.4 to 8 mW cm^{-2} by changing the number of lamps to study the effect of light intensity. For other experiments in this work, eight 20 W black light fluorescent lamps (Toshiba FL20S-BLB) were used as a light source and their light intensity, measured with a light power meter (OPHIR-Laser Power Meter), was around 8 mW cm^{-2} .

3. Analysis

An FTIR spectrometer (Nicolet 800 FT-IR spectrometer) was used for the quantitative and qualitative determination of TCE and products. We selected the light intensity of 8 mW cm^{-2} to investi-

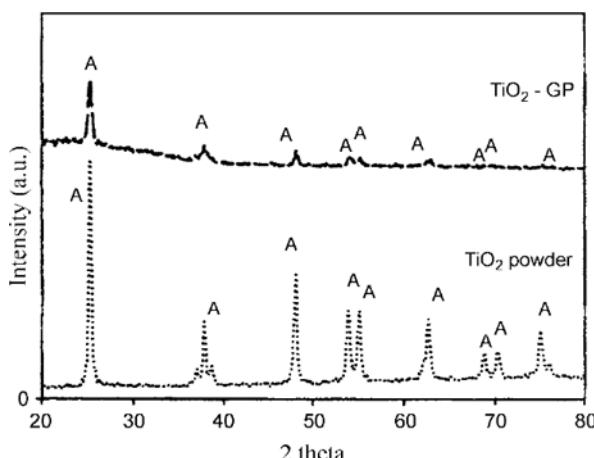


Fig. 1. XRD pattern of TiO_2 powder and TiO_2 -GP (A: anatase phase).

gate the reaction products because the kinds of species were found to be the same irrespective of the light intensity although the degradation rate of TCE was different. The peak height of 942 cm^{-1} for the C-Cl stretching vibration was used to determine the change in TCE concentration.

RESULTS AND DISCUSSION

1. Effect of Light Intensity

The concentration of TCE decreased slowly when the illumination was started but decreased rapidly after several minutes of illumination. Thus, since it was difficult to evaluate the initial reaction rate, the average degradation rate of TCE was calculated from the half-life of the reaction. Tests of the effect of light intensity were performed with the non-treated TiO_2 -GP.

Fig. 2 shows the TCE degradation rate against UV light intensity. No reaction took place in the absence of UV light or catalyst,

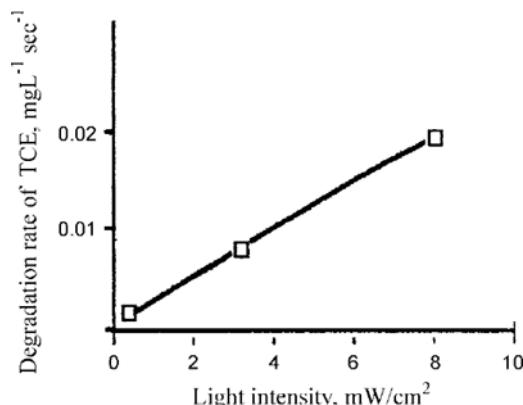


Fig. 2. Relationship between the degradation rate of TCE and the light intensity. Initial concentration of TCE was adjusted to be 4.6 mg/L with non-pretreated TiO_2 -GP.

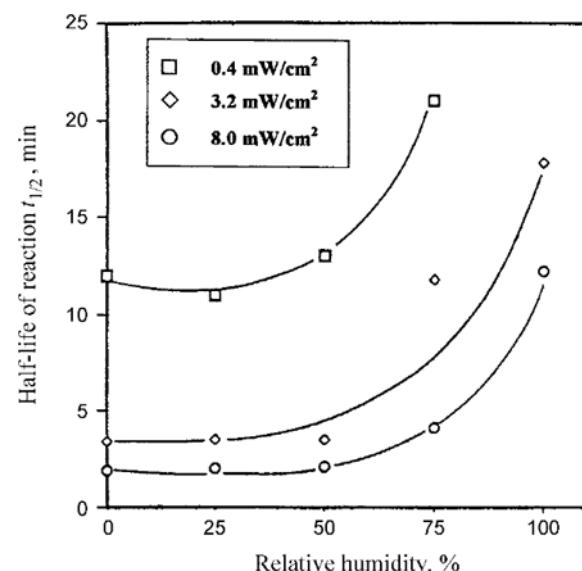


Fig. 3. Relationship between the relative humidity and the half-lives of TCE degradation reaction. The non-pretreated TiO_2 -GP was used.

and high conversion of TCE was obtained at strong light intensity of 8 mW cm^{-2} under our experimental conditions. These results were consistent with others reported elsewhere [Kutsuna et al., 1993].

Fig. 3 shows the relationship between the relative humidity and half-life at three different light intensities, 0.4, 3.2 and 8 mW cm^{-2} . For all three light intensities, the relative humidity up to 50% did not affect the half-lives of TCE degradation. However, as the humidity increased over 50% the reaction became slower for all light intensities. From these results it can be said that the relative humidity

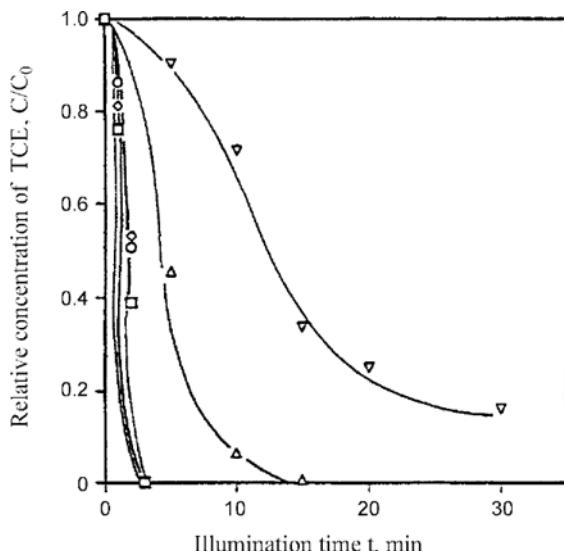


Fig. 4. Effect of water vapor on the gas-phase photocatalysis of TCE over the non-treated TiO_2 -GP. Symbols, \square , \circ , \diamond , \triangle and ∇ indicate the relative humidity of 0%, 25%, 50%, 75% and 100%, respectively.

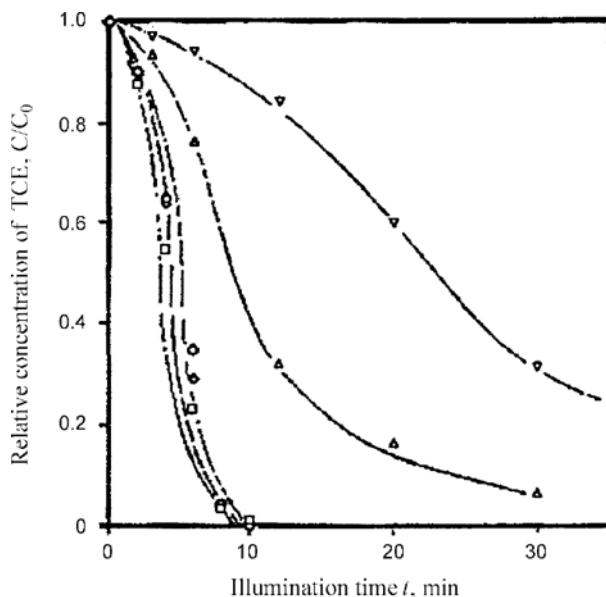


Fig. 5. Effect of water vapor on the gas-phase photocatalysis of TCE when the TiO_2 -GP washed with water and dried at 100°C for 20 min was used. Symbols, \square , \circ , \diamond , \triangle and ∇ indicate the relative humidity of 0%, 25%, 50%, 75% and 100%, respectively.

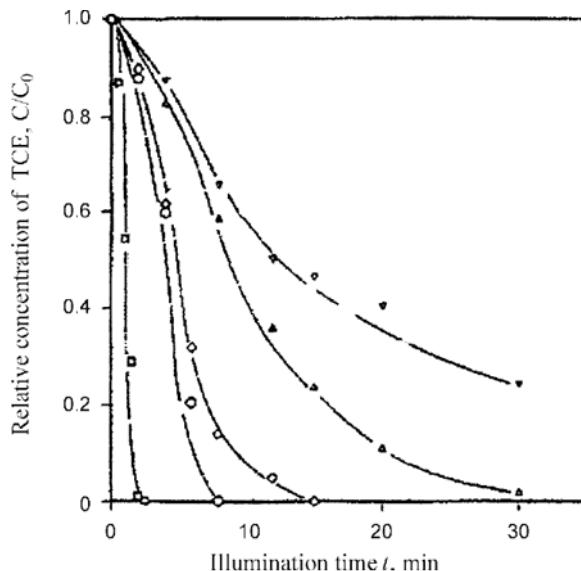


Fig. 6. Effect of water vapor on the gas-phase photocatalysis of TCE when the TiO_2 -GP pretreated by UV preillumination was used. Symbols, \square , \circ , \diamond , \triangle and ∇ indicate the relative humidity of 0%, 25%, 50%, 75% and 100%, respectively.

played the same role on the degradation rate of TCE regardless of light intensity.

2. Effect of Humidity

Fig. 4 shows the effect of humidity on the gas-phase photocatalytic degradation of TCE. In this experiment, the TiO_2 films coated on glass plates were non-treated. The degradation rates of TCE were not changed at relative humidity in the range of 0-50%. However, the increase of relative humidity higher than 75% made the reaction proceed slowly compared to that below 50%.

Figs. 5 and 6 also show the effect of humidity on the gas-phase photocatalytic degradation of TCE, but films were pretreated by washing with water and dried at 100°C for 20 min (Fig. 5) and by pre-illuminating UV light (Fig. 6), respectively.

From Fig. 5, it was observed that the trend of the change in degradation rate was similar with non-treated films (Fig. 4) in the whole range of 0-100% of relative humidity in our experiment. When the TiO_2 films were washed with water, the surface would be covered with water molecules and they might keep the reaction from proceeding [Kim et al., 1999]. Moisture added to increase the humidity would be difficult to adsorb onto the TiO_2 surface if it was already occupied with other water molecules. From these reasons, it would be thought that water vapor added within this range exhibits a negative role on the reaction.

Our results were different from those of Kutsuna et al. [1993] due to the lower initial concentration of TCE than ours. But for both results it is true that the adsorption of the compounds onto the surface of catalyst was shown to be important. When the amount of water vapor in the reactor increased, the adsorption of TCE onto the photocatalyst surface would be restricted due to the competitive adsorption with water molecules. This might be the reason why the degradation rates of TCE in the presence of water vapor of 75% and 100% decreased.

On the other hand, as shown in Fig. 6, when the TiO_2 films were

used after being washed with water and then pre-illuminated by UV light, the degradation rate was the fastest at relative humidity of 0%, but decreased with the increase of relative humidity. It is possible to explain that water molecules adsorbed onto the surface of film after washing with water desorbed or decomposed by UV pre-illumination, and therefore TCE can be easily adsorbed and degraded. The decrease of the degradation rates of TCE with the increase of the relative humidity would be also due to the competitive adsorption of water molecules on the surface of TiO_2 film.

3. Intermediates

The series of FTIR spectra taken during the photocatalytic degradation of TCE over TiO_2 -GP with the light intensity of 8 mW cm^{-2} are shown in Fig. 7. We confirmed the production of ClCH_2COCl

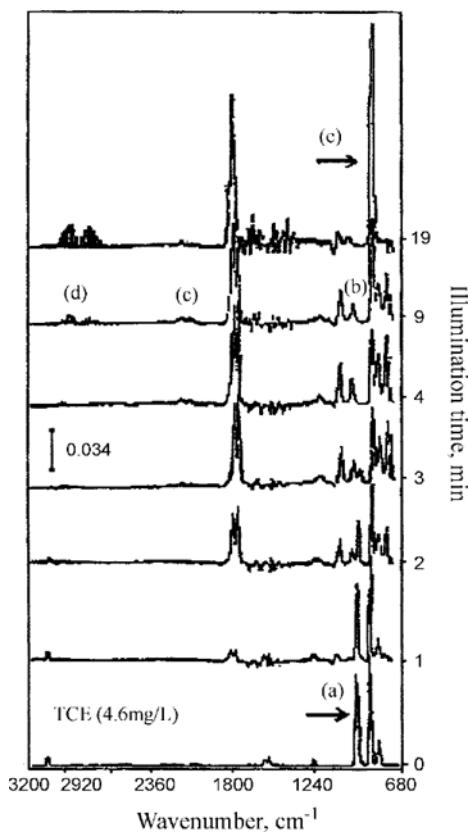


Fig. 7. A series of FTIR spectra taken during the photocatalytic degradation of TCE with light intensity of 8 mW/cm^2 . (a), (b), (c), (d) and (e) are the peaks used to determine the concentration of TCE, DCAC, CO, HCl, and COCl_2 , respectively. TiO_2 -GP was used.

Table 1. Main standard peaks of products obtained from the library spectra supplied by Nicolet

Compounds	Main peaks of FTIR (cm^{-1})
TCE	782, 845, 942, 1253, 1556, 3097
DCAC	739, 803, 991, 1077, 1218
COCl_2	858, 1835
CO	2112, 2140
CO_2	675, 2400
HCl	2703-3020, 2906

(dichloroacetyl chloride, DCAC), which was the main intermediate, together with COCl_2 , CO, CO_2 and HCl. The production of CO_2 was identified mainly from the peak at $2,400 \text{ cm}^{-1}$ but could not be determined quantitatively because of the strong interference of that in air. The standard peak positions in FTIR spectra of TCE, DCAC, COCl_2 , CO, CO_2 and HCl are listed in Table 1. The change in the concentration of products with the illumination time during the photocatalytic degradation of TCE was illustrated in Fig. 8.

Fig. 9 shows the relationship between the production of DCAC and the relative humidity. The production amount of DCAC was decreased with the increase of relative humidity. This might be due to the fact that the produced DCAC reacts immediately with water, and

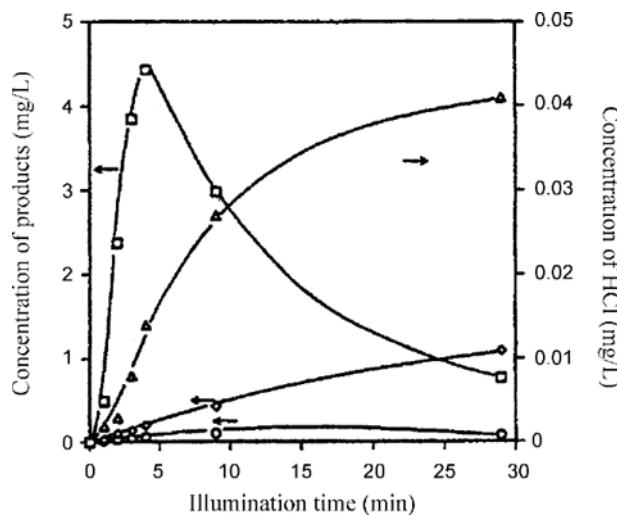


Fig. 8. The change in the concentration of products with the illumination time for the photocatalytic degradation of TCE. TiO_2 -GP and blacklight fluorescent lamps having the light intensity of 8 mW/cm^2 were used. □: DCAC, ◇: COCl_2 , ○: CO, △: HCl.

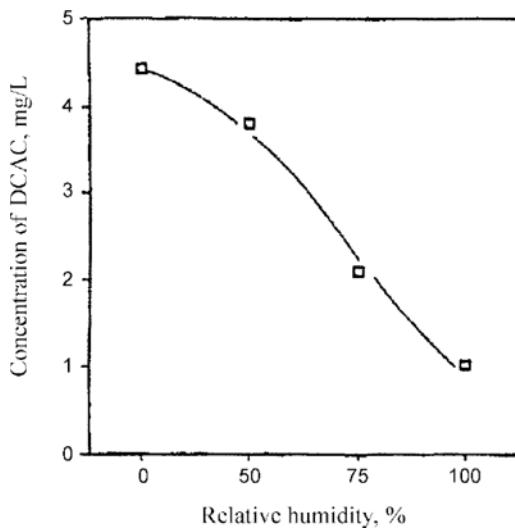


Fig. 9. Relationship of the production of DCAC during TCE photocatalysis with the relative humidity; the concentration of DCAC was the highest in the reaction. TiO_2 -GP and blacklight fluorescent lamps having the light intensity of 8 mW/cm^2 were used.

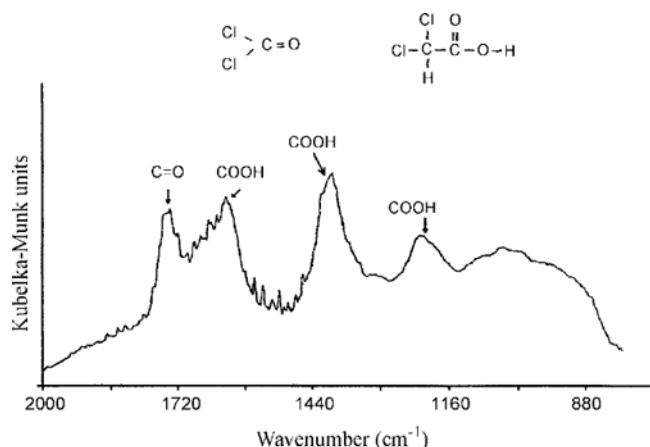
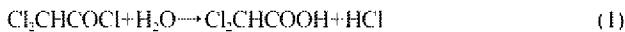


Fig. 10. DRIFT spectrum of TiO_2 powder after the photocatalytic degradation of TCE.

soon produces Cl_2CHCOOH (DCAA) on the TiO_2 surface through hydrolysis as follow.



In fact, DCAA was confirmed on the TiO_2 surface by the observation of three peaks of COOH by using a DRIFT (Diffuse Reflectance Infrared Fourier Transform Spectroscopy), as shown in Fig. 10.

CONCLUSIONS

Through detailed experiments it was found that the effect of humidity on the photocatalytic degradation rate of TCE in gas phase depended on the pretreated states of the TiO_2 films. It was also observed that the photocatalytic activity of the TiO_2 films was affected more strongly by the pretreatment conditions (especially UV pre-illumination) compared to the moisture content. When the relative humidity was over 50%, the reaction rates decreased regardless of treatment conditions of photocatalyst. These results indicate that water vapor could be easily adsorbed on the clean TiO_2 surface pretreated by UV illumination, and the adsorbed water vapor hinders the reaction.

The photocatalytic decomposition rate of TCE increased with the increase of light intensity. The intermediates and byproducts of the reaction were not changed in different humidity conditions.

From our results, the UV illumination on the surface of TiO_2 film after washing with water was the most effective pretreatment method to increase the activity of TiO_2 films. Consequently, in order to regenerate the photocatalytic activity of the TiO_2 films, the UV pre-illumination after washing with water is recommended before their reuse.

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