



The photocatalytic degradation of trichloroethane by chemical vapor deposition method prepared titanium dioxide catalyst

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Abstract

The purpose of the investigation was to study the photocatalytic reaction of trichloroethane using a TiO₂ catalyst deposited in an annular reactor by the chemical vapor deposition (CVD) method. The experimental results indicated the highest decomposition rate of the trichloroethane was 2.71 μmol/(s m²) and the conversion ratio reached a maximum of 99.9%. When the humidity was below 154 μM, the reaction rate slightly increased with increasing humidity. However, the reaction rate decreased as the humidity increased >154 μM. Oxygen played a role as an electron acceptor in the reaction, and reduced the recombination of the photogenerated electron–hole pairs. Therefore, the reaction rate rose as the oxygen concentration increased. Nevertheless, after the oxygen concentration reached 12%, the reaction rate reached its maximum and was constant in spite of increasing oxygen concentration. As the initial reactant concentration increased, the reaction rate increased, but the conversion ratio dropped. An increase of light intensity resulted in an increase in the number of photons and thus increased the reaction rate. Accordingly the decomposition of trichloroethane could be fitted by the semi-empirical bimolecular Langmuir–Hinshelwood model. Moreover, the reaction rate was proportional to the 0.48-order of the light intensity.

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1. Introduction

Trichloroethane is commonly used in industrial manufacturing processes, and can enter the human body by respiration or dermal absorption. Trichloroethane can damage the central nervous system, skin, heart, and circulatory system, or it may even cause cancer [1]. Generally, the method of treatment for controlling volatile organic compounds (VOCs) such as trichloroethane can be subdivided into two categories, namely combustible and non-combustible processes [2]. In the non-combustible control process, the VOCs released from the waste gas are collected. The major control technologies in this area include adsorption, absorption, condensation, and biological filtration. In the combustible control process, the VOCs in the waste gas are destroyed by thermal or catalytic incineration.

Both of these commonly used technologies have their disadvantages and limitations in practical applications. For example, the efficiency of activated carbon adsorption significantly decreases when the temperature reaches 38 °C. Moreover, disposal of the waste activated carbon presents a problem. Although thermal incineration is quite effective, it consumes significant amount auxiliary fuel. While, the catalytic incinerator may be operated at a lower temperature than thermal incinerator, catalytic incineration is relatively costly, and has waste disposal problem also.

In recent years, the use of semiconductors as a light excitation source for the heterogeneous photocatalytic decomposition of organic compounds in liquid and gas phases has received considerable attention. Obee and Hay [3], who treated ethane by the UV/TiO₂ process, pointed out that the reaction rate decreased with increasing humidity. Obee and Hay proposed that if the water molecules were hydrated first and then chemically adsorbed on a TiO₂ surface, the ethane on the TiO₂ surface would compete with the water molecules for adsorption. Therefore, the more the water molecules in the gas phase, the less favorable the reaction was. Larson and Falconer [4] detected the reaction species at the TiO₂ surface after photocatalytic decomposition of trichloroethylene (TCE) by X-ray diffraction (XRD). They observed that the reduction in activity of the catalyst was due to the chlorine ions and other intermediates adsorbed on the TiO₂. When there was an appropriate amount of water molecules, they would help to remove the substance deposited on the TiO₂ surface, and maintain the catalyst's activity.

Raupp and Junio [5] pointed out that the reaction rate of the photocatalytic decomposition of acetone increased as the oxygen concentration increased and would be constant until it exceeded 10%. Similarly, Hung and Marinas [6] studied the impact of oxygen on the photocatalytic decomposition of TCE. The experimental results showed that when the concentration of oxygen was <1000 ppmv, the conversion ratio increased as the oxygen concentration increased. While, when the concentration of the oxygen was >1000 ppmv, the conversion ratio did not increase significantly. Dibble and Raupp [7] pointed out that the reaction rate increased as the TCE concentration increased, and changed from a first-order reaction to a zero-order reaction. When the titanium dioxide lost its activity, it could be regenerated by water vapor.

Luo and Ollis [8] mixed TCE with toluene to perform the photocatalytic decomposition reaction. Their results showed that TCE promoted the decomposition of toluene, but toluene suppressed the decomposition of TCE. They deduced that free chlorine radicals generated in the TCE decomposition process participated in the decomposition reaction of the toluene

and enhanced its decomposition rate. However, the free radicals that should participate in the original TCE reaction mechanism are consumed by toluene and in turn slowed the TCE decomposition.

The chemical vapor deposition (CVD) activates a chemical reaction by offering an energy, such as heating to the gaseous raw materials and to deposit the reaction product onto target substance [9]. CVD's advantages include: (1) the ability to control the composition and the structure of the deposited compounds, (2) the ability to deposit the film on the reactor surface with different geometric shapes. Therefore, in this investigation a titanium dioxide catalytic membrane was prepared by CVD method, and its effect on the trichloroethane decomposition was studied with the purpose of developing a convenient, effective, and adherent catalyst.

2. Experimental

The experimental apparatus utilized in this research is shown in Fig. 1. The trichloroethane liquid was supplied to the apparatus by a gas tight syringe placed on the micro-syringe pump (kd-Scientific, Model 250), and evaporated in the stainless steel pipe wrapped with heating tape. The concentration was controlled by the injection speed of the syringe pump. The moisture was generated by passing the highly pure nitrogen gas through an aeration flask containing de-ionized water. The two streams were mixed with oxygen. The moisture and oxygen concentration were controlled by a mass flow controller (MKS, Model 247C). The humidity was monitored by a dew point meter (General Eastern, Hygro M4). The stainless steel pipeline was wrapped with heating tape and heated to 110 °C to prevent the gaseous trichloroethane and water vapor from condensing. The effluent gas was injected

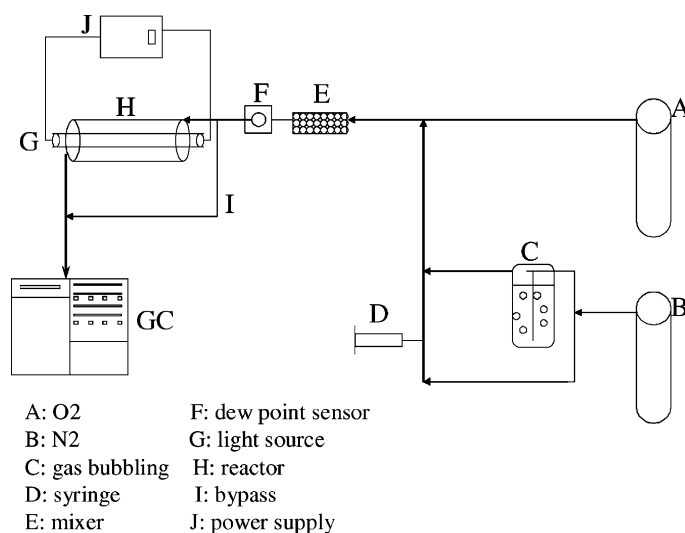


Fig. 1. Experimental apparatus used in the photocatalytic reaction.

via the manual sample injection valve into the gas chromatograph (China Chromatograph, 8900) and analyzed by a flame ionization detector. To avoid a residue of reactants and products, and to keep the TiO_2 hydrated, the pipe system was purged with a nitrogen stream containing water under UV illumination after each experimental run. All the experiments including every sample analysis and experimental run were repeated once to measure the reproducibility of results. The reactions were carried in a 45-cm long annular reactor that was composed of an external Pyrex glass tube with an internal diameter of 3.7 cm and an internal quartz glass tube with an external diameter of 3.0 cm. A UV light tube (Sankyo Denki, F10T8BLb 10 W) with 365 nm major wavelength was placed in the center of the reactor so that the light intensity could be controlled by adjusting the voltage. The light intensity was measured by an actinometer (International Light, IL-1700). The calculation of reaction rate was shown as in the following formula:

$$r = \frac{Q(C_0 - C)}{A} \quad (1)$$

where reaction rate ($\mu\text{mol}/(\text{s m}^2)$) is denoted by r , Q the flow rate (l/s), C_0 the influent concentration (μM), C the effluent concentration (μM) and A is the illumination area (m^2).

The effluent concentration of the reactant was analyzed after the reaction reached steady state at about 3 min. The experiments were continued for 30 min after reaching steady state to ensure the reproducibility of the experimental data. Because the deposited catalyst was strong adherent, it could not get a sufficient amount of catalyst sample to analyze the BET specific surface area. In addition, the photocatalytic reaction occurred only in the light radiation area. Thus, the illumination area in Eq. (1) was defined as the internal surface area of external tube on the annular reactor coated with TiO_2 film.

The TiO_2 film was deposited on the internal surface of the external pipe by the CVD method. Its preparation apparatus is shown in Fig. 2.

Both the $\text{Ti}(\text{OC}_3\text{H}_7)_4$ liquid and de-ionized water were placed in the aeration flask, and heated in a water bath to 60°C . Two separate highly pure nitrogen streams were flowed into

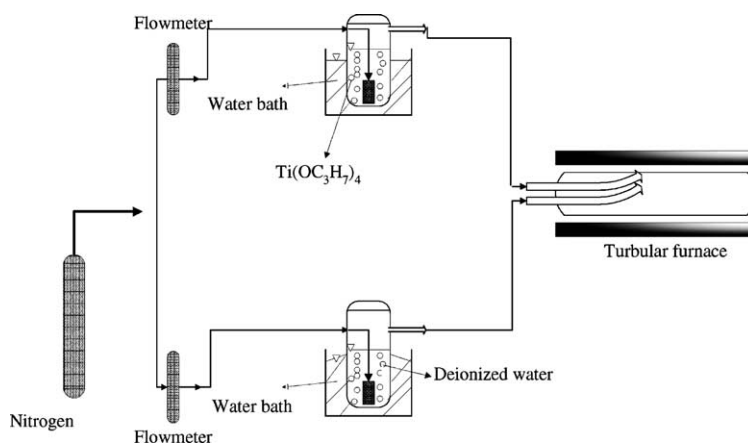


Fig. 2. Apparatus for initial preparation of chemical vapor deposition method.

the aeration flask and carried out the organic titanium and water vapors. The gas flow rates were 100 ml/min for the $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and 50 ml/min for the de-ionized water. The exit of the aeration flask was connected by a Teflon tube to the external tube of the reactor.

The Teflon tube and the external reactor tube were wrapped with heating tape, and kept at 110 and 300 °C, respectively by a temperature controller. The external reactor tube was slowly rotated during the preparation period and to allow the TiO_2 membrane to deposit evenly on the internal wall of the reactor tube. After approximate a 6-h reaction period, the catalyst was calcined at a temperature of 550 °C for 18 h. The TiO_2 was analyzed by scanning electron microscopy (SEM) (Cambridge, Model S-360) and an XRD analyzer (Shimadzu, Model XD-5).

3. Results and discussion

After the deposition at 300 °C and calcination at 550 °C, the internal wall of the external tube of the reactor formed an evenly distributed white membrane. This catalytic membrane was analyzed by the XRD under the conditions of 40.0 kV, 300 mA, and 4.0 °C/min. The spectrum is shown in Fig. 3. The spectrum indicated that the XRD spectrum matched with the card number 21-1272 of Joint Committee on Powder Diffraction Standards (JCPDS). It showed that the catalyst prepared in this study was the anatase crystal of TiO_2 . Fig. 4

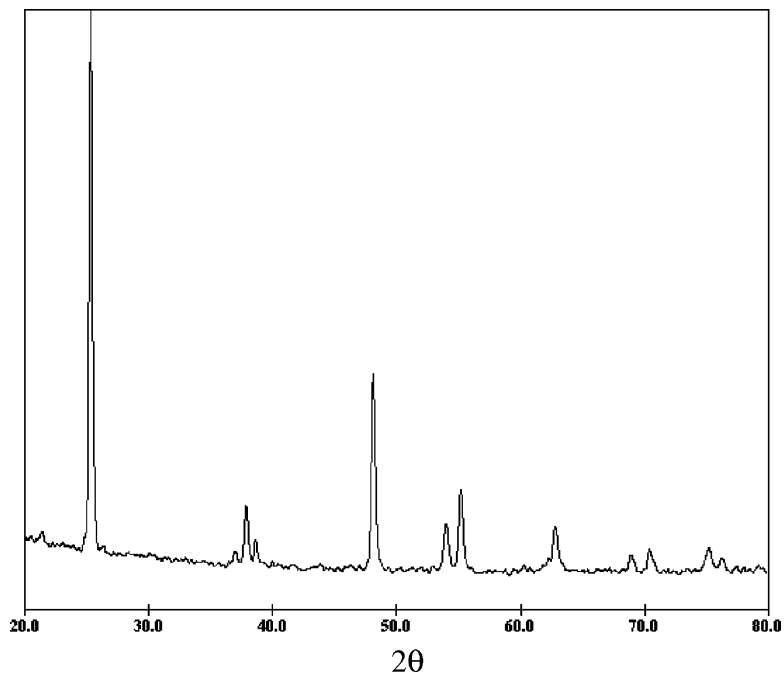
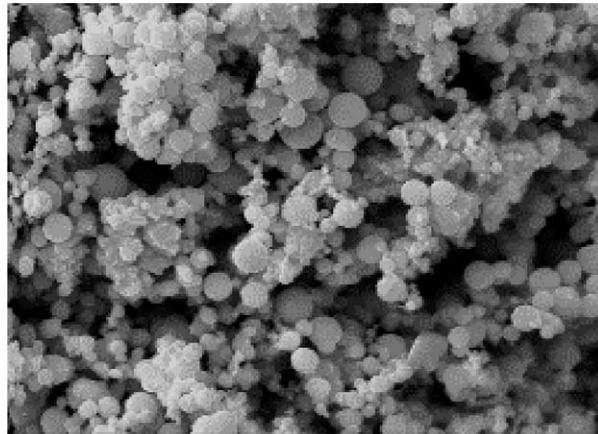
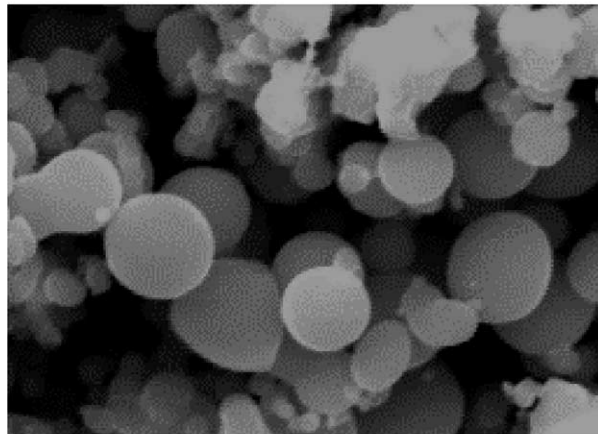


Fig. 3. The XRD spectrum of TiO_2 membrane.



(a)



(b)

Fig. 4. The scanning electron micrograph (SEM) of TiO₂ catalyst: (a) 2000 \times ; (b) 7500 \times .

shows the SEM of TiO₂ catalyst. The image shows the delicate structure and sphere form of catalyst, and the size distribution is $<1\ \mu\text{m}$.

For operating conditions with flow rate 364 ml/min, oxygen concentration 20%, trichloroethane concentration $15.1\ \mu\text{M}$, light intensity $3.14\ \text{mW}/\text{cm}^2$, and $32.0\text{--}1270.8\ \mu\text{M}$ of humidity, the experimental results are shown in Fig. 5. When the humidity was $<154.4\ \mu\text{M}$, the reaction rate and the conversion ratio increased slightly as the humidity increased, but when the humidity was $>154.4\ \mu\text{M}$, both the reaction rate and the conversion ratio decreased with the increasing humidity.

In the photocatalytic reaction, hydroxyl free radical plays an important role in promoting the oxidation, and its source mainly comes from water molecule and electron hole. Dibble

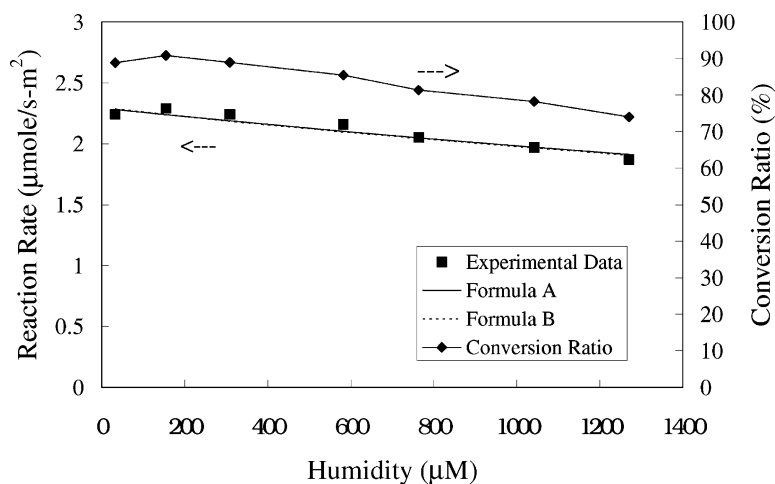


Fig. 5. The reaction rate and conversion ratio at different humidities under the operating conditions of flow rate 364 ml/min, oxygen concentration 20%, trichloroethane concentration 15.1 μM , light intensity 3.14 mW/cm^2 .

and Raupp [7] also pointed out that the activation of the titanium dioxide would gradually decrease with dry gas. Therefore, under the condition of low humidity, an increase in humidity would increase the OH free radicals and increase the reaction rate. However, when the humidity increased, the water molecules and TCE might form hydrogen bonds with the hydroxyl groups on the TiO_2 surface. Thus, the water molecules and TCE were adsorbed onto the activated sites of the TiO_2 surface. A competition for adsorption ensued between the water molecules and TCE for the same adsorption sites. When the TCE concentration remained constant and the concentration of water molecules gradually increased, the adsorption would tend to favor the water molecules. In addition, as Gonzalez-Elipse et al. [10] have indicated, the excited mechanism for the TiO_2 by the illumination produced an exciting center ($\text{Ti}^{+3}-\text{O}^-$), and received photogenerated electron-hole pairs to form a reaction intermediate in the exciting process. Then, a coordinate bond was formed by desorption of water molecule and the oxygen molecule was allowed to link with it and the hydroxyl free radical was released. Because of high humidity, it was possible to retard the removal of water molecules from this excited process, and hindered the sequent release of hydroxyl free radicals. Therefore, when the humidity was increased, the reaction rate decreased accordingly due to the competitive adsorption and the suppression of the water molecule desorption from the exciting center.

Fig. 6 shows the relation of the reaction rate and the conversion ratio at the different oxygen concentrations under the operating conditions of a flow rate 364 ml/min, humidity 154.4 μM , light intensity 3.14 mW/cm^2 , trichloroethane concentration 15.2 μM . By increasing the oxygen concentration from 0 to 4%, the reaction rate and the conversion ratio increased. Moreover, when the oxygen concentration was >4%, the reaction rate and conversion ratio increased gradually. When the oxygen concentration was >12%, the reaction rate would no longer rise but was almost at a steady state.

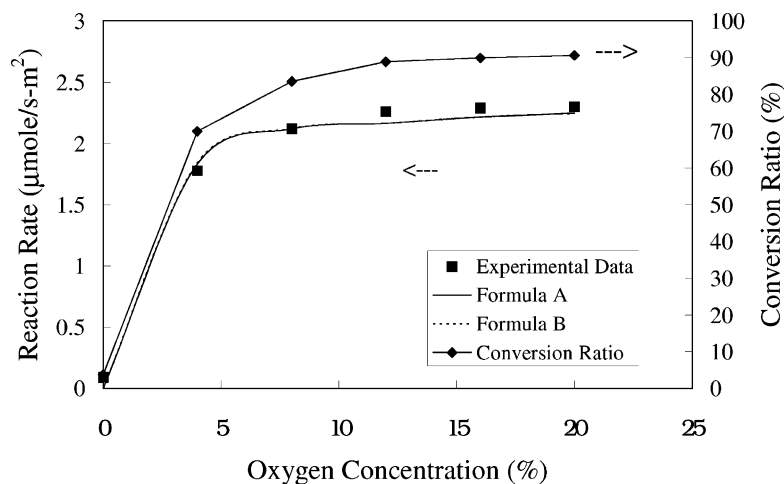
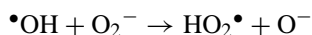
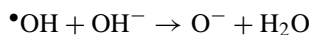
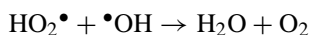
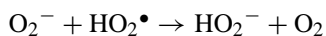
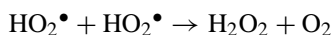
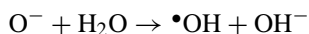


Fig. 6. The reaction rate and conversion ratio at different oxygen concentrations under the operating conditions of a flow rate 364 ml/min, humidity 154.4 μM , light intensity 3.14 mW/cm^2 , trichloroethane concentration 15.2 μM .

When the oxygen molecule was adsorbed onto the TiO_2 surface, it would react with the photogenerated electrons to form a $\bullet\text{O}_2^-$ radical, and decreased the rate of the recombination of the photogenerated electrons and positive holes. In addition, the $\bullet\text{O}_2^-$ would form $\bullet\text{OH}$ after a series of reactions. Therefore, when there was oxygen in the reaction system, it helped facilitate the decomposition reaction for the trichloroethane. This result might explain why the reaction rate increased as the oxygen concentration increased. However, when the oxygen concentration kept increasing, the adsorption of the oxygen molecules on the TiO_2 surface gradually reached saturation consequently, the continuous increase in oxygen did not have any significant effect in increasing the reaction rate and the conversion ratio. On the other hand, the captured positive holes formed the hydroxyl free radicals with the OH^- and would proceed with the following reactions on the hydrated TiO_2 surface [11]:



The O^- and $\text{HO}_2\bullet$ formed in the previous reactions might proceed with the following reactions:



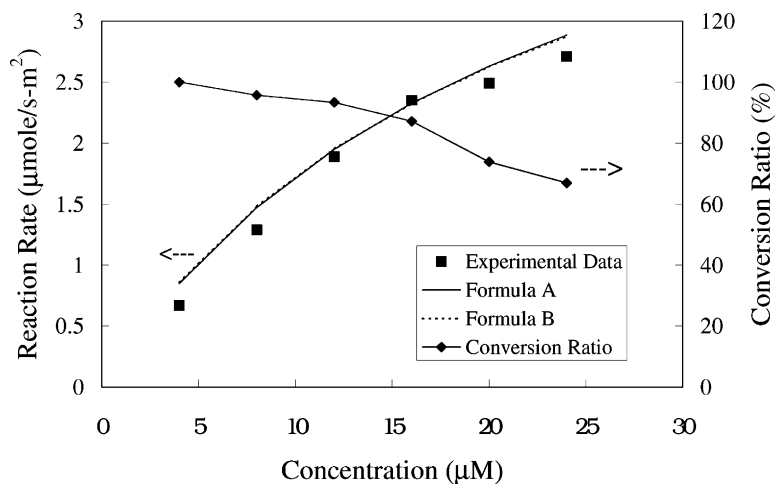


Fig. 7. The reaction rate and conversion ratio at different initial trichloroethane concentrations under the operating conditions of flow rate 364 ml/min, oxygen concentration 20%, humidity 154.4 μM , light intensity 3.14 mW/cm^2 .

In the foregoing reactions, it reached a kinetically steady state of adsorption–desorption for oxygen on TiO_2 surface. The existence of the oxygen promoted the reaction rate, but at a high oxygen concentration, the increase of oxygen would not raise the reaction rate.

Fig. 7 shows the influence of different initial concentrations of trichloroethane on the reaction rate and conversion ratio under the operating conditions of flow rate 364 ml/min, oxygen concentration 20%, humidity 154.4 μM , light intensity 3.14 mW/cm^2 . The results showed that the reaction rate increased with the increasing concentration, but it decreased at high initial concentrations. When the trichloroethane concentration was relatively low, the conversion ratio reached 100%. However, when the concentration was increased to 24 μM , the conversion ratio declined to 67%.

From this figure, one can see a typical adsorption–desorption control reaction [12]. At a constant humidity and at a lower trichloroethane concentration, the increase of the trichloroethane concentration increased the concentration gradient of trichloroethane between the bulk phase and TiO_2 surface. Therefore, the reaction rate limitation was the diffused rate of the reactant to the TiO_2 surface. The reaction rate would increase as the concentration increased. However, when the concentration continued to rise, the surface adsorption sites provided by the TiO_2 were limited. It did not increase the adsorption quantity of the reactant. At that time, the limitation condition of reaction was controlled by a reaction product desorption, and the increasing tendency of the reaction rate slowed down [12]. On the other hand, the conversion ratio was not like the reaction rate that increased as the concentration of trichloroethane increased, but decreased as the concentration of trichloroethane increased. This result indicated that the increasing reaction rate, or the increasing change of decomposed trichloroethane concentration in a time interval, the decomposition quantity increased was not greater than the change of increasing initial trichloroethane concentration, therefore, the conversion ratio showed an opposite tendency to the reaction rate.

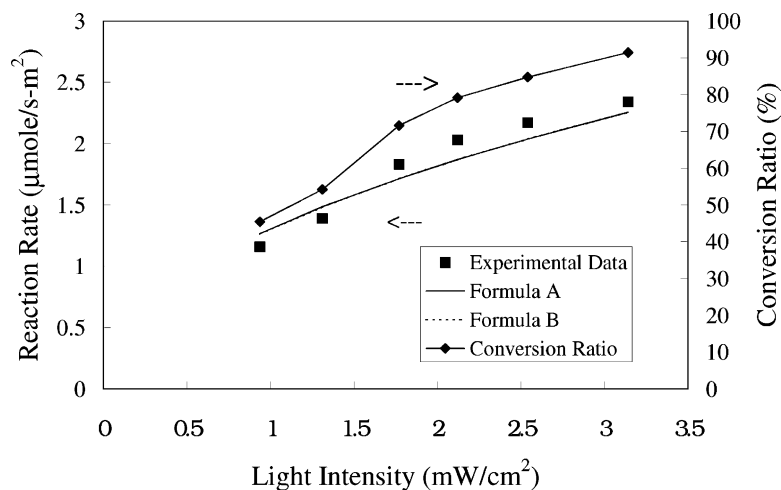


Fig. 8. The reaction rate and conversion ratio at different light intensities under the operating conditions of flow rate 364 ml/min, oxygen concentration 20%, humidity 154.4 μM , trichloroethane concentration 15 μM .

The experimental results in Fig. 8 show the influence of different light intensity on the photocatalytic reaction at a flow rate of 364 ml/min, oxygen concentration of 20%, humidity of 154.4 μM , and trichloroethane concentration of 15 μM . Both the reaction rate and the conversion ratio increased as the light intensity increased.

When the energy of the incident photon exceeds the energy gap, the electron at the valance band may be excited to the conduction band, leaving a positive hole in the valance band [13]. Since the energy of the incident photon kept illuminating, the electron–positive hole pair would be generated continuously. While, the recombination of the electron and positive hole would offset the input energy or it might move to the surface of the semiconductor and proceed to oxidation–reduction reaction with the electron donor or electron acceptor. Therefore, the larger the light intensity, the larger was the formation of the electron–positive hole pairs. Hence, the reaction rate was increasing. In addition, when the light intensity was $>2.12 \text{ mW/cm}^2$, the increase in reaction rate slightly decreased. This result showed that the proportion of the increasing photogenerated electron–hole pair participated in the oxidation–reduction reaction was not increased. It tended to make the photogenerated electron–hole pairs to recombine.

It was found on that if there was no oxygen, the reaction could not proceed. Oxygen acted as an electron acceptor that prohibited the recombination of the electron and the positive hole and formed the free radicals. Therefore, although oxygen did not participate in the trichloroethane decomposition reaction directly, it was a major factor in the reaction. Jacoby et al. [14] indicated that the existence of oxygen would not affect the adsorption of the reactant on the TiO_2 surface. Therefore, the trichloroethane and O_2 were assumed to adsorb onto different activated sites, and the coverage of trichloroethane and O_2 on the TiO_2 surface would not influence each other [14].

The reaction rate can be expressed as follows:

$$r = -\frac{dc}{dt} = k\theta_{\text{TCEA}}\theta_{\text{O}_2} \quad (2)$$

$$\theta_{\text{TCEA}} = \frac{K_{\text{TCEA}}C_{\text{TCEA}}}{1 + K_{\text{TCEA}}C_{\text{TCEA}}} \quad (3)$$

$$\theta_{\text{O}_2} = \frac{K_{\text{O}_2}C_{\text{O}_2}}{1 + K_{\text{O}_2}C_{\text{O}_2}} \quad (4)$$

where k is the rate constant, θ_{TCEA} the coverage of trichloroethane on TiO_2 , θ_{O_2} the coverage of O_2 on TiO_2 , C_{TCEA} the concentration (μM) of trichloroethane, C_{O_2} the concentration (% v/v) of O_2 , K_{TCEA} adsorption constant (μM^{-1}) for trichloroethane, and K_{O_2} is the oxygen adsorption constant (μM^{-1}).

When the humidity is taken into consideration, this study agrees with other results in the literature [3,7]. Specifically the increase in humidity would suppress the reaction rate. Therefore, it is assumed that the water molecule itself did not participate in the reaction and would compete with trichloroethane for the activated sites. Thus, the following formula was obtained:

$$r = k \frac{K_{\text{TCEA}}C_{\text{TCEA}}}{1 + K_{\text{TCEA}}C_{\text{TCEA}} + K_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}} \frac{K_{\text{O}_2}C_{\text{O}_2}}{1 + K_{\text{O}_2}C_{\text{O}_2}} \quad (5)$$

where $K_{\text{H}_2\text{O}}$ is the competitive adsorption constant for water molecules and TCEA (μM^{-1}), and $C_{\text{H}_2\text{O}}$ is the water molecule concentration (μM).

If both the water molecules and trichloroethane would also compete with the water molecules for the adsorption sites, the following formula was obtained:

$$r = k \frac{K_{\text{TCEA}}C_{\text{TCEA}}}{1 + K_{\text{TCEA}}C_{\text{TCEA}} + K_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}} \frac{K_{\text{O}_2}C_{\text{O}_2}}{1 + K_{\text{O}_2}C_{\text{O}_2} + K'_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}} \quad (6)$$

where $K'_{\text{H}_2\text{O}}$ is the competitive adsorption constant for water molecules and oxygen (μM^{-1}).

Peral and Ollis [15] indicated that the reaction rate was proportional to the exponential of light intensity, therefore Eqs. (5) and (6) were modified as following.

Formula A (for the reaction model that water molecules will only compete with trichloroethane for the adsorption):

$$r = k \frac{K_{\text{TCEA}}C_{\text{TCEA}}}{1 + K_{\text{TCEA}}C_{\text{TCEA}} + K_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}} \frac{K_{\text{O}_2}C_{\text{O}_2}}{1 + K_{\text{O}_2}C_{\text{O}_2}} I^N \quad (7)$$

Formula B (for the reaction model that water molecules will compete with both the TCEA and the oxygen for the adsorption):

$$r = k \frac{K_{\text{TCEA}}C_{\text{TCEA}}}{1 + K_{\text{TCEA}}C_{\text{TCEA}} + K_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}} \frac{K_{\text{O}_2}C_{\text{O}_2}}{1 + K_{\text{O}_2}C_{\text{O}_2} + K'_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}}} I^N \quad (8)$$

where I is the light intensity (mW/cm^2), N the constant, k the rate constant ($\mu\text{mol}/(\text{s m}^2)/(\text{mW}/\text{cm}^2)^N$).

Table 1
The coefficients of Eqs. (7) and (8)

	k	K_{TCEA}	$K_{\text{H}_2\text{O}}$	$K'_{\text{H}_2\text{O}}$	K_{O_2}	N
Eq. (7)	3.40356	0.046950	0.000266	–	0.832225	0.478027
Eq. (8)	3.322610	0.049157	0.000333	0.788938	–0.000425	0.479901

Performing a non-linear regression using commercial software “STATISTICA” for the experiment results shown in Figs. 5–8 with two Eqs. (7) and (8), we obtained the results shown in Table 1. Figs. 5–8 showed the modeling results were very close to the experimental data. In order to discern the applicability of these two models in other conditions, we performed experiments under the operating conditions shown in Figs. 5–7 at higher humidity (1270.8 μM), lower oxygen concentrations (4%), and higher trichloroethane concentrations (24 μM). For higher humidity and higher trichloroethane concentration, these two models were still applicable, but for lower oxygen concentration as shown in Fig. 9, the difference between experimental data and Eq. (8) increased with the increasing humidity. These results indicated that Eq. (8) had a larger error for the reaction forecast under these operating conditions. Therefore, Eq. (7) was applicable for the reaction predicted in this research. Furthermore, the reaction-order (0.48) for light intensity was obtained from this model. Jacoby et al. [14] indicated that the first-order reaction of the light intensity and reaction rate was mainly based on the consumption of the photogenerated electron–hole pairs. In the 0.5-order reaction, the reaction was preceded mainly following the recombination of the electron–positive hole pairs. The light intensity reaction-order of this research was

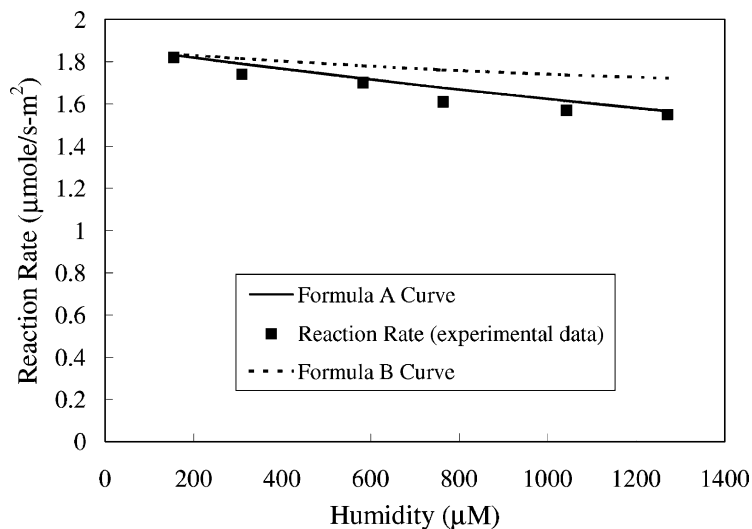


Fig. 9. The experimental data and predicted equation curves at oxygen concentration 4% and different humidity under the operating conditions of flow rate 364 ml/min, trichloroethane concentration 15.1 μM , light intensity 3.14 mW/cm^2 .

0.48. Thus, this study was in agreement with Jacoby's that the reaction mechanism in the light intensity ranges of this study was likely belong to the photogenerated electron–hole recombination.

4. Conclusions

1. The titanium dioxide catalyst prepared by the CVD was identified by the XRD and the result showed that its composition was of the anatase crystal structure.
2. Since water molecules were the main source for the hydroxyl free radicals, the increase in water molecule concentration at low humidity increased the reaction rate slightly. However, the excess amount of water molecules competed with the reactant for the adsorption. Hence, as the humidity increased, the reaction rate and the conversion ratio decreased accordingly.
3. Without oxygen molecules, the lowest reaction rate $0.09 \mu\text{mol}/(\text{s m}^2)$ occurred and it rose to $1.78 \mu\text{mol}/(\text{s m}^2)$ as the oxygen increased. However, when the oxygen content reached 12% (v/v), the reaction rate did not rise.
4. The initial concentration of the reactant was positively related to the reaction rate and it increased from $0.67 \mu\text{mol}/(\text{s m}^2)$ up to $2.71 \mu\text{mol}/(\text{s m}^2)$. However, the increase of initial concentration was negatively related with the conversion ratio, and the conversion ratio dropped from 99.9 to 66.9%.
5. The higher the light intensity, the more the excited electron–hole pairs. Therefore, the reaction rate rose from 1.16 to $2.34 \mu\text{mol}/(\text{s m}^2)$. However, when the light intensity was $>2.12 \text{ mW}/\text{cm}^2$, the increase in reaction rate slowed down slightly due to the increase in recombination of electron and positive hole pairs.
6. The results of this study could be successfully fitted by the Langmuir–Hinshelwood bimolecular equation:

$$r = 3.40356 \frac{0.046950 C_{\text{TCEA}}}{1 + 0.046950 C_{\text{TCEA}} + 0.000266 C_{\text{H}_2\text{O}}} \frac{0.832225 C_{\text{O}_2}}{1 + 0.832225 C_{\text{O}_2}} I^{0.48} \quad (9)$$

7. The reaction rate was proportional to the 0.48-order of light intensity, indicating that the recombination of the electron–positive hole pairs dominated the photo-reaction.

References

- [1] W.T. Tsai, *Ind. Pollut. Prev.* 43 (1992) 175.
- [2] K.T. Liu, *Ind. Pollut. Prev.* 48 (1993) 15.
- [3] T.N. Obee, S.O. Hay, *Environ. Sci. Technol.* 31 (1997) 2034.
- [4] S.A. Larson, J.L. Falconer, *Appl. Catal. B Environ.* 4 (1994) 325.
- [5] G.B. Raupp, C.T. Junio, *Appl. Surf. Sci.* 72 (1993) 321.
- [6] C.H. Hung, B.J. Marinas, *Environ. Sci. Technol.* 31 (1997) 562.
- [7] D.A. Dibble, G.B. Raupp, *Catal. Lett.* 4 (1990) 345.
- [8] Y. Luo, D.F. Ollis, *J. Catal.* 163 (1996) 1.
- [9] K.Y. Lai, *The Technology of Coating Film for Ceramic Material*, 1st Edition, Fu-Han Publishing, Tainan, Taiwan, 1989, p. 38.

- [10] A.R. Gonzalez-Elipe, G. Munuera, J.J. Soria, Chem. Soc., Faraday Trans. I 72 (1976) 1642.
- [11] G. Munuera, V. Rivrs-Arnau, A. Saucedo, J. Chem. Soc., Faraday Trans. I 75 (1979) 736.
- [12] O. Levenspiel, Chemical Reaction Engineering, Wiley, New York, 1972.
- [13] P.S. Rominder, J. Lin, D.W. Hand, J.C. Crittenden, D.L. Perram, M.E. Mulins, Water Environ. Res. 65 (1993) 655.
- [14] W.A. Jacoby, D.M. Blake, R.D. Noble, C.A. Koval, J. Catal. 157 (1995) 87.
- [15] J. Peral, D.F. Ollis, J. Catal. 136 (1992) 554.