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A Kinetic Study on the Photocatalytic Degradation of Gas-Phase VOCs Using TiO_2 photocatalyst

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Abstract

The present paper examined the kinetics of photocatalytic degradation of volatile organic compounds (VOCs) including gaseous trichloroethylene (TCE) and acetone. In this study, we examined the effects of the initial concentration of VOCs and the light intensity of ultra-violet (UV). A batch photo-reactor was specifically designed for this work. The photocatalytic degradation rate increased with the initial concentration of VOCs but remained almost constant beyond a certain concentration. It matched well with the Langmuir-Hinshelwood (L-H) kinetic model. When the effect of light intensity was concerned, it was found that photocatalytic degradation occurs in two regimes with respect to light intensity.

Key words : Kinetics of photocatalytic degradation, Volatile organic compounds, Gas phase, Batch photo-reactor

1. INTRODUCTION

VOCs are widely used in industrial processes and domestic activities. These extensive uses of VOCs have led to water and air pollution, particularly in indoor air pollution (EPA, 1987). Many VOCs are known to be toxic and considered to be carcinogenic. The most significant problem related to the emission of VOCs is centered on the potential production of photochemical oxidants; for example, ozone and peroxyacetyl nitrate (PAN).

Photocatalytic degradation of organic compounds using TiO_2 as a catalyst has been proposed as an alternative advanced oxidation process (AOP) for the decontamination of water and air. AOP is initiated from the generation of hole-electron pairs on the semiconductor upon absorbing UV light with energy equal to or higher than the band gap energy. Electrons and holes photogenerated in the bulk of the semiconductor upon absorbing UV move to the particle surface. The electrons can reduce electron acceptors such as molecular oxygen, and the holes can oxidize electron donors including adsorbed water or hydroxide anions to give

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hydroxyl radicals (Hoffmann *et al.*, 1995).

The common VOCs such as halogenated hydrocarbons, ketones, ethers, alcohols and aromatic compounds, among which TCE has been widely used in industries, therefore it was easily found in the emission from chemical processing (e.g. cleaning processing), dumping ground, hazardous material disposal site, groundwater remediation site and even in the indoor air (Shen *et al.*, 1993). And acetone represents a serious air pollutant for indoor environment. Photocatalytic oxidation has a number of advantages for treating air pollutants, especially for the removal of organic admixtures. Many researchers have recently examined TCE in gas phase photocatalytic degradation. In order to determine the kinetics of conversion of trace (0～100 ppm) TCE, Dibble and Raupp (1992) systematically investigated the photo-oxidation of it in air using both a fixed-bed reactor and a fluidized bed reactor. According to the study by Anderson *et al.* (1993), it was found that the TCE photocatalytic degradation rate depends on light intensity, feed composition (TCE, O_2, H_2O), and temperature in a bed reactor packed with TiO_2 pellets. The reaction rate was the first order with respect to light intensity, and was independent of the concentration in the range of 37～450 ppm of TCE with the oxygen mole fraction 0.01～0.2 and water vapor mole fraction 0.001～0.028. Wang *et al.* (1998) examined the kinetics of photocatalytic degradation of TCE in gas phase over TiO_2 supported on glass bead.

Photocatalytic oxidation of acetone in the gas phase has been discussed in several recent publications (El-Maazawi *et al.*, 2000; Vorontsov *et al.*, 2000; Vorontsov *et al.*, 1999; Alberici and Jardim, 1997; Peral and Ollis, 1992). Peral and Ollis (1992) studied the photocatalytic oxidation of organics including acetone. The study showed that the integral conversion rate data from single component runs could provide the parameters of kinetics for a L-H rate expression. El-Maazawi *et al.* (2000) examined adsorption and photocatalytic oxidation of acetone on TiO_2. They showed that the adsorption of acetone has been followed as a function of coverage on clean TiO_2 surfaces. Vorontsov *et al.* (2000) investigated the kinetics of the photocatalytic oxidation of gaseous acetone over Pt/TiO_2 prepared by photodeposition as well as by reduction with $NaBH_4$. They showed that the increased activity of Pt/TiO_2 prepared by reduction with $NaBH_4$ is related to the stronger adsorption of acetone and higher rate constant.

In the present work, the kinetics of photocatalytic degradation of the representative VOCs such as TCE and acetone in the gas phase on TiO_2 was closely studied. Photocatalytic degradation reaction was carried out using a thin film of TiO_2 coated on the internal surface of a glass tube. A batch photo-reactor experiment was carried out prior to the acquisition of fundamental data for a scaled-up photo-reactor design and the application of continuous process for the gas-solid heterogeneous photocatalytic reaction. The L-H kinetics was successfully applied to describe the heterogeneous gas-solid reaction. A batch reactor under UV light was applied for the photocatalytic degradation rate as a function of the initial concentration of VOCs and the light intensity of UV.

2. EXPERIMENTAL

2. 1 Preparation of photocatalyst

All of the chemicals used in this work were reagent-grade. The liquid phase VOCs were products of Aldrich (TCE-anhydrous, 99%, acetone-A.C.S. reagent, 99.5%). The photocatalyst was prepared from TiO_2 solution (STS-01, anatase, 7 nm in diameter, 300 $m^2 g^{-1}$ for specific surface area, Ishihara Sangyo Co., Japan), tetraethyl orthosilicate (TEOS, 98%, Aldrich, U.S.A.), dimethoxy dimethyl silane (DMDMS, 95%, Aldrich, U.S.A.), isopropyl alcohol (IPA, anhydrous, 99.5%, Aldrich, U.S.A.) and nitric acid (65 wt.% solution in water, Aldrich, U.S.A.). Deionized and doubly distilled water was used for the generation of water vapor and the preparation of the photocatalyst.

The photocatalyst solution was prepared through a three-step process as follows: TEOS (2 g) and DMDMS (1 g) were added to the IPA (10 g) on a vessel con-

nected to a condenser at room temperature (1st step). A solution combined with IPA (10 g), deionized water (0.5 g) and nitric acid (0.03 g) was dropped in the solution prepared in the first step at a temperature of about 5°C for 60 min, and stirred for two hours (2nd step). STS-01 (35 g) was then dropped in a solution combined with IPA (15 g), deionized water (15 g) and the solution (22.5 g) prepared in the second step at a temperature of about 5°C for 60 min, and stirred for three hours (3rd step).

A TiO_2 thin film photocatalyst was formed by the dip-coating method. After filling a Pyrex glass tube with the TiO_2 photocatalyst solution, it was removed from the Pyrex glass tube at a constant rate of 5 mm min^{-1}. Then, the Pyrex glass tube coated with TiO_2 was dried at 120°C for one hour.

2. 2 Reactor system

The apparatus used for this work was depicted previously (Kim *et al.*, 2001). A batch reactor made of Pyrex glass had a 100 mm inside diameter, 210 mm height and 1,600 cm^3 total volume. The upper part of the reactor was sealed with a Teflon lid. A vertical UV lamp (15.5 mm outside diameter, 210.5 mm length) was vertically inserted in the center of the reactor. Germicidal lamp (Model G6T5, 6 W, Sankyo Denki Co., LTD, Japan) and fluorescent black light lamp (Model F6T5 BL, 6 W, Sankyo Denki Co., LTD, Japan) were used as light sources. The wavelength of the germicidal lamp ranged from 200 to 300 nm with the maximum light intensity at 254 nm, and that of the black light lamp ranged from 315 to 400 nm with the maximum light intensity at 352 nm. Pyrex glass tubes (inside diameters: 20, 26, 30, 35 and 60.5 mm, height: 165 mm) coated by a TiO_2 photocatalyst solution at the internal surface were fixed to the exterior of the UV lamp. The distance between the surface of the UV lamp and the TiO_2 thin film photocatalyst was increased to 3.25, 5.25, 7.25, 9.75 and 22.5 mm, respectively. Varying the distance between the surface of the UV lamp and the TiO_2 thin film photocatalyst controlled the photon flux of UV light. A magnetic stirrer at the bottom of the reactor achieved effective dispersion. A thermoregulated bath -circulator (Model TB-85, Shimazu, Japan) unit was connected to the reactor jacket to control the temperature of the reactor. The concentration of VOCs was measured by a gas chromatograph (Model HP 6890, Hewlett-Packard, U.S.A.). The gas chromatograph was equipped with a capillary column (Model HP-5, Agilent Technologies, U.S.A.) of 30 m length, 0.25 μm film thickness and 0.32 mm internal diameter.

2. 3 Experimental methods

The batch reactor was flushed and filled with dry air prior to the injection of liquid phase VOCs and water. The desired amount of water was then injected and allowed to evaporate, mix and reach adsorption equilibrium with the TiO_2 thin film photocatalyst. Next, the desired amount of VOCs was injected in the liquid phase and allowed to evaporate, mix, and reach gas-solid adsorption equilibrium. Once the concentration of VOCs stabilized, the UV lamp was turned on and the concentration of VOCs was recorded with the reaction time throughout the test. Sampled VOCs were circulated by a low-flow diaphragm pump (Model SP 600 EC -LC, SP J. Schwarzer GmbH u. Co., Germany) and injected through a six-port external injection GC valve (6890 Valve system, Agilent Technologies, U.S.A.) with a 250 μl automatic sample loop. The samples were then transferred to a gas chromatograph with pure helium as a carrier gas. Temperatures of the injector and column were maintained at 120 and 200°C, respectively. The flame ionization detector was maintained at 250°C.

2. 4 Characterization of photocatalyst

In this experiment, the TiO_2 thin film was prepared by dip-coating method using TEOS, DMDMS, and STS-01 as starting materials. In order to form thin particulate films of TiO_2 (STS-01) with superior adhesion onto a Pyrex glass support, TEOS and DMDMS as coupling agents were used together.

A uniform and transparent TiO_2 thin film with a thickness of about 65 nm was prepared onto an internal surface of a Pyrex glass tube. Scanning electron mi-

croscopy (SEM, Philip SEM-535M) images were depicted previously (Kim *et al.*, 2001). The film consists of small crystalline particles with an average diameter of about 40 nm. Since the average particle size in the TiO_2 solution was about 7 nm, it is assumed that the particles aggregated during heat treatment. TiO_2 used was found to be Anatase by means of X-ray diffraction (Rigaku D/MAX-III (3 kW) diffractometer). As previously depicted (Kim *et al.*, 2001), there were four remarkable peaks at the angles of 2θ : 25.38, 38.14, 48.04 and 55.02. Specific surface areas of the particles were determined by the BET (Model ASAP 2100, Micrometritics, U.S.A.) method. The BET surface area of the prepared TiO_2 particles was 277 $m^2 g^{-1}$.

3. RESULTS AND DISCUSSION

3. 1 Effect of initial concentration

In general, the kinetics would follow the L-H model, in which the reaction rate (r) varies proportionally with the surface coverage (θ) as;

$$r = k\theta = \frac{kKC}{1+KC} \tag{1}$$

where k and K are the reaction rate constant and the adsorption equilibrium constant, and C is the concentration of VOCs (Ollis *et al.*, 1991).

Owing to the complex mechanism of reactions, it is difficult to develop a model for the dependence of the photocatalytic degradation rate on the experimental parameters during the whole period of the treatment. Thus, kinetic modeling of the photocatalytic process is usually restricted to the analysis of the initial rate of photocatalytic degradation. This can be obtained from the initial slope and the initial VOCs' concentration in an experiment in which the variation of the VOCs concentration is measured as a function of time. The extrapolation of the photocatalytic degradation rate to time = 0 avoids the possible interference from by-products. The initial photocatalytic degradation rate (r_o) is observed to be a function of the initial VOCs' concentration (Co). A linear plot of r_o^{-1} versus C_o^{-1} is often obtained, that gives k as the L-H rate constant and K as the Langmuir adsorption constant of the VOCs in the photocatalytic degradation reaction (Eq. (2)).

$$r_o = \frac{kKC_o}{1+KC_o} \quad \text{or} \quad \frac{1}{r_o} = \frac{1}{kK}\frac{1}{C_o} + \frac{1}{k} \tag{2}$$

In order to find the effect of initial concentration on the photocatalytic degradation rate, more detailed analysis was fulfilled based on the kinetics of photocatalytic degradation reaction. Fig. 1 shows the variation of concentration of TCE and acetone in air with the

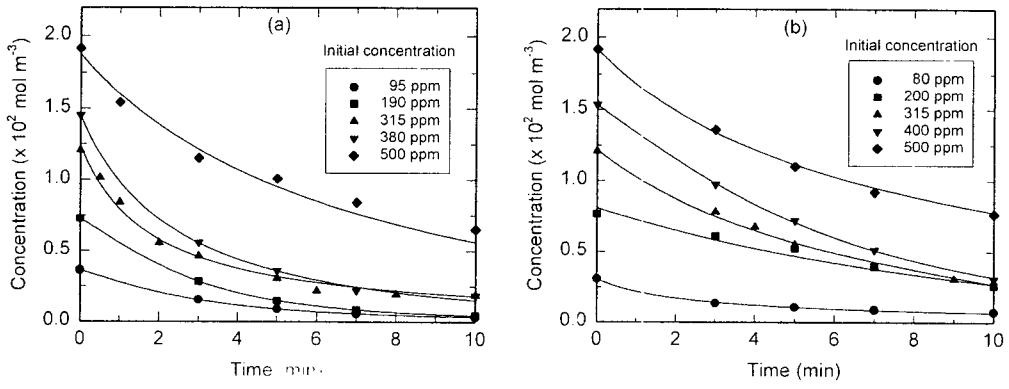

Fig. 1. Photocatalytic degradation of each VOC according to initial concentrations ((a) TCE (water vapor, C_{H_2O} = 3.83 (10^{-1} mol m^{-3}), (b) Acetone (C_{H_2O} = 0.0 mol m^{-3}); UV source: germicidal (254 nm) lamp, light intensity: 2,095 μW cm^{-2}; reaction temperature: 45°C).

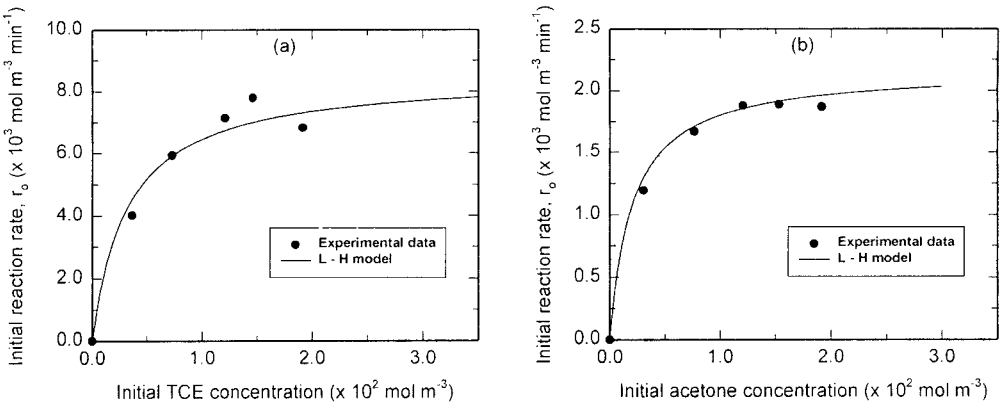

Fig. 2. Initial reaction rate of each VOC photocatalytic degradation versus initial VOCs concentration ((a) TCE (water vapor, C_{H_2O} = 3.83 (10^{-1} mol m^{-3}),(b) Acetone (C_{H_2O} = 0.0 mol m^{-3}; UV source: germicidal (254 nm) lamp, light intensity: 2,095 μW cm^{-2}; reaction temperature: 45°C).

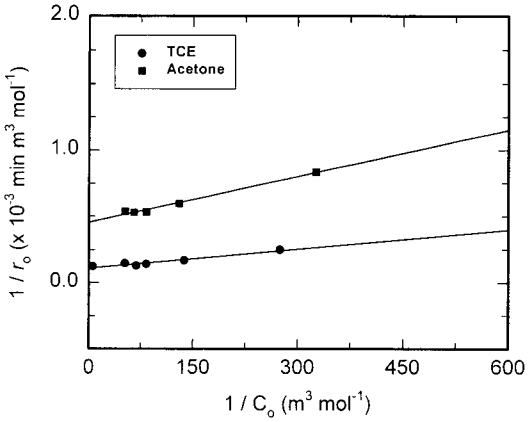

Fig. 3. Langmuir-Hinshelwood plots of the reciprocal of the initial reaction rate versus the reciprocal of the initial VOCs' concentration (the same experimental conditions as in Fig. 2).

reaction time for five different initial levels. As can be seen in Fig. 1, the initial slope increased with increasing initial concentration of TCE and acetone, but maintained almost constant beyond a certain concentration. Fig. 2 describes the initial photocatalytic degradation rate (r_o) for initial concentration of TCE and acetone. The steep rise of the rate at low levels of TCE and acetone and the subsequent mild variation are a typical behavior of L-H kinetics. Fig. 3 shows plot of the reciprocal of the initial rate, r_o^{-1}, versus the reciprocal of the initial concentration of TCE and acetone, C_o^{-1}, for photocatalytic degradation of TCE and acetone. The kinetic parameters k and K were obtained using linear regression analysis. Table 1 summarizes the kinetic parameters of photocatalytic degradation reaction for the identical conditions. By substituting the k and K values into Eq. (2), the analytical relationship between r_o and C_o is obtained. The solid line drawn in Fig. 2 represents this relationship; a good fitting of the model to the experimental data may be observed, thus confirmed the L-H nature of the photocatalytic degradation reaction mechanism.

Table 1. Langmuir-Hinshelwood parameters obtained in the photocatalytic degradation of TCE and acetone.

Compounds	k (mol m^{-3} min^{-1})	K (m^3 mol^{-1})	kK (min^{-1})
TCE	9.108×10^{-3}	229.2	2.087
Acetone	2.199×10^{-3}	392.3	0.863

In the mean time, as shown in Table 1, photocatalytic degradation rate constant of TCE is much higher than that of acetone. It should be due to the rapid chain reaction of chlorine radicals, as reported by several researchers (Luo and Ollis, 1996; Sauer *et al.*, 1995). It is interesting to note that the photocatalytic degradation

rate relates to k and K; therefore, a higher adsorption constant does not always result in a higher reaction rate. Although it could be thought that a high rate constant leads to a rapid reaction, the reaction rate based on the L-H kinetic model depends simultaneously on k and K. In practice, acetone was larger than TCE for the adsorption constant, but TCE was larger than acetone for the multiplied products of k and K.

3. 2 Effect of light intensity

Photon energy from the irradiation source is an important factor in photocatalytic reaction. Photocatalytic reaction occurs in two regimes in association with light intensity of UV light: first-order regime and half-order regime. In the former, the electron-hole pairs are consumed more rapidly by chemical reactions than by recombination reaction decreasing the photocatalytic degradation rate; whereas in the half-order regime the recombination rate is dominant (Wang *et al.*, 1998; Jacoby *et al.*, 1995; Ollis *et al.*, 1991).

In order to find the effect of the light intensity of UV on the photocatalytic degradation rate, varying the distance (3.25, 5.25, 7.25, 9.75, and 22.50 mm) between the surface of the UV lamp and the TiO_2 thin film photocatalyst controlled the light intensity of UV. The light intensities for two lamps (germicidal and black light lamp) are summarized in Table 2. In this experiment, two different reaction rate regimes as a function of the light intensity of UV were observed by using different UV lamps. As shown in Fig. 4, it was found that the reaction rate depends on the light intensity (I) of UV in a power law (Ollis *et al.*, 1991) such as;

$$r = r' I^{\alpha} \tag{3}$$

where is the reaction rate independent of light inten-

Table 2. Light intensities for germicidal and black light lamp according to distance between the surface of the UV lamp and the TiO_2 thin film photocatalyst.

Distance (mm)	Light intensity ($\mu W\ cm^{-2}$)	
	Germicidal lamp	Black light lamp
3.25	3384.6	–
5.25	2095.2	1178.6
7.25	1517.2	853.5
9.75	1128.2	634.6
22.50	–	275.0

Table 3. Exponent values (α) for germicidal and black light lamp in the photocatalytic degradation for TCE and acetone.

Compounds	Germicidal lamp (254 nm)	Black light lamp (352 nm)
TCE	0.35	0.90
Acetone	0.42	0.94

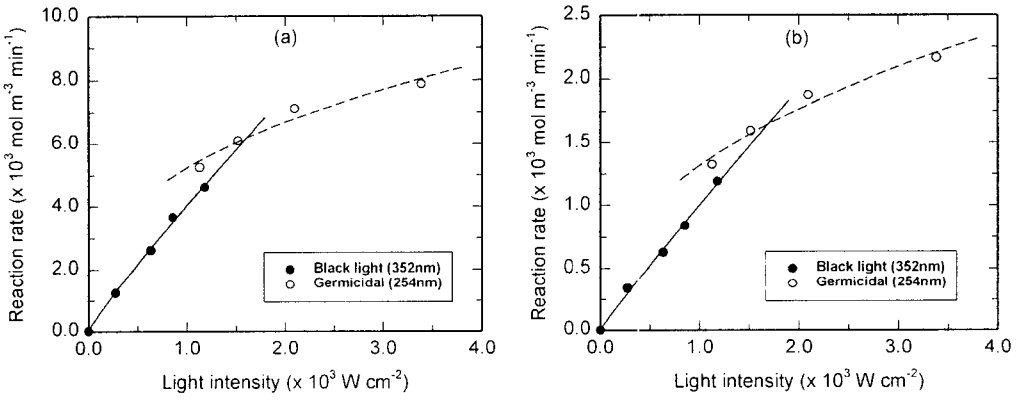

Fig. 4. The effect of light intensity on the photocatalytic degradation rate of each VOC ((a) TCE (initial concentration C_o = 1.206 (10^{-2} mol m^{-3}, water vapor C_{H2O} = 3.83 (10^{-1} mol m^{-3}), (b) Acetone (C_o = 1.208 (10^{-2} mol m^{-3}, C_{H2O} = 0.0 mol m^{-3}); reaction temperature: 45°C).

sity. The exponent value (α) could be estimated from the plot of Fig. 4 and is summarized in Table 3. The tendency of the effect by light intensity was similar to the previous result (Obee and Brown, 1995). For the illumination level appreciably above 1,000~2,000 $\mu W\ cm^{-2}$, the photocatalytic degradation rate increases with the square root of light intensity. For light intensities below 1,000~2,000 $\mu W\ cm^{-2}$, the photocatalytic degradation rate increases linearly with light intensity.

Another factor that might have an influence on the photocatalytic degradation rate of VOCs is wavelength of the UV light. In the present experiment, a germicidal lamp and black light lamp were used to compare the effect of light wavelengths. The wavelength of the germicidal lamp ranged from 200 to 300 nm with the maximum light intensity at 254 nm, and that of the black light lamp ranged from 315 to 400 nm with the maximum light intensity at 352 nm. For both compounds, the germicidal lamp showed higher photocatalytic degradation rate than the black light lamp (Fig. 4). Both lamps have sufficient energy to promote electrons from the valence band to the conduction band of TiO_2. However, since the light intensities of germicidal lamp are higher than those of black light lamp, the higher photon flux output of the germicidal lamp should lead to higher photocatalytic degradation rate.

4. CONCLUSIONS

The photocatalytic degradation rate of VOCs including gaseous TCE and acetone as a function of the initial VOCs' concentration and the light intensity of UV was investigated in a batch photo-reactor. The reactor was designed to be suitable for the proposed test of something, and some results were attained as follows. The photocatalytic degradation rate increased with increasing initial concentration of TCE and acetone, but kept constant rates beyond a certain concentration. The L-H kinetic model was successfully applied to correlate the obtained data. For the effect of the light intensity of UV, it was found that photocatalytic degradation reaction occurs in two regimes with respect to the light intensity: for illumination levels appreciably below 1,000~2,000 $\mu W\ cm^{-2}$, the photocatalytic degradation rate increases linearly with light intensity; while for light intensities above 1,000~2,000 $\mu W\ cm^{-2}$, the photocatalytic degradation rate increases with the square root of light intensity.

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