Degradation of Gaseous Trichloroethylene Over a Thin-Film TiO₂ Photocatalyst

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Abstract: Photocatalytic degradation (PCD) of gaseous trichloroethylene (TCE) over thin-film TiO₂ was examined in a continuous flow system with regard to the mixing condition of the baffle, the inlet concentration of TCE, and the face velocity of the gas flow. The effect of mixing with the baffle on the PCD rate of TCE was found to be positive under conditions of a simultaneous low inlet concentration and a high face velocity. It was found that the effect of mixing could be improved by installation of a baffle, based on the tanks-in-series and dispersion models using residence time distribution (RTD) data in the existence of a baffle. The baffles exhibited continuous-stirred tank reactor (CSTR) behavior in the reactor. The PCD rate continuously increased linearly with the TCE inlet concentration, regardless of the tendency of the Langmuir-Hinshelwood (L-H) kinetics. The face velocity also increased the PCD rate. In the long run, it could be concluded that the PCD rate of TCE may be controlled by mass transfer.

Keywords: photocatalytic degradation rate, trichloroethylene, mass transfer control, surface reaction control, continuous flow system

Introduction

Volatile organic compounds (VOCs) are widely used in industrial processes and domestic activities. Thus, one of the most important technical issues of recent years is the effective and economical disposal of VOCs in air. 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, aldehydes, and peroxyacetyl nitrate. Among these VOCs, TCE represents an especially serious air pollutant for industrial processes or even indoor environments [1]. The PCD of organic compounds using TiO₂ 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 photogenerate in the bulk of the semiconductor and move to the particle surface; electrons reduce electron acceptors (such as molecular oxygen), and holes can oxidize electron donors (including adsorbed water or hydroxide anion) to give hydroxyl radicals [2-4].

The PCD of TCE was first reported by Dibble and Raupp [5] to be much faster than that of hydrocarbons and oxygenates, and apparent quantum yields exceeding 100 % have often been measured for TCE degradation. These very high photon efficiencies imply that a chain mechanism occurs on the TiO₂ surface. To determine the kinetics of conversion of trace (0~100 ppm) TCE, Dibble and Raupp [6] systematically investigated the photo-oxidation in air using both a fixed-bed reactor and a fluidized bed reactor. The observed reaction rate was a positive to zero apparent order in the TCE and oxygen vapor phase mole fraction, depending on the concentration of each species. A trace water vapor presence was found to be necessary to maintain photocatalytic catalyst activity for extended periods of time, but higher water vapor levels were strongly inhibitory. Anderson and coworkers [7] examined the dependency of the TCE
photocatalytic degradation rate on the light intensity, feed composition (TCE, O2, H2O), and temperature in a bed reactor packed with TiO2 pellets. They found that the TCE reaction rate was independent of the flow rate when the conversion was less than 10%, which suggests that external mass transfer was not controlling the reaction rate.

The purpose of the present work was to find the optimum conditions for the PCD of gaseous TCE in a continuous flow system with regard to the mixing conditions (by baffle), the inlet concentration of TCE, and the face velocity of the gas flow.

**Experimental**

**Materials and Preparation of TiO2 Photocatalyst**

All of the chemicals used in the work were reagent-grade. TCE was obtained from Aldrich (anhydrous, 99%). The photocatalyst was prepared from TiO2-sol (STS-01, anatase, 7 nm diameter, 300 m² g⁻¹ specific surface area, Ishihara Sangyo Co.), tetraethyl orthosilicate (TEOS, 98%, Aldrich), dimethoxy dimethyl silane (DMDMS, 95%, Aldrich), isopropyl alcohol (IPA, anhydrous, 99.5%, Aldrich) and nitric acid (65 wt% solution in water, Aldrich). Deionized and doubly distilled water was used for the preparation of the photocatalyst and the generation of water vapor.

The suspension of TiO2 photocatalyst was prepared through a three-step process. TEOS (180 g) and DMDMS (90 g) were added to the IPA (900 g) on a vessel connected to a condenser at room temperature (1st step). A solution combined with IPA (900 g), deionized water (45 g) and nitric acid (2.7 g) was dropped into the solution prepared in the first step at a temperature of ca. 5°C for 60 min, and stirred for 2 h (2nd step). STS-01 (3150 g) was then dropped into a solution combined with IPA (1350 g), deionized water (1350 g), and the solution (2025 g) prepared in the second step at a temperature of ca. 5°C for 60 min, and then stirred for 3 h (3rd step).

A TiO2 thin-film photocatalyst was formed by the dip-coating method. After filling a Pyrex glass reactor with the TiO2 photocatalyst suspension, it was removed from the reactor at a constant rate of 5 mm min⁻¹. Then, the reactor coated with TiO2 was dried at 120°C for 1 h.

**Reactor System**

A schematic representation of the experimental set-up of the continuous flow system used for performing photocatalytic degradation of TCE at the gas-solid interface is shown in Figure 1. It includes three parts: the generator of the gas mixture containing TCD and water vapor, the continuous flow photo-reactor, and the...
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Figure 2. Configuration of baffles in the continuous flow reactor.

Experimental Methods

Once the gas mixture was introduced, the reactor inlet/outlet TCE levels reached adsorption equilibrium. After the adsorption process had reached equilibrium as indicated by equality between the inlet/outlet TCE concentrations, the UV lamp was turned on. The concentration of TCE was recorded with respect to the reaction time throughout the test. The influent/effluent gas sample of the reactor was moved by a low-flow diaphragm pump (Model SP 600 EC-LC, SP J. Schwarzer GmbH u. Co.) and injected through a six-port external injection GC valve (6890 Valve system, Agilent Technologies) possessing a 250 µL automatic sample loop. The sample was then transferred to a gas chromatograph (Model HP 6890, Hewlett-Packard) with pure helium as the carrier gas. The temperatures of the injector and column were maintained at 120 and 200 °C, respectively. The flame ionization detector was maintained at 250 °C.

To examine the effect of the installing baffle on the RTD, the RTD function was determined experimentally through pulse injection of a tracer, methane, into the reactor at the time \( t = 0 \). The concentration of the tracer in the effluent stream was measured as a function of time. Pure methane (5 cc) was injected instantaneously by a gas-tight syringe into the nitrogen feed stream. The outlet concentration of methane was measured using a non-dispersed infrared analyzer (Uras 10 E, Hartmann & Brown Co.).

Results and Discussion

Characterization of TiO₂ Photocatalyst

In this work, the TiO₂ thin film was prepared through the dip-coating method using TEOS, DMDMS, and STS-01 as starting materials. To form thin particulate films of TiO₂ (STS-01) exhibiting superior adhesion onto a Pyrex glass support, TEOS and DMDMS were used together as coupling agents.

A uniform and transparent TiO₂ thin film having a thickness of ca. 65 nm was prepared onto the internal surface of a Pyrex glass reactor. The scanning electron analytical instrument.

A source of main air was supplied from the compressed air cylinders. The gas containing TCE as a model pollutant and water vapor of a desired concentration was generated from a bubbler. This bubbler consisted of a reservoir containing the pure (liquid phase) TCE and water, and it was immersed in a thermoregulated bath-circulator (Model TB-85, Shimazu). The temperature of the thermoregulated bath and the gas flow rate determined the concentration of TCE in air. The volumetric flow rate of the gas stream was controlled electronically by a mass flow controller (Model 8272, Metheson Gas Products). A continuous flow photo-reactor made of Pyrex glass was of annular type and had a 1500 mm length, 75 mm inside diameter, and 80 mm outside diameter. This annular type consisted of a Pyrex glass reactor coated on the inner surface with a TiO₂ photocatalyst and UV lamp (15 mm outside diameter, 1553.6 mm length) inserted in the center of the reactor. A UV lamp (Model G64T5L, Light Sources, INC., 65 W) of the germicidal type was used as a light source. The wavelength of the UV lamp ranged from 200 to 300 nm with the maximum light intensity at 253.7 nm. The concentration of TCE was measured using a gas chromatograph (Model HP 6890, Hewlett-Packard). The gas chromatograph was equipped with a HP-5 capillary column (Agilent Technologies) of 30 m length, 0.25 µm film thickness, and 0.32 mm internal diameter.

The configuration of the baffle in the continuous flow photo-reactor is shown schematically in Figure 2. The aluminum baffle of 70 mm diameter and 0.5 mm thickness was designed with a hole of 20 mm diameter at the center.
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Figure 3. SEM and TEM images of TiO$_2$ film on the Pyrex glass reactor (a) SEM image, top view, (b) SEM image, cross-sectional view, and (c) TEM image.

microscopy (SEM, Philip SEM-535M) images in Figures 3(a) and 3(b) show top and cross-sectional views, respectively. The film consists of small crystalline particles having an average diameter of ca. 40 nm. Because the average particle size in the TiO$_2$ solution was ca. 7 nm, it is assumed that the particles aggregated during heat treatment. A transmission electron microscopy (TEM, Hitachi H-800) image is shown in Figure 3(c). From these Figures, the average diameter of the crystalline particles could be estimated to be ca. 10 nm. The used TiO$_2$ was found to have Anatase form by means of X-ray diffraction [Rigaku D/MAX-III(3 kW) diffractometer]. As shown in Figure 4, there are four remarkable peaks at angles of 2$\theta$ of 25.38, 38.14, 48.04, and 55.02. Specific surface areas of the particles were determined by the BET (Micromeritics ASAP 2100) method. The BET surface area of the prepared TiO$_2$ particles was 277 m$^2$ g$^{-1}$.

Effect of Mixing by Baffle

The most primary parameter in the design of a reactor is the reactor size, including the reactor length or diameter. An annular reactor in which the UV lamp was inserted horizontally in the center of the reactor was used in this study. In the annular reactor, the length and diameter of the reactor are closely associated with the dimensions of the UV lamp. Thus, the reactor diameter is one of the essential process variables in reactor design. In the continuous flow process, the most significant parameter to determine the throughput is the gap between the outside of the UV lamp and the internal surface of the reactor coated with the photocatalyst. Expanding the gap to increase the throughput causes a decrease in the photon flux and a reduction in the mass transfer to the photocatalyst surface in the bulk flow. It thereby results in a decrease of the PCD efficiency. To overcome this problem, a baffle was inserted into the reactor. The baffle affected the flow pattern and the RTD of the gas flow in the reactor, and was supposed to improve the mass transfer by effective mixing. In consequence, the function of baffle was investigated, focusing on the RTD.

From the RTD experiment (Figure 5), the mean residence time and variance can be expressed, respectively, as Equations (1) and (2) [8].

Figure 4. X-ray diffraction patterns of TiO$_2$ film.
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Figure 5. Residence time distribution profiles according to the volumetric flow rate in the (a) absence and (b) presence of the baffle.

\[ t_m = \frac{\int_0^\infty tE(t)\,dt}{\int_0^\infty E(t)\,dt} = \int_0^\infty tE(t)\,dt \]  

(1)

\[ \sigma^2 = \frac{\int_0^\infty (t-t_m)^2E(t)\,dt}{\int_0^\infty E(t)\,dt} = \int_0^\infty (t-t_m)^2E(t)\,dt \]  

(2)

where \( t_m \) (sec) is the mean residence time, \( E(t) \) (sec\(^{-1}\)) is the function of RTD, and \( \sigma^2 \) (sec\(^2\)) is the variance of the RTD function.

There are many situations where the fluid in a reactor is neither well mixed nor approximates plug flow. Thus, we needed to model real reactors in a number of ways. Examples of one-parameter models for tubular reactors include the tanks-in-series model and the dispersion model [8]. That is, one approach involves modeling the non-ideal tubular reactor as a series of identically sized CSTRs. The other approach (the dispersion model) involves a modification of the ideal reactor by imposing axial dispersion on plug flow. For the tanks-in-series model, the parameter is the number of tanks, \( n \); for the dispersion model, it is the dispersion coefficient \( D_a \) [or Peclet number (Pe)]. From the tanks-in-series model and dispersion model, the number of tanks and the Peclet number can be expressed, respectively, as Equations (3) and (4) [8].

\[ n = \frac{t_m^2}{\sigma^2} \]  

(3)

\[ \frac{\sigma^2}{t_m^2} = \frac{2}{Pe} + \frac{8}{Pe^2} \]  

(4)

Table 1. Mean Residence Times, Variance, Number of Ideal Tanks, and Peclet Numbers Obtained from RTD Data in the Absence and Presence of Baffle

<table>
<thead>
<tr>
<th>Flow rate (L min(^{-1}))</th>
<th>In the absence of baffle</th>
<th>In the presence of baffle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( t_m ) (sec)</td>
<td>( \sigma^2 ) (sec(^2))</td>
</tr>
<tr>
<td>5</td>
<td>53.15</td>
<td>11.21(^2)</td>
</tr>
<tr>
<td>10</td>
<td>29.31</td>
<td>6.99(^2)</td>
</tr>
<tr>
<td>20</td>
<td>19.54</td>
<td>5.10(^2)</td>
</tr>
<tr>
<td>30</td>
<td>18.89</td>
<td>4.54(^2)</td>
</tr>
</tbody>
</table>
Effect of Inlet Concentration

In the PCD reaction of the continuous flow system, the PCD rate could be evaluated through a differential method of Equation (5) [9-12].

$$-\dot{Y}_A = \frac{C_{A, in} X_A Q}{S} \tag{5}$$

where, $-\dot{Y}_A$ (mol m$^{-2}$ s$^{-1}$) is the PCD rate; $C_{A, in}$ (mol m$^{-3}$) is inlet concentration of reactant A; $X_A$ is the fractional conversion of reactant A; $Q$ (m$^3$ s$^{-1}$) is the total volumetric flow rate; and $S$ (m$^2$) is the geometric area of the TiO$_2$ photocatalyst coated-glass reactor. Many researchers [6,7,9] have reported that the photocatalytic reaction rate increased linearly with the inlet concentration of TCE at a low inlet concentration, and became constant over a certain inlet concentration, which would obey the typical L-H equation. To observe the effect of the inlet concentration on the PCD rate of TCE in the experiment, the PCD rate was evaluated under the operation conditions of a 5 to 40 L min$^{-1}$ total volumetric flow rate, a 3.83×10$^{-1}$ mol m$^{-3}$ (1.0 vol. %) water vapor content, and a 5.740×10$^{-4}$ to 3.446×10$^{-2}$ mol m$^{-3}$ inlet concentration (Figure 6).

As shown in Figure 6, a high total volumetric flow rate resulted in a higher PCD rate, and the increasing gradient was linear for both low and high total volumetric flow rates. Mass transfer from bulk flow to photocatalyst surface hardly occurs at the low total volumetric flow rate. Then, the PCD rate increased linearly with increasing TCE inlet concentration, because mass transfer could be improved as a result of the increase of molecular diffusion and residence time becoming sufficient.

Meanwhile, despite a short residence time at the high total volumetric flow rate, the photocatalytic degradation reaction of TCE proceeds very rapidly. The photocatalytic degradation rate, after all, increases continuously even at a high total volumetric flow rate. Moreover, differing from the former results, Figure 6 does not show the tendency of the L-H equation. The PCD rate continued to increase linearly with the TCE inlet concentration, suggesting that a dilute reactant in the low inlet TCE concentration may result in the rare possibility of adsorption onto the photocatalyst surface. Thus, an increased inlet concentration merely induces much adsorption, eventually leading to an increase reaction rate. The PCD reaction pretends to be the first-order reaction. Although the surface of the photocatalyst is gradually saturated with reactant molecules at a high inlet concentration of TCE, the PCD rate increases consistently, probably because of the rapid chain reaction of chlorine radicals.
Figure 8. PCD rates and conversions of TCE according to face velocities; inlet concentration: (a) \(2.680 \times 10^{-3}\) and (b) \(5.742 \times 10^{-3}\) mol m\(^{-3}\); the same other conditions as those described in Figure 7.

**Effect of Face Velocity**

The ratio \(Q/S\) in Equation (5) can be defined as a face velocity, which means the flow velocity passing through the reactor \([10,13]\). According to former studies, the reaction rate increases linearly with the face velocity up to a certain face velocity, and then it is kept constant. The region of linear increase is generally dominated by mass transfer control, while the constant region is controlled by the surface reaction.

The present work was performed with the variation of face velocity (\(0.2358 \times 10^{-3}\) to \(1.8864 \times 10^{-3}\) m s\(^{-1}\)) with a fixed water vapor content (\(3.83 \times 10^{-1}\) mol s\(^{-3}\), Figures 7~9). Increasing the face velocity increased the PCD rate linearly because of the dilute phase of TCE at a low inlet concentration. Fewer TCE molecules should result in a lower degree of adsorption. As a consequence, a high face velocity led to better adsorption by the improved mass transfer effect. Because a low inlet concentration could not cause fast saturation of TCE on the surface of photocatalyst, the PCD rate is proportional to the face velocity. Thus, it could be defined as a mass transfer control region. On the other hand, as previously explained, for a high inlet concentration, although the photocatalyst surface is saturated with reactant molecules, TCE participates in a very rapid reaction on the surface. Subsequently, mass transfer increases with increasing face velocity. Therefore, it could be found that the region of high inlet concentration was also controlled by mass transfer.

As already stated, we found that the effect of mixing could be improved by installing a baffle, based on the tanks-in-series and dispersion models using RTD data in the existence of baffle. The baffles induced CSTR behavior in the reactor. Figures 7 and 8(a) show the effectiveness of the baffle. The PCD rate is promoted by using baffles under the conditions of a simultaneous low inlet concentration and a high face velocity. The PCD reaction was controlled by mass transfer at a low inlet concentration. Thus, the baffle aids the mixing of the gases and improves mass transfer, thereby increasing the
PCD rate. Moreover, the reactant in a high face velocity would pass through without effective contact between the reactant and the photocatalyst surface because of the decreased residence time. As a consequence, baffles enable the reactants to contact the photocatalyst surface effectively, and, thus, the PCD rate can be increased.

Conclusions

The conclusions drawn from this study are summarized as follows:

1) The effect of mixing could be improved by installing a baffle under the conditions of a simultaneous low inlet concentration and a high face velocity, based on the tanks-in-series and dispersion models using RTD data in the existence of a baffle. The baffles induced CSTR behavior in the reactor of tubular type.

2) For the effect of the inlet concentration on the PCD rate of TCE, the rate continued to increase linearly with the TCE inlet concentration.

3) For the influence of the face velocity of the gas flow, the PCD rate increased with increasing the face velocity at both low and high TCE inlet concentrations. Thus, it could be found that the PCD rate of TCE was controlled by mass transfer.

References


