

Gas-phase photocatalytic decomposition of trichloroethylene adsorbed on TiO₂/silica gel beads in an O₂ gas atmosphere

Y. Kojima¹, S. Kanda¹, M. S. Onyango¹, H. Matsuda¹,
K. Ushiroebisu² & Z. Yamada³

¹*Research Center for Advanced Waste and Emission Management,
Nagoya University, Japan*

²*Shintokogio, Ltd., Sinto Ecotec. Co., Japan*

³*Shinto V-Cerax, Ltd., Japan*

Abstract

A robust technique for trichloroethylene (TCE) decomposition using a tubular reactor containing 0.13g TiO₂/g-catalyst-supported silica gel bead was investigated. The TiO₂ was used due to its low cost, mineralization of a wide range of VOCs, and operation at ambient temperature. Likewise, the silica gel supporting material is transparent and allows for light transmission, and has adsorption capability on its large internal surface area. In this work, the effects of the variables; gas flow rate, catalyst dose, water vapor content and temperature on the extent of the decomposition and formation of intermediates and products were studied. In an O₂ atmosphere, the decomposition of TCE was relatively constant at gas flow rates up to 200x10⁻⁶ m³/min while the decomposition decreased linearly with an increase in gas flow rates above 200x10⁻⁶ m³/min. At the optimum gas flow rate, the decomposition of TCE steeply increased with an increase in photocatalyst dose. It was considered that increases in external surface area and reaction sites were responsible for the increased decomposition. Similarly, the presence of water vapor up to 1% in the gas stream raised the decomposition of TCE. On the contrary, water vapor content above 1% caused a reduction in the decomposition due to competitive adsorption between TCE and water molecules. The photocatalytic process proceeded with the formation of intermediates such as CHCl₃, COCl₂, and CCl₄ and products; CO₂ and HCl.

Keywords: TCE, photocatalyst, titanium oxide, silica gel beads, gas-phase.



1 Introduction

Noxious volatile organic compounds (VOCs) such as Trichloroethylene (TCE) are widely used and found in emissions from the chemical industries and laundries. Strict environmental policies that have been adopted in the recent times put a major constraint on the manufacturing and service industries. Strategies for waste management must therefore be reconsidered.

Several TCE treatment systems such as incineration, adsorption, absorption, biofiltration and air bubbling, among others are in use (Lim and Kim [1]). The drawbacks of some of these systems are that they simply transfer the waste from one phase to another and thus create secondary wastes (adsorption and absorption), require high energy leading to high energy costs (incineration) and in some cases the efficiency is low (biofiltration). Photocatalytic decomposition is arguably the most dependable treatment technique for TCE. For this technique, the temperature of operation is mild and hence low energy requirements, and complete mineralization is possible.

Research works on the removal of TCE from gas streams by photocatalytic decomposition are enormous (Lim and Kim [1], Kim et al. [2,3], Demeestere et al. [4], Wang et al. [5]). Although the principal objective, reduction of TCE concentration, has always remained the same, the approach has always varied as far as the reactor configuration and mode of operation are concerned. In a recent work, Wang et al. [5] studied the reaction pathway of gas-phase photodegradation of TCE using fixed bed and batch reactors containing TiO_2 -loaded glass beads while Lim and Kim [1] used an annulus fluidized bed photoreactor to degrade TCE. The latter authors explained that such a reactor would enhance contact of photocatalyst and reactant gas and UV light penetration efficiency into the interior of the photocatalyst bed.

The objectives of the current work are to present the extent of photocatalytic degradation of TCE and formation of intermediates and products under varying process conditions including gas flow rate, catalyst dose, water vapor content and temperature. A fixed bed reactor containing TiO_2 -loaded silica gel beads (chosen after preliminary tests) and light source placed at the centre of the bed was used. The silica gel beads were chosen as supporting material because the beads are transparent and allow for light transmission, and have adsorption capability on their large internal surface area. Moreover, larger beads used in this study ensured that light passed through the large gaps between the beads to reach the TiO_2 and thus the photo-efficiency was not compromised.

2 Materials and methods

2.1 Apparatus

The reactor consisted of an outer pyrex tube (56mm inside diameter and 200mm length) and an inner quartz glass tube (32mm outside diameter and 300mm length). The light source used was a cold cathode fluorescent lamp (Toshiba



Lightec Co., 2W and 365nm lamp) fixed to the inner glass tube as shown in Fig.1.

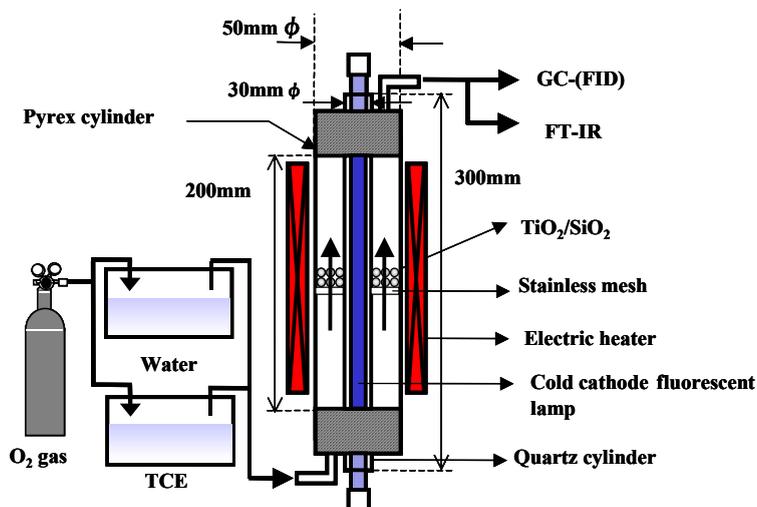


Figure 1: Experimental apparatus.

The outer pyrex tube of the reactor vessel was covered with aluminum foil to shield it from the outside light. The annular part of the reactor vessel between the outer and the inner tubes was filled with photocatalyst-supported beads and the beads held in the column by stainless mesh. The set up was such that the amount of photocatalyst beads packing in the reactor could easily be varied. An electric heater attached over most of the reactor length was used to maintain constant temperature during the photocatalytic reaction.

2.2 Photocatalyst-supporting materials

In this work, two TiO_2 -supported materials namely; silica gel and glass beads were used. The TiO_2 -supported silica gel beads were supplied by Sinto V-Cerax, Toyokawa, Japan whilst TiO_2 -supported glass beads were supplied by Photocatalytic Materials Inc. From the preliminary photodecomposition results it was found that the silica gel beads were superior to the glass beads. Other features that are in favour of the silica gel beads include, but not limited to, their large internal surface area and pore diameter, and their transparent nature. In Table 1 a summary of both the characteristics of TiO_2 -loaded silica gel and glass beads are given. However, in Fig. 2 we present only the internal distribution of the relative intensity of the photocatalyst TiO_2 as a function of the silica gel bead radius, measured from the particle surface. It is observed that the distribution of the photocatalyst TiO_2 is positively skewed towards the core of the silica gel

beads, and thus most of the photocatalyst is deposited near the periphery of the silica gel beads.

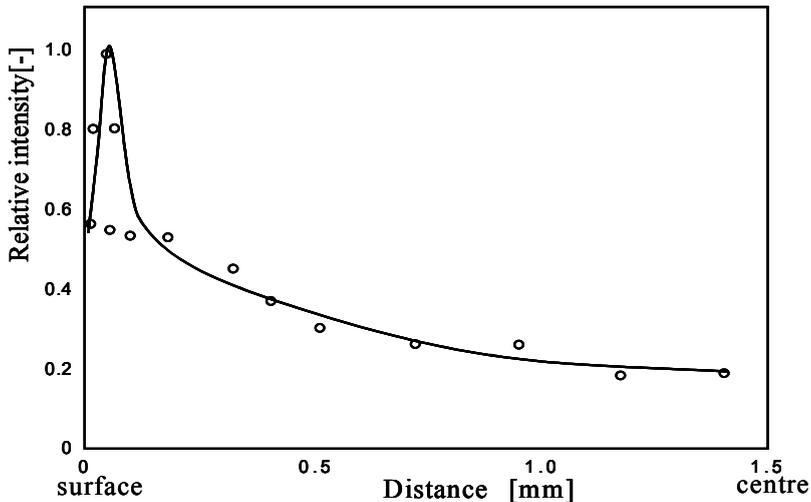


Figure 2: Distribution of photocatalyst on $\text{TiO}_2/\text{silica}$ gel.

2.3 Experimental

First, the gas sample was prepared by mixing a 500ppm TCE with oxygen. The sample was then passed through the reactor in an upward flow mode until the silica gel beads were saturated with the TCE; when the concentration of TCE at the reactor inlet was the same as that at the outlet. The light source was then switched on at which time the photocatalytic decomposition of TCE started. In the first set of the series of experiments, the effect of gas flow rate (50-500ml/min) on the decomposition of TCE and formation of intermediates and products was studied. Using an optimum flow rate obtained in the preceding experiment, the effects of $\text{TiO}_2/\text{silica}$ gel catalyst dose (4.5-36g) and water vapor content (0-2%) were studied. The temperature was controlled at 303 K using an electrical heater fitted to the outer tube of the reaction vessel. Meanwhile, concentrations of TCE and CO_2 at the outlet of the reactor were measured by gas chromatograph equipped with a methanizer (SHIMADZU, Methanizer MNT-1) and flame ionization detector (SHIMADZU, GC-14-FID). The concentration of HCl was measured by an FTIR (SHIMADZU, FTIR-8700) whilst those of byproducts measured by gas detector tubes (Gastec). In addition, it was envisaged that the product, HCl, produced during the decomposition of TCE might have remained adsorbed on the $\text{TiO}_2/\text{silica}$ gel beads surface without being discharged out of the reactor. Subsequently, at the end of each experiment, 4.5g of the catalyst in 50 ml water was shaken for 1 hr at 200 rpm by a mechanical shaker to extract the sorbed HCl in the form of Cl^- ions. The chloride ions concentration in the water was measured by an ion chromatograph (SHIMADZU, electroconductivity detector type: CDD-10Avp).

2.4 Calculations

The TCE decomposition ratio (X), CO_2 formation ratio (F_{CO_2}) and HCl formation ratio (F_{HCl}) were determined according to the following expressions:

$$X [\%] = \left[1 - \frac{\text{TCE concentration at the outlet of the reactor [ppm]}}{\text{TCE concentration at the inlet of the reactor [ppm]}} \right] \times 100 \quad (1)$$

$$F_{\text{CO}_2} [\%] = \frac{\text{amount of CO}_2 \text{ generated [mol]}}{\text{amount of TCE decomposed [mol]} \times 2} \times 100 \quad (2)$$

$$F_{\text{HCl}} [\%] = \frac{\text{amount of HCl generated [mol]}}{\text{amount of TCE decomposed [mol]} \times 3} \times 100 \quad (3)$$

Table 1: Characteristics of $\text{TiO}_2/\text{silica}$ gel and $\text{TiO}_2/\text{glass}$ beads.

	$\text{TiO}_2/\text{silica}$ gel bead	$\text{TiO}_2/\text{glass}$ bead
BET Surface Area [m^2/g]	135	0.0062
Pore Volume [ml/g]	0.72	0.00034
Particle Diameter [mm]	2.5~3.0	2.5
Amount of TiO_2 [g/g - catalyst]	0.13	0.001

3 Results and discussion

Preliminary experiments were performed to serve as control and to rate the performance of silica beads against glass beads. When the process was performed in the absence of UV light source, there was no TCE decomposition and neither were there decomposition products; CO_2 and HCl. Likewise, in the absence of the photocatalyst, the UV light could not decompose the TCE. Using photocatalyst-loaded glass beads, the extent of decomposition and formation of products were marginally in the range 10 to 15% while higher values were observed when silica beads were used. It was considered that glass beads had poor adsorption ability. Moreover, the amount of TiO_2 -supported material per amount of glass beads was much lower than that of silica gel beads. For these reasons, silica beads were used in all subsequent experiments.

3.1 Effect of gas flow rate

The experimental design used in this work was such that a given process variable was first optimized and used in the subsequent experiments. In the first series of the experiments, the TCE decomposition and gaseous products concentration



dependence on gas flow rate in an oxygen atmosphere was investigated and results are shown in Fig.3. There is a twofold function played by oxygen in this process as given in Eqs. 4, 5 and 6 that needs to be examined. First, the incumbent heterogeneous photocatalytic reaction was initiated by illuminating the TiO_2 with photons (Eq.4) thus exciting the valence band electrons to the conduction band resulting in the creation of electron-hole pairs (Wang[5]). Then, to ensure that these electron-hole pairs did not recombine, oxygen was used to scavenge the electrons. Second, the interaction of oxygen with the electrons created the super oxide radicals (Eq.5) which attacked the TCE to form intermediates (such as CHCl_3 , COCl_2 , and CCl_2) from which the terminal products (CO_2 and HCl) were formed (Eq.6).

Back to Fig.3, it was observed that a change in the gas flow rate up to $200 \times 10^{-6} \text{ m}^3/\text{min}$ did not alter the extent of the decomposition (X). However, increasing the gas flow rate above $200 \times 10^{-6} \text{ m}^3/\text{min}$ diminished the extent of the decomposition.

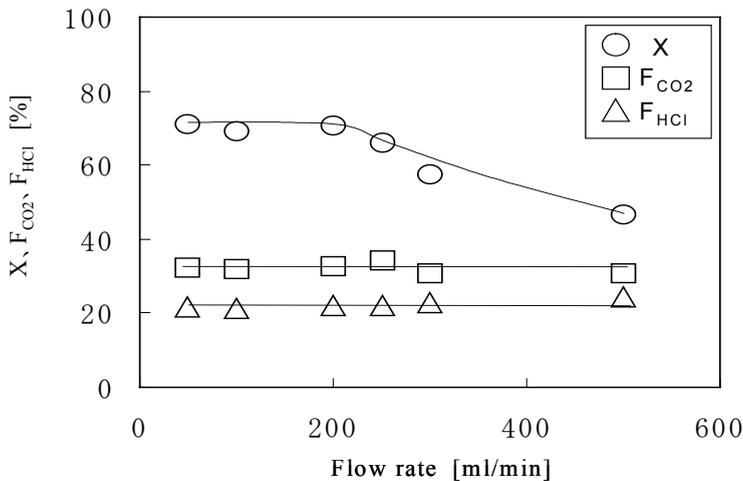
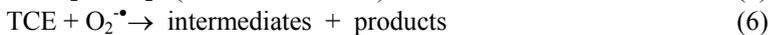
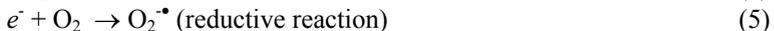


Figure 3: Effect of TCE flow rate on the decomposition ratio of TCE(X) and fractions of CO_2 and HCl (F_{CO_2} , F_{HCl}) formed. Concentration of TCE: 500ppm, Temperature: 30°C , $\text{TiO}_2/\text{silica gel}$ amount: 4.5g.

In heterogeneous reactions, both mass transfer and reaction kinetics may control the overall process depending on the prevailing conditions. Though, the extent (X) of decomposition of TCE did not depend on gas flow rate in the low range values, it was found that the photodecomposition transient curves (not shown) were a function of gas flow rate suggesting that film diffusion played a



limiting role in this process. At higher flow rates, however, the residence/retention time was too low to allow for the adsorptive to adsorb on the catalyst surface and interact sufficiently with the super oxide radical. This resulted in an approximate linear reduction of the extent of decomposition with the gas flow rate. There are mixed findings reported in literature for various reactor configurations but principally, mass transfer resistance and residence times are the determining factors. As an example, in a similar study by Lim and Kim [1] using a fluidized bed reactor, they found the extent of TCE photodecomposition to be optimal at a given gas velocity, below or above which the photodecomposition was retarded. The extent of photodegradation in their work at TCE initial concentration of 500ppm, however, was lower than our results. By contrast, Mohseni and David [6] found the extent of the gas-phase vinyl chloride oxidation using TiO_2 to increase monotonously with increase in residence time.

Meanwhile, the extent of formation of the terminal products defined in this work as the amount of the terminal products formed per amount of TCE degraded (Fig. 3) remained relatively constant as the gas flow rate was varied. The basic reason for this observation which can too be derived from Eq.3 is that changes in flow rate did not change the proportion of intermediates formed during TCE degradation and further suggests that the rate of gas supply does not alter the photocatalytic degradation mechanism. Considering the fact that higher flow rate is better for higher productivity, a value of $200 \times 10^{-6} \text{ m}^3/\text{min}$ was chosen for subsequent experiments over the lower values even though the extents of degradation were the same.

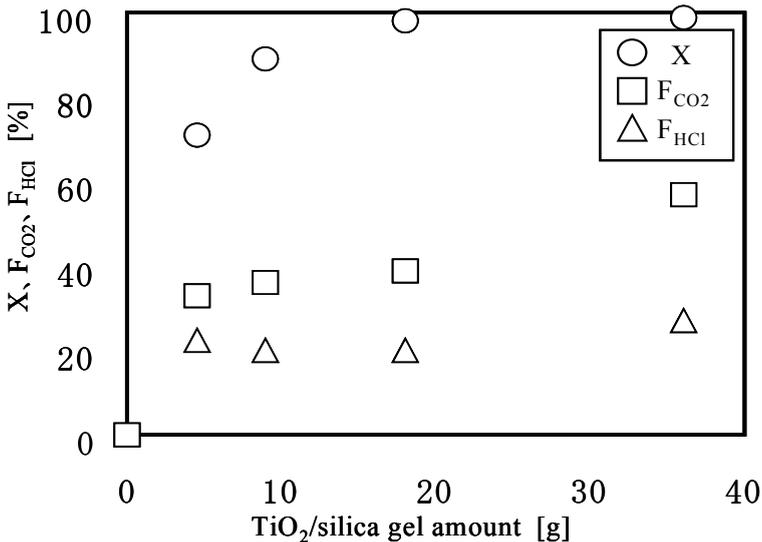


Figure 4: Effect of $\text{TiO}_2/\text{silica gel}$ amount on the decomposition ratio of TCE(X) and fractions of CO_2 and HCl ($F_{\text{CO}_2}, F_{\text{HCl}}$). Conc. of TCE: 500ppm, Temperature: 30°C , Flow rate: 200ml/min.



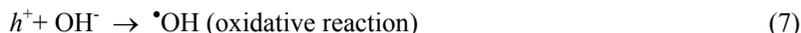
3.2 Catalyst dose

A study was undertaken to investigate the effect of catalyst dose on X and formation of products as shown in Fig.4. A steep increase in X was observed with an increase in the dose. At catalyst doses $\geq 18\text{g}$, the decomposition of TCE was nearly complete. It was considered that an increase in surface area, contact time and reaction sites were responsible for the increased decomposition. In the preceding statement, it is assumed that the catalyst mass in the reaction bed had no effect on the transmission (or scattering) of light through the silica beads and that the sole determining factors were increased surface area, contact time and active sites.

Interestingly, the formation of products (CO_2 and HCl) was relatively constant with an increase in catalyst dose between 4.5g and 18g. However, significant increases in CO_2 and HCl were observed between catalyst doses of 18g and 36g, coinciding with complete decomposition of TCE. It seems that after complete decomposition of TCE, the photocatalyst then decomposed the byproducts (intermediates) to form CO_2 and HCl . In all cases, the extent of formation of CO_2 was higher than that of HCl .

3.3 Water vapor dependence of TCE photodecomposition

Dissociation of chemisorbed water provides the hydroxyl groups that enter the photocatalytic decomposition chain reaction by scavenging the holes and thus minimizing the latter's ability to recombine with the electrons. When a surface hydroxyl group captures a hole, hydroxyl and hydroperoxyl radicals are formed according, but not limited, to the scheme (Wang et al. [5]):



The radicals created in Eqs. 7 and 8 can additionally (i.e. in combination to the reactions described in 3 through 5) attack the TCE to form intermediates and/or products. It follows therefore that the presence of water vapor in the reactant supply would enhance photocatalytic decomposition of TCE. Two experimental runs were performed using 4.5g and 18g silica gel beads at different water vapor concentrations. When the reactor was loaded with 4.5g (Fig. 5) silica gel beads, the decomposition of TCE and formation of CO_2 and HCl increased significantly with a rise in water vapor content from 0 to 1%. Kim and Hong [2] suggest that continuous consumption of the water vapor-induced radicals requires replenishment to maintain catalytic activity. Thus, under low water vapor content, a suitable equilibrium is maintained between consumption and sorption leading to observed increase in TCE decomposition. On the contrary, water vapor content above 1% caused a reduction in the decomposition and formation of products due to the competitive adsorption between TCE and water molecules. Closely similar results for photocatalytic decomposition of VOCs are reported in literature (Kim et al. [2,3], Muradov et al. [7], Pengyi et al. [8]). The concentration of the byproducts; CHCl_3 , COCl_2 , and CCl_4 , were



relatively insensitive to changes in water vapor content at the prevailing conditions.

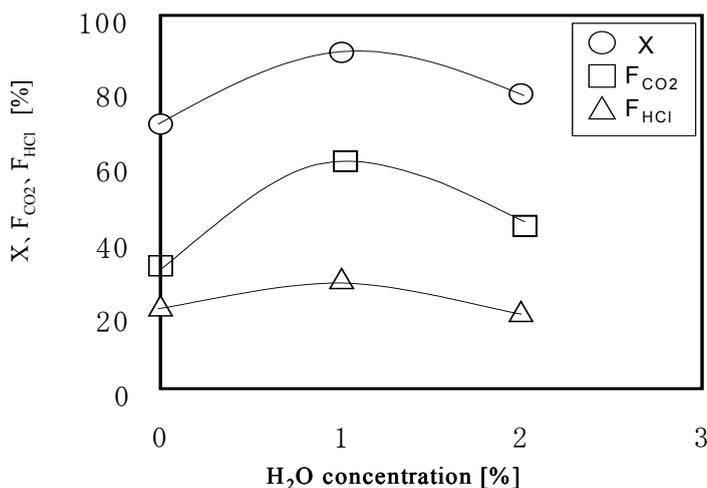


Figure 5: Effect of H₂O concentration on the decomposition ratio of TCE (X) and fractions of CO₂ and HCl (F_{CO_2}, F_{HCl}). Conc. of TCE: 500ppm, Temperature: 30°C, Flow rate: 200ml/min, TiO₂/silica gel amount: 4.5 g.

When the mass of the silica gel was raised to 18g (figure not shown) at the same conditions, an improvement was observed in the formation of the products. In all cases except at 2% water vapor, the decompositions of TCE were nearly uniform and maximum. Quantitative analysis of the byproducts at photocatalyst dose of 18g revealed a reduction in the quantity of byproducts. This was not surprising, though, as there was an improvement in the formation of products (complete mineralization).

4 Conclusions

Gas-phase TCE was successfully photodegraded to CO₂, HCl and intermediates such as CHCl₃, COCl₂, and CCl₄, Cl₂, using TiO₂-loaded silica gel beads in a tubular reactor. The TCE conversion was found to be affected by gas flow rate, photocatalyst mass, water vapor and temperature. Likewise, the byproducts /intermediates formation, identified by gas detector tubes, was also affected by the process variables. Complete mineralization of TCE was achieved at photocatalyst dose ≥ 18 g. Given the major problems associate with air streams contaminated with TCE, removal efficiencies achieved in this work are

significant and comparable to those achieved by other researchers using different photoreactor configurations.

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