Photocatalytic Degradation of Gas-Phase Methanol and Toluene Using Thin-Film TiO₂ Photocatalyst

I. Influence of Water Vapor, Molecular Oxygen and Temperature

Sang Bum Kim*, Hyun Tae Jang*, and Sung Chang Hong**

Department of Chemical Engineering, Korea University, Seoul 136-701, Korea
*Department of Chemical Engineering, Hanseo University, Seosan 356-706, Korea
**Department of Environmental Engineering, Kyonggi University, Suwon 442-760, Korea

Received September 29, 2001; Accepted February 8, 2002

Abstract: In the present work, photocatalytic degradation of volatile organic compounds (VOCs) including gas-phase methanol and toluene over illuminated TiO₂ was closely examined in a batch photo-reactor as a function of water vapor, molecular oxygen, and temperature. Water vapor enhanced the photocatalytic degradation rate of toluene, while there was an optimum water vapor concentration in decomposing methanol. In pure nitrogen atmosphere, it showed lower photocatalytic degradation rate than in air and pure oxygen. Thus, the effect of molecular oxygen on photocatalytic degradation of methanol and toluene was significant. As for the influence of reaction temperature, it was found that photocatalytic degradation was more effective at the room temperature than at an elevated temperature for both compounds.

Keywords: photocatalytic degradation, thin-film TiO₂, photocatalyst, gas-phase, volatile organic compound, batch scale of photo-reactor

Introduction

VOCs such as alcohols, aromatic compounds, ketones, and halogenated hydrocarbons are widely used in industrial process and domestic activities. These extensive uses have led to water and air pollution, even indoor work-place air pollution [1]. Many VOCs are known to be toxic and considered to be carcinogenic. The most significant problem related to the emission of VOCs is the potential production of photochemical oxidants; for example, ozone and peroxyacetyl nitrate.

Photocatalytic degradation 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 [2-4]. 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 are photo-generated in the bulk of the semiconductor, and move to the particle surface; electrons reduce an electron acceptor such as molecular oxygen and holes can oxidize electron donors including adsorbed water or hydroxide anion to give hydroxyl radicals.

Photocatalytic oxidation of alcohols has been studied previously, mostly in steady state or batch reactors with the alcohol in the gas-phase. Blake and Griffin [5] proposed two parallel pathways for the gas-phase photocatalytic oxidation of 1-butanol on TiO₂. They observed 1-butanal and 1-buten with selectivity of 89 and 11%, respectively. Although their reactions were performed with a 100 W Hg lamp in 22% O₂, the feed contained 1% butanol and CO₂ was not observed. In addition, varying the oxygen concentration from 2 to 22% had no effect on the rate or selectivity of the reaction. Sauer and Ollis [6] used a recirculating batch reactor system to study photocatalytic oxidation of ethanol in humidified air. For the fully illuminated reactor, they proposed that ethanol reacts to acetaldehyde, which then forms CO₂ both directly and through a formaldehyde intermediate.

Ibusuki and Takeuchi [7] investigated the photo-
oxidation with the trace toluene 80 ppm in air over UV irradiated TiO$_2$ at an ambient temperature. They observed that the CO$_2$ concentration with 10 min residence time increased linearly with increasing water vapor content between 0% and 60% relative humidity. Obee and Brown [8] studied the photo-oxidation of toluene and other organic pollutants by using polycrystalline TiO$_2$ photocatalyst. In particular, the influence on the photo-oxidation rate through the competitive adsorption between water and toluene vapors was closely investigated.

The purpose of this work is to find the optimum condition in the photocatalytic degradation of VOCs including methanol and toluene as a function of water vapor, molecular oxygen, and temperature. A batch scale of photo-reactor was applied 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.

**Experimental**

**Materials and Reactor System**

All of the chemicals used in this work were reagent-grade. The liquid phase VOCs were products of Aldrich (methanol-anhydrous, 99.8%, toluene anhydrous, 99%). Photocatalyst was prepared with TiO$_2$ suspension (STS-01, anatase, 7 nm in diameter, 300 m$^2$/g of specific surface area, Ishihara Sangyo Co., Japan), tetraethyl orthosilicate (or tetraethoxy silane, 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.

A batch photo-reactor made of Pyrex glass depicted schematically in Figure 1 had a 100 mm inside diameter, 210 mm height and 1600 cm$^3$ total volume. The upper part of the reactor was sealed with a Teflon lid. A vertical UV lamp (outside diameter of 15.5 mm, length of 210.5 mm) was centered of the reactor. Pyrex glass tube coated by the photocatalyst (TiO$_2$) at the internal surface was fixed at the outside of UV lamp resulting in a 3 mm gap. The effective dispersion was achieved by a magnetic stirrer. The concentration of VOCs could be measured by a gas chromatograph (Model HP 6890, Hewlett-Packard, U.S.A.) equipped with a capillary column (30 m length, 0.25 \( \mu \)m film thickness and 0.32 mm internal diameter; Model HP-5, Agilent Technologies, U.S.A.) and a flame ionization detector.

The light source was the germicidal lamp (Model G6T5, 6 W, Sankyo Denki Co., LTD, Japan). The wave-length of the germicidal lamp ranged from 200 to 300 nm with the maximum light intensity at 254 nm.

**Preparation of Photocatalyst**

Photocatalyst suspension was prepared through a three-step process as follows: TEOS (2 g) and DMDMS (1 g) were added to the IPA (10 g) in a vessel connected to a condenser at room temperature (1$^{st}$ 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 (2$^{nd}$ step). STS-01 (35 g) was dropped in the 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 (3$^{rd}$ 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 suspension, it was removed from the Pyrex glass tube at a constant rate of 5 mm/min. Then, the Pyrex glass tube coated with TiO$_2$ was dried at 120°C for one h.

**Characterization of Photocatalyst**

The photocatalytic degradation of organic compounds in particulate semiconductor catalyst suspension has been well studied. However, several practical problems with using powders in photocatalytic processing are apparent: (1) separation of the catalysts from the suspension after the reaction is difficult, and (2) particulate suspensions are not easily applicable to continuous processes. In order to avoid these technical problems several approaches have been taken. For example: (1) powder-type photocatalysts have been immobilized on various supports, and (2) catalysts were prepared in film form.
Thus, a key element in the experimental approach was to use thin particulate films of TiO₂ to enable full illumination of the particulate film. In this experiment, the TiO₂ thin film was prepared by dip-coating method using TEOS, DMDMS, and STS-01 as starting material. In order to form thin particulate films of TiO₂ (STS-01) with superior adhesion onto a Pyrex glass support, TEOS and DMDMS as a coupling agent were used together.

A uniform and transparent TiO₂ thin film with a thickness of about 65 nm was prepared onto an internal surface of a Pyrex glass tube. Scanning electron microscopy (SEM, Philip SEM-535M) images are shown in Figures 2 (a) and (b), which show top and cross-sectional views, respectively. The film consists of small crystalline particles with an average diameter of about 40 nm. Since the average particle size in the TiO₂ solution was about 7 nm, it is assumed that the particles aggregated during heat treatment. The used TiO₂ was found to be Anatase by means of X-ray diffraction (Rigaku D/MAX-2500 diffractometer). As shown in Figure 3, 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 (Micrometrics ASAP 2100) method. The BET surface area of the prepared TiO₂ particles was 277 m² g⁻¹.

Experimental Method

The batch reactor was flushed and filled with dry air or N₂ 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 TiO₂ 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. The concentration of VOCs was monitored using an automated sampling system. Right after the concentration of VOCs was stabilized, the UV lamp was turned on and the concentration of VOCs was recorded with the reaction time throughout the test.

Samples were circulated by a low-flow diaphragm pump (Model SP 600 EC-LC, SP J. Schwarz GmbH u. Co., Germany). Injections were made by a six-port external injection GC valve (6890 Valve system, Agilent Technologies, U.S.A.) with a 250 µL automatic sample loop. Analysis was made by 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 attached in gas chromatograph was maintained at 250°C.

Results and Discussion

When the kinetic data of photocatalytic degradation is interpreted by the differential method, owing to the complex mechanism of reactions, it is difficult to develop a model for dependence of the photocatalytic degradation rate on the experimental parameters for the whole treatment time. Thus, kinetic modeling of the photocatalytic process is usually restricted to analysis of the initial rate (i.e., (dC/dt)₀ of photocatalytic degradation) [9]. This can be obtained from the initial slope of curves in which the variation of the VOC's concentration is measured as a function of time. The extrapolation of the photocatalytic degradation rate to time, t = 0 avoids the possible interference from by-products.

Effect of Water Vapor

Numerous studies have revealed a dual function of water vapor. The influence of water vapor in gas phase photocatalytic degradation reaction depends on the species of contaminant. It has been known that water vapor strongly inhibits the oxidation of isopropanol, trichloroethylene, and acetone; enhances oxidation of toluene and formaldehyde; and has no significant effect on 1-butanol oxidation [10-13].

In the presence of water vapor, the hydroxyl radicals formed on the illuminated TiO₂ can not only directly attack VOC molecules but also suppress the electron-hole recombination [2,14]. Hydroxyl group or water

Figure 2. SEM photographs of (a) top and (b) cross-sectional views of the TiO₂ film on the Pyrex glass tube.

Figure 3. X-ray diffraction patterns of TiO₂ film.
molecules behave as a hole trap, forming surface adsorbed hydroxyl radicals. However, under higher humidity conditions, the water molecules could compete with the VOC molecules on the catalyst surface sites during the adsorption [10,11,13].

In order to examine the effect of water vapor, different concentrations of water vapor were applied to a fixed concentration of VOCs. Figure 4 (a) shows the photocatalytic degradation rate of methanol \((1.151 \times 10^{-2} \text{ mol m}^{-3})\) (300 ppm) initial concentration) versus initial water vapor concentrations varying from 0 to 1.149 mol m\(^{-3}\) (3.0 vol.%). As can be seen from Figure 4 (a), the photocatalytic degradation rate of methanol is more or less enhanced by water vapor with concentrations up to 0.383 mol m\(^{-3}\) (1.0 vol.%), and inhibits above 0.383 mol m\(^{-3}\). Since methanol has a hydroxyl group itself, it may produce hydroxyl radicals even in the absence of water. Thus, the effect of hydroxyl radicals generated from the water molecules might be insignificant. On the contrary, when excess water vapor was admitted, the photocatalytic degradation rate decreased. As previously stated, it seems that the water molecules could compete with the methanol molecules on the catalyst surfaces during the adsorption.

In the case of toluene, a toxic compound resistant to oxidation, phenomenon of catalyst deactivation was observed. Photocatalytic degradation reaction of toluene with low water vapor concentration (below 0.766 mol m\(^{-3}\) (2.0 vol.%)) deactivated the catalyst being implicated by the change of color to brown. In this experiment, the examination of photocatalytic degradation of toluene is thus fulfilled with a low toluene concentration of 3.835 \(\times 10^{-3} \text{ mol m}^{-3}\) (100 ppm). As shown in Figure 4 (b), the photocatalytic degradation rate of toluene increases with increasing water vapor. Carboxylate formation and carboxylic acid accumulation postulated by previous investigators could be a major cause of catalyst deactivation [11,15-17]. An important role of water vapor is regeneration of catalysts. That is, the increase of toluene reaction rate in the presence of water vapor could lead to desorption or degradation of carboxylic molecules which were accumulated on the catalyst surface. In the meantime, as a result of analysis (GC/MS (HP 6890/HP 5971, equipped with a HP-5S capillary column)) of material extracted from TiO\(_2\) surface by using ethanol, it was observed that the species of this catalytic deactivation was benzoic acid (molecular weight: 122). It was also observed that the deactivated catalyst was restored to its inherent transparent appearance as well as activity observed prior to deactivation after UV illumination for three hours with enough water vapor concentration (above 0.766 mol m\(^{-3}\) (2.0 vol.%)) and pure air.

**Effect of Oxygen**

When the TiO\(_2\) particles are illuminated by photons with appropriate energy, the valence band electrons of the TiO\(_2\) can be excited to the conduction band, creating highly reactive electron \((e^-)\) and hole \((h^+)\) pairs (reaction (1)). Those migrate to the TiO\(_2\) solid surface and are trapped at different sites. Those electrons and holes play a part in the reduction and oxidation of photocatalytic reaction, respectively. The photo-generated holes may be trapped by hydroxyl ions on the surface forming hydroxyl radicals (reaction (2)) [18,19], and the electrons may be trapped by an electron acceptor of oxygen forming oxygen species (O\(_2^\cdot\) ·; super oxide radical) on the surface (reaction (3)).

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(e^- + h^+) \quad (1)
\]

\[
h^+ + \text{OH}^- \rightarrow \text{OH}^\cdot \quad (2)
\]

\[
\text{O}_2 + e^- \rightarrow \text{O}_2^\cdot \quad (3)
\]

If water vapor takes part in the gas-solid photocatalysis,
the super oxide radicals will be involved in the reaction with water molecules, eventually forming the hydroxyl radicals as shown in reaction (4). Thus, the photocatalytic degradation of VOCs can be increased due to the formation of hydroxyl radicals [20].

\[
2O_2^- + 2H_2O \rightarrow 2OH^- + OH^- + O_2
\] (4)

In order to examine the effect of oxygen on the photocatalytic conversion of VOCs, the photocatalytic degradation tests were carried out at an atmosphere of synthetic air (20.9 vol.% O₂), pure oxygen, and pure nitrogen with O₂-free. Figure 5 shows the oxygen dependency on the photocatalytic degradation rate of methanol and toluene. From these figures, it can be noticed that the oxygen facilitates the photocatalytic degradation rate of methanol and toluene. As previously stated, while oxygen as an electron acceptor forms hydroxyl radicals, nitrogen cannot form hydroxyl radicals. Thus, the effect of oxygen on photocatalytic degradation rate of methanol and toluene was significant.

**Effect of Temperature**

As a whole, temperature is one of the most important factors in gas-solid heterogeneous reactions. However, photocatalytic reactions are not sensitive to minor variation in temperature [2]. From Pitchat and Hermann's study [21] for dehydrogenation of alcohol over Pt/TiO₂, it was found that the desorption step of hydrogen was rate determining at lower temperature. On the contrary, the photocatalytic reaction rate decreased over 70°C. In this case, adsorption should be the rate determining step.

The effect of reaction temperature on the photocatalytic degradation rate of methanol and toluene was investigated at three different temperatures (25, 45 and 75°C). Figure 6 demonstrates the temperature dependency on the photocatalytic degradation rate of methanol and toluene. Since the adsorption of reactants on the photocatalyst surface was the rate-determining step at higher temperature, it can be noticed that the photocatalytic degradation was more effective at the room temperature than at an elevated temperature for both compounds.

![Figure 5](image-url) **Figure 5.** The effect of molecular oxygen on the photocatalytic degradation rate of each VOC. (a) Methanol \((C_0 = 1.151 \times 10^2 \text{ mol m}^-3, C_{H_2O} = 0.383 \text{ mol m}^-3)\); (b) Toluene \((C_0 = 3.835 \times 10^3 \text{ mol m}^-3, C_{H_2O} = 0.766 \text{ mol m}^-3)\); UV source: germicidal (254 nm) lamp, light intensity: \(2.095 \times 10^3 \text{ W cm}^-2\); temperature: 45°C.

![Figure 6](image-url) **Figure 6.** The effect of temperature on the photocatalytic degradation rate of each VOC. (a) Methanol \((C_0 = 1.151 \times 10^2 \text{ mol m}^-3, C_{H_2O} = 0.383 \text{ mol m}^-3)\); (b) Toluene \((C_0 = 3.835 \times 10^3 \text{ mol m}^-3, C_{H_2O} = 0.766 \text{ mol m}^-3)\); UV source: germicidal (254 nm) lamp, light intensity: \(2.095 \times 10^3 \text{ W cm}^-2\).
Conclusions

The photocatalytic degradation of VOCs including gaseous methanol and toluene, as a preliminary study prior to the continuous process for the gas-solid heterogenous reaction, was investigated in a batch photo-reactor as a function of water vapor, molecular oxygen, and temperature. Water vapor enhanced the photocatalytic degradation rate of toluene, while there was an optimum water vapor concentration in decomposing methanol. For the effect of oxygen on the photocatalytic degradation rate of methanol and toluene, oxygen is an essential component in photocatalytic reactions because it traps photo-generated electrons on semiconductor surfaces and decreases recombination of electrons and holes. Thus, oxygen facilitates the photocatalytic rate of methanol and toluene. As for the effect of reaction temperature on the photocatalytic degradation rate of methanol and toluene, it can be noticed that the photocatalytic degradation was more effective at the room temperature than at an elevated temperature for both compounds because the adsorption of reactants on the photocatalyst surface was the rate-determining step at higher temperature.

Acknowledgement

The authors thank the Korea Institute of Industrial Technology-National Center for Cleaner Production and MAGGREEN INC. for support of this work.

References