

Removal of gaseous toluene by using TiO₂ film doped of Ru-dye/Pt in a pilot scale photoreactor

Moon-Sun Kim*, Ji Sun Kim**, and Byung-Woo Kim**,[†]

*Bio/Nano-Fusion Material Research Center, Sungkyunkwan University, Suwon 440-746, Korea

**Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

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Abstract—The photodegradation efficiency (PE) of gaseous toluene was investigated by using titanium dioxide (TiO₂) film doped of ruthenium (Ru)-dye/platinum (Pt) in a 3,600 L pilot reactor. Ru-dye was applied as a sensitizer to enhance PE of toluene in both UV and visible wavelength range since its major peaks are 225 nm, 325 nm, 375 nm, and 525 nm. PE by using Pt/TiO₂ was more enhanced since Pt plays a role as an electron trapper in UV light range. The 3.2 μm thickness of TiO₂ film was optimized for the highest PE. The highest PE was 75%, 85%, and 90% by TiO₂, Pt/TiO₂, and Ru-dye/Pt/TiO₂ film, respectively.

Key words: Gaseous Toluene, Ru-dye/Pt/TiO₂, Pilot-photoreactor, Continuous Flow Reactor

INTRODUCTION

As volatile organic compounds (VOCs) are major environmental components with a harmful effect on human health, their removal has an attracted study. The major VOCs, toluene is extensively used as a solvent for coating, painting, and adhesive and is known to cause skin diseases and respiratory problems at low concentrations [1,2]. Many studies have been performed for the effective removal of gaseous toluene, and first of all, photocatalytic oxidation has attracted much attention due to its easy handling and high photodegradation efficiency (PE) [3-6]. TiO₂ is used as a photocatalyst for the degradation of organic compounds in the UV wavelength range from 380 nm to 410 nm [7,8]. Many studies have been performed to increase PE of gaseous toluene using photocatalytic oxidation for a few years. Jothiramingalingam and Wang [2] synthesized a porous TiO₂ doped with manganese oxide for the removal of toluene and Maira et al. [4] removed gaseous toluene using nanoparticles less than 6 nm of TiO₂. However, these studies have a limitation for removing gaseous toluene due to their low PE and performances in a laboratory scale.

To resolve these problems, we needed an improved photocatalytic system by doping Ru-dye and Pt on TiO₂ to enhance PE and to keep PE constant for a long time in the pilot scale reactor. There were reports on increasing of PE of VOCs by doping Ru-dye on TiO₂ [9,10]. Higher photocatalytic activity of Pt-TiO₂ was obtained by exiting efficiently of band-gap irradiation to generate electron-hole pairs [11-14]. Both Pt and Ru were doped on TiO₂ to enhance the photocatalytic activity [15].

In this paper, gaseous toluene was efficiently removed by using a TiO₂ film doped with Ru-dye and Pt in the 3,600 L photoreactor. We investigated the effect of coating thickness of TiO₂ film on PE of gaseous toluene at input concentration of 100 ppm. Varying PE of toluene for 20 h with TiO₂, Pt/TiO₂, and Ru-dye/Pt/TiO₂ film was

compared as well.

MATERIALS AND METHOD

The photoreactor system for the removal of gaseous toluene is shown in Fig. 1.

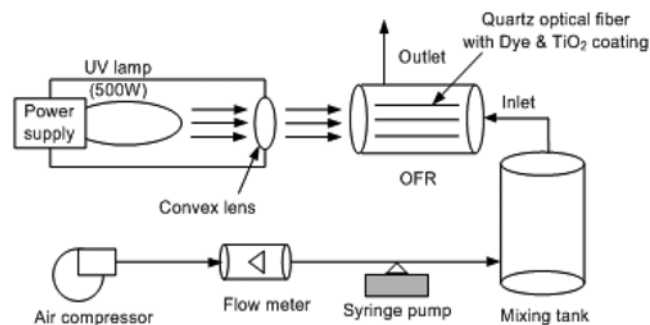


Fig. 1. Schematic diagram of the photoreactor for the removal of gaseous toluene.

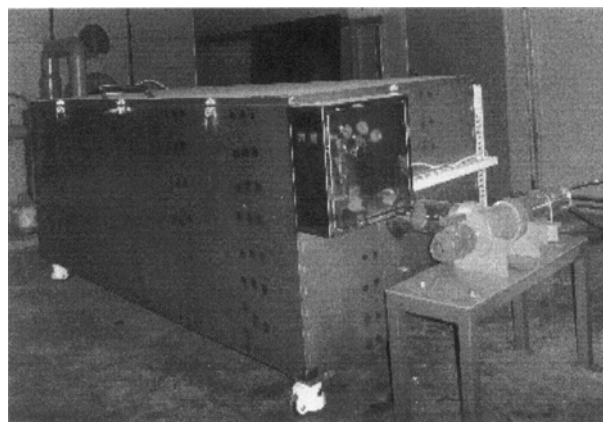


Fig. 2. Photograph of the photoreactor of 3,600 L.

[†]To whom correspondence should be addressed.

E-mail: bwkim@skku.edu

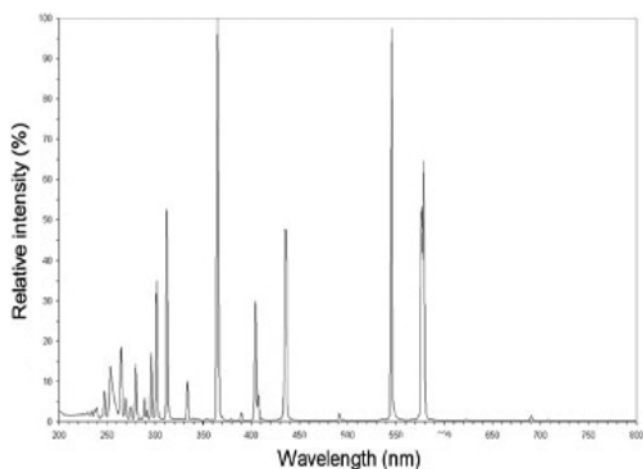


Fig. 3. Wavelength of 500 W-Hg UV lamp.

Table 1. Operation conditions for the pilot photoreactor

Items	Operating conditions
Inlet concentration of toluene	100 ppm
Feed rate	10,000 L/min
Temperature in reactor	25 °C
No. of UV lamps	12 pieces of 500 W Hg
Volume of photoreactor	1,000 mm×800 mm×4,500 mm

In the photoreactor, air was supplied to the mixing tank at constant flow rate by an air compressor. Liquid toluene was spurred into the mixing tank by a syringe pump (KDS-100, K.D. Scientific Co, Korea), where air and toluene were constantly mixed to 100 ppm. The mixed toluene was discharged to the photoreactor shown in Fig. 2 at 10,000 L/min and 25 °C.

The photoreactor (U-IL Eng, Korea) is a type of rectangular parallel pipe with 3,600 L volume (1,000 mm×800 mm×4,500 mm) and combined with optical-fibers (BFL37-1500, Thorlabs, U.S.A.). Photo-oxidation was performed in the reactor with 15 pieces lamps of 500 W Hg (Samil, Korea) as the UV light source and its wavelength is shown in Fig. 3.

The photocatalytic film was immobilized onto the external surface of optical fibers with an outside diameter of 1.5 mm. The operating conditions for the reactor used in the experiment are shown in Table 1.

Ru-dye/Pt/TiO₂ film was prepared as shown in Fig. 4. TiO₂ particles were doped by Pt according to the steps shown in Fig. 4(a).

To a blend with 1,750 mL of 2 M sodium carbonate (Na₂CO₃, MERCK, Germany) and 0.1 g of hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·H₂O, ACROS, U.S.A.) was added 3.8 g of TiO₂ particles (P-25, Degussa, Hanau, Germany), whose average diameter, BET surface area, and density were 20±5 nm, 50±15 m²/g, and 3.89 g/cm³ at 20 °C, respectively. The mixture was stirred for 5 h under a 500 W Hg lamp. After drying at 120 °C for 1 h via washing with distilled water, Pt/TiO₂ particles were obtained.

Fig. 4(b) shows the preparation of Ru-dye/Pt/TiO₂ film immobilized on the optical fibers by dip-coating. After blending 9.47 mL of tetra-titanium-isopropoxide (TTIP, with a purity over 98%, Junsei

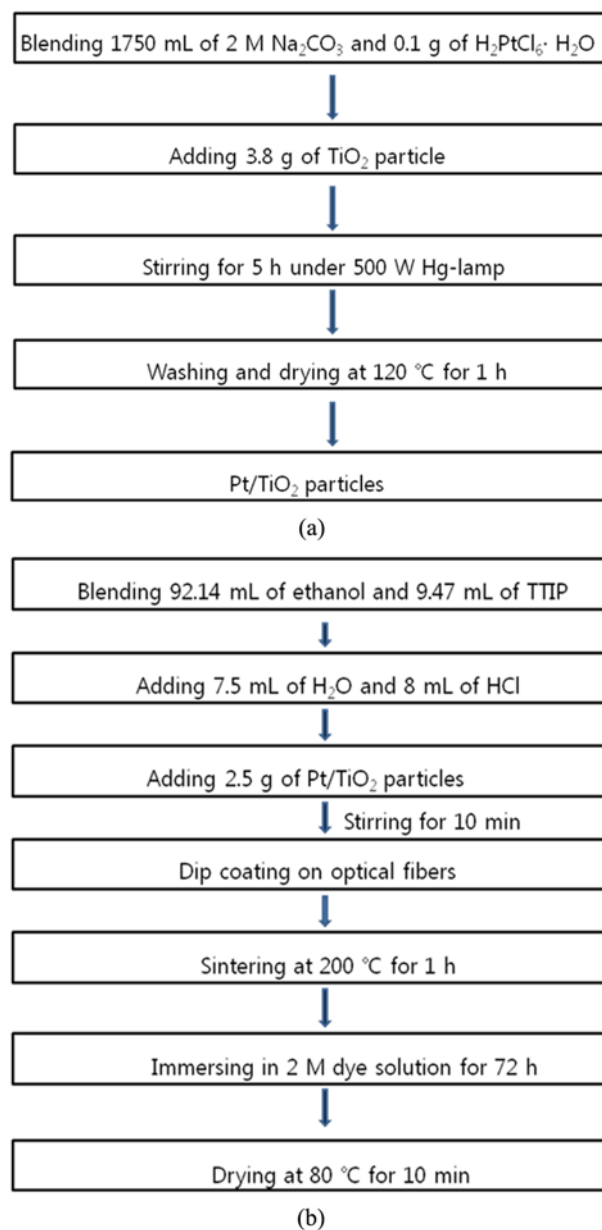


Fig. 4. Preparation of Ru-dye/Pt/TiO₂ photocatalyst.

Chem. Co. Ltd., Japan) and 92.14 mL of ethanol (Samchun, Korea), 7.5 mL of distilled water and 8 mL of HCl (Daejung Chem. & Metals Co., Korea) were added. A total of 2.5 g of Pt/TiO₂ from Fig. 4(a) was added to the synthesized solution and stirred for 10 min. The prepared coating-solution was immobilized on the optical fibers by dip-coating. The coated photocatalytic film was sintered at 200 °C for 1 h. The Pt/TiO₂ film was immersed in 2 M dye solution for 72 h. The Ru-dye (N719, Ruthenium 535-bis TBA, C₅₈H₈₆O₈S₂Ru) was supplied by Dyesol Co., Australia, and its chemical structure is shown in Fig. 5.

After drying at 80 °C for 10 min, the dye/Pt/TiO₂ film was used for the removal of gaseous toluene. The average amount of Pt and Ru-dye doped on TiO₂ particle was 200±10 mg/kg and 20±2 mg/kg, respectively. The Pt doped on TiO₂ particles was shown as classical structure of Pt with X-ray diffraction spectroscopy (XRD, SMART

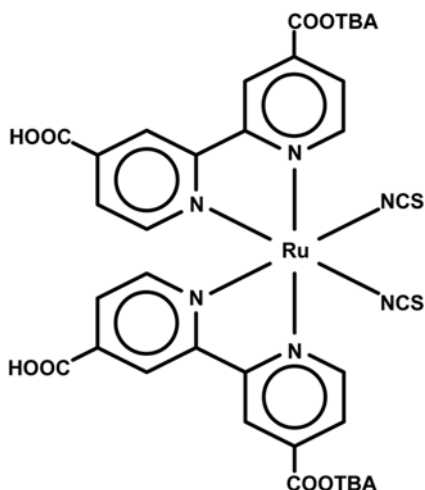


Fig. 5. Chemical structure of Ru-dye (Ruthenium 535-bis TBA).

APEX, Bruker Co., U.S.A.) and the structure of Ru in Ru-dye after doping could not be determined.

The thickness of the coated Ru-dye/Pt/TiO₂ film was measured with a surface profilometer (Alpha Step 500, KLA Tencor Co., U.S.A.) and scanning electron microscopy (SEM; JSM7000F, JEOL, U.S.A.). Amount of Ru and Pt doped on TiO₂ was measured with inductively coupled plasma spectrometer (ICP-MS, Agilent 7500, Agilent Technologies Inc., U.S.A.). The concentration of toluene and the intermediates derived from toluene was determined by gas chromatographer-mass spectrometer (GC/MS, HP 6890, Hewlett Packard Co., U.S.A.) with an HP-5MS column (model 190915-143, Hewlett Packard Co., U.S.A.). The absorption spectra of TiO₂, Pt, and Ru-dye (N719) were dissolved in ethanol and measured with UV-vis absorption spectrometer (Cary 5000, Varian Inc., U.S.A.).

PE of gaseous toluene by a photoreactor is evaluated according to Eq. (1) [16]:

$$PE (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the input and output concentrations of toluene, respectively.

RESULTS AND DISCUSSION

1. Absorbance Spectra of Ru-dye, Pt, and TiO₂ as Raw Materials

The absorbance of spectra of TiO₂ (P-25), Pt, and Ru-dye (N719) by spurring 0.002 g of a sample in 100 mL of ethanol, respectively, are shown in Fig. 6.

Major peaks of Ru-dye are 225 nm, 325 nm, 375 nm, and 525 nm and that of TiO₂ (P-25) are observed only at 325 nm. That of Pt was determined to be under 250 nm. Ru-dye was used as a sensitizer in both the UV and the visible light range and Pt was applied as an electron trapper in the UV wavelength range [10]. PE of toluene was compared by using Ru-dye/Pt/TiO₂ film as a photocatalyst in the 3,600 L photoreactor.

2. Effect of TiO₂ Film Thickness on PE of Gaseous Toluene

TiO₂ film was immobilized on the optical fiber by a dip-coating from one to five coating times, and SEM images of cross section

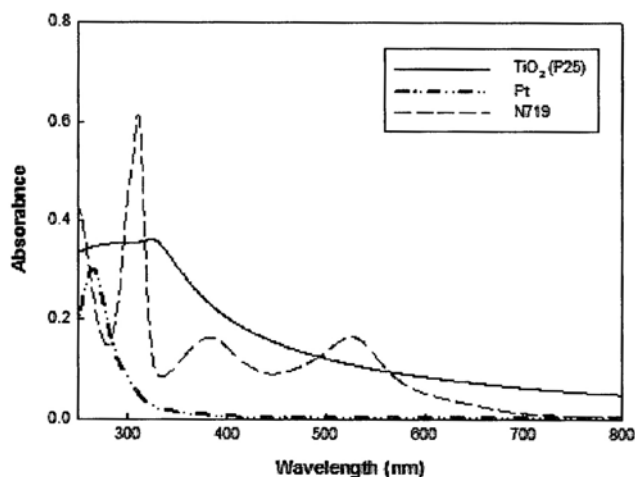


Fig. 6. Absorbance spectra of TiO₂ (P-25), Pt, and Ru-dye (N719) in ethanol.

of coated film are shown in Fig. 7.

Thickness of film was (a) 1.0 μm , (b) 2.6 μm , (c) 3.2 μm , (d) 3.9 μm , and (e) 4.2 μm with a coating of 1-, 2-, 3-, 4-, and 5-times, respectively. PE of gaseous toluene in 1 h by a thickness of TiO₂ film is shown in Fig. 8.

PE of gaseous toluene was 65%, 72%, 75%, 70%, and 67% at 1.0 μm , 2.6 μm , 3.2 μm , 3.9 μm , and 4.2 μm thickness, respectively. From these results, it was determined 3.2 μm was the thickness of TiO₂ film to obtain the highest PE. Thickness of TiO₂ film is one of major parameters to enhance PE of toluene [17]. The thickness of TiO₂ film was optimized on their purpose since it was affected by inlet concentration, feed rate, temperature, reactor system, and so on. It is relates to the reduction in the recombination of UV-activated electron and hole and affects on concentration of OH radical on surface of the film [18,19]. The OH radicals are to degrade toluene to H₂O and CO₂ finally. Concentration of OH radicals increased with an increasing to 3.2 μm thickness and started to decrease over 3.2 μm thickness.

3. PE of Gaseous Toluene by TiO₂, Pt/TiO₂, and Ru-dye/Pt/TiO₂ Film

Fig. 9 shows the PE of gaseous toluene by using TiO₂, Pt/TiO₂, and dye/Pt/TiO₂ film.

For the pure TiO₂ (P-25) film, PE was 70% in 0.5 h and reached 75%, the highest PE, in 1-5 h. Over 10 h, PE was observed to decrease, and 72%, 70%, and 65% were in 10 h, 15 h, and 20 h, respectively. For Pt/TiO₂ film, PE was 78% in 0.5 h and reached 85% in 1-20 h. Value of PE was the highest and kept constant during this time. For Ru-dye/Pt/TiO₂ film, PE was 85% in 0.5 h and the highest of PE was 90% in 1-5 h. The initial concentration of toluene and UV light intensity were optimized as 100 ppm and 7,500 W (15 pieces of 500 W UV lamp) in 3,600 L reactor since PE of VOCs is affected by initial concentration and UV light intensity. At initial toluene concentration under 90 ppm, PE was 100% in 5 h; however, PE was 87%, 82%, and 75% with an increasing of 120 ppm, 150 ppm, and 200 ppm. At initial toluene concentration of 100 ppm, PE was 88%, 85%, 80%, 75%, and 70% in 5 h with a decreasing of 14 pieces, 13 pieces, 12 pieces, 11 pieces, and 10 pieces of the UV lamp with 500 W.

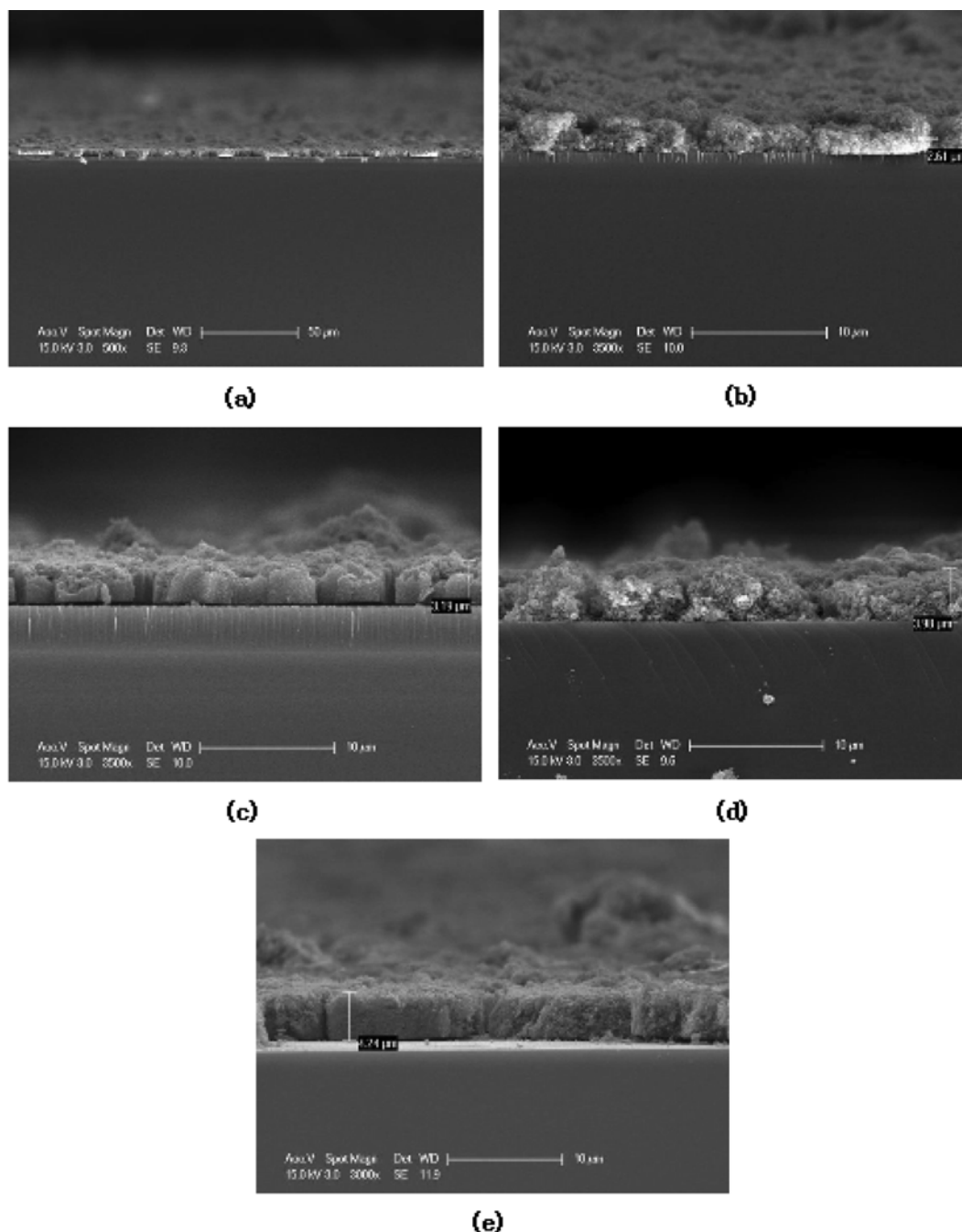


Fig. 7. SEM images of thickness of TiO_2 film by (a) 1- (b) 2-, (c) 3-, (d) 4-, and (e) 5-coating times.

Over 10 h, PE decreased from 90% to 88%, 85%, and 80% in 10 h, 15 h, and 20 h, respectively. The highest value of PE was 75%, 85%, and 90% by TiO_2 , Pt/TiO_2 , and Ru-dye/Pt/TiO_2 film, respectively. The PE of gaseous toluene obtained from the experiment could not be compared with that of other works since they had performed by only lab-scale equipments. In Jothiramalingam and Wang' [2], Ban et al. [20], and Juyoung et al. [21], the highest PE of toluene was 41%, 60%, and 84%, respectively.

The role of Ru-dye doped TiO_2 was to enhance PE of gaseous toluene since absorbance capacity of Ru-dye is higher than TiO_2 and Pt in UV wavelength range. The presence of Ru and Pt in the photocatalytic layer significantly influenced the charge carrier recom-

bination rates and interfacial electron-transfer rates [14]. However, PE by using of Ru-dye/Pt/TiO_2 film decreased from 90% to 88% and 80% in 10 h and 20 h, respectively, due to a low heat-resistance of dye. In other work [10] on the photodegradation by using dye/ Pt/TiO_2 , PE of methane increased from initial stage until 3 h but PE was not mentioned over 3 h. In the study of solar cell using dye sensitized TiO_2 , photovoltage increased with an increasing for a long day and decreased over 80 days due to its low heat- and light-stability [22].

In case of Pt/TiO_2 , PE was kept constant at 85% in 1-20 h since heat-resistance of Pt is better than dye. Pt film increases the O_2 concentration on the TiO_2 surface, so that the photocatalytic oxidation of Pt/TiO_2 was higher than that of TiO_2 [23]. It is reasonable that Pt

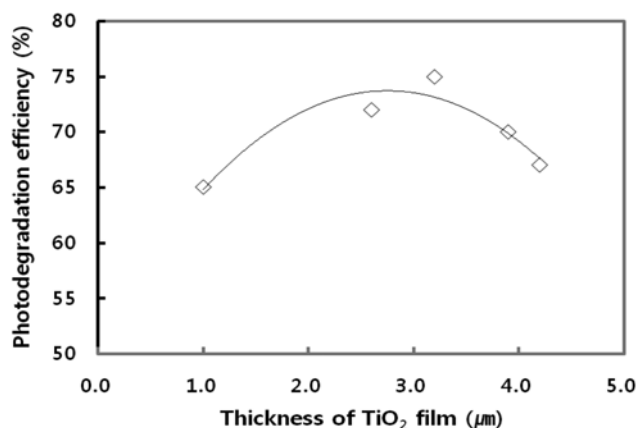


Fig. 8. Effect of thickness of TiO₂ film on PE of gaseous toluene.

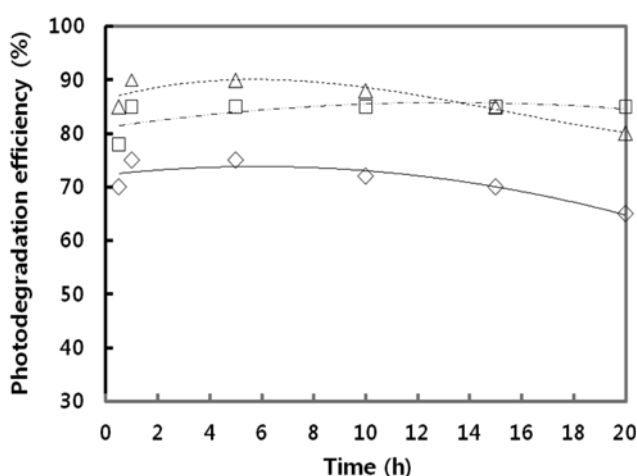


Fig. 9. PE of gaseous toluene by 3-type photocatalytic films: TiO₂ (◇), Pt/TiO₂ (□), and Ru-dye/Pt/TiO₂ (△) at 25°C and 100 ppm of input concentration.

was first doped on the TiO₂ to keep PE constant, and then Ru-dye was secondly doped as a sensitizer on the Pt/TiO₂ to enhance PE in the UV wavelength range [24].

4. Intermediates Derived from Photodegradation of Gaseous Toluene by Ru-dye/Pt/TiO₂ Film

Gaseous samples from the photoreactor were analyzed by GC-

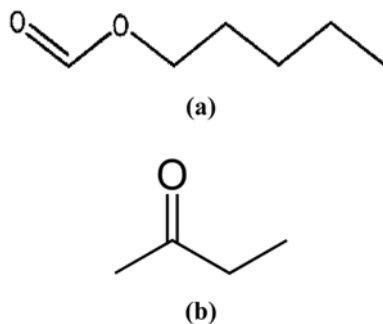


Fig. 10. Intermediates observed from the photooxidation of gaseous toluene by GC-MS: system (a) amyl formate and (b) ethyl formate.

MS to investigate the noxiousness of the intermediates. The results are shown in Fig. 10.

Over 90% of the organic compounds were identified as amyl formate and ethyl formate, as shown in Fig. 10(a) and (b), respectively. The remainder was low molecular weight compounds. Formic and acetic acids have been previously observed through the photodegradation of toluene using TiO₂/H₂O and TiO₂/HCl, respectively [23, 24]. From these results, we considered that toluene was photodegraded to amyl formate first, then to ethyl formate, and finally to CO₂ and H₂O.

CONCLUSIONS

From the removal of gaseous toluene by Ru-dye/Pt/TiO₂ film in the 3,600 L photoreactor, the following conclusions were drawn.

PE of gaseous toluene was 65%, 72%, 75%, 70%, and 67% at 1.0 μm, 2.6 μm, 3.2 μm, 3.9 μm, and 4.2 μm thickness, respectively. It was determined to be 3.2 μm thickness of TiO₂ film for the highest PE.

The highest PE was 75%, 85%, and 90% by TiO₂, Pt/TiO₂, and Ru-dye/Pt/TiO₂ film, respectively. The role of Ru-dye and Pt film doped on TiO₂ was to enhance PE and to keep PE constant for a long time, respectively.

Intermediates derived from photodegradation of gaseous toluene were amyl formate and ethyl formate, which are non-toxic.

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