

Experimental Study on the Treatment of Volatile Organic Compound Vapors Using a Photoreactor Equipped with Photocatalyst-Coated Fabrics

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ABSTRACT: In this study, methods were developed to enlarge the scope of traditional applications of titanium dioxide (TiO_2) and to increase the value of felted fabric by allowing volatile organic compound (VOC) degradation as well as dust filtration in a photoreacting fabric filter. In the past, when a V-Ti mixed catalyst was used, the application of felted fabric as a support material for the catalyst was difficult because the active temperature of the catalyst ranged from 250 to 400°C. Thus, in this study catalyst-coated felted fabric was manufactured at normal temperature conditions, and then fundamental de-VOC performance tests were conducted under irradiation condition to develop a fabric filter having a de-VOC function in addition to a dust-filtration function. Toluene vapor was selected as a sample VOC because it poses health hazards, has been widely used as an organic solvent, and has been known as a compound

that is difficult to dissociate. To manufacture and use a fabric filter that degrades VOC_s , and removes dust particles through using photocatalyst-coated fabrics and light sources, optimum operating conditions were obtained by observing the degradation attributed to varying the toluene-vapor flow rate, the initial toluene concentration, flue gas humidity, TiO_2 loading onto the surface of the fabric, and the intensity and wavelength of a near ultraviolet light lamp. To keep the flue gas humidity at a relatively constant level, a system to automatically control the humidity was constructed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3174–3179, 2004

Key words: TiO_2 ; photocatalyst; toluene degradation; dip coating; fabric filter

INTRODUCTION

Volatile organic compounds released from organic solvents (VOC_s), used in various industrial fields, cause pollution in various media such as air, water, and soil. For the last two decades, to cope with these problems a number of investigations to treat these organic materials—without promoting further environmental stresses—have been actively carried out using metal oxides as photocatalysts. Among these studies, the field dealing with photocatalyst TiO_2 has recently received special attention. Moreover, catalyst-oxidation technology is economical and environmentally friendly compared with existing technologies including activated carbon adsorption, chemical treatment, air stripping, and incineration. The TiO_2 /UV process is an advanced oxidation process and a heterogeneous system by which an OH radical is produced and oxidizes pollutants. TiO_2 is superior to other oxidants in terms of oxidation capacity and reaction velocity, and the photocatalyst reacts with almost all organic material. The sol-gel method is generally used to coat TiO_2 onto a material's surface,

and it refers to establishing a mesh structure of TiO_2 particles through a condensation reaction after conducting hydrolysis by using metal alkoxide. Even in a sol-gel method, the characteristics of the final products depend on manufacturing conditions such as alkoxide, pH, catalyst, and temperature; thus serious caution is required when applying this method. However, most of the TiO_2 produced by the sol-gel method is not crystalloidal; therefore, transformation to the anatase phase by a heating process should be performed as in the sedimentation method. For these reasons, ceramic materials that endure high temperature have been mainly used for the manufacture of boards/carriers; fabric and/or plastic materials with less temperature resistance have not been used for these applications.

This study was carried out to appropriately respond to VOC pollution through the development of a new method vesting a de-VOC function to felted fabrics under the following objectives:

1. To review the usefulness of polyester fabric as a substrate for photocatalyst coating, which has been scarcely used compared with glass beads or ceramics.
2. To check whether the fabric coated with a photocatalyst can be used as a filter material for

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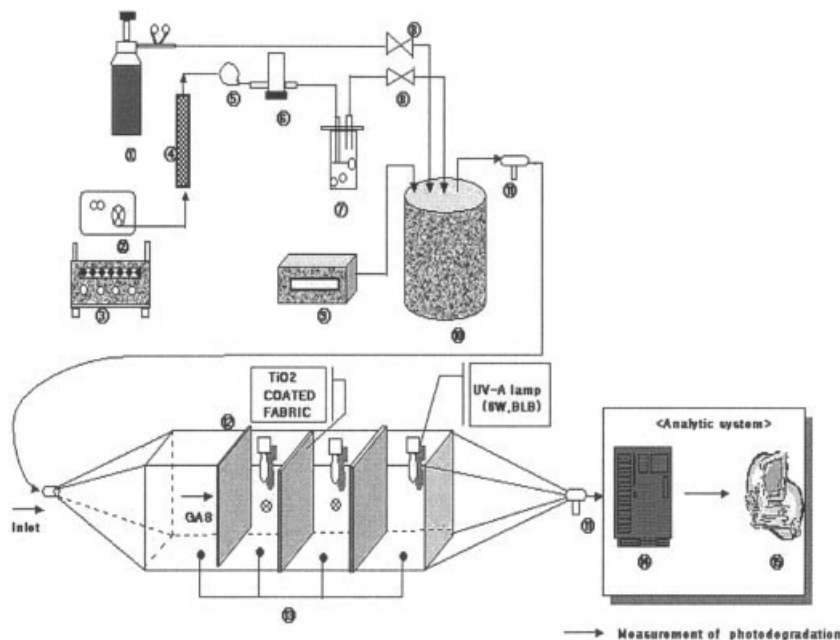


Figure 1 Schematic diagram of a photoreactor equipped with fabrics, coated with TiO₂, in series.

VOC purification as well as dust filtration in a photoreacting fabric filter.

3. To accumulate and present fundamental measurements on the photocatalysis effect with respect to variations of various operating conditions.

EXPERIMENTAL

Photoreactor

A lab-scale apparatus to observe the photodegradation of VOC_s by a photocatalyst coated onto a fabric’s surface is shown in Figure 1. A photoreactor (dimensions 80 × 25 × 35 cm) was made of acrylic resin. The reactor was equipped with a thermostat (SD-506, Sanup Electric Co.) with a measurable temperature range of 0 to 400°C and with a cylindrical-type water jacket (15 cm diameter) outside a mixer so that the influent flue gas temperature could be kept at a constant level of 25 ± 1°C by circulation of warm water from a water bath. To precisely measure the sample gas concentration for determining the VOC_s removal performance by the photocatalyst, a calibration curve was drawn using a standard toluene vapor manufactured at the Korean Standard Science Institute. A mass flow controller was used to control the airflow diluting the toluene vapor, and a flow meter was used to control the required sample-gas concentration. Again, a valve was facilitated to control the sample gas flowing into the photoreactor. The inlet and outlet of the photoreactor were manufactured in a gradual expanding and contracting shape, respectively, to cause less

energy loss. The use of Teflon tubes and junction parts made with stainless-steel minimized toluene vapor loss resulting from adsorption. Reactors consisted of three units, connected in series, to improve VOC removal efficiency and to observe the various steps in the relationship between the photocatalyst-coated fabric’s surface and the reaction results including adsorption and photocatalysis. Considering the future use of the photocatalyst-coated fabric in a fabric filter where dust-laden gas gets into the bags through interstices of the fabric, the sample fabric coated with TiO₂ sol was placed perpendicularly to the air stream in the lab-scale apparatus. To remove the adsorption effect on the toluene photodegradation measurements, sample gas collection for measuring toluene concentrations at the inlet and outlet of the reactor were conducted when inlet and outlet gas concentrations became sta-

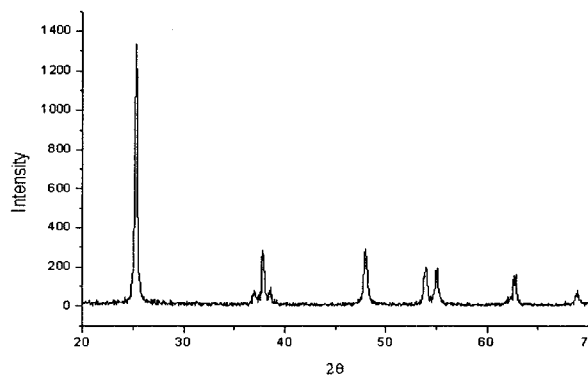


Figure 2 X-ray diffraction pattern of titanium dioxide sol.

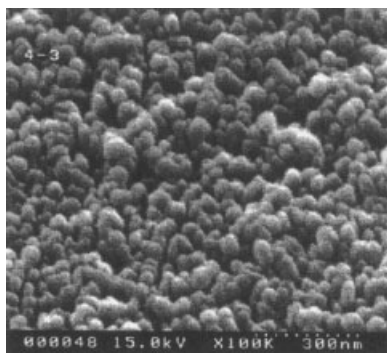


Figure 3 SEM micrograph of titanium dioxide sol.

bilized after the reduction of toluene vapor by adsorption had disappeared.

Property and material of photocatalyst

The raw material that was used as a photocatalyst, which has been studied most intensively in the treatment of both gaseous and liquid phase VOCs, was TiO₂ powder (P-25, Degussa, Germany) of the crystalline anatase structure. An X-ray diffraction and a SEM micrograph of TiO₂ sol (Slost-100, E Co.), which was used in this study, are shown in Figures 2 and 3, respectively. Physical and chemical properties of the TiO₂ sol diluted with distilled water are described in Table I. As sources of UV light-activating photocatalysis, four blacklight blue lamps (BLB; Philips, The Netherlands), requiring low power and emitting radiation of relatively long wavelength ranging from 350 to 390 nm, and four germicidal lamps (Sankyo, Denki, Japan), requiring light power and emitting extreme ultraviolet radiation of 250–265 nm wavelength, were used. The resulting wavelengths of peak radiations from the above sources, determined by using a UV radiometer (Minolta, Tokyo, Japan), were about 370 and 250 nm, respectively.

Properties of fabric used in this study

The fabric used in this study to coat the photocatalyst was a felted fabric of polyester material, which is cheap and commonly used in industry. Its properties are as described in Table II. The process for coating of titanium dioxide thin film on the fabric's surface is shown in Figure 4.

TABLE II
Properties of the Polyester Fabric Used in This Study

Polyester property (normal)	Value
Weight (g/m ²)	500
Thickness (mm)	1.8
Air permeability (cc/cm ² /sec)	11.3
Tensile strength (kg/25 mm)	>170
Thermal resistance (°C)	≈ 130°C
Chemical resistance	Strong against acid

RESULTS AND DISCUSSION

Variation of toluene conversion with flow rate

Measurement results of toluene removal obtained at conditions of constant concentration (7 ppm) and various flow rates ranging from 500 to 7000 mL/min are shown in Figure 5. This figure reveals that the toluene removal efficiency increases with retention time within the reactor, probably because of the longer contact between the vapor and the photocatalyst-coated fabric. A relatively low efficiency of 27% for 500 mL/min may be partly attributable to less-intense radiation (25.2 μW/cm²) from a light source installed on the side wall so as not to interfere with the smooth air stream. To see the photocatalysis effect according to the clearance between the catalyst-coated fabric and a UV light source, a relationship of UV intensity versus irradiation distance (from Yoon¹) is shown in Figure 6. It may be observed that the light intensity rapidly decreases with distance from the fabric to the lamp. Considering that the distance was 3.5 cm in this experiment, it can be expected that by adjusting the irradiation distance, it is possible to attain greater degradation of VOCs. Figure 7 shows that the light intensity reached at the fabric varies with the electric power of the light source and the air stream velocity within the reactor. To improve vapor purification, it is necessary to determine an optimum air stream velocity through measurement of light intensity variation attributed to electric power and air stream velocity as the figure suggests.

Variation of toluene conversion with inlet concentration

Toluene is an aromatic compound that does not decompose easily and has a chemical property that deactivates catalysts. Considering the deactivation prop-

TABLE I
Physical and Chemical Properties of Titanium Dioxide Sol

Catalyst model	Solid content (%)	Structure type	Particle size (nm)	pH	Particle shape	Solvent
Slost-100w	4	Anatase	30–40	10–11	Spherical type	Water

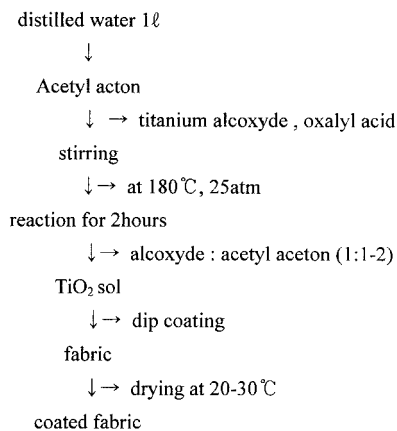


Figure 4 Process for coating of titanium dioxide thin film on the fabric’s surface.

erty, the initial inlet concentration was set up at a somewhat low level. To observe the toluene degradation as the inlet concentration varies, the experimental results of the degradation for concentrations of 2 and 20 ppm at a fixed flow rate of 1 L/min are displayed in Figure 8. It was observed that the toluene decomposition efficiency for 2 ppm reached beyond 80–90% of final attainment when the irradiation time lasted 30–40 min. The reason that the curves showing the decomposition efficiencies for 2 and 20 ppm remain parallel later in the experiment appears to be because of the products of the initial photocatalytic reaction, such as CO₂ and H₂O, which remain near the photocatalyst-coated fabric and interfere with the later contact between toluene vapor and the catalyst.²

The degradation of toluene vapor that instantaneously passes through the fabric for irradiation lasting for >1 h does not significantly improve compared with irradiation lasting for only 30 min, probably because of the short contact time between toluene vapor and catalyst. This finding is very different from that

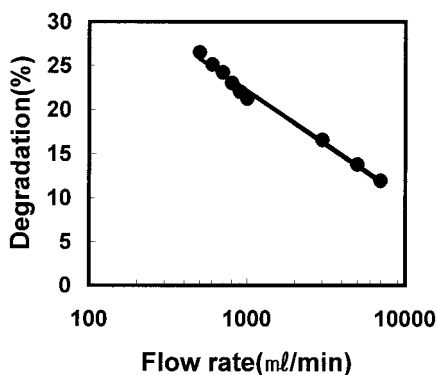


Figure 5 Variation of photocatalytic degradation of toluene vapor with flow rate [$C_0 = 7$ ppm, humidity = 38%, irradiation duration = 100 min, temperature = 20°C, catalyst loading = $6(\pm 0.4)$ mg (TiO₂)/cm² (fabric)].

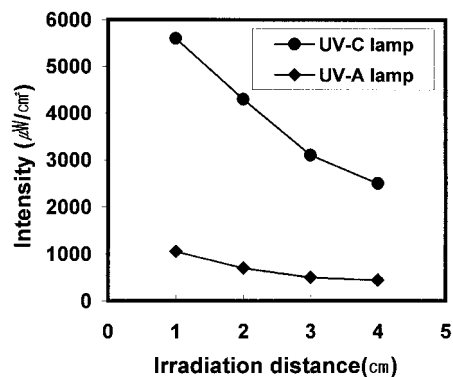


Figure 6 Measured UV radiation intensity on the fabric’s surface as a function of irradiation distance from lamps to a UV sensor (from Yoon¹).

for a packed tower in which many glass beads, coated with a photocatalyst, are filled as packing and the vapor retention time increases with tower height. If air and the VOC stream pass through the photocatalyst-coated fabric and flow across the fabrics in series, then VOC_S degradation would increase.

Variation of toluene conversion with humidity

It was previously established that moisture produces OH radicals upon adsorption onto a photocatalyst surface, commences photocatalysis reaction, and induces chain reactions afterward.^{3,4} However, moisture does not have a synergistic action in every reaction and even reduces the reaction velocity attributed to competitive adsorption between moisture and organic material. Ibusuki and Takeuchi⁵ studied toluene photooxidation using the photocatalyst TiO₂ when water vapor exists at normal temperature. They found that CO₂ products increased linearly with relative humidity (RH) up to 60%, and the amount of CO₂ for 60%

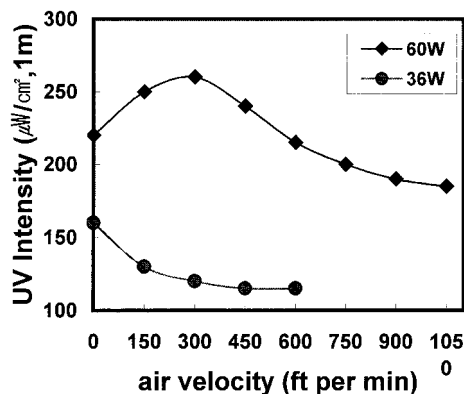


Figure 7 Variation in UV radiation intensity with various combinations of the light source power and the air stream velocity within the reactor (from Hansung Ultraviolet Co., 2002).

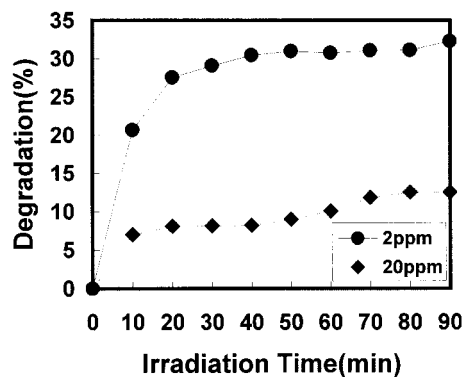


Figure 8 Effect of an initial toluene concentration in air crossing through a photocatalyst-coated fabric on its degradation [flow rate = 1 L/min, humidity = 38%, temperature = 20°C, catalyst loading = $6(\pm 0.4)$ mg (TiO₂)/cm² (fabric)].

corresponded to 10 times that for dry air. On the other hand, they reported that the benzaldehyde concentration decreases with relative humidity, and the moisture range most effective for toluene photooxidation was 0–30%. Through this study, it was confirmed that toluene conversion increases with RH up to about 55%, but decreases beyond the level as shown in Figure 9. This phenomenon appears to occur because the moisture controls the deactivation of catalyst to RH about 55% during the photooxidation reaction of toluene, and more moisture beyond that level with the increase in reunion frequency of electron-hole pairs.

Variation of toluene conversion with TiO₂ coating thickness

The photocatalytic degradations of toluene vapor at conditions of varying thickness of catalyst were investigated for constant concentration and are presented in

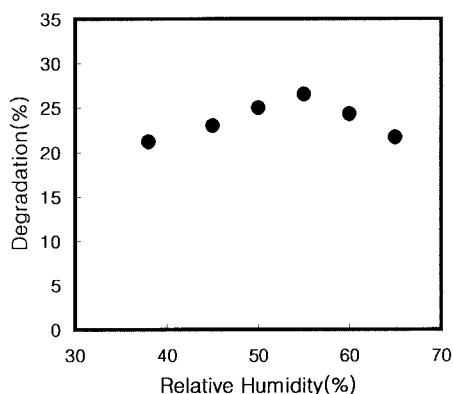


Figure 9 Effect of flue gas humidity on the photocatalytic degradation of toluene vapor [$C_0 = 7$ ppm, flow rate = 1 L/min, temperature = 20°C, irradiation time = 100 min, catalyst loading = $6(\pm 0.4)$ mg (TiO₂)/cm² (fabric)].

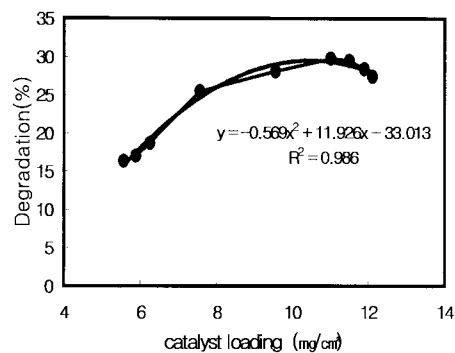


Figure 10 Effect of catalyst loading on the photocatalytic degradation of toluene vapor ($C_0 = 7$ ppm, flow rate = 1 L/min, temperature = 20°C, irradiation time = 100 min, relative humidity = 38%).

Figure 10. This figure reveals that toluene decomposition increases with the amount of catalyst loading up to 11.02 mg (TiO₂)/cm² (fabric), but decreases beyond the loading. This result appears to occur because more radiation energy is absorbed into the catalyst, and the potential of photocatalysis increases as the catalyst loading increases to the critical value.⁶ However, if an excessive amount of catalyst is coated onto the fabric, the transmission of radiation is significantly hindered and, as a result, the toluene conversion reaction can mainly take place only on the surface of the catalyst; thus, additional catalyst coating appears not to cause further increase in degradation of VOCs.^{7,8} Figure 11 expresses the relationship between catalyst loading and air permeation measured using the Erazier method. If maximum catalyst loading for cleaning of dust-laden air was taken as $6(\pm 0.4)$ mg (TiO₂)/cm² (fabric), then air permeation would be about 9.3 cm³ (air)/cm² (fabric) s⁻¹, which suggests an air passage closure of 16–17%. The closure ratio for the catalyst loading of 11 mg (TiO₂)/cm² (fabric) was about 25%, but the closure would be minimized through (i) improvement of the coating method and (ii) control of catalyst particle size. Figure 12 contrasts a SEM micro-

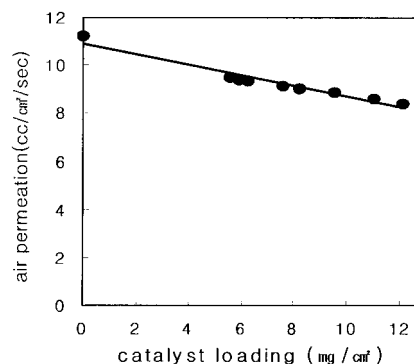


Figure 11 Variation in measured air permeation with catalyst loading.

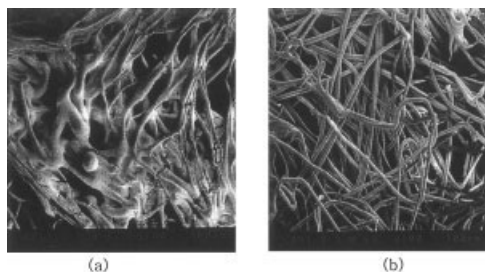


Figure 12 SEM micrographs of (a) catalyst-coated fabric [loading = 11.02 mg (TiO₂)/cm² (fabric)] and (b) uncoated fabric.

graph of a catalyst-coated fabric with that of an uncoated fabric.

CONCLUSIONS

This study was carried out to develop a new fabric coated with TiO₂ photocatalyst, which would be used in fabric filters having de-VOCs as well as dust-filtration function. To determine the optimum operating conditions for use of photocatalyst-coated fabrics, a series of experiments were performed on the variation of toluene vapor degradation under varying conditions of various important parameters. Significant conclusions were obtained as follows:

1. Toluene vapor conversion by photocatalyst-oxidation increases with radiation energy and the contact time of the vapor with a photocatalyst-coated fabric. To improve the vapor removal efficiency, an investigation on the variation of light intensity with light-source power and air

stream velocity should be conducted; it is thus necessary to determine the optimum velocity.

2. Flue gas moisture up to 55% (RH) contributes to keeping the photocatalyst active; however, it was confirmed that VOC_S removal performance of a photocatalyst-coated fabric decreases as the moisture increases beyond the critical level because the competitive adsorption between water vapor and VOC_S as well as the reunion of electron-hole pairs occur.
3. VOC_S decomposition efficiency increases with photocatalyst loading up to about 11 mg (TiO₂)/cm² (fabric), leading to air permeation reduction by about 25%; however, further conversion does not occur beyond the critical loading probably because of the limitation of UV light transmission into a catalyst cake. Air passage closure attributed to the catalyst coating would be minimized through (i) improvement of the coating method and (ii) control of particle size of the catalyst.

References

1. Yoon, J. K. M.S. Thesis, Yunsae University, Korea, 1998.
2. Park, S. J. M.S. Thesis, Chung-Ang University, Korea, 1999.
3. Hager, S.; Bauer, R. *Chemosphere* 1999, 38, 1549.
4. Whang 2000.
5. Ibusuki, T.; Takeuchi, K. *Atmos Environ* 1986, 20, 1711.
6. Yasumori, A.; Ishizu, K. *J Mater Chem* 1998, 8, 2521.
7. Campion, L. L.; Giannotti, C.; Ouazzani, J. *Chemosphere* 1999, 38, 1561.
8. Lee, S. J.; Cho, I. H. *J Korean Soc Elec Eng* 2002, 24, 1071.
9. Glaze, W. H.; Kang, J. W.; Chapin, D. H. *J Am Water Works Assoc* 1988, 80, 57.
10. Glaze, W. H.; Kang, J. W.; Chapin, D. H. *Ind Eng Chem Res* 1989, 28, 1580.
11. Einaga, H.; Futamura, S.; Ibusuki, T. *Appl Catal B* 2002, 38, 215.