Article

Photoreactor-Initiated Acetaldehyde Conversion Rate of a TiO₂-Surface-Treated Alumina Photocatalyst Prepared Using the Sol–Gel Method

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Abstract: In this study, a TiO₂–alumina photocatalyst was manufactured by coating a surface-treated alumina substrate with TiO₂ sol using the sol–gel method, and the photolysis and conversion of acetaldehyde in the gas phase were evaluated. The effects of acetaldehyde flow rate (i.e., retention time), ultraviolet wavelength, moisture, and catalyst heat-treatment temperature on the conversion of acetaldehyde were investigated. The experiments confirmed that a decrease in flow rate (i.e., increase in retention time), increase in moisture level, and decrease in the ultraviolet wavelength of the light source increased the conversion rate of the gaseous acetaldehyde. Among the three heat-treatment temperatures (450, 650, and 850 °C) used in the catalyst manufacturing process, the catalyst treated at 650 °C had the highest acetaldehyde conversion rate. As a result of its increased acetaldehyde decomposition and photoefficiency, the newly manufactured TiO₂–alumina photocatalyst is expected to be used alongside a photoreactor as an air-purifying filter. Furthermore, the photocatalyst surface treatment demonstrated herein can be adopted to fabricate various environmentally friendly materials in the future.

Keywords: photolysis; titanium dioxide; sol–gel; alumina; photocatalyst

1. Introduction

Various studies have explored the incorporation of photocatalytic technology to reduce the amount of particulate matter in air. Among the diverse functions of photocatalysts, their indoor and outdoor “air purification” function has rapidly gained attention owing to the recent worldwide outbreak of a novel, contagious respiratory disease, COVID-19. Photocatalysts can reduce or decompose nitrogen oxides (NOx), sulfur oxides, and volatile organic compounds (VOCs), which are precursors that generate particulate matter through the absorption of light (ultraviolet and visible rays). Owing to their photodegradation of harmful organic substances and bacteria, reduction of air pollutants, and photooxidation capabilities, photocatalysts can be applied to preserve the environment and combat viruses that affect daily life [1,2]. Materials that can be used as photocatalysts include TiO₂, SiO₂, ZnO,WO₃, CdS, and ZrO₂, as well as perovskite-type composite metal oxides (e.g., SrTiO₃ and BaTiO₃), which are known to exhibit photocatalytic effects [3–6]. Among these, TiO₂ is widely used as a photocatalyst because its physical and chemical
stabilities do not change even when exposed to light. With its high oxidation and reduction power, it can decompose NO\(_x\) (substances that are converted to fine dust) into nitric acid and VOCs into carbon dioxide (CO\(_2\)) and water (H\(_2\)O) [7,8]. Furthermore, TiO\(_2\) is considered a safe and environmentally friendly material [9,10].

When treating pollutants using a TiO\(_2\) photocatalyst, fine photocatalyst powder is difficult to separate from the suspension after reaction and suspended particles tend to agglomerate, so the fine particle suspension cannot be easily applied in a continuous flow process; rather, it can act as dust and TiO\(_2\) powder must be recovered after the reaction is completed [11]. Therefore, to overcome the problem, research on TiO\(_2\) thin-film manufacturing has been reported using thermal oxidation [12], sputtering [13,14], pyrolysis [15], thermal deposition [16,17], chemical vapor deposition (CVD) [18–21], atomic layer deposition (ALD) [22,23], and sol–gel methods [24–27].

Among the aforementioned methods, sol–gel is one of the most important methods for the synthesis of various functional coating films and holds several advantages over other thin-film manufacturing techniques, such as low-temperature treatment, easy coating of large surfaces, and the possibility of forming porous thin films and homogeneous composite oxide thin films [28,29].

In addition, several studies emphasizing the immobilization of TiO\(_2\) particles or sols on a support are in progress, and the characteristics of ceramic materials as TiO\(_2\) supports for the photocatalytic decomposition of VOCs have been widely emphasized [30,31]. When TiO\(_2\) nanoparticles are dispersed on the surfaces of ceramic materials, photocatalytic activity is improved due to the high specific surface area of TiO\(_2\), high adsorption capacity, large pore volume, chemical stability, and excellent mechanical properties [32,33]. Among such materials, alumina has been extensively used as a substrate due to its high strength, durability, cost-effectiveness, and versatility [34]. A porous support facilitating such an appropriate photo-interaction can be extremely advantageous in preventing oxidation reduction [35].

TiO\(_2\) was coated on surface-treated porous alumina using a sol–gel method, heat-treated at a different firing temperature, and then a photocatalyst was inserted into the prepared functional photo reactor to perform a photo-oxidation test of acetaldehyde. The characteristics of the TiO\(_2\) photocatalyst were observed depending on the firing temperature, and the conversion rate of acetaldehyde was evaluated using the photocatalyst of surface-treated alumina by applying flow change, light source type, moisture presence, initial concentration change, and various variables. In addition, the applicability of a functional photoreactor to an environmentally friendly reactor was evaluated.

2. Materials and Methods

2.1. Materials and Reagents

For the experiments, titanium tetraisopropoxide (TTIP, 98%; Junsei Chemical Co., Tokyo, Japan) was used as a starting material for TiO\(_2\); whereas hydrochloric acid (HCl, 35%; Duksan) and acetaldehyde (Sigma-Aldrich Korea, Seoul, Korea) were used as the catalyst and target VOC, respectively. Ethanol (EtOH, 99.9%; Carlo Erba Co.) was used as a solvent and tertiary distilled water (DW; Milli-Q IQ 7000, Merck, Korea) was used for hydrolysis. Sodium hydroxide (NaOH, 50%; Duksan) and acetone (CH\(_3\)COCH\(_3\), pure grade; Duksan) were used to clean the surface of the donut-shaped alumina substrate (Al\(_2\)O\(_3\), diameter: 4.6 cm, inner diameter: 2.6 cm, width: 1 cm; Ju-Hyoung Ceramics Co., Gumi, Korea). All the reagents used in the experiment were reagent grade.

2.2. Alumina Substrate Preparation

Four holes with diameters of 2 mm were drilled into the alumina substrate to prevent any channeling phenomena (Figure 1a). To remove impurities on the surface of the substrate, the substrate was immersed in 0.1 N NaOH for 1 day and then washed five times with DW. The surface was rewashed with acetone before being washed with an ultrasonic
cleaner (NXP1505P, KODO) at 60 °C for 30 min. After washing with water, it was sufficiently dried in an oven (ON-21E, JEIO TECH) and then used as the catalyst substrate.

![Figure 1](image1.png)

**Figure 1.** Schematics of the (a) alumina substrate and (b) photoreactor.

2.3. Preparation of the TiO$_2$ Photocatalyst Using the Sol–Gel Method

TiO$_2$ sol was prepared by mixing TTIP (0.1 mol, 29 mL) and EtOH (100 mL) using a stirrer (10 min, room temperature, 800 rpm). Thereafter, a mixture of aqueous HCl (0.7 N, 2.7 mL) and EtOH (100 mL) was added, and the solution was stirred at room temperature at 800 rpm for 1 h (Figure 2). The resulting sol, which was yellowish and transparent, comprised TTIP, EtOH, and HCl (aq., 0.7 N) in a molar ratio of 1:37.2:1.5. The TiO$_2$ sol was applied to the alumina substrate via dip coating [36].

After putting the alumina substrate in and out of the TiO$_2$ sol, the process of drying it in an oven at 100 °C for 30 min was repeated three times, and after the final drying it was dried in an oven at 80 °C for 24 h to sufficiently dry the solvent remaining on the surface. The dried TiO$_2$–alumina sample was heat-treated at 450, 650, and 850 °C for 3 h to compare properties according to the firing temperature; the temperature was increased at a rate of 28 °C/min for each condition.

![Figure 2](image2.png)

**Figure 2.** Preparation of the TiO$_2$ catalyst.

2.4. Photoreactor Manufacturing and the TiO$_2$–Alumina Catalyst Immobilization

A stainless steel photoreactor with a diameter of 50 mm and length of 360 mm was used. UV lamps (254 nm UV-C (Easywork Co., Ansan, Korea) and 365 nm UV-A (Easywork Co. Ansan, Korea)) inside quartz tubes were used at 15 W. An injection-molded component was separately manufactured so that it could be inserted from the upper part of the reaction tube (Figure 1b). After the insertion of the injection-molded part connected to the quartz tube in the photoreactor, the screw connecting the O-ring was sufficiently tightened to prevent the leakage of internal gas. The catalyst-coated alumina substrates were placed in the center of the reaction tube by inserting 10 catalyst plates at regular intervals outside the quartz tube. An O-ring that fitted around the quartz tube was inserted under the samples to fix them at the center of the reaction tube.
2.5. Acetaldehyde Degradation Experiments

To measure the acetaldehyde degradation abilities of the catalysts, acetaldehyde was flowed through an evaporation tube installed in a low-temperature thermostat (ThermoFisher Scientific, Seoul, Korea) to a dilution tube by concomitant evaporation with air. The acetaldehyde in the dilution tube was diluted again with air to control its concentration. The concentration of acetaldehyde was adjusted, with a three-way valve in front of the dilution tube to monitor the change in moisture, and a needle valve was installed to control the flow rate entering the reaction tube (Figure 3).

A gas chromatograph and data analysis system (GC-14A, Shimadzu Scientific Korea, Seoul, Korea) equipped with Porapak Q and T columns (50–80 mesh, Ø 3 mm × 3 m) was used to analyze the reactants and products.

![Figure 3. Schematic diagram of the experimental setup.](image)

2.6. Conversion(X) of Acetaldehyde

Before it was introduced into the photoreactor, acetaldehyde was sent only to the GC to calculate the concentration of the initial material. When the concentration of acetaldehyde became constant while continuously flowing through the GC, the light source (UV-A or UV-C) of the photoreactor was switched on, and acetaldehyde (in the gas phase) was allowed to flow into the reactor for the experiment.

The photocatalytic activity percentage of the TiO2-coated alumina substrate was calculated using the following Equation (1) [37,38]:

\[
X(\%) = \frac{(A_0 - A_t)}{A_0} \times 100
\]  

(1)

where \(X\) indicates the percentage of conversion, \(A_0\) is the gas chromatography peak area of the initial acetaldehyde concentration before irradiation under UV light, and \(A_t\) is the acetaldehyde concentration expressed as the integrated area of gas chromatographic peak at a sampling time \(t\) (min).

2.7. Characterization

X-ray diffraction (XRD; DMAX/1200, RIGAKU, Tokyo, Japan) was employed in continuous scan mode to identify the structural state of the catalyst (scan speed: 3°, scan step: 0.02°, scan range: 10–70°). The XRD analysis sample was measured only with TiO2 powder excluding alumina substrates. Field-emission scanning electron microscopy (FE-SEM; S-
4700 microscope, HITACHI, Tokyo, Japan) was used to analyze the surfaces of the catalysts; platinum was coated on the sample surfaces prior to the FE-SEM analysis to prevent surface deformation (acceleration voltage: 15 kV, vacuum pressure: 10⁻⁶ Torr).

3. Results and Discussion
3.1. Photodegradation Characteristics of Acetaldehyde against Heat-Treatment Temperature during Catalyst Preparation

The optimum firing temperature was first determined among the three heat-treatment temperatures of 450, 650, and 850 °C. Acetaldehyde decomposition experiments were performed on three heat-treated catalysts, and the best conversion was obtained using the catalyst heat-treated at 650 °C. At an initial concentration of 1800 ppm, a maximum conversion rate of 57% was observed after 30 min of light source irradiation, which stabilized at 50% after 2 h of irradiation. The lowest conversion rate was achieved while testing catalysts heat-treated at 850 °C. The rate increased from 8% after the initial 30 min to 23% after 75 min, with a marginal conversion rate of 17–18%. The maximum conversion rate achieved using the catalyst treated at 450 °C was 43%, which was lower than that of the catalyst treated at 650 °C (Figure 4).

Figure 4. Acetaldehyde photodegradation of the catalyst according to heat-treatment temperature: (a) 450 °C, (b) 650 °C, and (c) 850 °C (cc (sccm): standard cubic centimeter per minute (cm³/min)).

FE-SEM analysis was performed to observe the surface morphology of the three catalysts (Figure 5). Overall, the sol–gel thin film shrank on the surface of the alumina substrate, the pores disappeared, and the surface density increased as the heat treatment temperature increased. This was not observed for the alumina substrate without TiO₂ surface treatment (control). However, surface cracks occurred in the heat-treated sample, and the density and number of cracks increased as the heat-treatment temperature increased. At
450 °C, the TiO2 thin film was not uniformly coated on the surface of the alumina substrate and cracks in the thin film appeared to coexist. Increasing the temperature from 450 °C to 650 °C and 850 °C increased the density and number of cracks, and most cracks were observed in the catalyst heat-treated at 850 °C.

![Image](a)![Image](b)

**Figure 5.** FE-SEM photographs (2000×) of the catalyst on (a) an alumina plate and (b–d) heat-treated at (b) 450 °C, (c) 650 °C, and (d) 850 °C.

The TiO2 thin film tended to shrink as the heat treatment progressed, causing the pores to disappear and densify. In addition, as the heat treatment temperature increased, tensile stress was generated. Moreover, because the thermal expansion coefficient of the alumina substrate was low, it seemed that cracks occurred on the surface when the thin film was accompanied by additional shrinkage. This can be noted in a previous study that stated the effect of annealing temperature on the crystallization stage of TiO2 thin films [39]. For cracks in such shrinkage, it seems necessary to consider the variables of the type of solvent in the initial synthesis or the firing temperature increment conditions.

Figure 6 shows the anatase phase, coexisting rutile phase, and anatase and rutile phases of the catalysts heat-treated at 450, 650, and 850 °C, respectively. In particular, the coexistence of the rutile and anatase phases occurred in the catalyst at 650 °C, which had the highest conversion rate in our experiment. As the firing temperature increased, the rutile phase was formed and showed low photocatalytic activity. The photocatalytic activity of the TiO2 thin film coated on alumina was highly dependent on the firing temperature, and the surface area of the rutile phase decreased due to the sintering and growth of the TiO2 crystal phase [40]. The crystal sizes of the treated catalysts at 450, 650, and 850 °C were calculated to be 14, 31, and 33 nm, respectively, using the Scherrer equation. Therefore, as the sintering temperature increased, the crystal size increased. This is because the sintering temperature can increase the grain size and TiO2 crystal growth can be induced as the sintering temperature rises. It can be seen that they correspond [41,42].
Figure 6. XRD patterns of the catalysts prepared at different heat-treatment temperatures: (a) 450 °C, (b) 650 °C, and (c) 850 °C (● anatase (JCPDS no. 21-1272); □ rutile (JCPDS no. 21-1276)).

In this study, the highest conversion rate of the catalyst, in which the anatase and rutile phases coexisted, is consistent with the results of a previous study [43] which reported increased conversion rates for a catalyst with anatase and rutile phases mixed in a ratio of 8:2; therein lies a correlation. This is because a mixed-phase catalyst has more active sites than a catalyst having a pure crystalline phase of rutile or anatase, as the separation efficiency of electron–hole pairs is improved due to the multi-phase nature. In addition, the higher conversion rate of the catalyst treated at 450 °C (anatase phase) compared to the catalyst treated at 850 °C (rutile phase) indicates that the anatase phase is more effective in enhancing photocatalytic activity than the rutile phase. This was indirectly supported by other reports stating that the photocatalytic activity of anatase-like materials is superior to that of rutile-like materials because such materials show a higher Fermi level and surface hydroxylation on anatase than on rutile [44].

3.2. Acetaldehyde Degradation Characteristics according to Changes in Flow Rate

The effects of the flow rate at which acetaldehyde was introduced to the photoreactor were determined; flow rates of 40, 60, and 100 sccm were used. The conversion rate increased as the flow rate decreased, which seemed to affect the photo-oxidation of acetaldehyde on the surface of the photocatalyst according to the change in the flow rate of the reaction gas entering the photoreactor. When a UV light source was used, photons and various radicals were generated on the surface of the photocatalyst. Longer residence times of the reaction gas on the photocatalyst surface led to higher conversion rates; this was due to the photons and various radicals that allow sufficient oxidation [45].

3.3. Acetaldehyde Degradation Characteristics according to the Initial Inflow Concentration

The concentration of acetaldehyde initially introduced into the reactor was also varied. At an initial aldehyde concentration of 1,500–1,800 ppm, the conversion rate of acetaldehyde was maintained at approximately 60%, with the catalyst treated at 650 °C (Figure 4). This is consistent with a study [46] that reported incomplete photocatalytic oxidation owing to the active part of their catalyst being covered by the excess amount of contaminant molecules initially introduced; this reduced the generation of radicals on the surface of the catalyst. Notably, using the catalyst heat-treated at 650 °C with a significantly reduced initial acetaldehyde concentration (750 ppm) resulted in a conversion rate of 100% after 30 min when irradiated with a UV-C light source (Figure 7).
Figure 7. Change in the conversion rate of acetaldehyde with the initial acetaldehyde concentration (650 °C catalyst, UV-C light, flow rate: 40 sccm).

3.4. Acetaldehyde Degradation Characteristics according to Light Source Conditions

Different light sources were also tested. When the catalysts were irradiated using the UV-A (365 nm) light source, all three showed conversion rates of less than 5% (Figure 4). Irradiation with the 365 nm light resulted in almost no oxidation of the contaminants, which is consistent with a previous paper [47]. Conversely, with the UV-C light source, the conversion rate achieved with the catalyst heat-treated at 450 °C reached 42% before leveling out; additionally, the conversion rate of the catalyst heat-treated at 650 °C reached up to 57% 45 min after irradiation and that of the catalyst heat-treated at 850 °C was 23% at its highest; however, this gradually decreased and stabilized in the 10% range. Therefore, the UV-C light source induced higher conversion rates than those of the UV-A source, presumably because UV-C light has a higher light flux than that of UV-A light. Another study demonstrated greater photon flux of short-wavelength light than long-wavelength light, along with the high acetaldehyde removal efficiency of short-wavelength light [48].

Furthermore, experiments with and without a catalyst in the reactor were conducted to determine the possibility of direct acetaldehyde decomposition in the presence of a light source only. The conversion rate was 4.7% when only UV-C irradiation was used in the reactor for 45 min, which decreased to a constant value of 3% after 120 min (Figure 8). However, when the catalyst was present in the reactor (flow rate: 40 sccm, UV-C light), the conversion rate of acetaldehyde reached as high as 57%, suggesting that irradiation with a light source did not affect the direct oxidation of acetaldehyde.

Figure 8. Comparison of the conversion rate of acetaldehyde with and without catalyst (catalyst calcined at 650 °C, UV-C light, flow rate: 40 sccm).
3.5. Effects of Moisture on Organic Matter Degradation Characteristics of the Catalysts

To determine the effects of moisture on the photocatalytic conversion rate, experiments were conducted with and without moisture; a vapor evaporation tube was installed in front of the dilution tube for use while the gas-phase acetaldehyde was flowed in the reactor. A three-way valve was used to block the inflow of water into the photoreactor, and acetaldehyde photodegradation experiments were conducted using three catalysts heat-treated at 450, 650, and 850 °C. The gas flow rate was 40 sccm, and UV-C was used as the light source. As a result of the experiment, the conversion rates in the absence of water were 24%, 30% and 11%, respectively. This is a much lower result than when the reaction was induced by supplying moisture (Figure 9).

![Figure 9](image_url)

**Figure 9.** Comparison of the conversion rate of acetaldehyde in the (a) presence and (b) absence of moisture.

Acetic acid, which is typically the predominant byproduct of acetaldehyde degradation, was evidently not produced in any of the reaction experiments. However, a thorough analysis revealed that acetic acid was formed but decomposed over time into CO₂ and H₂O; the conversion rates were calculated taking this into account. Considering that direct contact between superoxide radicals and acetaldehyde occurs while acetaldehyde is adsorbed on the catalyst surface, the following reaction can be considered [49]:

\[ \text{CH}_3\text{CHO} + \text{O}_2^- \rightarrow \text{CH}_3\text{CO}^- + \text{HO}_2^- \]  
\[ \text{CH}_3\text{CHO} + \text{O}_2^- \rightarrow \text{CH}_3\text{CO}^- + \text{HO}_2^- \]  
\[ \text{CH}_3\text{CHO} + \text{HO}_2^- \rightarrow \text{CH}_3\text{CO}^- + \text{H}_2\text{O} \]  
\[ \text{CH}_3\text{CO}^- + \text{OH} \rightarrow \text{CH}_3\text{COOH} + e^- \]

The total reaction is:

\[ 2\text{CH}_3\text{CHO} + \text{O}_2 \rightarrow 2\text{CH}_3\text{COOH} \]

Under strong illumination, further oxidation proceeds similarly.

\[ 2\text{CH}_3\text{COOH} + \text{O}_2 \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O} \]

The enhanced acetaldehyde conversion that was observed in the presence of moisture is likely because of the introduction of species such as OH and HO₂⁻ radicals to the surface of the catalyst. Additionally, our results are consistent with those of a study [50] on the role of moisture in the photocatalytic degradation of gaseous pollutants.
4. Conclusions

In this study, a TiO$_2$–alumina photocatalyst was prepared using the sol–gel method and inserted into a functional photoreactor to evaluate the conversion rate of gaseous acetaldehyde. Photocatalysts of three types were prepared, according to the firing temperatures, and their properties were evaluated for various conditions in the gas phase experiment.

The experimental results confirmed that the acetaldehyde conversion of the TiO$_2$–alumina catalyst at 650 °C was superior to that of the catalyst treated at 450 °C or 850 °C. As the calcination temperature increased, the conversion rate decreased as the anatase phase changed to the rutile phase, and the calcination temperature also affected the crystal size. Moreover, the conversion rate was higher as the residence time of the reaction gas flowing in the photoreactor increased, a light source of a low wavelength region was irradiated, and moisture was continuously supplied into the photoreactor. By optimizing these various factors, a photocatalyst at a firing temperature of 650 °C was applied to the functional photoreactor, and the highest conversion rate was achieved when a flow rate of 40 sccm and a UV-C light source were used.

The TiO$_2$ photocatalyst coated on the surface-treated alumina substrate showed the potential to remove various gaseous contaminants when used in a functional photoreactor and is expected to be applied as a novel material for air purification systems.

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