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Adsorption and Photocatalytic Decomposition of Gaseous 2-Propanol Using TiO₂-Coated Porous Glass Fiber Cloth

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Abstract: Combinations of TiO₂ photocatalysts and various adsorbents have been extensively investigated for eliminating volatile organic compounds (VOCs) at low concentrations. Herein, TiO₂ and porous glass cloth composites were prepared by acid leaching and subsequent TiO₂ dip-coating of the electrically applied glass (E-glass) cloth, and its adsorption and photocatalytic ability were investigated. Acid leaching increased the specific surface area of the E-glass cloth from 1 to 430 m²/g while maintaining sufficient mechanical strength for supporting TiO₂. Further, the specific surface area remained large (290 m²/g) after TiO₂ coating. In the photocatalytic decomposition of gaseous 2-propanol, the TiO₂-coated porous glass cloth exhibited higher adsorption and photocatalytic decomposition ability than those exhibited by the TiO₂-coated, non-porous glass cloth. The porous composite limited desorption of acetone, which is a decomposition intermediate of 2-propanol, until 2-propanol was completely decomposed to CO₂. The CO₂ generation rate was affected by the temperature condition (15 or 35 °C) and the water content (2 or 18 mg/L); the latter also influenced 2-propanol adsorption in photocatalytic decomposition. Both the conditions may change the diffusion and adsorption behavior of 2-propanol in the porous composite. As demonstrated by its high adsorption and photocatalytic ability, the composite (TiO₂ and porous glass cloth) effectively eliminates VOCs, while decreasing the emission of harmful intermediates.

Keywords: photocatalyst; microporous material; composite; adsorption; air purification; TiO₂; porous glass

1. Introduction

Indoor air pollution by volatile organic compounds (VOCs) is considered to be a serious health problem. Construction materials emit various VOCs, including formaldehyde, acetaldehyde, toluene, xylene, hexane, acetone, and 2-propanol, which can cause the sick building syndrome even at VOC concentrations lower than 1 ppm [1]. Further, the VOC concentrations in the work spaces are strictly limited to prevent health damage from prolonged exposure. However, the imposed concentration limits of the major solvents are in the range of 10–10³ ppm [2]. Titanium dioxide (TiO₂) photocatalysts have been extensively investigated in VOC decomposition because of their strong oxidation abilities under ultraviolet (UV) irradiation and because of their ability to decompose various organic compounds [3–6]. However, the VOC decomposition rates are observed to be insufficient

at considerably low concentrations because the photocatalytic decomposition reaction tends to be diffusion controlled under such conditions [7].

A promising solution to this problem is to combine TiO_2 with an appropriate adsorbate material. Further, the proposed mechanism of VOC elimination by composites can be given as follows. The concentration of VOC molecules can be obtained based on the adherence of VOC molecules in bulk air to the adsorbate surface. The VOC molecules in bulk air are concentrated on the adsorbate surface by adsorption. The adsorbed molecules are diffused to the vicinity of the TiO_2 surface and are photo-catalytically decomposed by TiO_2 [8,9]. The adsorbate is a porous material, including activated carbon [9,10], zeolite [9,11,12], silica gel [13], or mesoporous silica [14,15]. The composites require a free-standing structure for maintaining sufficient mechanical strength in practical applications. Further, because it is generally difficult to prepare the composites from porous adsorbates, they are used in powder form or are supported on another substrate [12]. Porous glass is an adsorbate candidate exhibiting sufficient mechanical strength for TiO_2 support. Thus, a composite photocatalyst of TiO_2 and porous glass exhibits superior photocatalytic activity to powder TiO_2 , or non-porous composite photocatalyst in case of gaseous and aqueous systems [16–19].

The electrically applied glass (E-glass) fiber is a mass-produced glass fiber with low alkaline metal content. E-glass fiber and its cloth are primarily used to form the fiber-reinforced plastics. The typical composition of E-glass fiber is 52–62 wt % SiO_2 , 16–25 wt % CaO , 12–16 wt % Al_2O_3 , 0–10 wt % B_2O_3 , and 0–5 wt % MgO , along with small amounts of alkaline metal oxides (TiO_2 and Fe_2O_3) and fluorides [20]. When the E-glass fiber is corroded in an acid solution [21,22], a porous structure is formed. The pores are formed by the dissolution of Al_2O_3 , B_2O_3 , and the ions of alkaline metals and alkali earth metals, leaving the SiO_2 structure. The acid-leached E-glass fiber and cloth are the porous materials that had been investigated in previously conducted studies [23–25]. The properties of porous glass cloth, such as the high adsorption capacity for VOCs, high optical transparency, low weight, and sufficient mechanical strength, are considered to be advantageous for photocatalyst support. Very low alkali metal content is another advantage because the diffusion of alkaline metal ions from the glass substrate to the TiO_2 photocatalyst deteriorates the photocatalytic activity of TiO_2 [26,27]. Kitamura et al. prepared air filters by combining the TiO_2 photocatalyst and the porous glass fiber cloth that was prepared by acid leaching [25]. They further examined the filter's ability to eliminate gaseous formaldehyde; however, they did not measure the concentration of the decomposition products. Therefore, they could not discuss the contributions of adsorption and photocatalytic decomposition in the elimination process.

In this study, a composite material was fabricated from the TiO_2 photocatalyst and porous glass fiber cloth; further, its adsorption and photocatalytic decomposition ability has been examined with respect to gaseous air-diluted 2-propanol. The TiO_2 -porous glass cloth composite was prepared by acid leaching the glass cloth and by subsequently dip-coating it using TiO_2 . The pore formation process was investigated by observing the microstructure, analyzing the chemical composition, and measuring the N_2 adsorption of the acid-leached glass cloth. Further, the effects of TiO_2 loading on the composite properties were also investigated. Subsequently, the adsorption and photocatalytic properties of the TiO_2 -coated porous glass cloth were investigated using 300 ppm of gaseous 2-propanol. The concentration changes in the 2-propanol, acetone as an intermediate oxidative product of 2-propanol, and CO_2 as a final product of 2-propanol decomposition were measured during the adsorption and photocatalytic decomposition. Further, the effects of temperature and water content on the adsorption and photocatalytic decomposition abilities of the composite were also investigated because these factors affect the photocatalytic decomposition rates of 2-propanol [28–31] and acetone [32,33], and because they may affect the adsorption and diffusion of organic molecules in the porous glass. Finally, based on the experimental results, we discuss the adsorption and photocatalytic decomposition mechanisms of the TiO_2 -coated porous glass cloth.

2. Results and Discussion

2.1. Microstructure Analysis and Mechanical Strength Test

The micro-structural change of the E-glass cloth that was prepared by acid leaching and TiO₂ coating was investigated using field emission scanning electron microscopy (FE-SEM). Hereafter, the unleached and leached samples are referred to as the non-porous and porous glass samples, respectively. Panels (a–c) of Figure 1 denote the cross-sectional images of the non-porous and porous glass fibers comprising cloth samples. After leaching for 1 h, the structure of the glass fibers changed from uniform and dense with no pores (Figure 1a), to a dense core surrounded by a porous surface layer with a thickness of 2–3 μm (Figure 1b). After 3 h of leaching, the glass fiber was observed to become completely porous. The SEM images indicate that the porous structure was formed from the surface to the center as the leaching time increased, as previously reported by Tanaka et al. [24]. Panels (d–f) of Figure 1 denote the side views of the non-porous and porous glass fibers. A larger number of cracks developed in the porous fibers when compared to that in the non-porous fibers. The cracks that were observed on the 1-h leached fibers were mainly observed to be perpendicular to the fiber elongation direction and propagated only in the porous layer. This indicated that the cracks were generated by the tensile stress in the porous layer. During the drying process, the generation of strong capillary forces in the porous structure could shrink the porous surface layer. The different shrinkage ratios between the core and the porous layer could further result in crack generation. In contrast, the cracks on the 3-h leached fibers progressed along the fiber elongation direction and near the fiber center. Further, the mechanism of crack generation differed between the samples that were prepared after 1 and 3 h of leaching. The residual stress that was derived from the fiber spinning process may explain this type of crack generation, as will be discussed in our subsequent report. Despite the generation of clacking by acid leaching, the flexibility of the porous glass cloth was maintained at a high level. When the 3-h leached glass cloth was curved with a curvature radius of 3 mm, the glass cloth did not break; further, its form was recovered without any deformation. Panels (g–i) of Figure 1 denote the side views of the TiO₂-coated fibers. Agglomerates of the TiO₂ nanoparticles are observed on the surfaces, and the coating is observed to be in-homogeneous. Because the glass cloth samples have high fiber density, homogeneous coating of each fiber by dip-coating the cloth sample would be difficult. Further, the sampling process before FE-SEM observation can cause some damage to the TiO₂ coating. Figure S1 depicts the surface and fracture cross-section of TiO₂ coating on the porous glass cloth at a position where plenty of TiO₂ is loaded and where only little sample damage is observed. The TiO₂ coating exhibited a porous structure, and VOCs can penetrate the coating.

2.2. Crystalline Phase of TiO₂

The TiO₂-coated glass cloth samples, and the TiO₂ powder sample that was prepared from TiO₂ suspension used in the dip-coating process, were ground with a pestle in an agate mortar, and their X-ray diffraction (XRD) patterns were measured. Figure 2 depicts the XRD patterns of the aforementioned samples. The TiO₂ suspension comprised anatase (TiO₂) nanoparticles and solvent; therefore, the TiO₂ powder sample prepared from the TiO₂ suspension exhibited anatase peaks (Figure 2a). The crystalline size that was estimated from Scherrer's equation using 101 reflection is 6.9 nm. The TiO₂-coated non-porous glass cloth exhibited no anatase peak (Figure 2b). This can be attributed to the lesser amounts of TiO₂, and will be explained in the following elemental analysis in Section 2.3. The broad peaks that can be observed at around 26° denote the glass halo, whereas the peaks that can be observed at around 42° denote the graphite oxide generated by incomplete organic molecule combustion. The TiO₂-coated 3-h leached porous glass cloth did not exhibit the strongest 101 reflection of anatase because it was overlapped with glass halo at around 24° (Figure 2c). However, the 220, 105, 211, and 204 reflections of anatase can be clearly observed. Based on these results, the TiO₂ on the porous sample was observed to be in the anatase form. Further, the TiO₂ on the non-porous sample was also in the anatase form because it was prepared in the same manner as the porous sample.

It indicates that the use of black light lamp (center wavelength: 365 nm), in the following photocatalytic decomposition experiments, is suitable for the photo-excitation of this composite because anatase exhibits a bandgap of 3.2 eV (388 nm) [34].

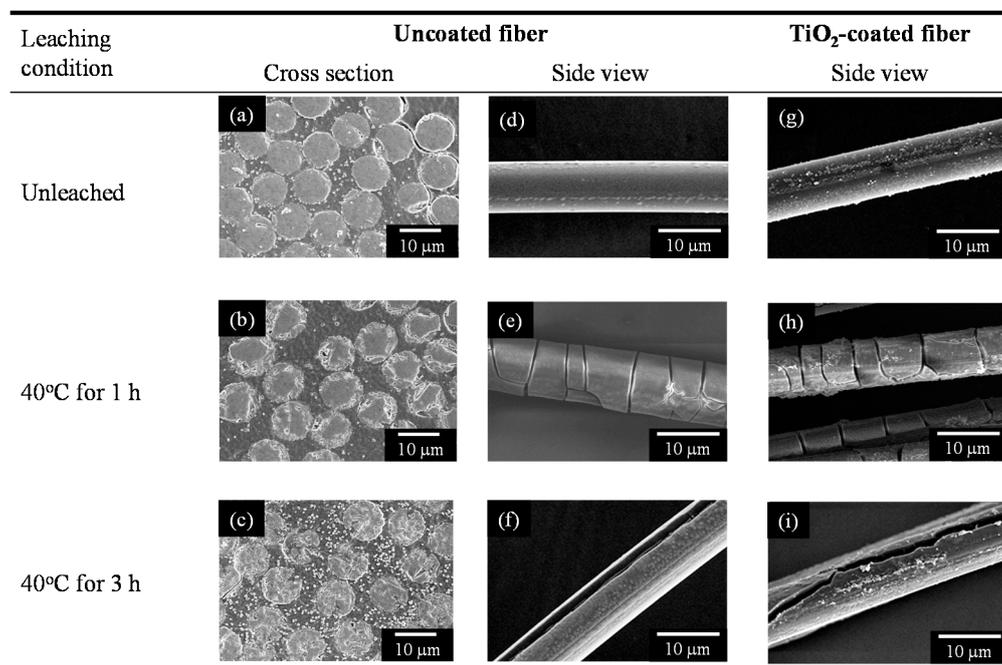


Figure 1. SEM images of the non-porous and porous glass fibers before (left and center panels) and after (right panel) TiO₂ coating.

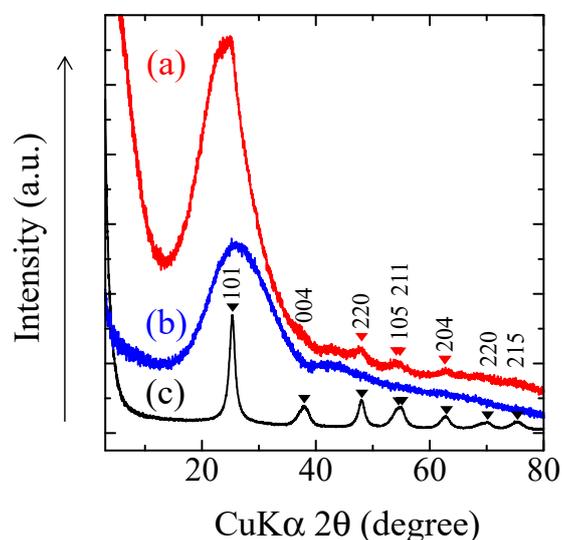


Figure 2. Powder X-Ray diffraction (XRD) pattern of the ground samples: (a) dried and heated TiO₂ suspension; (b) TiO₂-coated non-porous glass cloth; and (c) TiO₂-coated porous glass cloth. *hkl* are reflection indices of anatase.

2.3. Chemical Composition Analysis

Figure 3 depicts the chemical compositions of the non-porous and porous glass cloths that have been estimated using the X-ray fluorescence (XRF) measurements. In this figure, the porous cloths were obtained after leaching for 1, 3, and 12 h. While estimating the compositions of the 3- and 12-h leached glass cloths, sodium oxide was assumed to be zero because the sample pellets were prepared using Na₂CO₃. With an increase in leaching time, the composition ratios of the alkali earth metal oxides,

boron oxide, alkali metal oxides, and alumina decreased, whereas the silica content was maintained to be almost constant. The leaching of the non-silica components from the glass fiber resulted in the formation of the observed microporous structures in the glass cloths Panels (b,c,e,f) of Figure 1. The composition almost ceased to change after 3 h of leaching (the time of core disappearance in the acid-leached fibers).

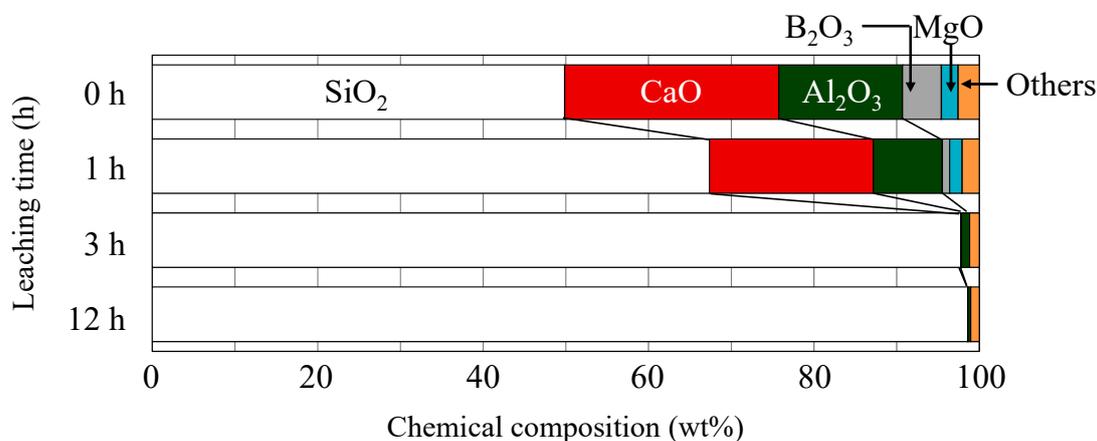


Figure 3. Chemical compositions of the non-porous (0-h leaching time) and porous glass cloths estimated from the X-ray fluorescence (XRF) measurements. The “Others” category includes TiO₂, Na₂O, K₂O, Fe₂O₃, and SrO.

Further, the TiO₂ contents in the TiO₂-coated non-porous and porous glass cloths were evaluated using XRF. Figure 4 plots the TiO₂ content and weight loss of the glass cloth as functions of the acid leaching time. The weight loss of the glass cloth was calculated as follows:

$$\text{Weight loss (\%)} = \frac{\text{Weight change of glass cloth after acid leaching}}{\text{Weight of glass cloth before leaching}} \times 100$$

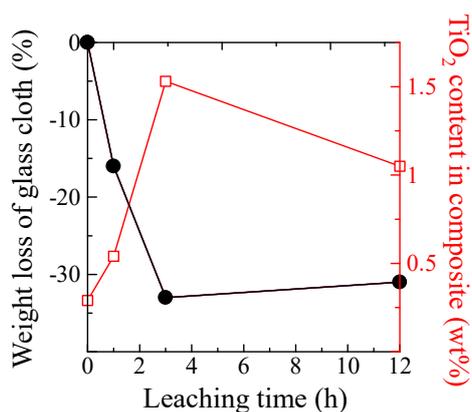


Figure 4. TiO₂ content in the TiO₂-coated porous glass cloth (open squares) and weight loss of the porous glass cloth (filled circles) versus the acid leaching time.

Both the TiO₂ loading amount and weight loss of the glass cloth increased at the maximum leaching time of 3 h. Even if the TiO₂ loading amount was unaffected by the leaching time, the TiO₂ composition ratio was observed to increase because of the weight loss of the glass cloth. However, the increase in the TiO₂ composition ratio exceeded the expected value corresponding to this weight loss, demonstrating the remaining factors that were responsible for this increase in TiO₂ composition ratio. As will be discussed subsequently, the TiO₂ particles cannot penetrate the pores in the glass fiber structure; therefore, the increased volume of pores cannot be explained by the increased loading

amount of TiO_2 . However, the large cracks that are observed in the SEM images (Figure 1e,f) are considered to be the likely support sites of the TiO_2 particles in the dip-coating process. Further, the pore formation can also increase the TiO_2 content by increasing the surface roughness or the wettability of the glass surface. In contrast, the increase in leaching time from 3 to 12 h decreases the TiO_2 amount. However, the factors that can affect the TiO_2 loading, weight loss, cracking, and surface conditions were not significantly altered in this time range. Therefore, the loading amount of TiO_2 was observed to be saturated rather than decreased.

2.4. N_2 Adsorption

Figure 5 depicts the N_2 adsorption and desorption isotherms of the non-porous and the 3-h leached porous glass cloths before and after TiO_2 coating. The non-porous samples (Figure 5a) yielded a type III adsorption isotherm, confirming the absence of micrometer- or nanometer-sized pores [35]. However, the porous samples (Figure 5b) yielded a type I adsorption isotherm, indicating the existence of nanometer-sized pores (<2 nm) [35]. The sample that was prepared in an extended leaching time (12 h) yielded a type I adsorption isotherm, indicating that the pore size will not be significantly changed by prolonging the leaching time. Figure 6 plots the specific surface areas (Sg) of the TiO_2 -coated and uncoated glass cloth samples versus the acid leaching time. The Sg values of both the samples increased up to approximately 4 h of leaching time and remained almost constant thereafter, indicating that the microporous structure was completely formed after 4 h of leaching. However, in the SEM images, the fiber core disappeared after 3 h of leaching (Figure 1c), implying that the microporous structure continued to evolve after the fiber center was subjected to acid leaching. After the disappearance of the core, Sg was probably increased by the leaching of the non-silica components that remained in the porous glass cloth and by the precipitation of silica gel in the pores. The latter process is typically observed during the leaching of the phase-separated borosilicate glasses [36,37].

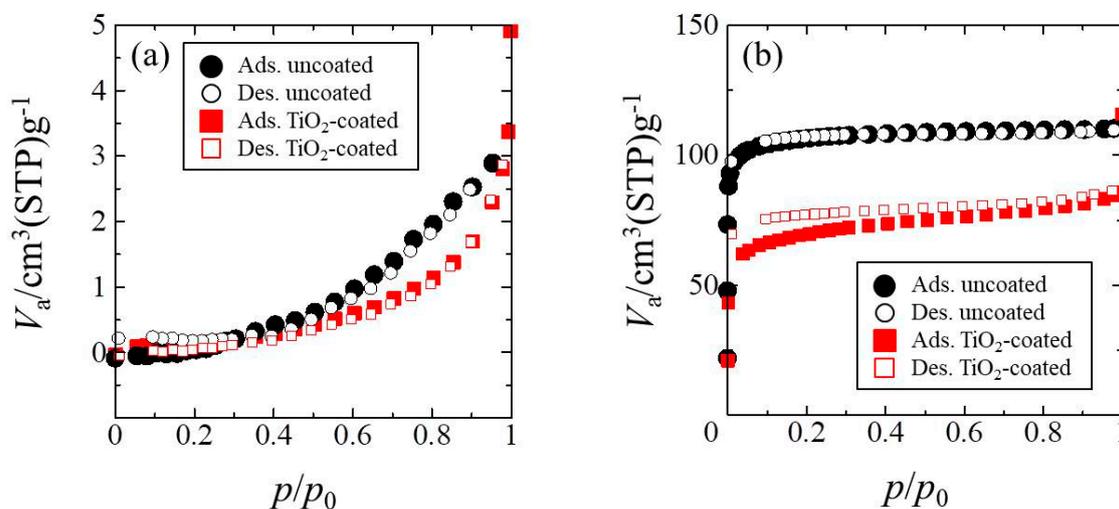


Figure 5. Adsorption (Ads.) and desorption (Des.) isotherms of (a) a non-porous glass cloth and (b) a porous glass cloth before and after TiO_2 coating.

As depicted in Figure 5b, the TiO_2 coating reduced the adsorbed/desorbed N_2 in the low pressure region or the isotherm. This decrease corresponds to the lower Sg value of the TiO_2 -coated samples when compared to that of the uncoated samples depicted in Figure 5. This decrease cannot be ascribed to the filling of nanometer-sized pores by TiO_2 particles because even the primary particle size of TiO_2 (6 nm) is considerably larger than the estimated pore diameter (<2 nm). To elucidate the reason that the Sg decreased during the TiO_2 coating process, we investigated the manner in which heat treatment after dip-coating affected the Sg of the samples. The porous glass cloth that was prepared by 3 h of leaching was subjected to the same heat treatment as that used in the dip-coated samples

(300 °C for 2 h), and its measured S_g was compared with that of the samples obtained before heat treatment. The heat treatment decreased the S_g from 370 to 200 m²/g, indicating that heating was mainly responsible for the loss of S_g in the TiO₂-coated sample. To verify the effects of coating and heating on the porous properties, we investigated the pore-size distribution in the samples. Figure S2 depicts the adsorption isotherms of the uncoated and TiO₂-coated porous glass cloths and their pore-size distributions estimated by Saito–Foley fitting [38,39]. The majority of the pores were observed to be less than 1 nm in diameter, and the TiO₂ coating and heating process reduced the volume of the large pores. The reduced S_g and enlarged pores in the heat-treated sample may have arisen from dehydration condensation of the silanol groups on the surface of the pores [40]. However, because the subsequent heat treatment ensured that a high specific surface area of the TiO₂-coated glass cloth was retained, the organic-molecule adsorption ability of the TiO₂-coated sample should not have been significantly degraded.

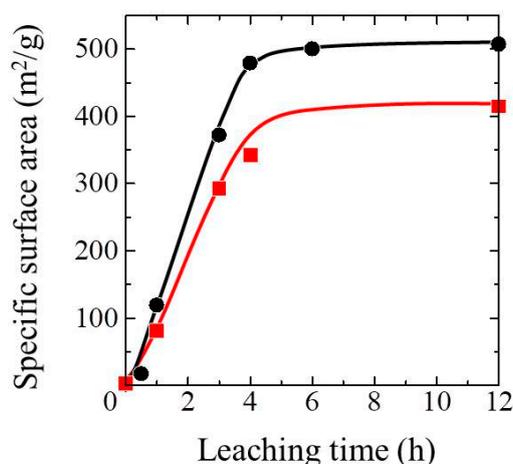


Figure 6. Specific surface area versus leaching time of the TiO₂-coated porous glass cloths (squares) and the uncoated porous glass cloth (circles).

2.5. Adsorption and Photocatalytic Ability of 2-Propanol

First, the adsorption and photocatalytic decomposition abilities of the TiO₂-coated porous glass cloth, that was prepared by 3 h of leaching, and the TiO₂-coated non-porous glass cloth were compared at 15 °C and a low water content (2 mg/L). Figure 7a plots the 2-propanol concentration versus time under dark conditions. The non-porous sample gradually reduced the concentration of gaseous 2-propanol during the initial 60 min, whereas the porous sample rapidly reduced the 2-propanol concentration within the initial 10 min, reducing it to lower than the detection limit in 20 min. These results indicate the strong absorbency of the porous sample for gaseous 2-propanol. The panels (b,c) of Figure 7 depict the temporal changes of 2-propanol concentration under UV light irradiation for the TiO₂-coated non-porous and porous glass cloths, respectively, after the adsorption experiment is conducted in dark conditions. Further, the photocatalytic oxidation decomposition of gaseous 2-propanol tends to desorb acetone from the TiO₂ surface; consequently, acetone is formed as a typical decomposition intermediate of this process [33]. The acetone concentration that was desorbed from the TiO₂-coated non-porous glass cloth increased to its maximum at 2.5 h of irradiation time and gradually decreased. Meanwhile, the CO₂ concentration monotonically increased with the UV light irradiation time. However, acetone was not detected from the porous glass sample, and the CO₂ concentration rapidly increased until approximately 1.5 h of the irradiation time; further, it gradually increased up to 4 h of irradiation time. These results indicate that the acetone that was generated on the porous sample was not desorbed from the surface but was decomposed to CO₂. Further, a similar reaction process has been reported for the TiO₂–zeolite composite [12]. The rapidly increasing amount of CO₂ indicates

the effectiveness of photocatalytic decomposition during the early stages because of the 2-propanol concentration in the composite.

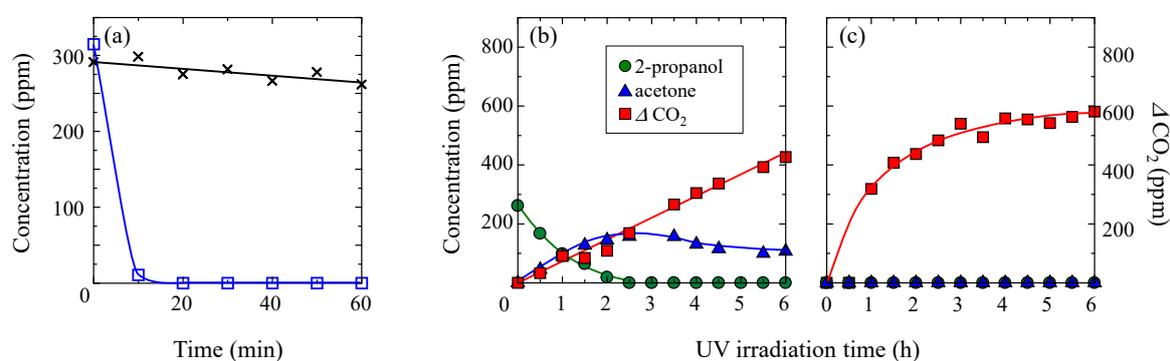


Figure 7. (a) Temporal concentration changes of gaseous 2-propanol under dark conditions for the TiO₂-coated non-porous (crosses) and porous (open squares) glass cloths. (b,c) Concentrations of gaseous 2-propanol, acetone, and CO₂ under subsequent UV light irradiation for the TiO₂-coated non-porous and porous glass cloths, respectively. The porous sample was prepared by 3 h of leaching. The dark adsorption and photocatalytic deposition experiments were conducted at 15 °C and in the presence of low water content (2 mg/L) in a 2-propanol atmosphere.

Further, the effects of temperature and water content on the adsorption and decomposition abilities of the TiO₂-coated porous glass cloth were investigated. Figure 8a depicts the trends of the 2-propanol adsorption under dark conditions in 2-propanol atmospheres with both high (18 mg/L) and low (2 mg/L) water contents. Both the experiments were conducted at 35 °C. A higher amount of 2-propanol was adsorbed from dry air when compared to that adsorbed from moist air. In the presence of high water contents, the alcohol and water molecules compete to be adsorbed on the silanol sites of the silica surface [41], thereby reducing the amount of adsorbed 2-propanol. The concentration changes of 2-propanol, acetone, and CO₂ in dry and moist atmospheres during UV irradiation are depicted in Panels (b,c) of Figure 8. Acetone was not detected under either condition, which was similar to that observed in the experiment that was conducted at 15 °C in the presence of a low water content (Figure 7c). Meanwhile, more CO₂ was generated at 35 °C than at 15 °C with low water content. In addition, at 35 °C, slightly more CO₂ was generated under the high-water atmosphere when compared to that generated under the low-water atmosphere.

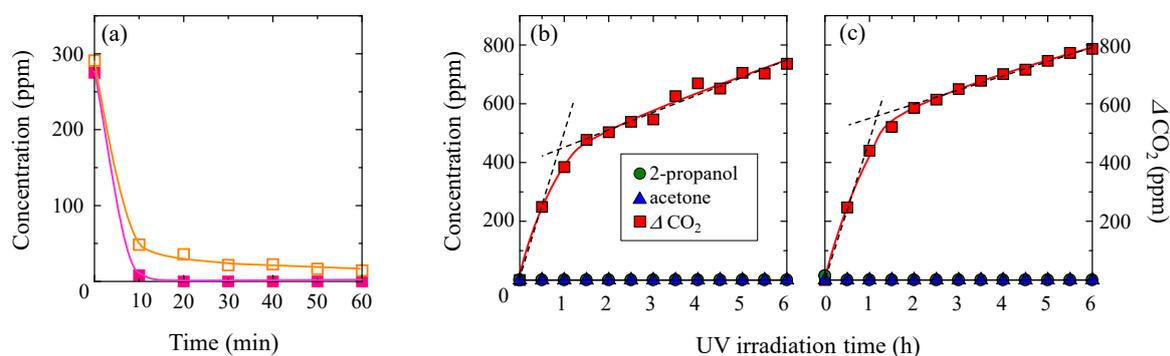


Figure 8. (a) Temporal concentration changes of 2-propanol during the dark storage of TiO₂-coated porous glass cloth in gaseous 2-propanol with 2-mg/L water content (closed squares) and 18-mg/L water content (open squares). (b,c) The concentration changes of 2-propanol, acetone, and CO₂ during UV irradiation of the TiO₂-coated non-porous glass cloth in gaseous 2-propanol with 2-mg/L and 18-mg/L water contents, respectively. All the experiments were conducted at 35 °C.

The rate of CO₂ generation by the decomposition of 2-propanol in the TiO₂-coated porous glass cloth (Figures 6c and 7b,c) changed after approximately 1.5 h of UV irradiation. No rate change could be observed in the non-porous sample (Figure 6b), confirming that the rate change phenomenon originated from the porous structure. The proposed decomposition model is depicted in Figure 9. In the TiO₂-coated porous glass cloth, the TiO₂ particles are mainly supported on the external surface of the porous glass fibers and do not penetrate the pores. Therefore, the photocatalytic reaction occurs on the external fiber surface, whereas the porous interior provides the adsorption sites of 2-propanol, acetone, and water. When the dried sample is inserted into a reactor filled with gaseous 2-propanol, the 2-propanol and water molecules are competitively adsorbed on the SiO₂ walls of the pores. Wu et al. clarified that the water and alcohol molecules emit comparatively large adsorption heat when they are adsorbed onto a bare SiO₂ surface than that emitted when they are adsorbed onto or when they form cluster with the molecules that have already being adsorbed onto the SiO₂ surface [42]. This observation indicates that the weakly and strongly adsorbed molecules coexist on the SiO₂ walls of the pores (Figure 9a). Under UV illumination, the 2-propanol molecules near the TiO₂ surface are decomposed to CO₂ via the acetone intermediate. In the early phase of photocatalytic decomposition, the weakly adsorbed 2-propanol molecules on the SiO₂ walls are preferentially desorbed and diffuse from the interior of the fiber to near the TiO₂ surface. Further, 2-propanol diffusion provides a sufficient supply of 2-propanol for sustaining CO₂ generation at a high rate (Figure 9b). The reaction rate gradually decreases as the supply of weakly adsorbed 2-propanol reduces. In the later phase, the CO₂ generation rate is limited by the desorption and diffusion of the strongly adsorbed 2-propanol molecules (Figure 9c). This limiting rate corresponds to the decelerated CO₂ generation rate after 1.5 h of light illumination in the photocatalytic decomposition of 2-propanol on the TiO₂-coated porous glass cloth (Figures 7c and 8b,c).

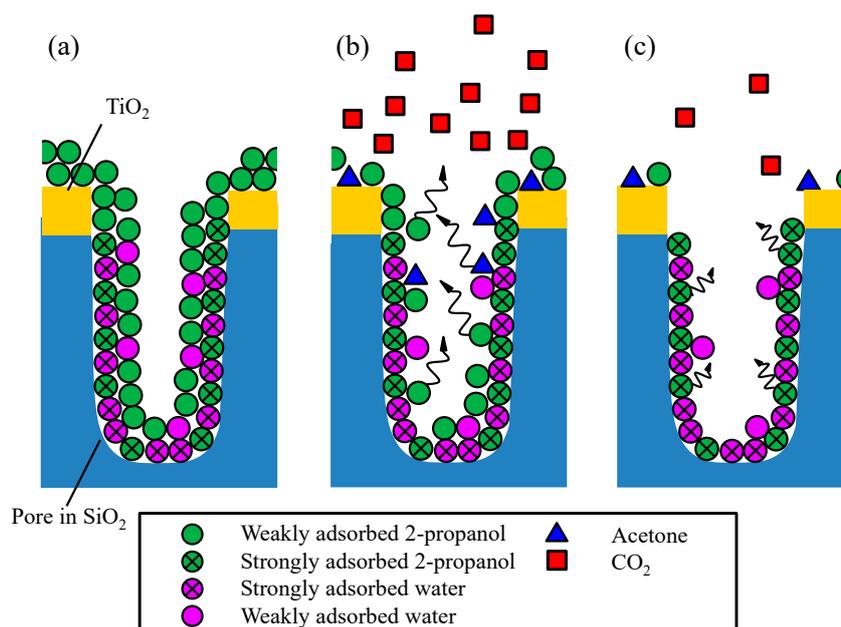


Figure 9. Schematics of (a) adsorption, (b) early-phase photocatalytic oxidation, and (c) late-phase photocatalytic oxidation on the TiO₂-coated porous glass cloth.

Based on this decomposition model, we compared the results of photocatalytic decomposition at 15 °C and 35 °C under a 2-propanol atmosphere with a low (2 mg/L) water content (Figures 7c and 8b). During the early phase of decomposition, the CO₂ generation rate was observed to be only slightly higher at 35 °C than that at 15 °C; however, during the later phase of decomposition, the CO₂ decomposition rates of the two conditions were observed to be clearly different. More specifically, the CO₂ generation rates after 2–6 h of UV light irradiation were 18 and 54 ppm/h at 15 °C and 35 °C,

respectively. The higher CO₂ generation rate observed at 35 °C can be explained by the accelerated diffusion of 2-propanol from inside the porous glass fibers to the TiO₂ surface by a higher temperature.

The effect of water content was further evaluated from the photocatalytic decomposition results at 35 °C in 2-propanol atmospheres with low (2 mg/L) and high (18 mg/L) water contents (Figure 8b,c). After 30 min of light illumination, the CO₂ concentrations in the dry and moist atmospheres were observed to be identical; however, the CO₂ generation rate changed at CO₂ concentrations of 440 and 560 ppm in dry and moist atmospheres, respectively. This result indicates that the CO₂ generation rate changed at a later stage of the decomposition process in the moist condition. This difference may be obtained from the condition of 2-propanol adsorption in porous glass fibers. As shown in the decomposition model (Figure 9), the weakly and strongly adsorbed 2-propanol molecules coexisted in the pores. In the moist condition, the abundant water molecules are expected to occupy a large portion of the strong adsorption sites on the bare SiO₂ surface, thereby decreasing the ratio of the amount of strongly adsorbed 2-propanol to that of the weakly adsorbed 2-propanol. Because the weakly adsorbed 2-propanol molecules are easily desorbed from the SiO₂ walls, a sufficient supply of 2-propanol can continue the generation of CO₂ at a constant rate for a certain time. In contrast, in the dry condition, the proportion of strongly adsorbed 2-propanol should be relatively high. Once the weakly adsorbed 2-propanol molecules have been consumed in the early phase, the CO₂ generation rate will gradually decrease.

We further discuss the reason why the CO₂ generation rates were identical during the earliest phase of 2-propanol decomposition. In the surface-reaction limited situation, the rate of mass transportation is generally greater than the rate of surface reaction; therefore, the decomposition rate is considered to be independent of the reactant concentration. In the mass-transportation limited situation, the rate of surface reaction is greater than the rate of mass transportation, and the decomposition rate is related to the reactant concentration near the reaction site [7]. In our experiments, the concentration of weakly adsorbed 2-propanol in the porous glass fiber was expected to be dependent on the water content; however, the initial CO₂ generation rate remained constant. This indicated that the photocatalytic decomposition was limited by the surface reaction on TiO₂ in this phase.

Finally, the effect of water on the radical reaction at the photo-illuminated TiO₂ surface is discussed. In the photocatalytic reaction on TiO₂, the adsorbed water molecules react with the photogenerated carriers at the TiO₂ surface and change to hydroxyl radicals [43]. These hydroxyl radicals further diffuse and decompose the organic compounds near the TiO₂ surface; therefore, a certain amount of water vapor can enhance the photocatalytic decomposition rate of organic compounds such as 2-propanol [29,44,45]. Further, excess water vapor prevents the adsorption of organic molecules on the TiO₂ surface, thereby decreasing the photocatalytic decomposition rate [29,32,44]. However, as noted above, the initial CO₂ generation rates estimated from the CO₂ concentration after 30 min of UV irradiation were observed to remain the same under both dry and moist conditions. It indicated that the CO₂ generation rates under both conditions were very similar because the amount of water in the gaseous phase was not significantly different under both conditions. The majority of the water in the present reactor was expected to be adsorbed on the large Sg of the porous glass fiber cloth. Large water adsorption will decrease the water concentration in the gaseous phase, which can be used to plausibly explain the similar CO₂ generation rates at high and low water contents in the earliest phase of 2-propanol decomposition.

In the later phase of the decomposition, the CO₂ generation rates were estimated in the UV light irradiation time ranging from 2 to 6 h. The rates were 54 and 46 ppm/h under low and high water content conditions, respectively. Within this range, the water content did not largely influence the CO₂ generation rates because the rates were limited by the diffusion of the strongly adsorbed 2-propanol molecules.

3. Materials and Methods

3.1. Materials

The glass fiber cloth was provided by Arisawa Manufacturing Co. Ltd. (Joetsu, Japan). Figure 10 is a photomicrograph of the glass fiber cloth. It has a plain weave structure, and approximately 400 E-glass fibers of 9.1- μm diameters form the warp and weft thread; further, the thread density, the number of warp and the weft thread per certain area of woven fabric was 44×32 in $25 \times 25 \text{ mm}^2$. The thickness of the cloth was 180 μm , and the weight per unit area was 203.5 g/m^2 . The TiO_2 (anatase) nanoparticles were dispersed in 2-propanol (TKD-701, 17.0 wt %, $d = 6 \text{ nm}$, TAYCA Co., Osaka, Japan). Further, reagent-grade aqueous hydrochloric acid (HCl; 5 mol/L), ethanol (99.5 wt %), 2-propanol (99.7 wt %), and sodium carbonate (99.5 wt %) were supplied by Wako Pure Chemical Industries Ltd. (Osaka, Japan) and were used without any purification.

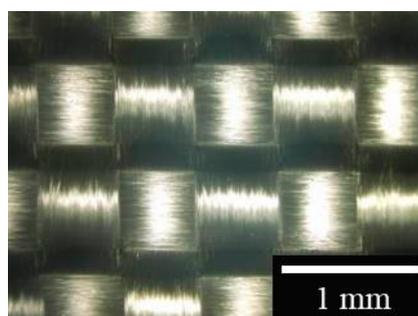


Figure 10. Photograph of the magnified surface of the E-glass cloth.

3.2. Preparation of the TiO_2 -Coated Porous Glass Cloth

The organic compounds on the fibers of two pieces of glass cloth (ca. $(30 \times 35) \text{ mm}^2 \times 2$, total weight 0.19 g) were eliminated by heating at 500 $^\circ\text{C}$ for 1 h. The heat-treated cloth samples were immersed in 13.3 ml of 2.5 mol/L HCl aqueous solution at 40 $^\circ\text{C}$ for 0.5, 1, 3, 4, 6, or 12 h in a screw-capped perfluoroalkoxy alkane (PFA) container without stirring. After leaching by HCl, the samples were washed several times in distilled water and were further immersed in 80 ml of distilled water for 10 min. This immersion process was repeated, replacing the water between each immersion, until the pH of the immersing water reached ca. 7 (in this case, after two washes). The samples were washed with ethanol and immersed in sufficient ethanol to perform solvent exchange in the sample pores. After 10 min in ethanol, the samples were dried at 120 $^\circ\text{C}$ for 10 min to form the porous glass cloth. A reference sample with a non-porous structure was prepared by heating the glass fiber cloth at 500 $^\circ\text{C}$ for 1 h without subsequent acid leaching. This sample was used as the non-porous glass cloth.

TiO_2 was coated on both the porous and non-porous glass cloths using the conventional dip-coating method. The TiO_2 coating solution was prepared by diluting the TiO_2 suspension to 1 wt % in 2-propanol. The glass cloth samples were dipped in the diluted TiO_2 suspension and were further pulled up at 1.0 mm/s. The dip-coated samples were subsequently dried at room temperature and at 120 $^\circ\text{C}$ for 10 min; further, they were finally heated at 300 $^\circ\text{C}$ for 2 h. The obtained samples were referred to as the TiO_2 -coated porous and non-porous glass cloths. On the other hand, as a reference in XRD measurement, the TiO_2 powder sample was also prepared from the TiO_2 suspension by drying at 120 $^\circ\text{C}$ and subsequently heating at 300 $^\circ\text{C}$ for 2 h.

3.3. Characterization

The surface morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-2400 and S-5200, Hitachi High-Technologies, Tokyo, Japan). Before the FE-SEM observation, the samples were platinum-coated using a sputtering method. The XRD patterns were collected using $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$, monochromatized by Ni filter) by

an X-ray diffractometer (MiniFlex 600, Rigaku Co., Tokyo, Japan) that was operated at 40 kV and 15 mA. The chemical compositions of the samples were analyzed using an X-ray fluorescence (XRF) spectrometer (ZSX Primus μ , Rigaku Co., Tokyo, Japan). For the XRF measurements, glass disks were prepared from the TiO₂-coated and uncoated samples as follows. First, 150 mg of the sample was ground with a pestle in an alumina mortar and was formed into a pellet by uniaxial pressing. For acid leaching (by varying the leaching time from 2 to 12 h), the porous samples were mixed with 25 mg of Na₂CO₃ as the flux. The pressed pellets were sintered by a 3-step heating process (700 °C for 2 h, 800 °C for 2 h, and 900 °C for 4 h), yielding the glass disks that were required to perform XRF analysis. Further, the porous properties of the samples were determined from the N₂ gas adsorption isotherms measured at 77 K (BELLSOAP mini II, BEL Japan Inc., Osaka, Japan). Prior to performing the N₂ gas adsorption measurements, all the samples were dried in vacuo at 120 °C for 2 h. Their specific surface areas were calculated using the Brunauer–Emmet–Teller (BET) multi-plot method. To analyze their pore-size distributions, the samples were dried in vacuo at 140 °C for 10 h, and the N₂ gas adsorption was measured at a very low pressure range (from 10⁻³ Pa, BELSORP-max-N-VP-CM, BEL Japan Inc., Osaka, Japan). The pore-size distribution was estimated by Saito–Foley fitting using the zeolite Y standard.

The adsorption and photocatalytic decomposition properties of 2-propanol were examined using the TiO₂-coated porous glass cloth and the TiO₂-coated non-porous glass cloth as reference. The samples were cut into divisions of 0.042 ± 0.001 g for performing the experiments. The cut samples were pre-treated by UV–vis light irradiation under a black light (BL) lamp (FL15BLB, Toshiba Lighting & Technology Co., Yokosuka, Japan, peak wavelength: 365 nm, light intensity at 365 nm: 3.5 mW/cm² at the sample surface) for 24 h and were subsequently heated at 120 °C in vacuo to eliminate the adsorbed organic molecules and water. Further, the concentrations of 2-propanol and water vapor were adjusted using the apparatus depicted in Figure 11. The air-diluted 2-propanol vapor that was produced by a calibration gas generator (Permeator PD-1B, GASTECH Co., Ayase, Japan) was mixed with the humid air, that was produced through two steps of water bubbling. The resulting mixed gas contained 300 ppm of 2-propanol and 2 or 18 mg/L of water. The 2-propanol concentration in the mixed gas was confirmed by a gas chromatograph (GC-8A, Shimadzu Co., Kyoto, Japan) using a thermal conductivity detector (TCD), a porous polymer beads column (Sunpak-A, 2 m, 160 °C, Shinwa Chemical Industries Ltd., Kyoto, Japan), and He carrier gas (20 mL/min). The water contents in the mixed gas were also confirmed in the gas detector tube (No.6, GASTEC Co., Ayase, Japan). The mixed gas flowed into a gas-tight bag containing two glass vial reactors (diameter: 4 cm; height: 6 cm, volume: approximately 65 mL). After 50 min of gas flow, the pre-treated cloth sample was transferred into one of the vials, and both the vial reactors were immediately sealed with a gas-tight septum. The sealed vials containing the sample, as well as the mixed gas or mixed gas only were transferred to an incubator (maintained at 15 °C or 35 °C) and left for 1 h in the dark. During this time, 2-propanol was adsorbed without conducting a photocatalytic reaction. The glass vials were illuminated by UV–vis light under a BL lamp (with 1.0 mW/cm² of light intensity at the sample position with no shielding of the glass vial) for 6 h in the incubator. The concentrations of 2-propanol, acetone, and CO₂ in the glass vial were determined at 10- and 30-min intervals during the 2-propanol adsorption and photocatalytic decomposition, respectively, by gas chromatography.

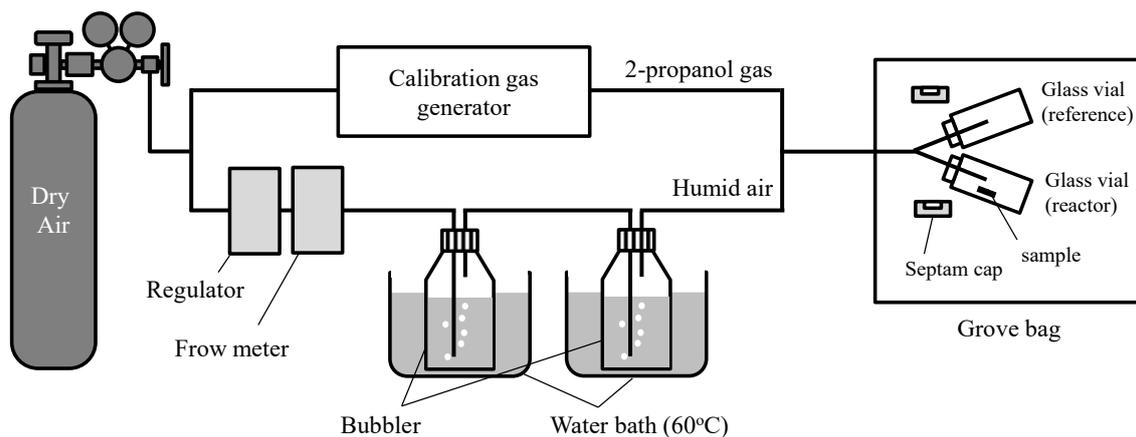


Figure 11. Apparatus settings for controlling the water content in gaseous 2-propanol.

4. Conclusions

A composite material of TiO_2 and porous glass cloth was prepared by acid leaching of an E-glass cloth and subsequent dip-coating of a TiO_2 photocatalyst. Working inward from the fiber surface, acid leaching resulted in the formation of a porous shell structure during an early stage. The fibers were observed to become completely porous after 3 h of leaching; however, the specific surface area of the acid-leached E-glass cloth continued to increase for another hour. Consequently, the specific surface area was maximized after 4 h of leaching. The compositional change was observed in the acid-leached E-glass by performing XRF analysis; Al_2O_3 and B_2O_3 were eliminated along with the ions of alkaline metals and alkali earth metals, leaving mainly the SiO_2 structure. During the photo-catalytic decomposition of 2-propanol, the TiO_2 -coated porous glass cloth exhibited considerable adsorption ability with respect to 2-propanol and generated CO_2 at a higher rate than that of the TiO_2 -coated non-porous glass cloth. The TiO_2 -coated porous glass cloth also adsorbed acetone until the decomposition to CO_2 was completed. Increasing the temperature from 15 to 35 °C clearly increased the CO_2 generation rate of the TiO_2 -coated porous glass cloth because the diffusion rate of the reactant molecules was accelerated. Further, increasing the moisture content from 2 to 18 mg/L at 35 °C slightly decreased the amount of adsorbed 2-propanol and delayed the change in the rate-controlling step from surface reaction to mass transportation. This indicated that the competitive adsorption of water and 2-propanol in the porous glass fiber decreased the amount of strongly adsorbed 2-propanol in the moist atmosphere. Finally, the porous glass cloth that was prepared from a commercial E-glass cloth provided a sufficiently strong TiO_2 support with a high specific surface area. The TiO_2 -coated porous glass cloth can adsorb and photo-catalytically degrade VOCs such as 2-propanol and acetone. Therefore, it is considered to be a strong candidate for ensuring the practical elimination of gaseous organic pollutants.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/1/82/s1>. Figure S1: (a) Surface and (b) fracture cross section of the TiO_2 coating on the porous glass cloth, Figure S2: (a) N_2 adsorption isotherms of the non-coated and TiO_2 -coated porous glass cloths and (b) pore-size distributions estimated by Saito–Foley fitting using the adsorption potential for N_2 on zeolite Y. V_a : adsorbed volume, d_p : pore diameter, V_p : pore volume.

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