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Innovative and stable TiO₂ supported catalytic surfaces removing aldehydes under UV-light irradiation.

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Abstract

The present study reports the photocatalytic degradation of aldehydes using TiO₂ impregnated polyester (PES) and glass fiber (GFT)-TiO₂ addressing the photocatalytic degradation aldehydes (air-solid interface). The PES-TiO₂ optical absorption was determined by diffuse reflectance spectroscopy (DRS). By X-ray diffraction (XRD), the formation of TiO₂ anatase on the PES surface was detected. The photocatalytic oxidation (PCO) of butyraldehyde and isovaleraldehyde was carried out in a batch photo-reactor equipped with a UV-mercury Philips 9W lamp and mediated by glass fiber GFT-TiO₂ and PES-TiO₂ surfaces. The removal of these two aldehydes was found to be a function of pollutant concentrations. The stable catalytic reuse of both catalysts reported. A Langmuir Hinshelwood (L-H) model describes the degradation kinetics on PES-TiO₂ and on GFT-TiO₂. The aldehyde degradation by-products were analyzed by gas chromatography mass spectrometry (GC-MS). Three organics intermediates identified during the aldehyde degradation were: acetones, alcohols and fatty acids.

Keywords:

TiO₂-PES; batch photo-reactor; kinetics; intermediate by-products, GC-MS, L-H isotherms, degradation kinetics

Introduction:

VOCs have been found to be hazardous to the human health and introduce collateral environmental damage. VOCs are discharged into the atmosphere by households and industry, and found in the exhaust gases from animal quartering, and residential cleaning agents. Damaging health effects have been reported on the eyes, nose and throat. They also lead to headaches, loss of coordination and nausea, damages to the liver, kidney and the central nervous system [1]. Moreover, they can induce cancer in animals; and can cause cancer in humans [2]. The technologies developed until now to remove VOCs have not been entirely successful and do not meet the regulatory levels becoming more demanding during the last decade. Recently studies report the aldehyde removal by adsorption [3], biological treatment [4] and advanced oxidation processes (AOP's).

Photocatalytic TiO₂ materials have been widely used during the last four decades due to their low cost, photo-activity and stability [5]. TiO₂ is widely used in catalytic processes occurring at the air-solid interface at room temperature and atmospheric pressure [6–8]. TiO₂ (titania) stands out as one of the most active photocatalyst [9] under UV-radiation. The electrons in the valence band of TiO₂ under light move to the conduction band generating electron (e⁻)-hole (h⁺) pairs. These electrons in contact with air are able to reduce the O₂ forming superoxide ions. Moreover, the holes oxidize water adsorbed on the TiO₂-surface generating hydroxyl radical (HO°) [10-11]. The later radical species oxidize organic compounds to produce CO₂ [12,13-15]. TiO₂ has been also used in chemical synthesis [16,17] and energy conversion [18].

Many research groups studied the photocatalytic oxidation for indoor and outdoor cleaning under UV and/or solar light. The reaction rate of a photocatalytic reaction depends on the catalyst, the applied light intensity, the concentration of reactants (in our case gaseous effluents), the flow rate and the type of reactor used (batch or continuous) [9,12].

This paper presents the optimization for the TiO₂ impregnation on two supports: polyester (from now PES) and Glass Fiber Tissue (from now GFT). It reports some properties of these surfaces [19] along the Langmuir Hinshelwood (L-H) isotherm followed during the photocatalytic degradation of the two aldehydes. The first

evidence for the degradation kinetics for gas-phase PCO of aldehydes is presented on PES-TiO₂ and GFT-TiO₂. Butyraldehyde and isovaleraldehyde were chosen as probes due to their abundant presence in exhaust gases from animal process/quartering [20].

2. Experimental Section

2.1. Chemical reagents

Chemicals were Sigma–Aldrich (USA). The isovaleraldehyde ($\geq 98\%$) and butyraldehyde ($\geq 99\%$) were p.a. reagents and used as received. Both aldehydes belong to the priority group of VOCs pollutants: aromatics (one, two or three rings) alkanes, ketones, alcohol, and chloro-carbons by the French Environment and Energy Management Agency (ADEME).

2.2. Apparatus and Analysis:

The batch reactor used was approximately 400 mm high and was able to contain a volume of 1.5 L. The catalytic samples used presented a surface of 330 cm² and were attached to the inner wall of the cylindrical reactor. The fluorescent UV-lamp in the photo-reactor was Philips PL-S 9W/10/4P. The outside wall of the reactor was covered with Al-foil during the irradiation experiments to prevent the lamp UV-emission to reach the outside of the reactor. A magnetic stirrer and a magnetic barrel allowed the homogenization of the gas phase.

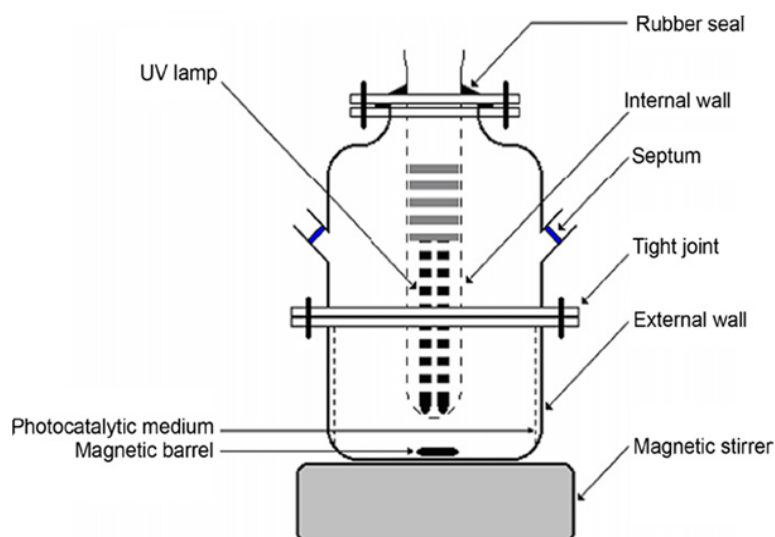


Figure 1. Schematic of the batch photo-reactor with the central co-axial mercury 9W mercury UV-light source

During the course of this study aldehyde samples were injected into the reactor. A magnetic stirrer and some glass spheres were used to homogenize of the inlet gas phase. When the equilibrium was reached, the UV lamp was turned on. Samples were taken regularly from the reactor for analysis.

The main reaction intermediates present in gas phase were analyzed to suggest at later stages during this study a reaction mechanism. Carbotrap compositions were used to concentrate the pollutants: Carbopack Y, is used for the selective retention of the C₁₂ to C₂₀ compounds. By way of Carbopack B C₅ to C₁₂, compounds were trapped while the lighter compounds C₂ to C₅ were adsorbed with Carboxen 1003. The initially concentrated aldehydes on different Carbotrap (Supelco) were then pumped by a Gillian LFS-113 pump under a flow rate of 50 mL/min. Subsequently, a Turbomatrix Perkin Elmer unit was used to thermally desorb these concentrated compounds. Then the gases were analyzed through a transfer line to the GC/MS Perkin Elmer Clarus 500 equipped with a Quadrupole mass spectrometer detector. The GC/MS column consisted of a capillary column FFAP-CB Chrompack 25 m long, 0.15 mm in diameter and a stationary phase's thickness of 0.25 µm. The temperature in the oven, the injection chamber and the detector were 100, 120 and 200 °C respectively.

2.3. Catalyst

2.3.1. Glass Fiber Tissue (GFT)

The glass-fiber(GFT) was provided by Ahlstrom Research/Services [12]. This material contained colloidal silica, a variable percentage of titanium dioxide, manganese dioxide nanoparticles and inorganic fibers as shown in Figure 2a. TiO₂ was deposited on the inorganic fibers by impregnation using an industrial-size press as shown in Figure 2b. A mixture of 50-wt% colloidal silica and different wt% of TiO₂ nanoparticles (PC500 Millennium) and manganese dioxide is suspended in pure water. In order to ensure the deposition of 13 g/m² of dry TiO₂ on the GFT support. The suspension was composed of 40% of dry powder and 60% of pure water. The PC500 TiO₂ nanoparticles consisted of anatase 5-10 nm in diameter with and TiO₂ SSA nanoparticles of 300 m²/g as shown in Figure 2a.

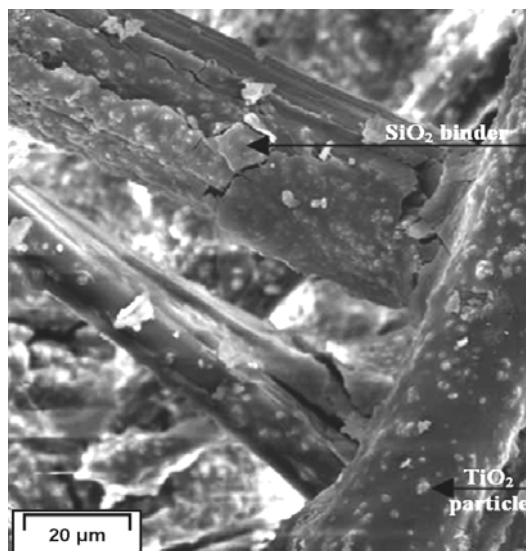


Figure 2a. Scanning electron micrographs (SEM) of the glass fibers (GFT).

An industrial type press was employed to impregnate fibers with the TiO₂ suspension, followed by the drying cstep arried out by Ahlstrom Research and Services.

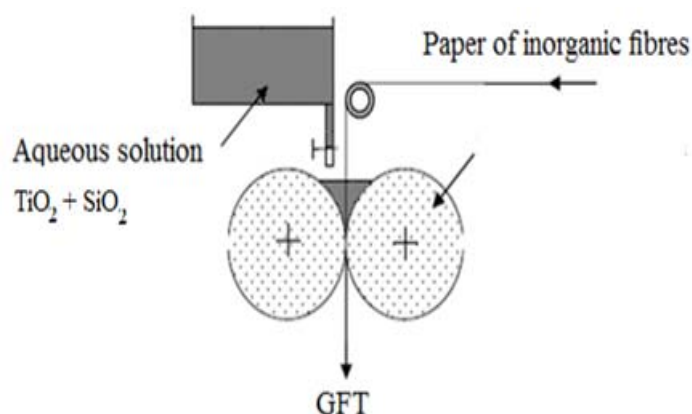


Figure 2b. Diagram of the impregnation technique for GFT synthesis "size press"

2.3.2. TiO₂ impregnated PES: TiO₂ loading, spectral absorption and isoelectric point.

PES-TiO₂ samples were prepared hydrothermal (HT) preparation treatment method. During the HT-preparation, the TiO₂ colloidal suspension was prepared dissolving titanium tetra-isopropoxide (TTIP, Sigma Aldrich) in isopropanol in a 1:3 volume ratio. Then, the solution was transferred into a beaker with 50 ml of 0.1M HNO₃. This way of preparation lead to a substantial TiO₂ aggregation. To study the effect of these aggregations on the photocatalytic activity, some samples were ultrasonicated for 10 min prior to the PES impregnation; these samples will be called US-TiO₂-PES along the manuscript. The polyester samples 10x10 cm was immersed into the acid TiO₂ precursor suspension and heated under stirring in a reflux condenser

for 2 hours at 80°C. The PES fabric was removed from the suspension, rinsed with demineralized water and treated in ultrasound bath for 2 min to remove the unbounded TiO₂ particles. The last operation was repeated three times and the TiO₂-polyester fabric dried for 2 hours in air at 70°C.

The low surface energy of polyester led to poor TiO₂ nanoparticles adhesion. In order to fix a higher amount of TiO₂ on PES, the PES was pretreated by UVC-light to induce a higher density of functional polar groups able to bind TiO₂ nanoparticles [21]. UVC pretreatment enhances the polarity, roughness and hydrophilicity of polyester improving its bondability and interfacial adhesion. The UVC pre-treatment induced negatively charged functional groups, e.g., carboxylic, percarboxylic, epoxide and peroxide groups due to the atomic and excited-O*. The polyester negative sites bind the slightly positive deposited Ti⁴⁺/(TiO₂) by electrostatic attraction involving chelation/complexation [23]. The TiO₂ was deposited immediately after the UVC-pretreatment due to the short lifetimes of the polar radical species.

To determine the TiO₂ isoelectric point (IEP), a Colloidal Dynamics Acousto Sizer II (Sydney, Australia) instrument was used. The zeta potential is calculated from the widely used Smoluchowski equation [23, 24] for thin double layers ($ka > 20$). The electro-acoustic determines the dynamic mobility, of the suspensions in 150 ml KNO₃ (0.01M). The pH adjusted with HNO₃ to around 3 and then titrated up to pH 10 or 11 by addition of KOH (0.01 M) 25°C. The colloid was dispersed under vigorous agitation and ultrasonic treatment for 5 minutes (150 watts, 20 kHz).

The Ti-content of the TiO₂-PES samples was determined in an Orbis PC Micro EDXRF analyzer equipped with a Rh micro-focus X-ray tube (50 kV and 1 mA) and X-ray multiple optic turret with 30 µm poly-capillary X-Ray optics/collimator.

Diffuse reflectance spectroscopy (DRS) was carried out in a Varian Analytical Instruments Cary 5 UV-VIS-IR spectrophotometer (controlled by the Cary Win UV software) within the wavelength range of 300-800 nm and a resolution of one nm. The spectral absorption of the samples was plotted in the Kubelka-Munk (KM) units vs. wavelength.

2.4. Pollutants degradation conditions

Degradation of isovaleraldehyde and butyraldehyde in the photocatalytic reactor was evaluated for several influent pollutant concentrations (Table 1).

Table 1. Experimental Conditions used during the degradation of aldehydes in the batch photo-reactor.

| Parameter | Value & domain |
|---|------------------------------|
| Gas Temperature | Ambient (293 K) |
| Gas Pressure | Atmospheric pressure (1 atm) |
| Volume of reactor | 1 L |
| Isovaleraldehyde Inlet Concentration [Isoval] | 1 to 22 g/m ³ |
| Butyraldehyde Inlet Concentration [Buty] | 1 to 20 g/m ³ |
| Relative humidity | 40-50 % |
| Intensity of UV lamp | 30 W/m ² |

3. Results and discussion

3.1. TiO₂ loading, IEP and spectral absorption

By X-ray fluorescence (XRF), HT PES-TiO₂ samples were found to have a 0.61 wt%TiO₂ / wt PES loading and the US PES-TiO₂ samples presented a TiO₂ loading of 0.39 wt%TiO₂ / wt PES. The quantity of TiO₂ was not very high as to affect the PES flexibility and/or other mechanical properties.

Figure 3 shows the spectral absorption of TiO₂-impregnated polyester prepared by both preparation methods HT or US.

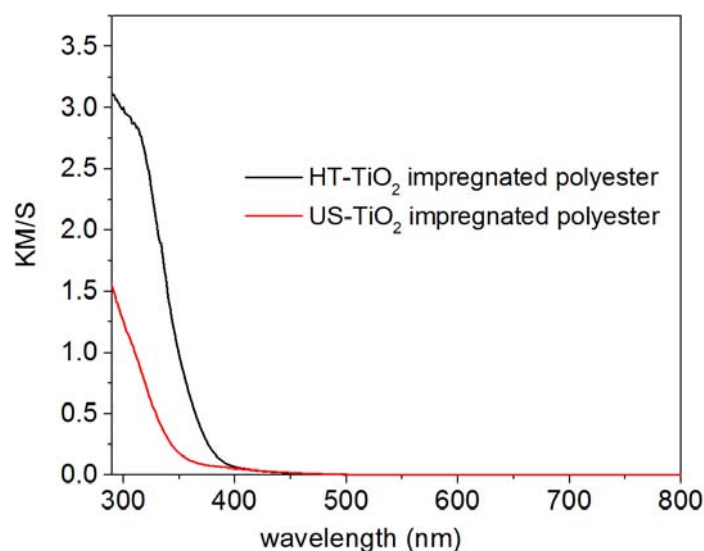


Figure 3. Diffuse reflection spectroscopy (DRS) absorption of PES-TiO₂.

The diffuse reflectance spectra (DRS) in Figure 3 show a higher optical absorption for the samples prepared by the HT-method compared to the samples prepared by the US-method. The higher TiO₂ loading on the HT-samples explains these DRS results as determined by (XFR) and can be explained by the different

aggregation of the TiO₂ clusters on the polyester surface. This leads to light reflectance in all directions increasing the signal registered in the optical integration sphere.

The rough UV-Vis reflectance data cannot be used directly when accounting for the absorption coefficient of the TiO₂-impregnated polyester due to the large scattering contribution. Normally, a weak dependence is assumed for the scattering coefficient *S* on the light diffusion.

In agreement with the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability, nanoparticle aggregation sets in at pH close to the TiO₂ IEP 6-7 used during the preparation of the TiO₂ colloidal suspensions due to the attractive Van der Waals forces. The TiO₂ single particles present sizes between 40-60 nm. The hydrodynamic diameter of the aggregates was found to be 170-240 nm and is approximately equivalent to 3-6 primary TiO₂ particles [19], aggregates involve a higher mass of TiO₂ but a lower surface *per* particle active intervening in the photocatalytic process.

3.2. Pollutant degradation

To separate the effects of photocatalysis and adsorption, the VOC with a concentration of several g/m³ were mixed with air and stirred for 30 min in the dark to reach adsorption-desorption equilibrium at time zero. Subsequently, the mixture was irradiated under UV-light for 180 min to test the photo-activity of PES-TiO₂. After the experimental conditions became stable, the PCO reaction was initiated and the VOC injected. Under steady-state conditions samples were taken to evaluate the degradation rate and the generation of by-products

Figure 4a and b show the variation of isovaleraldehyde) and butyraldehyde concentrations versus time at different inlet concentrations. The degradation rate first increased with the inlet concentration, due to the availability of the photocatalytic sites at a low concentration range [9, 11].

The concentrations of both aldehydes shown in Figures 4a/4b decreased with increasing irradiation time, going from 10 to 3 g/m³ and from 9 to 0.8 g/m³ within 15 min irradiation, at inlet concentration values of 10 and 9 g/m³ respectively. These rates were similar to the values reported for some VOCs [11-14]. We suggest that the degradation mechanism of the aldehydes on supported-TiO₂ involve TiO₂ electrons in the conduction band (cb) reacting with adsorbed O₂ on the TiO₂ yielding HO₂[°]

radical-anions and other highly oxidative protonated radicals leading to the oxidation of the aldehydes [10, 21-23].

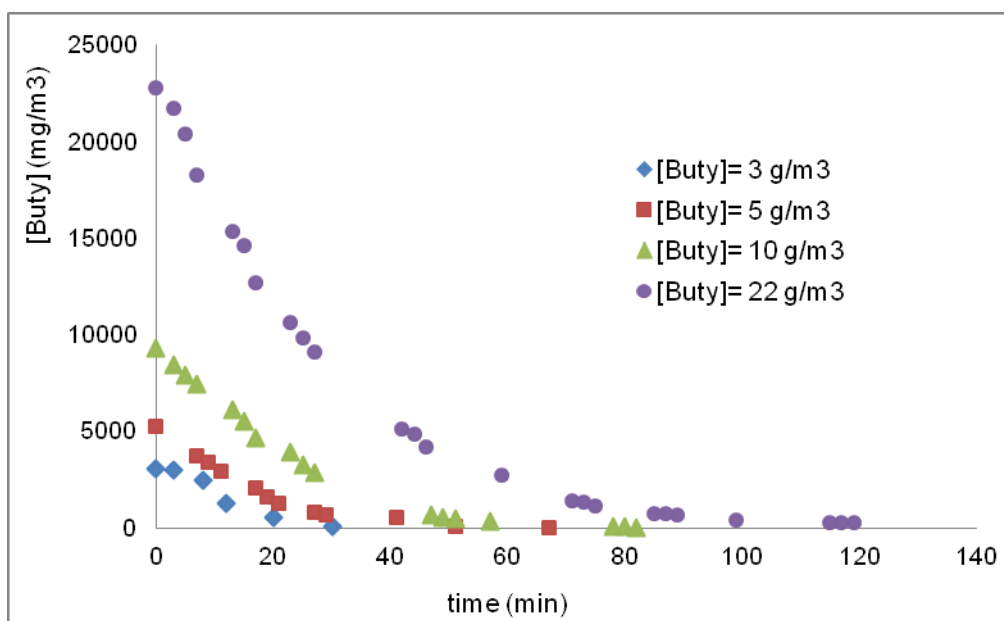


Figure 4a. Butyraldehyde degradation on PES-TiO₂ as a function of the initial aldehyde concentration) under a Philips UV 9W mercury lamp irradiation ($I=30W/m^2$).

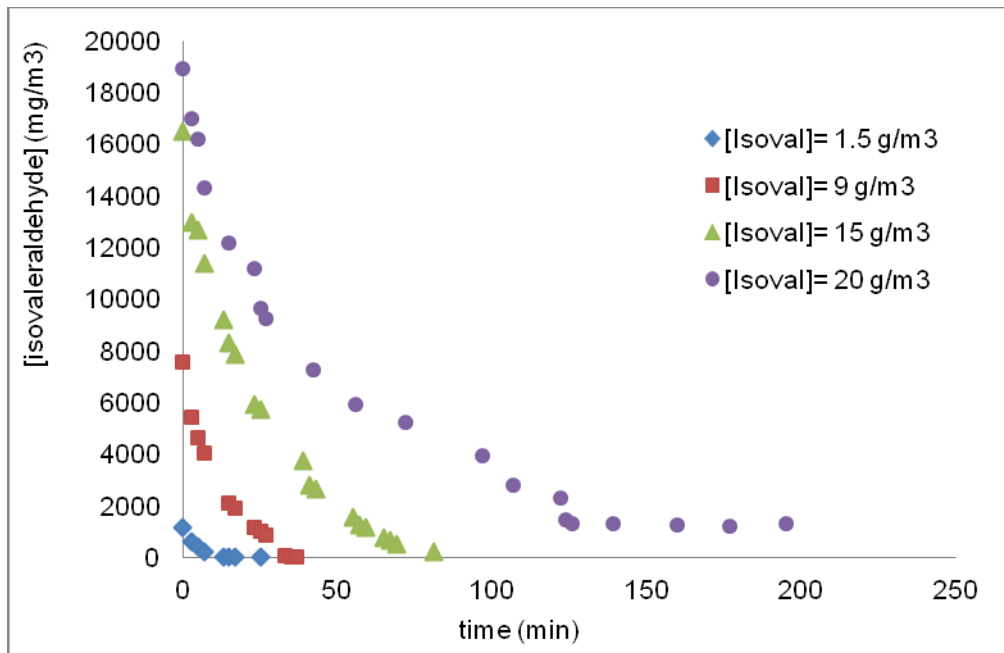


Figure 4b. Isovaleraldehyde degradation on PES-TiO₂ as a function of the initial aldehyde concentration under a Philips UV 9W mercury lamp ($I=30W/m^2$) irradiation.

3.3. Comparison with other photocatalyst (GFT)

The PES-TiO₂ and the (GFT)-TiO₂ samples presented a similar TiO₂ loading as determined by XRF of 0.61 wt%/wt-PES and 0.57 wt%/wt-GFT. PES and GFT did not led to aldehyde degradation in the dark or under light irradiation. Butyraldehyde, removal on GFT was about twice faster compared to PES, it reaches 90% removal in 30 minutes on GFT-TiO₂ as seen in Figure 5a. On PES-TiO₂ about 90% of butyraldehyde was removed within 60 min. The TiO₂ accessibility to lower depths in the GFT glass-wool containing TiO₂ dispersed nanoparticles offer a higher number of active sites *per* nanoparticle in the glass wool compared to the PES support. [14].

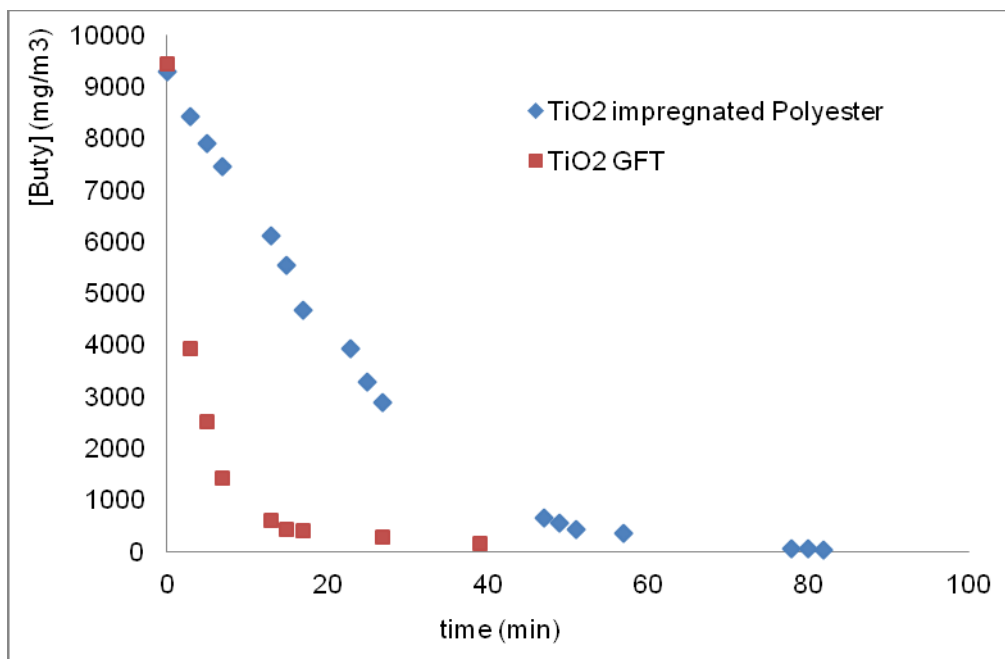


Figure 5a. Butyraldehyde photodegradation kinetics on GFT-TiO₂ and PES-TiO₂ samples under a Philips UV 9 W mercury lamp irradiation ($I=30W/m^2$).

To understand the kinetic and the adsorption process of butyraldehyde degradation on the two catalysts under investigation, the Langmuir-Hinshelwood (L-H) model was used according to the equation:

$$r_0 = -\frac{d[VOC]}{dt} = k_c \frac{K[VOC]_0}{1 + K[VOC]_0}$$

Where r_0 (mmol/g_{cat}xm³xs) is the initial photocatalytic degradation rate, [VOC] is the initial butyraldehyde concentration (mmol/m³), K is the adsorption constant (m³/mmol) and k_c is the kinetic constant (mmol.m⁻³xsxgTiO₂) at maximum coverage for the experimental conditions used could be expressed as:

$$k_c = k_0 \times I^\delta$$

where I is the light intensity (W/m^2), k_0 is a rate constant independent of the light intensity and δ is the order of I ($0 < \delta < 1$).

The linearized L-H equation reads:

$$\frac{1}{r_0} = \frac{1}{k_c K} \times \frac{1}{[\text{VOC}]_0} + \frac{1}{k_c}$$

The plot of $1/r_0$ versus $1/[\text{VOC}]_0$ allows to determine k_c and K values by the plot presented in Figure 5b.

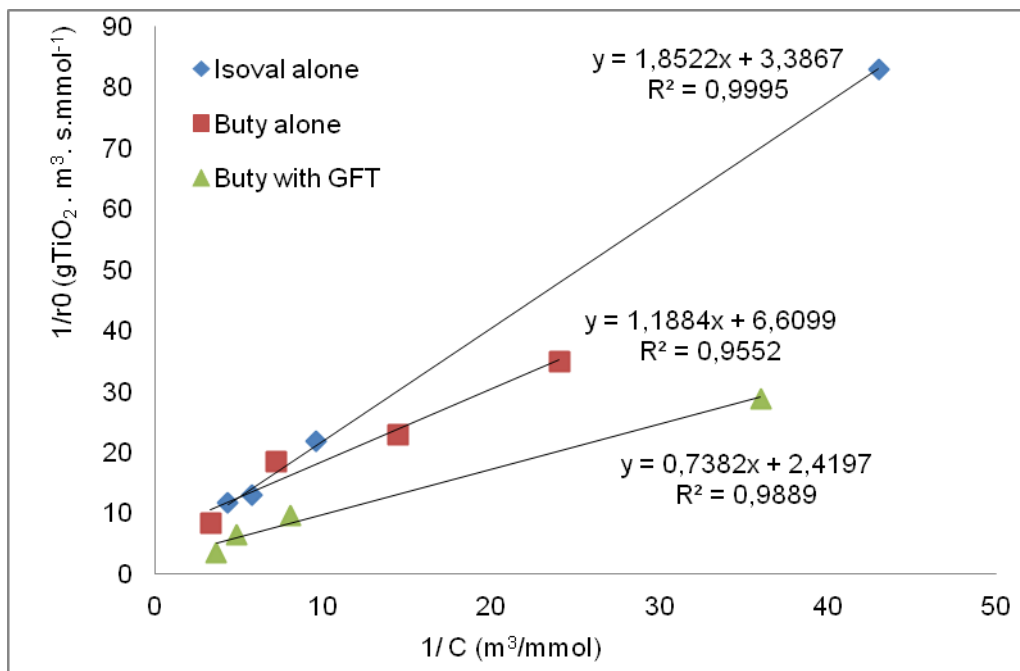


Figure 5b. Linear regression using L-H model for the butyraldehyde degradation and isovaleraldehyde alone and in the presence of GFT-TiO₂

According to the values reported in Figure 5b, the values of the L-H constants (k_c and K) are shown in the Table 2.

Table 2. L-H constants (k_c and K) at different catalysts tested

| Catalyst tested | Target pollutant | k_c : Kinetic constant of L-H ($\text{mmol} \cdot \text{m}^{-3} \cdot \text{s} \cdot \text{g}_{\text{TiO}_2}$) | K : Adsorption Constant of L-H ($\text{m}^3 \cdot \text{mmol}^{-1}$) |
|----------------------|------------------|--|--|
| PES-TiO ₂ | Isovaleraldehyde | 0.2953 | 1.8285 |
| | Butyraldehyde | 0.1513 | 5.5545 |
| GFT-TiO ₂ | Butyraldehyde | 0.4134 | 3.2769 |

Table 2 shows that GFT-TiO₂ leads to a faster butyraldehyde degradation compared with the PES-TiO₂. Anatase crystals are formed at around 300°C and rutile at around 600°C when heating TiO₂ colloids in the absence of a structure-forming surface like polyester [19,28]. These temperatures are significantly higher compared to temperatures of around 80°C used in the preparation of TiO₂-polyester surfaces (see section 2.3.2). This can lead to different crystallographic structures influencing the photocatalytic activity as recently reported [10,19]. These support materials present: a) a different catalytic site accessibility for the aldehyde and b) a distinct light exposure of the TiO₂ sites to the incoming UV-light [14].

3.4. By-products Identification

The by-products detected during the photocatalytic degradation of butyraldehyde on PES-TiO₂ were determined by GC-MS. The degradation by-products detected were: methanol (2) acetone (3), ethyl acetate (4), acetic acid (5) and propionic acid (6). Butyraldehyde (1) was also present after 30 minutes. These results are similar to those reported by Assadi et al. [25, 26], reporting acetic, propionic, and butyric acids. Assadi et al., used GFT-TiO₂ for the isovaleraldehyde photodegradation and detected propionic acid, acetone, acetic acid and CO₂ as the degradation products.

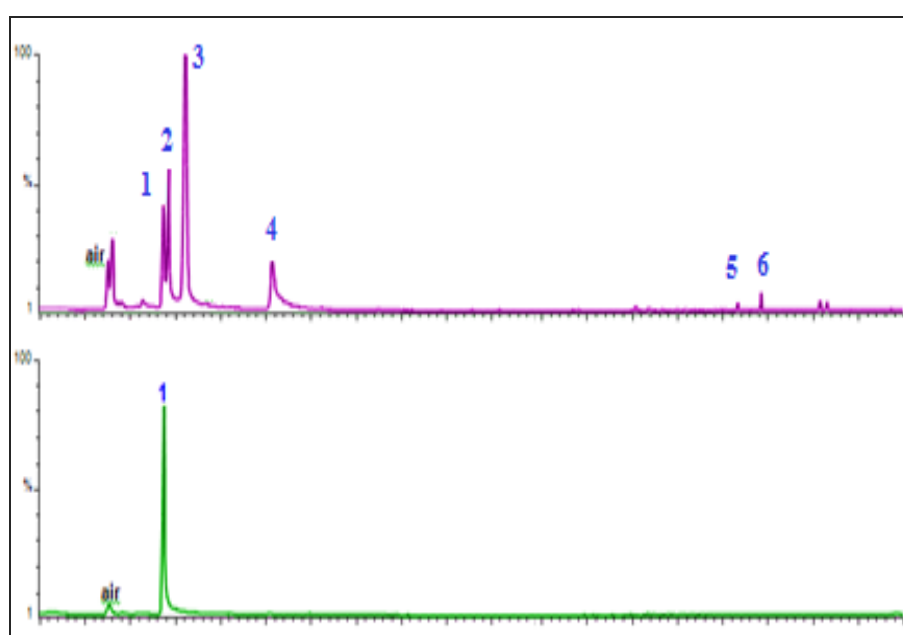


Figure 6. By-products observed during butyraldehyde degradation by GC-MS on PES-TiO₂

4. Catalyst recyclability

The reusability of the used catalyst is an important factor to investigate since it is a measure for its practical application potential degrading pollutants in the gas phase [27-28]. The repetitive use of the GFT-TiO₂ photocatalyst up to the 5th cycle leading to butyraldehyde degradation is shown below in Figure 7. No loss of activity was detected by the photocatalyst during its repetitive recycling as shown in Figure 7. The catalyst was thoroughly washed after each photodegradation cycle and reused. The results reported in Figure 7 show the potential of the GFT-TiO₂ samples for application in air treatment.

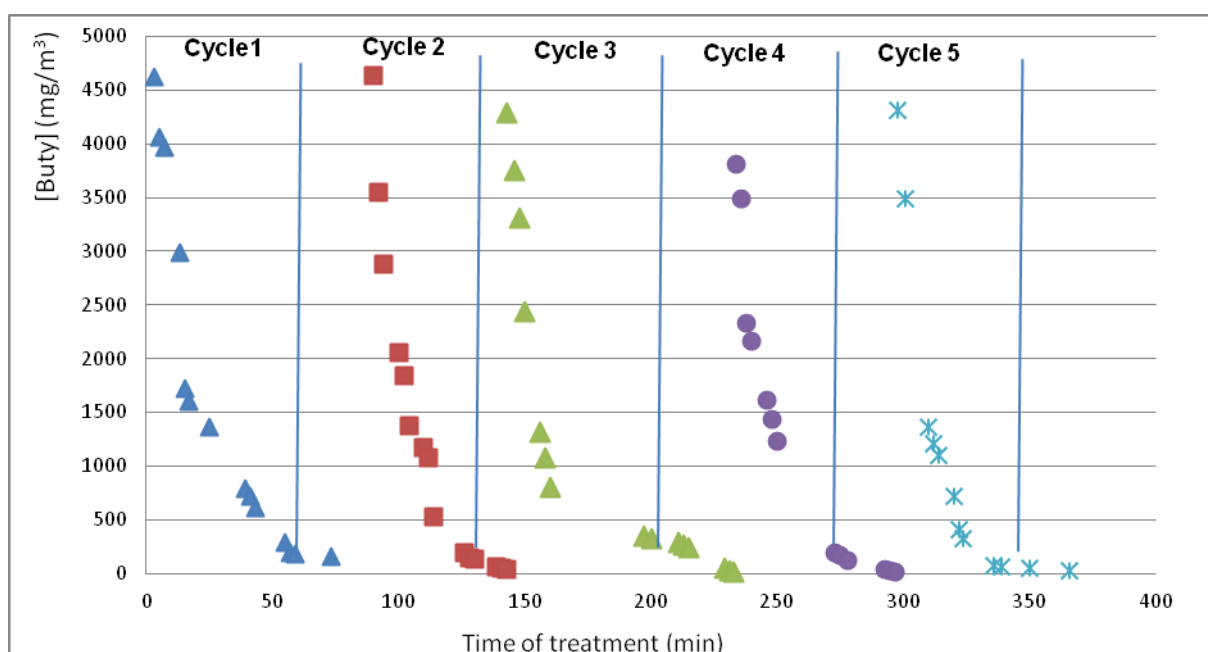


Figure 7. Repetitive degradation of butyraldehyde on a GFT-TiO₂ sample under 9W Philips mercury light. Further experimental conditions: $I=30\text{W/m}^2$, butyraldehyde concentration = 5g/m^3 .

5. Conclusion

Butyraldehyde and isovaleraldehyde degradation mediated by PES-TiO₂ and GFT-TiO₂ under mercury UV-light have been reported in this study. The by-products during the photocatalytic degradation of butyraldehyde on PES-TiO₂ were identified by GC-MS. The GFT-TiO₂ presented a larger photo-activity compared to PES-TiO₂ and this comparison was quantified by the k_c values found during in the L-H treatment of the experimental data. A stable degradation performance of the

aldehydes by the GFT-TiO₂ samples was observed during repetitive recycling under UV-light irradiation. This catalyst presents an application potential for application in air treatment.

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