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Modified-TiO_2 Photocatalyst Supported on β-SiC Foams for the Elimination of Gaseous Diethyl Sulfide as an Analog for Chemical Warfare Agent: Towards the Development of a Photoreactor Prototype

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Abstract: In the context of the increase in chemical threat due to warfare agents, the development of efficient methods for destruction of Chemical Warfare Agents (CWAs) are of first importance both for civilian and military purposes. Amongst possible methods for destruction of CWAs, photocatalytic oxidation is an alternative one. The present paper reports on the preparation of Ta and Sn doped TiO_2 photocatalysts immobilized on β-SiC foams for the elimination of diethyl sulfide (DES) used as a model molecule mimicking Yperite (Mustard Gas) in gaseous phase. Photo-oxidation efficiency of doped TiO_2 catalyst has been compared with TiO_2-P25. Here, we demonstrate that the Sn doped-TiO_2 with a Polyethylene glycol (PEG)/TiO_2 ratio of 7 exhibits the best initial activity (up to 90%) but is deactivates more quickly than Ta doped-TiO_2 (40% after 800 min). The activity of the catalysts is strongly influenced by the adsorption properties of the support, as β-SiC foams adsorb DES and other sulfur compounds. This adsorption makes it possible to limit the poisoning of the catalysts and to maintain an acceptable conversion rate even after ten hours under continuous DES flow. Washing with NaOH completely regenerates the catalyst after a firs treatment and even seems to "wash" it by removing impurities initially present on the foams.

Keywords: Chemical Warfare Agents; β-SiC foams; photocatalysis; doped TiO_2; diethyl sulfide

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1. Introduction

Due to the increased threat of chemical weapons and recent worldwide events, there is a renewed interest and need for neutralization and degradation of Chemical Warfare Agents (CWAs). Degradation of CWAs may also be an alternative to the destruction of stockpiles. Most of the methods for elimination of CWAs are focused on liquid or soluble decontamination procedures [1,2], and only few of them concern heterogeneous decontamination on solids [3–5]. Generally, elimination of CWAs can be non-catalytic (hydrolysis, combustion, biodegradation . . .) or catalytic (oxidation, enzymatic hydrolysis, methanolysis . . .) [6,7]. Amongst possible methods for destruction of CWAs, photocatalytic oxidation is an alternative one [8,9]. One of the main advantages of photocatalysis compared to combustion or thermal oxidation catalysis is to operate at room temperature and thus it allows to be applied in remote places or indoor environments where no heating facilities are available. Yperite (bis-2-chloroethyl sulfide) is a harmful vesicant agent. Due to the high toxicity of the agent, it is absolutely necessary to conduct studies using analogs and to use the most appropriate compounds to simulate the specific physico-chemical properties of interest [10]. Amongst numerous analogs, chloroethylethylsulfide (CEES) [11,12], and diethyl sulfide (DES) [13] are the most used in photocatalytic elimination of CWAs. TiO_2 is often considered as being one of the best candidates for using a photocatalyst for oxidation applications under UV-A light. However total mineralization of sulfur- or organo-sulfur compounds leading to the formation of sulfates deposited onto the surface generally ended to TiO_2 deactivation. To overcome this important limitation, strategies of increasing TiO_2 surface area by Ta or Sn-doping have been investigated and resulted in strongly hindering TiO_2 poisoning by sulfate species [9,14]. Furthermore, the treatment of large gas flows with low-pressure drops requires to overcome—or at least minimize—inherent drawbacks resulting from the use of a supported photocatalyst and including: a low exposed surface-to-volume ratio, possible mass transfer limitations, an increase in pressure drop, the complexity involved in the provision of light to the photocatalyst and to the reactor core and the possible loss of catalytic material due to poor adherence between the photocatalyst and its support. That means that the immobilization of the powdery photocatalyst onto a suitable support is necessary. This aspect remains highly challenging and requires the use of photocatalytic media providing a secure environment for both photocatalyst handling and recycling. Consequently, the deployment of cellular monolithic supports allows for a simplified usage of reactors, when compared to non-structured packed-bed configurations (easy loading; working and offloading operations possible without any dismantling of the system or fine formation, while at the same time maintaining a suitable exposed surface per volume unit and a good level of photocatalyst and reactant contact without drastic pressure drop). The interest in SiC foams as alveolar tridimensional medium and photocatalyst support [15] has increased in the last years, mainly due to their adaptable and flexible geometry allowing both good performance in light transmission and in fluid flow, thus promoting optimized contact between the photocatalytic coating and the polluted water [16,17], or air flow [18].

The present paper reports on the preparation of Ta and Sn doped TiO_2 photocatalysts immobilized on β-SiC foams for the elimination of Diethyl sulfide (DES) in gaseous phase. Photo-oxidation efficiency of doped TiO_2 catalyst has been compared with TiO_2-P25. The evolution of by-product concentrations during the photo-oxidation tests of DES under UV-A irradiation has been studied by GC-MS. Finally, we have tried to regenerate and to reuse the supported catalysts for a possible industrial use.

2. Results and Discussion

2.1. Optimization and Characterization of the Supported Photocatalytic Materials

2.1.1. Sn/Ta-Doped TiO_2 and PEG-Modified Catalysts

Optimization and characterization of Sn-doped TiO_2/PEG and Ta-doped TiO_2/PEG samples has been developed previously [9,14]. Therefore, they will not be detailed here. In the same manner Sn and Ta contents of doped TiO_2 samples have also been optimized in previous works and will not be presented here [9,14]. Thus, in the present study the two best sample photocatalysts (1% Sn and 8% Ta) have been chosen in order to be deposited onto SiC foams. To remind, the addition of PEG as a porogen with a TiO_2/PEG mass ratio of 1/7 has contributed to increase the specific surface and also to promote the anatase-rutile transition at low calcination temperature, which considerable increased Diethyl sulfide elimination under UV-A and solar irradiation [14].

2.1.2. β-SiC Foams Pre-Treatment to Optimize the Immobilization of TiO_2-Based Catalysts

In order to improve the quantity of catalyst immobilized by impregnation, an acidic chemical treatment has been made on the SiC foams. Because silica surfaces expose –OH groups thus allowing the attachment of TiO_2 by hydrogen bonds, or even by covalent bond by dehydration. As β-SiC and silica are materials resisting to acidic pH, the acid treatment aims to create/increase –OH or $–OH_2^+$ groups on the surface of the silica, without damaging the β-SiC structure (unlike heat treatment). In order to obtain many hydroxyl groups, a strong acid must be used. Nitric acid (HNO_3) was chosen to avoid the risk of contamination of the foam with anions like Cl^- (with HCl), SO_4^{2-} (with H_2SO_4), because the adsorption of HNO_3 on SiO_2 is reversible at room temperature [19]. In total, two concentrations were tested: 0.1 and 0.5 mol/L, and two times of immersion in the acid solution: 1 h and one night (approximately 17 h). A test was carried out by adding ammonia in the TiO_2 suspension to study the influence of the surface charge of TiO_2 nanoparticles, knowing that isoelectric point of TiO_2 P25 is close to 8.

Further experiments were carried out using TiO_2-P25 suspension with the automated system for 70 successive impregnation steps. As one can see in Table 1, the addition of NH_4OH does not improve the adhesion, and the $[H^+]$ concentration does not seem to have any influence on the adhesion of TiO_2. On the other hand, after one night of the foam immersion in the HCl solution, TiO_2 covers the SiC better than after only 1 h. The kinetics of the acid treatment could be slow, therefore a 0.1 mol/L concentration is chosen with an overnight treatment duration. The three tests were carried out under these conditions with pierced foams to assess the reproducibility of the impregnations. In terms of appearance, the three foams are well covered with TiO_2 in a homogeneous manner, as shown in Figure 1. The mass of TiO_2 added is reproducible. The samples contain approximatively 9% wt.% of TiO_2. However, this value is an estimated one because there some losses of SiC could occur during the impregnation process.

Table 1. Results of the different impregnations with TiO_2-P25 following the different chemical treatments of β-SiC foams.

Foam Samples	$[H^+]$ (mol/L)	Time (h)	NH_4OH (mol/L)	TiO_2 (% in Weight)	Appearance of Foam
Full sample	0.1	1	0	12.5	Partially covered
Full sample	0.1	1	0.1	5.4	Partially covered
Full sample	0.5	1	0	9.3	Some gray areas
Full sample	0.5	17	0	11.7	Well covered
Sample with hole	0.1	17	0	9.3	Well covered
Sample with hole	0.1	17	0	9.5	Well covered

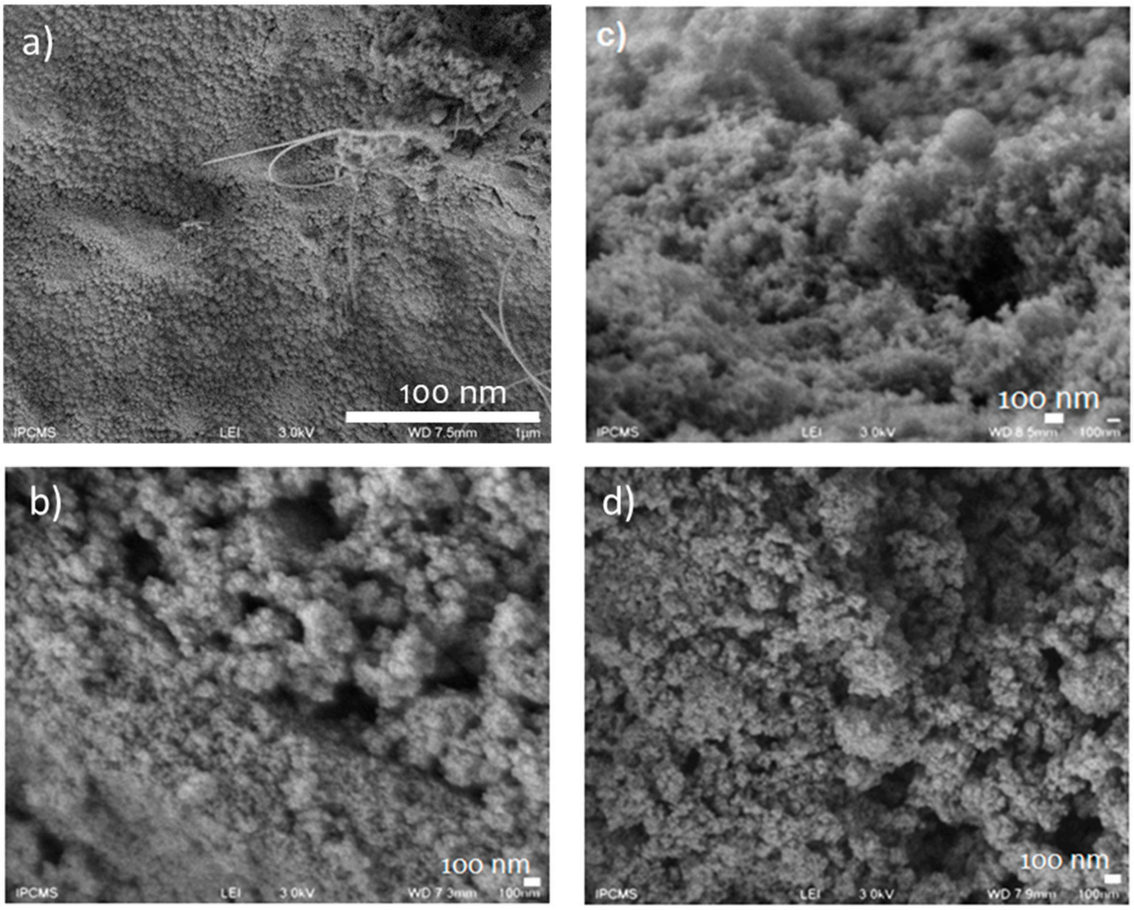


Figure 1. SEM images of β-SiC foams after HNO_3 treatment and calcined at 380 °C: (**a**) without catalyst, (**b**) with TiO_2-P25, (**c**) with 8% Ta-doped TiO_2/PEG and (**d**) with 1% Sn-doped TiO_2/PEG.

2.1.3. Characterizations of the Sn/Ta-Doped TiO_2 Immobilized Photocatalysts

The surface and texture of β-SiC foams were studied by SEM before and after the deposition of Sn/Ta-TiO_2 doped catalysts according to the previously optimized foam pretreatment. According to SEM images [20], the structure of the foams treated with nitric acid is similar to that of untreated foams, meaning that this chemical treatment did not visibly damage the foam morphology. The SEM images of the foams with TiO_2-P25 and Ta or Sn-doped TiO_2 synthesized by the sol-gel route with PEG, showed that for all the samples the catalyst is well distributed over the entire surface in a homogeneous manner (Figure 1). The porosity of the catalyst is preserved, which may allow the diffusion of molecules on the entire surface of the catalyst, or even on the SiO_2/SiC surface. Thus all the deposited catalyst should therefore be accessible by the reactants during the photocatalytic tests.

The specific surface area and the pore volume of the β-SiC foams before and after the deposition of catalysts were determined by N_2 isotherms at 77K. The values of the specific surface, as well as those of the pore volume are noted in Table 2.

Table 2. Values of specific area and pores volume of β-SiC foams with or without catalyst compared to powder catalysts.

Samples	Specific Area (m^2/g)	Pore Volume (cm^3/g)
8% Ta-doped TiO_2/PEG (catalyst)	116	0.43
1% Sn-doped TiO_2/PEG (catalyst)	68	0.48
β-SiC	26	0.09
β-SiC after drilling	26	0.12
β-SiC after drilling + 1% Sn-doped TiO_2/PEG	25	0.20
β-SiC after drilling + 8% Ta-doped TiO_2/PEG	28	0.23

The isotherms are close to type V with hysteresis H3 because the isotherms do not have any knee (point B), which is one of characteristic features in types II and IV, indicating the completion of monolayer coverage [21]. The isotherms of β-SiC foams with TiO_2 have a shape similar to the ones of raw foams (not shown). The specific surface of the raw foams is about 26 m^2/g, it does not change after drilling and after the various treatments. The pore volume increases when the foam is pierced (from 0.09 to 0.12 cm^3/g), which can be explained by the drilling which gives access to part of the internal porosity of the foam on the cut parts.

The specific surface increases very slightly with the addition of TiO_2. Ta and Sn-doped TiO_2/PEG have a larger specific surface area than β-SiC, but the surface of the foam is covered with a thin layer of TiO_2. The pore size distribution (Figure 2) of the two doped photocatalyst is very little modified after deposition on the β-SiC foams surface.

To summarize on the immobilization of TiO_2 and doped-TiO_2 onto a β-SiC support: the immobilization of photocatalysts on β-SiC foams was controlled with approximately 10% wt.% of catalyst added after a pretreatment of the foams with nitric acid and using an automated impregnation set-up. Catalyst weight losses, determined after ultrasound treatment in water, are negligible after calcination at 380 °C. The main steps of the optimized process can be summarized as follows:

- Decarbonation at 700 °C for 3 h (5 °C/min);
- Foam drilling;
- Treatment with HNO_3 (0.1 mol/L), overnight;
- Impregnation with home-made automated set-up (70 cycles);
- Calcination at 380 °C for 3 h (5 °C/min).

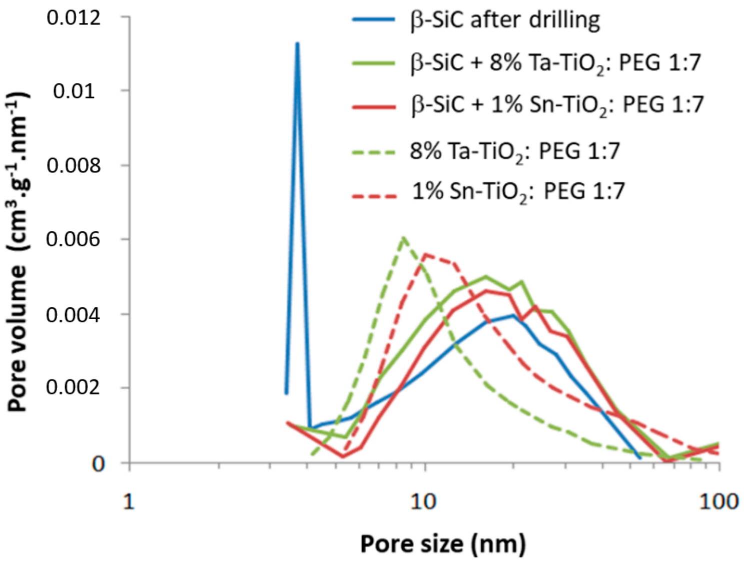


Figure 2. Porous distribution of β-SiC foams with or without catalyst compared to powdery material. The scale of [8% Ta-TiO_2: PEG 1:7] and [1% Sn-TiO_2: PEG 1:7] has been adjusted to be similar to the other curves.

2.2. Evaluation of Photocatalytic Efficiencies of Modified TiO_2 -Supported on β-SiC Foams toward Diethyl Sulfide Elimination

2.2.1. Preliminary Tests and Evaluation Method

Several preliminary tests were necessary to assess the ability of our photoreactor to remove DES by photocatalysis. It is shown that DES is not degraded by photolysis. For this purpose, a first control test was carried out under illumination, without β-SiC foam. No difference in concentration before, during and after illumination is observed.

A second test was carried out by integrating a sample of β-SiC foam (thickness 2 cm) without catalyst (Figure 3). After switching on the lamp, there is a significant increase in the DES concentration which comes back to the equilibrium value into the reactor after 60 min. After switching off the lamp, a decrease in the DES concentration is observed during 80 min before returning to equilibrium. This phenomenon can be explained by a significant adsorption of DES on the β-SiC foam before illumination. When the lamp is switched on, heating of the surface of the support happens leading to the desorption of the adsorbed DES due to the modification of adsorption and desorption equilibrium and therefore increases the concentration of the DES in gas phase, analyzed by GC-MS. When the lamp is turned off, the temperature drops and the initial adsorption and desorption equilibrium state is returned. One can also mention that under UV irradiation the surface chemistry of TiO_2 may also be modified thus impacting the adsorption and desorption equilibrium.

This adsorption and desorption of DES on the β-SiC support disturbs the results of the photo-oxidation tests of DES. Indeed, two phenomena may be superimposed during the 60 first minutes under irradiation, adsorption of DES onto the foam support and its photo-oxidation on TiO_2 (Equations (1) and (2)).

$$C_{desorbed} = C_{out(test\ \beta-SiC)} - C_{in(test\ \beta-SiC)} \tag{1}$$

$$C'_{out} = C_{out} - C_{desorbed} \cdot N \tag{2}$$

The new conversion rate used between 0 and 60 min is, therefore, calculated by:

$$\frac{C_{in} - C'_{out}}{C_{in}} \times 100 \tag{3}$$

This conversion rate (Equation (3)) is approximated because the β-SiC foams are not all identical in shape and in mass, they can therefore adsorb slightly a different amount of DES. This corrected conversion rate is nevertheless used to have a better readability of the results, because it avoids displaying negative conversion rates. In the remainder of the manuscript, the activity of the photocatalysts supported on β-SiC foams will preferably be compared after 60 min of illumination, according to this calculation protocol.

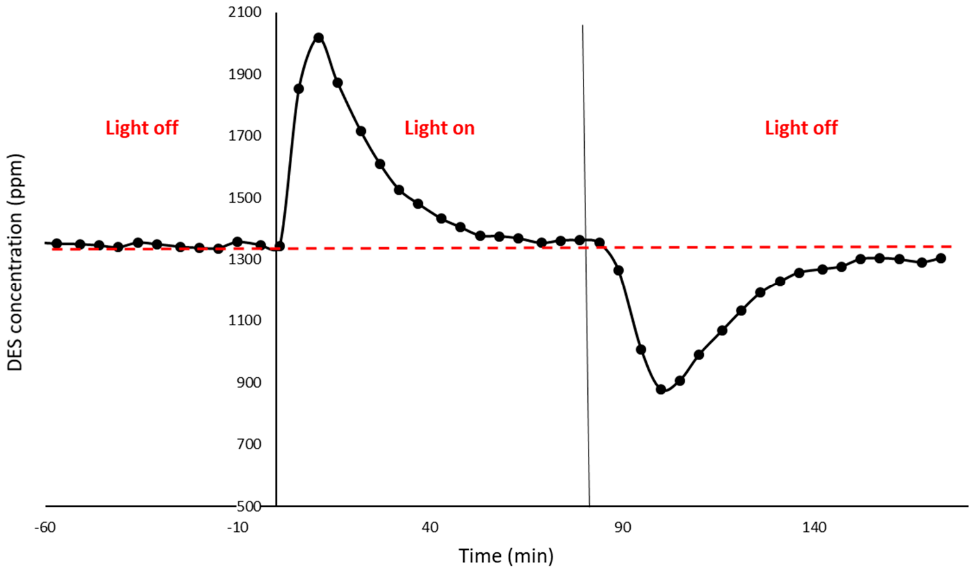


Figure 3. DES photolysis test with β-SiC foam without catalyst under UV-A illumination.

2.2.2. Degradation Tests of the DES with Sn/Ta-Doped TiO_2 and PEG-Modified Catalysts

The evaluation of the photocatalytic performances of the immobilized catalysts on β-SiC foams under UV-A illumination will be presented by the corrected conversion rate for DES as a function of the illumination time (as presented before). Reference tests were first carried out with TiO_2 P25.

2.2.3. DES Photo-Oxidation with TiO_2 P25 Supported on β-SiC FOAMS and Comparison with Powdery TiO_2 P25

Several tests were carried out with TiO_2 P25 immobilized on 1 and 4 samples of β-SiC foam, corresponding to 250 mg and 1 g of catalyst, respectively. In order to verify the reproducibility of the measurements of the macroscopic media, two tests were carried out under the same conditions with TiO_2 P25 immobilized on two different foam samples (containing 1 piece of foam). The conversion rate of DES under UV-A illumination is presented Figure 4.

The results show two distinct phases:

(1) The conversion rate increases until reaching a plateau. The catalyst seems to be activated gradually. Desorption of DES along with activation of the catalyst could explain these results.

(2) A second phase of slow and gradual deactivation of the catalyst.

The results show that the two tests with 1 foam piece are similar and reproducible after 80 min, which corresponds to the equilibrium time of adsorption and desorption of DES on the photocatalytic material. The difference in activity before may be attributed to non-reproducible coverage of TiO_2 from one foam to another. With single foam, the activity is very low for TiO_2 P25 (only 15% of DES conversion after 100 min of illumination under a continuous flow). As shown in Figure 5, the conversion rate with four foams pieces increases longer to reach a maximum of 70%, much better than with a single washer (30%) and for a longer duration. Deactivation is also relatively slow and the conversion rate is more than 50% after 250 min of test, about four times more than with one foam. The foam activity would therefore be cumulative under our test conditions. Therefore, in the continuation of our work, all the photocatalytic tests will be conducted with four SiC foam samples in order to obtain more important activities.

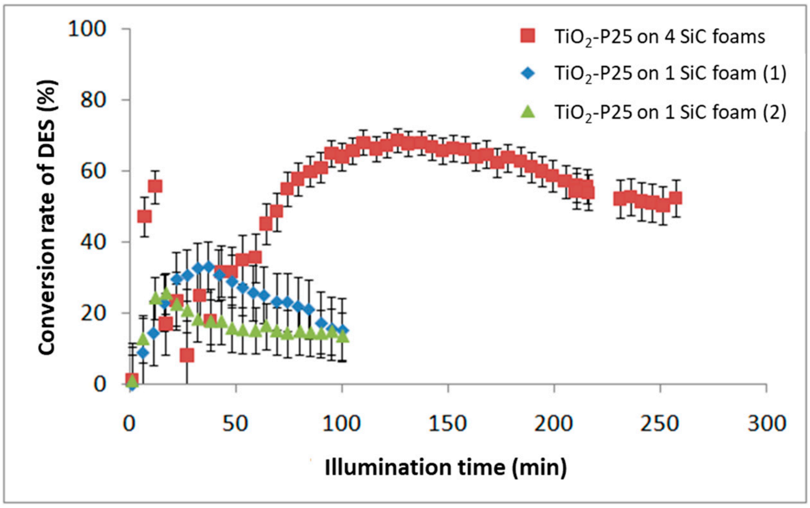


Figure 4. Degradation tests of DES under UV-A irradiation with TiO_2 P25 supported on 1 and four β-SiC foam samples.

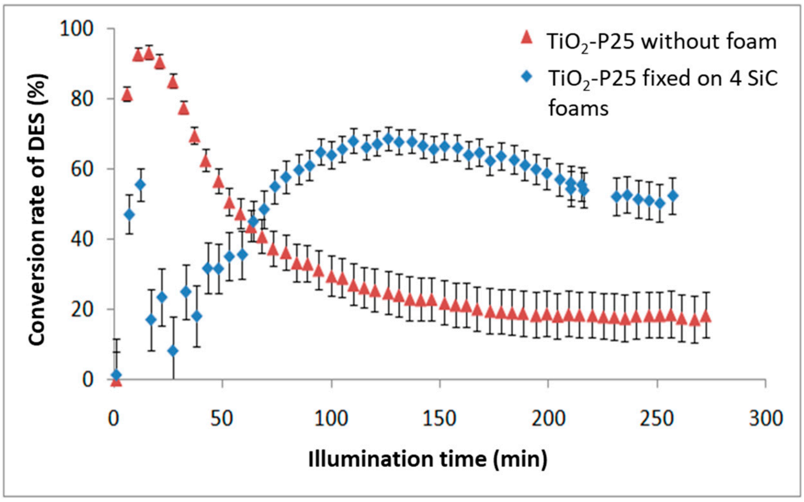


Figure 5. Comparison of DES degradation tests under UV-A illumination with 1 g of TiO_2 P25 supported on β-SiC foams and deposited directly on the walls of the same reactor.

In order to demonstrate the usefulness of a three-dimensional support of the cellular foam type with respect to a 2D surface, 1 g of powdered TiO_2 P25 was deposited on the reactor designed for the tests of supported catalysts (Figure 5), taking care to cover the same length of reactor (i.e., 8 cm) that the bed thickness to be crossed with four pieces of foam. In Figure 6, the photocatalytic activity of TiO_2 P25 deposited directly onto the reactor walls was compared with the one of TiO_2 P25 fixed on the SiC foams (four pieces of foam), considering the same amount of TiO_2. Although immobilization of the catalyst does not lead to an activity as significant as that observed on the powder material (conversion rate of 70% against 100%), the main advantage of the β-SiC support is to delay the deactivation of the catalyst. Indeed, the powdery catalyst deposited onto the walls of the reactor deactivates very quickly after 20 min of illumination to reach a conversion rate of 20% after 200 min (against 50% for the supported catalyst).

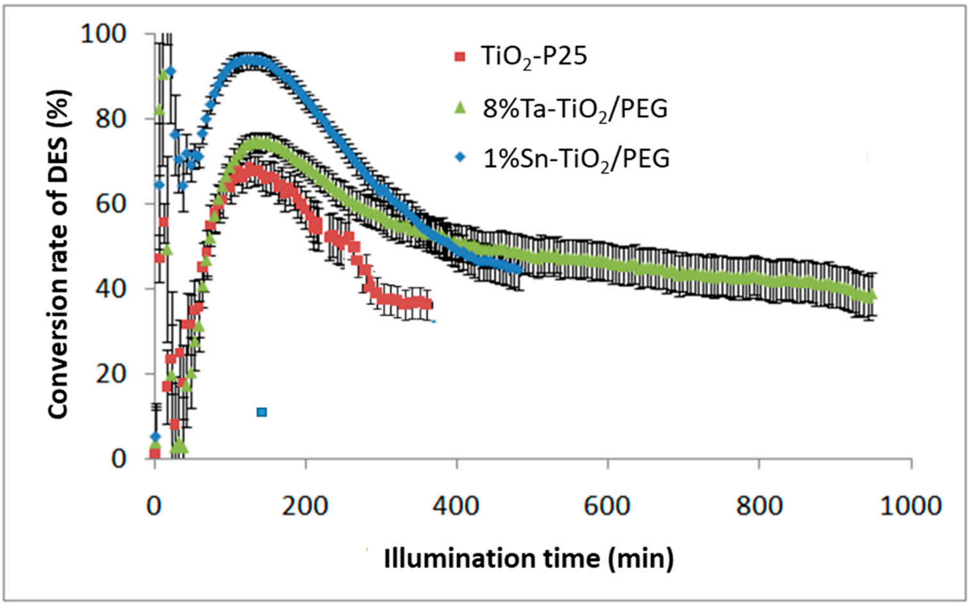


Figure 6. Photo-oxidation of DES under UV-A of TiO_2 P25, 8% Ta-TiO_2/PEG and 1% Sn-TiO_2/PEG supported on four samples of β-SiC foams.

It has already been shown that the alveolar foam of β-SiC makes it possible to mix the flow by dispersing the gaseous compounds throughout the volume of the reactor [18], which increases the contact of the DES molecules with the photocatalytic coating and therefore improves the conversion rate of DES.

2.2.4. DES Photo-Oxidation with 8% Ta-TiO_2/PEG and 1% Sn-TiO_2/PEG Immobilized on β-SiC

In Figure 6 are summarized the activity of the best TiO_2-modified catalysts compared to the activity of TiO_2 P25-deposited foam. As shown in Figure 6, Sn (1 wt.%)-TiO_2 foam exhibits a good initial activity with a conversion rate of 95% at 150 min of illumination. However, it deactivates from 150 min to reach a conversion rate of 40% after 400 min of illumination. Looking at Ta (8 wt.%)-TiO_2 foam activity a lower maximum of conversion rate (75%), comparable to that of TiO_2 P25 [9,14] is observed. However, the deactivation of Ta doped-TiO_2 is very slow since after 15 h of illumination the conversion rate is stable at more than 40%, which corresponds to approximately 440 mg of DES eliminated.

2.2.5. Evolution of Gaseous Products with Time under Irradiation

In a previous work [9,14], we analyzed DES and reaction products *on-line* by Gas Chromatography, coupled to a Mass Spectrometer (GC-MS). The gaseous compounds identified during DES photo-oxidation tests with catalysts supported on β-SiC foams are similar to those identified for unsupported catalysts. The only difference is a very low formation of SO_2 (a few ppm), its concentration as a function of time will therefore not be shown in this part. The studied compounds are CO_2, acetaldehyde (MeCHO) and diethyl disulfide (DEDS). These are the main degradation by-products identified during our previous works [9,14].

As shown in Figure 7, acetaldehyde is the main byproduct at the reactor outlet. Its concentration is proportional to that of DES, it is maximum after 15 min of illumination, and then gradually decreases. The high concentration of acetaldehyde from the beginning of the test proves that the photo-oxidation of DES by TiO_2 occurs as soon as the lamp is switched on. CO_2 and DEDS are present in very small quantities (less than 200 ppm), as we noticed during tests with powder catalysts. CO_2 follows the same evolution as acetaldehyde while the concentration of DEDS increases slightly throughout the test. This behavior is similar for the other DES degradation tests with the other supported catalysts. It will be compared more precisely between the different catalysts.

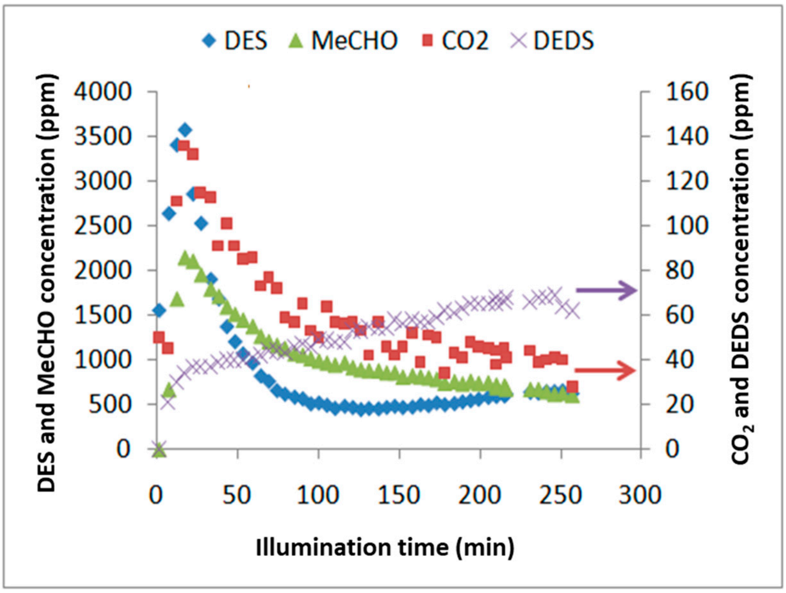
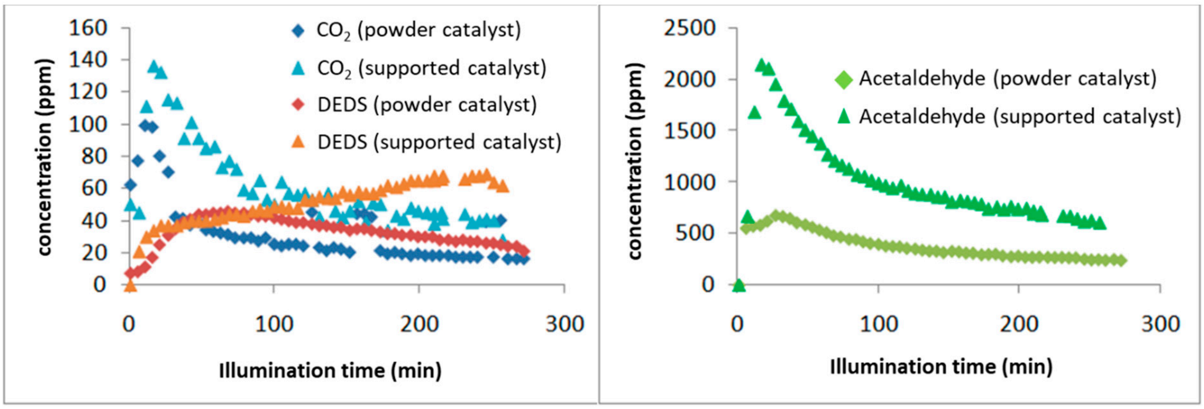


Figure 7. Evolution of the DES, CO_2, MeCHO, and DEDS concentration as a function of the UV-A irradiation time during the degradation of DES by TiO_2 P25 immobilized onto four foams.

2.2.6. Comparison of Powdery TiO_2 P25 and TiO_2 P25 Immobilized on β-SiC Foams

The evolution of by-product concentrations during the photo-oxidation tests of DES under UV-A irradiation for powdery and supported (β-SiC foam) TiO_2 P25 are presented in Figure 8.



(**a**) (**b**)

Figure 8. Evolution of CO_2, DEDS (**a**) and MeCHO (**b**) concentration as a function of the irradiation time during the degradation of DES by powdery and immobilized (on four foams pieces) TiO_2 P25 under UV-A illumination.

For CO_2, the concentration is relatively lower during the test carried out without support, which could be explained by the lower activity observed without foam. After 100 min, the DES concentration increases with the supported TiO_2 and decreases with the powdery catalyst. The β-SiC foams may adsorb the DEDS produced, which would limit the deactivation of the catalyst, and then the DEDS would slowly desorb. The presence of DEDS several hours after the activation of the UV-A lamp seems to support this hypothesis.

In the case of acetaldehyde, the concentration is three times higher at the beginning of the test for the supported catalyst. The adsorption of acetaldehyde on TiO_2 at the β-SiC surface therefore seems very low, the very high initial concentration may result from the oxidation of DES from two different sources, from continuous flow and DES adsorbed on the support. This is also explained by a larger active surface accessible with TiO_2 powder than supported (at equivalent mass). These results prove the high initial activity of the catalyst, masked by the desorption phenomenon of DES.

The carbon and sulfur balances were calculated according to the formula written in previous works (Figure 9) [9,14]. The carbon and sulfur balances are not complete, meaning that products remain adsorbed or deposited onto the surface of the catalyst and of the support, or that some products have not been detected. The overall balance is lower for supported-TiO_2 P25 that may be due to higher adsorption of the products on this immobilized catalyst, probably thanks to the support which also serves as an adsorbent. Note that the sulfur balance increases, which may be due to the progressive saturation of the surface of the support.

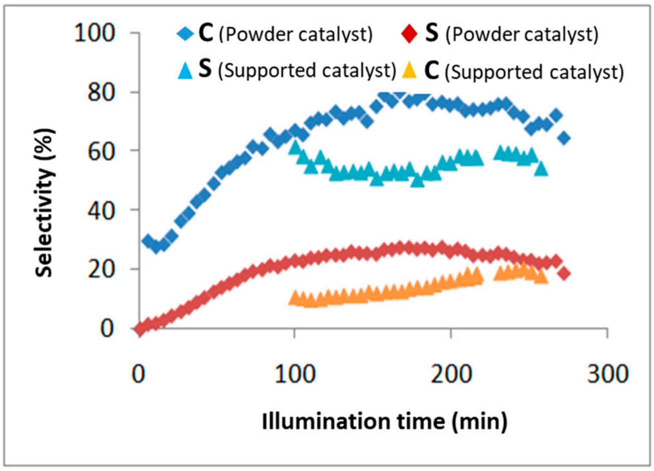


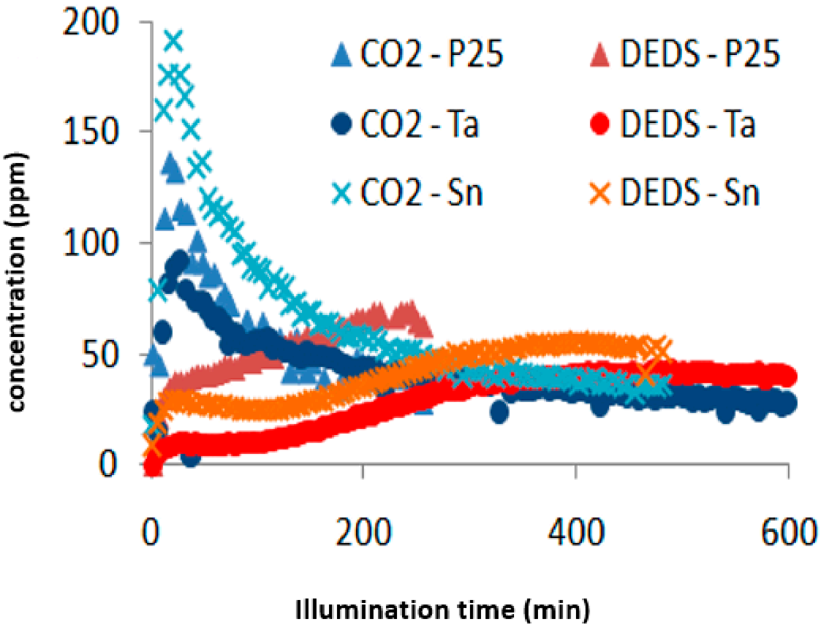
Figure 9. C and S balance for powdery and immobilized TiO_2 P25.

2.2.7. Porogen Effect on the Performance of Ta and Sn-Doped TiO_2 Immobilized on β-SiC Foam

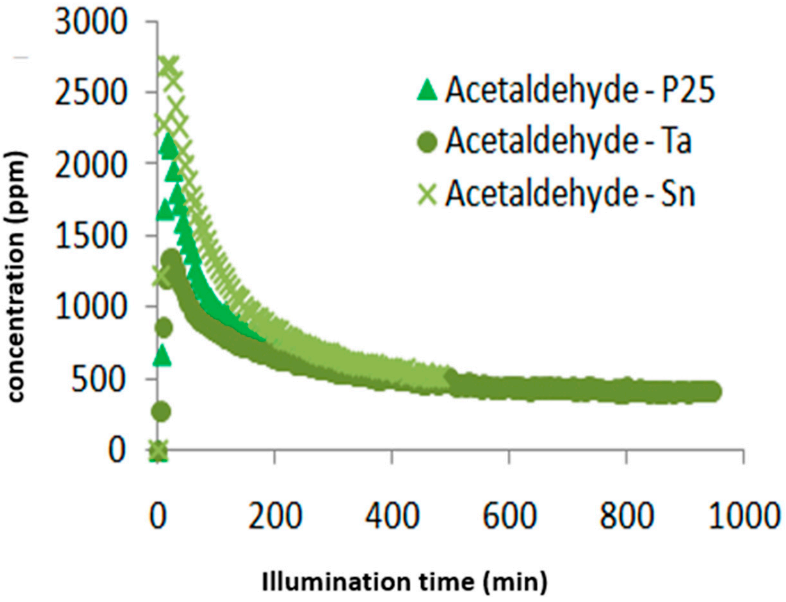
The influence of the porogen on the concentrations of CO_2, DEDS, and acetaldehyde has been followed during the photo-oxidation tests of DES under UV-A illumination in the presence of TiO_2 P25, 8 wt.% Ta-TiO_2/PEG and 1 wt.% Sn-TiO_2/PEG immobilized on 4 foam pieces (Figure 10). For CO_2 and acetaldehyde, the concentration is higher on Sn-doped TiO_2 than on Sn-doped TiO_2. Thus one may suppose better adsorption of carbon products on the Ta-doped catalyst, as we have already observed for powdery materials [14]. On the other hand, TiO_2 P25 seems to adsorb less DEDS than the doped catalysts, which could be explained by the more acidic surface of the doped catalysts or by their higher specific surface. The carbon and sulfur balances are very similar for all photocatalysts.

2.2.8. Regeneration and Reuse of the Supported Catalysts

For an application in a real situation, it is important that the photocatalytic materials have a sufficient long lifetime. Therefore, the aging of our materials and especially the possibility of regenerating them after photocatalytic tests have been studied. The study was performed on the two doped materials: 8% Ta-TiO_2/PEG and 1% Sn-TiO_2/PEG immobilized on β-SiC foam. The regeneration protocol aims at eliminating sulfates and other byproducts poisoning the surface of the catalyst and leading to its deactivation. For that purpose, two protocols were used. For the first, the photocatalytic media are immersed in distilled water for 30 min without stirring and then dried in an oven overnight at 100 °C. For the second regeneration, they are immersed in an NaOH solution at 0.01 mol/L for 30 min without stirring, they are rinsed with distilled water and then dried at 100 °C in an oven overnight. No significant loss of catalyst was observed during the regeneration (measurements by weighing before and after regeneration).



(**a**)



(**b**)

Figure 10. By-products evolution (CO_2 and DEDS in (**a**), acethaldehyde in (**b**)) during photo-oxidation of DES with TiO_2-P25 and Ta/Sn doped TiO_2.

According to Figure 11, after regeneration with water, the 8% Ta-TiO_2/PEG catalyst lost 40% of its initial activity. Washing with pure water therefore does not make it possible to remove all the products present onto the surface of the catalyst. On the other hand, after the regeneration with NaOH, the catalyst reaches for a short duration a better activity than initially which becomes again similar to the initial activity after 300 min of illumination. Washing with NaOH therefore completely regenerates the catalyst and even seems to "wash" it by removing impurities initially present on the foams. The results with 1% Sn-TiO_2/PEG are very similar and are not shown here.

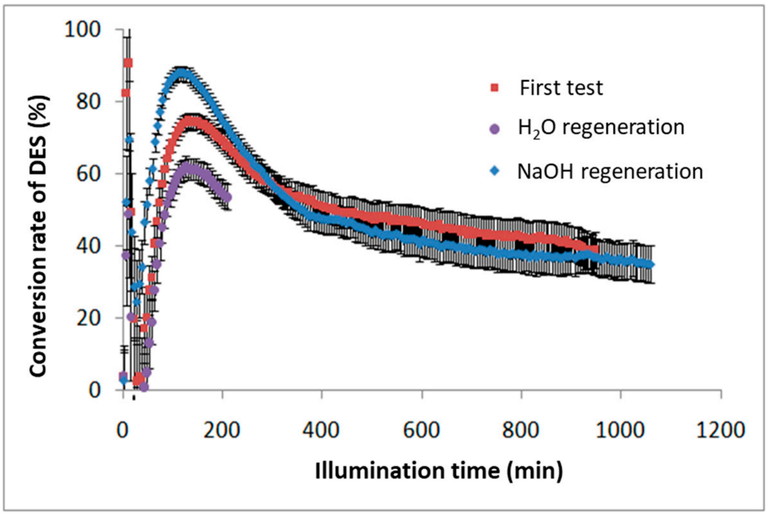


Figure 11. Photo-oxidation of DES with 8% Ta-TiO_2/PEG immobilized on β-SiC foams before and after regeneration with H_2O and NaOH.

The different gaseous compounds identified by GC-MS were followed for the different types of regeneration to understand why regeneration with sodium hydroxide is more effective than that with water. For CO_2 and acetaldehyde, no difference was observed, the concentration is broadly the same and it is proportional to the activity of the catalyst. For DEDS, its concentration is twice higher after regeneration with water than for the other two tests. Presumably DEDS was left on the water regenerated catalyst and it was desorbed when heated by the UV-A lamp, like DES. Water therefore does not seem to be able to remove all of the organosulfur compounds present on the surface of the catalyst. Finally, the sulfur compounds contained in the aqueous NaOH solution resulting from the washing of the Ta-doped TiO_2 were analyzed by GC-MS. With powdery materials, the concentration of compounds present on the surface was too low to be analyzed [9]. With the β-SiC-supported materials this concentration was higher and could be measured by GC-MS. It was obtained by an automatic injection of 2 μL of solution, the column remaining at a temperature of 40 °C for 4 min, followed by a temperature increase to 180 °C with a slope of 25 °C/min and finally by an isotherm of 4 min.

The products observed are DEDS, diethyl sulfide oxide, diethylsulfone and diethylsulfate. DEDS has already been observed in the gas phase. The other products come from the successive sulfur oxidation stages of DES. These are the same ones that allowed us to determine the photo-oxidation mechanism of DES [9].

3. Materials and Methods

3.1. Powder Photocatalyst Preparation

The catalysts are synthesized by sol-gel route in a basic medium. TiO_2 doped with Sn was obtained by dissolving 0.0486 mL of $SnCl_4$ (Sigma–Aldrich, Saint Louis, MO, USA, purity 99%) into absolute ethanol (purity 99.8%) before mixing with 18.6 mL of titanium isopropoxide (Sigma–Aldrich, purity 97%). The pH was adjusted around 9 by adding ammonia (Carlo Erba, 30% aqueous solution). Then, 35 g of the porogen, PEG 4000 (Merck), was dissolved in ethanol solution (TiO_2/PEG mass ratio 1/7). This sample was then calcined in a vertical oven integrating a filter, so that the PEG residues can be easily separated from the TiO_2 powder, at 500 °C using an air flow of 50 mL/min for 3 h with a heating rate of 5 °C/min [9]. The sample is named **1% Sn-doped TiO_2/PEG**.

TiO_2 doped with Ta was synthesized by mixing 18.6 mL of titanium isopropoxide with 40 mL of absolute ethanol at ambient temperature. Then, 40 mL of water and 0.792 mg of $TaCl_5$ (Sigma–Aldrich) were added. The pH was adjusted around 9 by adding ammonia (Carlo Erba, 30% aqueous solution). The rest of the procedure is the same as for the sample modified with Sn, the PEG is added and the whole is calcined at 500 °C [14]. The sample is named **8% Ta-doped TiO_2/PEG**.

3.2. Supported Photocatalyst Preparation

The alveolar foams of β-SiC have been supplied by SICAT company (Willstätt, Germany) [20]. The foam samples are shaped like a cylinder of 40 mm in diameter and 22 mm in height, with a cell size of 4.5 mm (Figure 12). The foam was calcined at 700 °C for 3 h under air, to remove residual organic carbon. To optimize the irradiation of the photocatalyst, the lamp is placed in the center of the foam for testing, so an inner hole has been drilled in the center of the foam. This hole is 20 mm in diameter and thus leaves a thickness of 10 mm of foam (Figure 12: photo on the right).

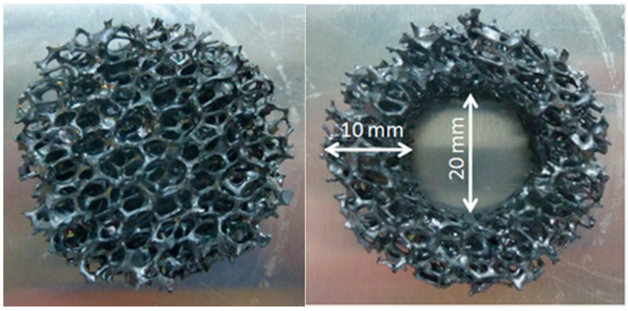


Figure 12. Pictures of a β-SiC foam before (**left**) and after (**right**) drilling.

3.2.1. Impregnation and Adhesion of TiO_2 on β-SiC Foams

The conditions for depositing the catalyst on the foams were optimized manually with TiO_2 P25. They were then transferred to the deposition of TiO_2 doped with 8% Ta and 1% Sn with a PEG: TiO_2 mass ratio of 7. The protocol previously established in our lab has been reproduced [21]. The foams are washed with a water–ethanol mixture, dried and dipped for 10 s in a solution of 10 g/L of catalyst dispersed in ethanol. A few drops of an ammonia solution are added up to a pH of 8 to better disperse the photocatalyst in the suspension. After each impregnation, the foam is washed with water or ethanol. These operations are repeated until the desired mass is immobilized onto the support. At the end of the procedure, the impregnated foam is calcined at 380 °C. However, the amount of TiO_2 immobilized after each impregnation step is very low and, thus, 45 cycles (for example) (impregnation + washing) are required to obtain a TiO_2 loading of 12 wt.%. It takes a long time and the risk of experimental error is high, especially since β-SiC foams are fragile and can break during quenching. For this reason, an automation of this process was carried out with the building of a home-made system adapted to the experimental conditions previously optimized.

3.2.2. Automated Impregnation Device

The automatic system for impregnating and washing carried out in the laboratory allows to perform the following steps:

(1) Dipping for 10 s in a suspension of catalyst dispersed in ethanol at a concentration of 10 g/L, the suspension is constantly left under stirring by a magnetic stirrer.

(2) Drying by an infrared lamp (UCI, IR-300W-118-R7S from IGLU Lighting France) and a small jet of compressed air, the foam is rotated by a motor.

(3) Washing by dipping for 10 s in ethanol

(4) Drying as step 2

(5) Steps 2 to 4 are repeated until the desired number of cycles (impregnation + drying) is reached.

The scheme of the automated system is presented in reference [22]. All the components are controlled by an electronic system including a microcontroller. The basic immobilization tests with the automated system do not allow a large amount of catalyst to be deposited on the β-SiC foams. Therefore, different approaches to increase the amount of TiO_2 immobilized by impregnation have been considered and optimized: a thermal treatment prior to the photocatalyst deposition by impregnation and the use of a chemical acid treatment prior to deposition. The results of these tests will be discussed later.

3.3. Characterization Techniques

SiC foams coated by photocatalysts were characterized by scanning electron microscopy at 20 kV with a Zeiss apparatus model EVO 50 equipped with a tungsten filament cathode. For analysis, a small fragment of a TiO_2/SiC foam was inserted in the SEM with a carbon adhesive tape from Soquelec Ltd (Québec-Canada).

Surface area and porosity measurements were carried out on a ASAP 2010 Micromeritics Tristar apparatus using N_2 as adsorbent at liquid N_2 temperature. Before N_2 adsorption, the material was outgassed under primary vacuum at 200 °C overnight. The specific surface area was calculated from the N_2 adsorption isotherm using the BET method, the micropore surface area was derived using the t-plot method, and the pore size distribution was obtained using the Barrett, Joyner et Halenda (BJH) method during the adsorption step. For each test, a "sample" of less than 100 mg is taken from the foam, but no grinding is carried out to keep the macroscopic structure of the foam as much as possible.

3.4. Experimental Device and Procedure

Gas phase photocatalysis was carried out in a 350 mm length single pass annular Pyrex reactor with a diameter of 44 mm, between which the reactant mixture was passing through (Figure 13). The reactor used is intended for the catalysts immobilized on β-SiC foams (with an external diameter of 40 mm and a thickness of 20 mm) supplied by our industrial partner (company SICAT). Extensive details concerning both photocatalytic reactor and device can be found elsewhere [21,23].

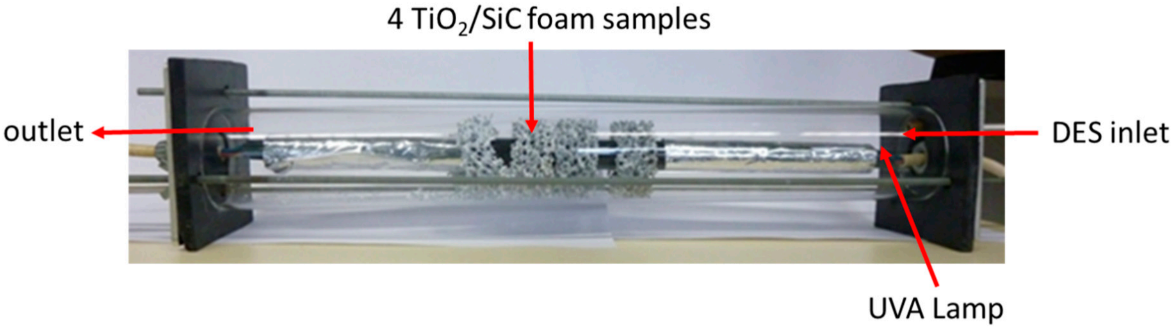


Figure 13. Photocatalytic reactor with TiO_2-based photocatalysts immobilized on β-SiC foams.

One or four foam samples are inserted into the reactor, which represents a bed thickness to be crossed of 2 and 8 cm, respectively. Since the length of the lamp (28.8 cm) is larger than the length of the foam bed studied, part of the lamp is masked with aluminum foil to consider only the radial illumination of the lamp. The UV-A lamp is a Sylvania F8W/BLB-T5 lamp with a total irradiance of 79.6 W/m^2, with a spectral peak centered around 365 nm. DES (Aldrich, 98%) and water were fed at ambient temperature and atmospheric pressure by bubbling air through two saturators, respectively, and mixed with additional air to obtain the required DES-water-air ratio with a constant total air flow.

The dry air flow rate is 71 mL/min, 50 mL/min for humid air and 1.5 mL/min for air saturated with DES. The total flow rate is 122.5 mL/min with a DES concentration of 1200 to 1500 ppmv (i.e., 4–5 g/m^3) which remains close to the test conditions for powdery materials (1200–1400 ppm DES, flow rate of 150 mL/min) [9,14].

Before the reaction, the catalyst was first exposed to the reactant-containing air stream with no illumination until dark-adsorption equilibrium was reached. Afterwards the illumination was switched on. Reactants and reaction products were analyzed on-line by an Agilent GC-6890N Gas Chromatography equipped with HP Plot Q and HP-5MS columns, coupled to a Thermal Conductivity Detector and a MS-5973N Mass Spectrometer, respectively.

4. Conclusions

The immobilization of the photocatalysts on β-SiC foams was controlled with ca. 10% uncertainty considering the weight % of catalyst deposited by automated impregnation after pretreatment of the foams with nitric acid. Catalyst losses are almost zero after calcination at a temperature of 380 °C when the foam is placed in water under ultrasound. The main steps of the optimized process are: decarbonation at a temperature of 700 °C for 3 h, then treatment overnight with HNO_3 (0.1 mol/L) and finally calcination at a temperature of 380 °C for 3 h. The degradation of DES on the photocatalysts immobilized onto β-SiC foams is never complete, unlike powdery catalysts, but it remains high after several hours of illumination. Sn doped-TiO_2 with, with a PEG/TiO_2 ratio of 7 exhibits the best initial activity (up to 90%) but is deactivates more quickly than Ta doped-TiO_2 (40% after 800 min). The activity of the catalysts is strongly influenced by the adsorption properties of the support, as β-SiC foams adsorb DES and other sulfur compounds. This adsorption makes it possible to limit the poisoning of the catalysts and to maintain an acceptable conversion rate even after 10 h under continuous DES flow. Desorption of DES at the beginning of the test is, however, troublesome in the case of degradation of true toxic chemical agents. Therefore, the reactor should be equipped with a cooling system to limit this desorption or coupled with a complementary adsorbent bed. Washing with NaOH completely regenerates the catalyst after a firs treatment and even seems to "wash" it by removing impurities initially present on the foams.

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