Photocatalytic degradation of TCE in air using TiO₂ porous thin films: influence of the relative humidity

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Abstract

Porous TiO₂-anatase thin films were prepared by the sol-gel route and used for the study of the influence of structural properties in their photocatalytic activity. Sols were prepared by using titanium isopropoxide with two types of modifier ligands, namely acetic acid and acetyl acetone, and pore generating agents such as polyethylene glycol, pluronic F-127 and polyethylene glycol hexadecyl ether (Brij 58). The photocatalytic activity for the degradation of trichloroethylene in air was evaluated under ultraviolet irradiation at different gas flows and water vapour contents. The photocatalytic activity depends on the nature of the pore generating agent which influences the TiO₂ crystallite size and the textural properties of the final material. The samples obtained by using acetic acid as the modifier ligand and either Brij 58 or PEG as pore the generating agent exhibited the best photocatalytic behaviour even in the presence of high quantities of water vapour. The direct **trichloroethylene** oxidation pathway to CO₂ is favoured at low water vapour contents, but an important generation of COCl₂ is observed even at low water partial pressures.

Keywords: Photocatalysis, **trichloroethylene degradation**, gas phase, **phosgene**, COCl₂, relative humidity, TiO₂ thin films, sol-gel, pore generating agent, PEG, Brij 58, F-127, porosity, spectral ellipsometry and environmental ellipsometric porosimetry (EEP).

1. Introduction

Photocatalysis is a well known Advanced Oxidation Process (AOP) for the abatement of volatile organic pollutants at mild conditions [1]. **Trichloroethylene (TCE)** is an organochloride compound that can be used as solvent, degreasing and/or cleaning agent [2] [3]. TCE can be found in industrial emissions, landfills, hazardous waste disposal sites or indoor air. The interest in this molecule accounts to the presence of chlorine groups, which are involved in the photocatalytic process and the formation of several partial oxidation products. Thus, a relationship between changes in the physico-chemical properties of the material and the CO₂ selectivity may be established. The excellence of TiO₂ as photocatalyst for the removal of pollutants both in water and gas-phase is well known [4]. TiO₂ immobilisation is a requirement for the feasibility of the treatment of pollutants in air mainly because it dodges the expensive filtration methods otherwise needed to avoid the release of nanoparticles into the atmosphere [5] [6].

Sol-gel process is an effective, versatile and the most commonly used method to prepare immobilized TiO₂ thin films on glass support. Properties such as particle size and textural properties can be adjusted by varying the synthesis method [7]. To achieve a precise control on the final characteristics of the material, complexing agents such as β diketones (e.g. acetylacetone) or carboxylic acids (e.g. acetic acid) are frequently used [8] [9] [10] [11] [12].

Another approach to tailor the photocatalytic properties of semiconductors is to promote the formation of porous structures. The higher photocatalytic performance of TiO₂ porous films has been reported by several groups. Polyethylene glycol (PEG) is considered as the archetypal and most effective polymer template for the formation of macroporous TiO₂ thin films [13] [14] [15] [16] [17] [18]. Surfactants such as Triton [19] or Tween [20] [21] have been used to synthesize nanocrystalline mesoporous TiO₂ films for the photodegradation of creatinine and methyl blue in water.

Phase composition, specific surface area, particle morphology, particle aggregation, bulk and surface OH groups and impurities are the most relevant parameters to describe the efficiency of photocatalysts [22] [23]. However, the accurate comparison of samples synthesized by using different routes is complicated. Contradictory results can be found in the literature. While some authors claim the predominant role of the specific surface area, [24] [25] others point out to the crystalline degree as the main influence [26]. In a previous work we have compared the

photocatalytic performance of porous TiO_2 thin films prepared with PEG as the pore generating agent with that of dense films [27]. The final heat treatment temperature and time of sintering was optimised and the results showed that the samples sintered at 450°C for 1 hour presented the best compromise between specific surface area and crystallinity resulting in a superior photocatalytic activity. Hitherto, no reports on the effect of the surfactant and nature of the chelating agent in the TCE conversion have been published.

Although the number of studies on the photo-oxidation of TCE is very high, the effect of water vapour partial pressure on the mineralization and formation of COCl_2 is elusive. Anderson et al. reported the conditions under which COCl_2 was not detected as reaction product [28] [29]. Blake et al. showed the increase of the COCl_2 carbon atom product fraction with increasing the water vapour partial pressure [30]. Fan and Yates [31] indicated that the presence of water causes a decrease in the level of DCAC (dichloroacetylchloride) and COCl_2 enhancing the CO_2 yield. Amama et al. reported that humidification promotes the phosgene hydrolysis reaction [32].

In this article, the photocatalytic performance of TiO_2 thin films for the degradation of TCE is analysed. The role of different molecules such as polyethylene glycol, pluronic F-127 and polyethylene glycol hexadecyl ether (Brij 58) as pore generating agents and chelating agents such as acetylacetone or glacial acetic acid has been studied. To this end, experiments at different total flows and relative humidity content (R.H.) were performed.

2. Experimental

2.1 Synthesis of TiO₂ and photocatalysts preparation

Titania sols were prepared via acid catalysis by using titanium isopropoxide (TISP) as precursor. TISP was chemically modified by mixing it with acetylacetone (AcAc) or glacial acetic acid (AcOH). The molar ratio TISP/complexing agent was set to 1 in order to control hydrolysis and condensation reactions. **The optimization of the synthesis parameters has been reported in a previous article [33].** The pore generating agents, provided by Sigma Aldrich, were incorporated to the sols in a surfactant/TISP molar ratio of 0.03 for polyethylene glycol (average molecular weight 400 g mol⁻¹), **0.0005** for Pluronic F-127 (average molecular weight 12,600 g mol⁻¹) and 0.07 for Polyethylene glycol hexadecyl ether P5884 (Brij 58, average molecular weight 1,124 g/mol). Finally, a mix of ethanol and acidulated water (0.1 M HCl) was added drop by drop into the solutions. By following the same route two reference sols, one with AcAc and another with **AcOH**, were prepared without surfactant addition. Final molar ratio of 1 TISP: 1 AcAc: 40 EtOH: 1 H₂O and TiO₂ concentration of 30 g L⁻¹ were fixed. All the sols were maintained at room temperature before use.

Films were deposited by dip-coating onto glass-slides at a withdrawal rate of 25 cm min⁻¹ for the reference sols and 35 cm min⁻¹ for the sols containing pore generating agents. All coatings were treated at **450°C** for 1h using a heating ramp of 10°C min⁻¹. Generally, all samples were prepared with two layers using an inter-medium heat treatment of 200°C/30 min for dense coatings and 350°C/1h for porous coatings, after each coating deposition. In order to optimize the TiO₂ loading, AcOH-Brij-58 samples with one and three layers were prepared. For the evaluation of the photocatalytic activity the glass slides were coated with a first layer of SiO₂ [34] (200 nm) to avoid the diffusion of Na⁺ cations from the glass substrate to the TiO₂ coating during firing.

2.2 Characterization of the coatings

Grazing X-ray diffraction (GXRd) studies were performed to analyse the crystallisation of TiO₂ in the anatase form and the crystal size, using CuK α radiation in a Panalytical diffractometer (X'Pert PRO theta/theta). The diffractograms were recorded in the range of 2 θ 20–70°, using a fixed counting time of 20 s/step and an increment of 0.05°.

The hydrophobic/hydrophilic character of TiO₂ coatings deposited on silicon wafers was evaluated through the contact angle using an Easy Drop equipment (“Drop Shape Analysis System” Kruss DSA 100). Silicon wafers were selected as support in order the obtained values to determine the pore size distribution using Environmental Ellipsometric Porosimetry (EEP) [35]. In this case, the EEP measurements were performed using the coating deposited on silicon wafer, in order to avoid the multiple reflections associated to use of glass substrates that extend the overlapping and complicates the fit of the experimental data.

Ellipsometry and Environmental Ellipsometric Porosimetry (EEP) measurements were performed using a spectral ellipsometer (WVASE32, (“Variable Angle Spectroscopic Ellipsometer”) J.A. Co., Woollam M-2000UTM). This equipment is used for measuring optical constants and thicknesses of films simultaneously. The measured values are expressed as psi (ψ) and delta (Δ) and the fit of parameters in the range of wavelengths allows determining the thickness and the refractive index at the same time. Thickness (e) and refraction index (n) were measured evaluating their variations with the R.H. from 0 to 100 % to calculate the adsorption-desorption isotherms. Pore size, pore volume, and specific surface area (S_s) of the films supported on silicon were determined from these isotherms following the approximation of Boissiere et al. [35]. An estimation of the exposed surface area per 1 cm² of sample was calculated considering the S_s , and thickness (cm). The density of the coatings was calculated using the Clausius Mossotti equation [36], and considering a refractive index of 2.4 for the bulk material.

2.3 Photocatalytic activity measurements

The photocatalytic oxidation of gas-phase trichloroethylene was studied in a continuous flow flat photoreactor with external dimensions 120x50x10 mm (length x width x depth). The photoreactor was made of stainless steel except for one face where a window of 30 cm², made out of borosilicate glass with low iron content, was placed for photocatalyst illumination, provided by two UVA (Philips TL-15W/05) fluorescent lamps with a maximum emission at 365 nm wavelength. A gas mixture of TCE and air was fed from a gas cylinder of TCE/N₂ (Air Liquide, 500 ppm) and compressed air free of water and CO₂. Flow rate, pressure, temperature, UV radiation and R.H. were controlled by automated equipment using electronic mass flow controllers and automated valves (Process Integral Development Eng&Tech S.L.). UV irradiation and

water vapour content were measured using specific sensors, GaAsP photodiode for the former and a polymer sensing element in the latter. TCE concentration was fixed to 90 ppm, and the total gas flow varied between 200-400 ml·min⁻¹ corresponding to gas hourly space velocities (GHSV) ranging between 5000-10000 h⁻¹, (residence times between 0.74 s and 0.37s). The study of the influence of the R.H. (0-90%) on the photocatalytic activity was performed at 90 ppm TCE and 200 ml min⁻¹ total flow. The gas composition was monitored continuously by using a FTIR Thermo-Nicolet 5700 spectrometer, equipped with a temperature controller multiple reflection gas cell (optical path 2 m) maintained at 110° C. The gas cell and the optic of the system was continuously purged with pure air, eliminating thus the contribution of atmospheric carbon dioxide. Thus, the determination of the carbon dioxide concentration along the reaction time was evaluated. IR spectra of 64 scans at a resolution of 2 cm⁻¹ were collected. The analysis of the reaction products was performed by following the evolution of the representative vibrational bands of the desired molecules at the following wavenumbers: TCE (965-903 cm⁻¹), CO₂ (2435-2233 cm⁻¹), COCl₂ (1873-1780 cm⁻¹), CO (2231-2027 cm⁻¹), HCl (2885-2662 cm⁻¹), DCAC-dichloroacetylchloride (1114-1037 cm⁻¹). The actual concentration of TCE, CO₂ and COCl₂ was evaluated against calibration mixtures provided by Air Liquid.

3. Results and discussion

3.1 Characterization of the TiO₂ films

The synthesis of the TiO₂ sols was optimised to obtain transparent and stable sols, since according to previous results, AcAc-sols displayed a yellowish colour [33]; meanwhile AcOH-sols were colourless. The synthesis of TiO₂ with F-127 and AcOH was ruled out because unstable sols were obtained in a wide range of compositions.

The crystallite size was estimated using Scherrer's equation from the GXRD peak broadening analysis (Table 1). In all cases, TiO₂-anatase was the only crystal phase observed (Figure 1 supporting information). The addition of surfactants as pore generating agents inhibited the growth of crystallites and the aggregation of the primary particles as reported by Choi [37]. Thus, the reference material and TiO₂-AcAc-PEG presented similar values of crystalline domain size of 40 and 42 nm, while the coatings prepared from surfactant derived sols present a smaller crystalline domain size between 25 and 30 nm. FE-SEM analyses were performed to identify titania particle size (Figure 2 supporting information). The calculation of the primary particle size by this technique is not a simple task. The micrographs indicate the presence of secondary particles with a Gaussian distribution of sizes and a mean size around 27 nm, in good agreement with XRD results. The size of Titania primary particles ranges between 13-15 nm. Moreover, transmission Electron Microscopy (TEM)) confirmed the presence of structures with porous in the range of the mesoporous. Bright and dark contrasts areas corresponding to porous and titania matrix respectively were identify for all samples (Figure 3 supporting information).

The bands corresponding to C-H bonds vibrations (1550, 1450, 1350 and 1140 cm⁻¹ [38,39]), C=C or C=O vibrations around 1650 and 1710 cm⁻¹ and those at 2930 and 2870 cm⁻¹, associated to asymmetric and symmetric vibrations of CH₂ group, were not detected by FTIR spectroscopy, suggesting the elimination of most of the surfactants. Only a band at 435 cm⁻¹ appears, assigned to the crystallisation of TiO₂ in the anatase phase [40] in agreement with GXRD results.

Spectral ellipsometry with water vapour technique allows determining the textural characteristics of mesoporous thin films. This is an extended and well known technique in the field of determination of the characteristics of mesoporous films [35] [41] [42] [43]. Details concerning the characterization of sample by spectral ellipsometry can be found elsewhere [33].

Environmental ellipsometric porosimetry (EEP) was used to study the structural characteristics of the porous coatings. Figure 1 shows the adsorption-desorption isotherms of TiO_2 -AcAc-Brij 58 and TiO_2 -AcAc-PEG obtained by EEP. The first coating presented a typical isotherm of a well-developed mesoporous material. A hysteresis loop between the adsorption and desorption branches was observed. The sharp drop on the desorption branch could be associated to mesoporous constrictions at the boundaries domains and/or smaller pores in the titania walls [44]. The pore size distribution from adsorption and desorption branches were 11 and 8 nm with a pore volume of 27% vol. For TiO_2 coating with PEG, the isotherm obtained is characteristic of a low porous material in the mesoporous range. In this case, pore size of 10 nm and pore volume of 4% was obtained.

Table 1 summarises the properties obtained by ellipsometric measurements (refraction index, pore volume, pore size, specific surface area and exposed surface) for all coatings. The incorporation of surfactants in the synthesis route leads to thicker layers and lower refractive indexes than the reference materials. For TiO_2 -AcAc and TiO_2 -AcAc-PEG coatings, the refractive index slightly changed from 2.11 to 2.09 suggesting that the coatings did not present porous in the mesoporous range. For the rest of compositions, lower refractive indexes were obtained and associated with higher pore volumes. The characteristic of porosity can be related to the properties of the surfactant. Thus, the porosity and the pore size increased with the hydrophobic tail length of the surfactant and with the surfactant concentration. In this case, the concentration was adjusted to obtain a similar pore size independently of the type of surfactant. Consequently similar high porosity (~30%) and pore size around 11 nm were obtained for TiO_2 -AcAc-F-127 and TiO_2 -AcOH/AcAc-Brij58 coatings.

In the case of TiO_2 -AcOH-Brij58 multilayer coatings, the thickness and the refractive index increased with the number of coatings. The successive heat treatments after the

incorporation of each layer provoked the partial collapse of the porosity. In this case, the pore size decreased from 11 to 5 nm while pore volume was reduced from 32 to 23%.

3.2 Photocatalytic results

The photocatalytic performance of TiO₂ thin films samples synthesised by using different pore generating agents and modifier ligands was evaluated in the TCE photo-oxidation reaction, using 90 ppm of TCE and residence times between 0.74 s to 0.37 s. Moreover the effect of film thickness and TiO₂ content was also evaluated. Finally experiments varying the R.H. of the gas stream were performed to analyse the partial oxidation products distribution in the presence of water vapour.

3.2.1 Influence of the synthesis route and TiO₂ loading

The photocatalytic oxidation of TCE at gas hourly space velocities between 5,000 and 10,000 h⁻¹ for dense samples and for those prepared with PEG, F-127 and Brij 58 is represented in Figure 2. TCE conversion and the formation of CO₂ and COCl₂ are shown in Figures 2a, 2b and 2c respectively as a function of the ratio between total flow and illuminated sample area (F/A). As expected, TCE conversion decreased with the increasing total flow. The photocatalytic activity was clearly influenced by the incorporation of surfactants in the sol synthesis. The TCE conversion increased according to the following sequence: AcAc < AcAc-F-127 < AcAc-PEG ≤ AcAc-Brij-58. The TiO₂-AcAc coating showed significantly lower degradation of TCE likely associated to its dense structure. The incorporation of surfactants resulted in an important improvement of the photocatalytic activity mainly due to the porous structure of the films.

TiO₂-AcAc-Brij58 and TiO₂-PEG coatings reached conversions 30% and 27% higher than the TiO₂-AcAc reference material. Although the refractive index of TiO₂-PEG coating is high, it is suggested that PEG induces the appearance of an open porosity that sharply increases the hydrophilicity, as proved by the decrease of the contact angle, Such open porosity enhanced the adsorption capacity and thus, the photocatalytic activity. TiO₂-AcAc-Brij58 coating recorded the best efficiency in the series. The low contact angle of this catalyst suggests that its hydrophilic surface facilitates the adsorption of the contaminants hence improving its photocatalytic activity [37,45].

During the heat treatment and elimination of the surfactant, the inorganic phase likely mimics the textural properties of the surfactant, modifying the hydrophilic/hydrophobic pore surfaces and, therefore, the photocatalytic performance of the coatings.

The main reaction products detected in the reaction outlet were CO_2 and COCl_2 (Figure 2.b and 2.c). As previously reported, CO , DCAC (dichloroacetylchloride) and HCl were also detected in the outlet gas stream in minor amounts [46], [47] (data not shown). As expected, the amount of reaction product decreases with the increasing gas flow. The photoactive materials that showed the fastest reaction rates were the ones that produced higher amounts of CO_2 and COCl_2 . The data obtained with $\text{TiO}_2\text{-AcAc-F127}$ indicated that TCE photodegradation is high due to the formation of DCAC, explaining the lower CO_2 and COCl_2 amounts (see section 3.2.2).

The influence of the complexing agent on the photocatalytic degradation of TCE is observed in Figure 3. The TCE conversion along with TCE, CO_2 and COCl_2 concentration in the outlet are shown in this figure. The superior performance of the samples prepared with acetic acid is clearly observed, increasing the TCE conversion around 20%. Both materials have a similar refraction index (around 2.1) and similar contact angle. The different behaviour could be associated to the modification of the textural properties. Moreover, according to XRD results, acetic acid favours the formation larger TiO_2 -anatase crystals and this feature seems to play an important role in the photocatalytic performance.

In order to optimize the effective use of photons by TiO_2 , samples with different number of layers were prepared. The results obtained with samples synthesised with acetic acid and Brij 58, the ones that showed the best photocatalytic activity results, is shown in Figure 4. A remarkable increase of the TCE conversion when the layer thickness changed from 160 to 240 nm, especially at a lower contact time, was observed. On the other hand, whereas the addition of a third layer increased the film thickness up to 360 nm it did not result in a significant change in the photocatalytic activity. Since thermal treatments at $350^\circ\text{C}/1\text{h}$ were performed after the deposition of each layer, the probable reduction of the porosity must be taken into account (Table 1) [48]. Consecutive heat-treatments likely collapsed the structure with the subsequent densification of the films. UV radiation penetrates only to a limited length and the

diffusion of TCE molecules from the gas phase to the photocatalyst active sites is possibly inhibited by the increasing number of layers and the densification of the coating. Thus, the optimum thickness of the TiO₂ layer for maximum efficiency was set around 250 nm.

3.2.2 Effect of the relative humidity

Since vapour water goes along within polluted gas streams, the effect of the R.H. in the photocatalytic degradation of TCE was studied. Values of TCE degradation and reaction products concentration were taken at steady state conditions, in order to avoid the effect of irradiance and temperature during the heating of the lamps. Examples of the FTIR spectra taken at different relative humidity for TiO₂-AcOH-Brij 58 (250 nm) are shown in Figure 5a. The ones corresponding to the 78 % water vapour content are not shown for the sake of clarity. Trichloroethylene has a characteristic band centred at 960 cm⁻¹. In the absence of water vapour, the presence of CO₂ (2,349 cm⁻¹), CO (2,144 cm⁻¹), phosgene (1,827 cm⁻¹) DCAC (1,076 cm⁻¹) and HCl (2,885 cm⁻¹) can be observed. The presence of water vapour in the feed leads to the appearance of two sets of strong bands between 4000-3400 cm⁻¹ and 2100-1200 cm⁻¹ overlapping with those of CO, COCl₂, DCAC and HCl. The signal corresponding to water was subtracted from the original spectrum (Figure 5.b.). The intensity of the COCl₂ band is constant within 0% to 50% RH but decreased significantly at 78% RH. Thus, a relationship between the CO₂/COCl₂ ratio and the water vapour content can be deduced.

TCE conversions as well as CO₂ and COCl₂ quantities at steady state conditions are shown in Figure 6 for the different photocatalysts. The results corroborate the effects observed in the absence of water. Coatings prepared from sols with AcOH, dense or porous, record a higher photocatalytic activity than those deposited from sols with acetyl acetone. Moreover, the increase of the porosity due the addition of surfactants improved the photocatalytic properties of the TiO₂ thin films even in the presence of high quantities of water vapour. The incorporation of water vapour at contents above 50 % led to a drastic decrease of the photocatalytic activity and consequently to lower CO₂ and COCl₂ formation. This feature can be explained by considering that TCE and H₂O compete for the same active sites. Figure 7 shows the adsorption isotherm of the AcOH-Brij-58 coating obtained by spectral ellipsometry compared to the evolution of the TCE

conversion. At low RH, $V_{\text{ads}}/V_{\text{film}}$ and TCE conversion changed very slowly. Above 50% RH, $V_{\text{ads}}/V_{\text{film}}$ sharply increased, associated to the filling of the pores with molecular water. As a consequence, the exposed surface decreased and therefore, TCE conversion began to fall. When the pores were practically full, condensation of water took place and TCE absorption was impeded because the surface suffered a violent decrease. This result is in line with the photocatalytic behaviour described above.

It is important to notice that TCE conversion was not modified within R.H. range between 0-50% but, on the contrary, mineralization was promoted. Considering that the amount of COCl_2 is constant in this RH range, the main reaction pathway at this condition is the direct decomposition of TCE into CO_2 according to eq. 1.

Nevertheless, others side reactions must be taken into consideration in order to justify the behaviour of COCl_2 . One such possible reaction could be the direct oxidation of TCE (Eq. 2) but at slower reaction rates than in the absence of water vapour in the stream.

In the case of DCAC formation (data not shown) a progressive decrease of the reaction rate with water vapour content was observed. These results seem to indicate that the decomposition of DCAC into COCl_2 could be a side reaction pathway and a source of COCl_2 as previously suggested by Blake et al. [30] [46] (Eq. 3-4). Thus, the net balance for COCl_2 was close to zero, and apparently no differences in the COCl_2 concentration were appreciated.

Our results show that the incorporation of hydroxyl groups from water vapour increases the TCE reaction rate for Eq.1 but do not favour hydrolysis of COCl_2 at the operating conditions selected, as suggested by other authors [30][31][32].

Either (or both) increasing the residence time or including an adsorbent bed to promote the hydrolysis reaction [30] could be possible strategies to minimise the concentration of non desirable reaction compounds even in the presence of water vapour.

Conclusions

The incorporation of surfactants as pore generating agents resulted in titania coatings with smaller crystallite size, refractive index, and higher pore volume. The presence of mesoporosity reduces internal mass transfer limitations increasing the photocatalytic activity. The best results were obtained with TiO_2 -AcOH-Brij58 coatings. The studies on the influence of the complexing agent showed a better photocatalytic behaviour for the coatings prepared from the acetic acid containing sols with respect to those synthesised with acetyl acetone.

Finally, the effect of the R.H. in the photocatalytic degradation of TCE showed that the direct TCE oxidation pathway was favoured in the presence of water vapour. The quantification of the different reaction products have to be carefully analysed. Although a general overview of the spectra seems to indicate that the COCl_2 signal disappears, the subtraction of the water signal showed the formation of COCl_2 . The concentration of COCl_2 did not change with water vapour content between 0-50% R.H., suggesting that the hydrolysis reaction did not take place under the reaction conditions studied here.

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Photocatalytic degradation of trichloroethylene in dry and wet air conditions with TiO₂ porous thin films

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Abstract

Porous TiO₂-anatase thin films were prepared by the sol-gel route to study the influence of structural properties in their photocatalytic activity. Sols were prepared using titanium isopropoxide with two types of modifiers ligands, acetic acid and acetone, and different types of pore generating agents such as polyethylene glycol, pluronic F-127 and polyethylene glycol hexadecyl ether (Brij 58). The photocatalytic activity was evaluated for the degradation of trichloroethylene in air as a model volatile organic compound molecule under ultraviolet irradiation at different gas flows and water vapour content. The photocatalytic activity depends on the nature of the pore generating agent which influence the TiO₂ crystal size and the textural properties of the final material. The samples obtained by using acetic acid as modifier ligand and Brij 58 or PEG as pore generating agent exhibited the best photocatalytic behaviour even in the presence of high quantity of water vapour. The direct TCE oxidation pathway to CO₂ was favoured at low water vapour contents, but an important generation of COCl₂ was appreciated even at low water partial pressure.

Keywords: Photocatalysis, TCE degradation, gas phase, COCl₂, relative humidity, TiO₂ thin films, sol-gel, pore generating agent, PEG, Brij 58, F-127, porous structures, spectral ellipsometry and environmental ellipsometric porosimetry (EEP).

1. Introduction

Photocatalysis is a well known Advanced Oxidation Process (AOP) for the abatement of volatile organic pollutants in mild conditions [1]. Trichloroethylene (TCE) is an organochloride commonly used as solvent, degreasing or cleaning agent [2] [3]. It is found in industrial emissions, landfills, hazardous waste disposal sites or indoor air. The interest in this molecule accounts to the presence of chlorine groups, which are involved in the photocatalytic process and the formation of several partial oxidation products. Thus, a relationship between the changes in the physico-chemical properties of the material synthesised and the CO₂ selectivity may be stabilised. The excellence of TiO₂ as photocatalyst for removal of pollutants both in water and gas-phase is well known [4]. TiO₂ immobilisation is a requirement for treatment of pollutants in air in order to dodge the expensive filtration methods indispensable to avoid the release of nanoparticles into the atmosphere [5] [6].

Sol-gel process is an effective, versatile and the most commonly used method to prepare immobilized TiO₂ thin films on glass support. Properties such as particle size and textural properties can be adjusted by varying the synthesis method [7]. To get precise control on the final characteristics of the material, complexing agents such as β diketones (e.g. acetylacetone) or carboxylic acids (e.g. acetic acid) are frequently used [8] [9] [10] [11] [12].

Another approach to tailor the photocatalytic properties of a semiconductor is to promote the formation of porous structures. The higher photocatalytic performance of TiO₂ porous films has been reported by several authors. PEG (polyethylene glycol) is considered as the archetypal and effective polymer template for the formation of macroporous TiO₂ thin films [13] [14] [15] [16] [17] [18]. Surfactants such as Triton [19] or Tween [20] [21] have been used to prepare nanocrystalline mesoporous TiO₂ films for the photodegradation of creatinine and methyl blue in water.

Phase composition, specific surface area, particle morphology, particle aggregation, bulk and surface OH groups and impurities are the most relevant parameters to describe the photocatalytic efficiency [22] [23]. The accurate comparison of samples synthesized using different routes is complicated. Contradictory results can be found in the literature. While some authors claimed the predominant role of the specific surface area [24] [25] others pointed out crystallinity degree as the main influence [26]. In a previous work we have compared the photocatalytic performance of

porous TiO₂ thin films prepared with PEG as pore generating agent with that of dense films [27]. The final heat treatment temperature and time of sintering was optimised. The results showed that samples sintered at 450°C for 1 hour presented the best compromise between specific surface area and crystallinity, with the subsequent benefit in the photocatalytic activity. Hitherto, no reports on the effect of the surfactant and chelating agent nature in the TCE conversion have been published.

Although abundant studies on the photo-oxidation of TCE are available, the effect of the water vapour partial pressure on the mineralization and on the formation of COCl₂ is elusive. Anderson et al. have reported the conditions under which COCl₂ was not detected as reaction product [28] [29]. Blake et al. showed the increase of the COCl₂ carbon atom product fraction with increasing the water vapour partial pressure [30]. Fan and Yates [31] indicate that the presence of water causes a decrease in the level of DCAC and COCl₂ enhancing the CO₂ yield. Amama et al. reported that humidification promotes the phosgene hydrolysis reaction [32].

In this article, the photocatalytic performance of TiO₂ thin films in the degradation of TCE was analysed. The role of different molecules such as polyethylene glycol, pluronic F-127 and polyethylene glycol hexadecyl ether (Brij 58) as pore generating agents and chelating agents such as acetylacetone or glacial acetic acid has been studied. To this end, experiments at different total flows and relative humidity content (RH) were performed.

2. Experimental

2.1 Synthesis of TiO₂ and photocatalysts preparation

Titania sols were prepared using titanium isopropoxide (TISP) as precursor via acid catalysis. TISP was chemically modified by mixing with acetylacetone (AcAc) or glacial acetic acid (AcOH) in a molar ratio TISP/complexing agent = 1, to control the hydrolysis and condensation reactions. The pore generating agents, provided by Sigma Aldrich, were incorporated to the sols in a surfactant/TISP molar ratio of 0.03 for polyethylene glycol (average molecular weight 400 g mol⁻¹), 5 · 10⁻⁴ for Pluronic F-127 (average molecular weight 12,600 g mol⁻¹) and 0.07 for Polyethylene glycol hexadecyl ether P5884 (Brij 58, average molecular weight 1,124 g/mol). Finally, a mix of ethanol and acidulated water (0.1 M HCl) was added drop by drop into the solutions. Following the same route two reference sols, one with AcAc and another with AcH, were prepared without surfactant addition. Final molar ratio of 1 TISP: 1 AcAc: 40 EtOH: 1 H₂O and TiO₂ concentration of 30 g/l were fixed. All the sols were maintained at room temperature before use.

Films were deposited by dip-coating onto glass-slides at a withdrawal rate of 25 cm min⁻¹ for the reference sols and 35 cm min⁻¹ for the sols with pore generating agents. All the coatings were treated at 450° C for 1h using a heating ramp of 10° C min⁻¹. Generally, all samples were prepared with two layers using an inter-medium heat treatment of 200°C/ 30 minutes for dense coatings and 350°C/1h for porous coatings, after each coating deposition. In order to optimize the TiO₂ loading, AcOH-Brij-58 samples with one and three layers were prepared. For the evaluation of the photocatalytic activity the glass slides were coated with a first layer of SiO₂ [33] (200 nm) to avoid the diffusion of Na⁺ cations from the glass substrate to the TiO₂ coating during firing.

2.2 Characterization of the coatings

Grazing X-ray diffraction (GXRD) studies were performed to analyse the crystallisation of TiO₂ in the anatase form and the crystal size, using CuKα radiation in a Panalytical diffractometer (X'Pert PRO theta/theta). The diffractograms were recorded in the range of 2θ 20–70 °, using a fixed counting time of 20 s/step and an increment of 0.05°.

The hydrophobic/hydrophilic character of TiO₂ coatings deposited on silicon wafers was evaluated through the contact angle using an Easy Drop equipment (“Drop Shape Analysis System” Kruss DSA 100).

Ellipsometry and Environmental Ellipsometric Porosimetry (EEP) measurements were performed using a spectral ellipsometer (WVASE32, (“Variable Angle Spectroscopic Ellipsometer”) J.A. Co., Woollam M-2000UTM). Thickness (*e*) and refraction index (*n*) were measured evaluating their variations with the relative humidity from 0 to 100 % to calculate the adsorption-desorption isotherms. Pore size, pore volume, and specific surface area (*S_s*) of the films supported on silicon were determined from these isotherms following the approximation of Boissiere et al. [34]. An estimation of the exposed surface area per 1 cm² of sample was calculated considering the *S_s*, and thickness (cm). The density of the coatings was calculated using the Clausius Mossotti equation [35], and considering a refractive index of 2.4 for the bulk material.

2.3 Photocatalytic activity measurements

The photocatalytic oxidation of gas-phase trichloroethylene was studied in a continuous flow flat photoreactor with external dimensions 120x50x10 mm (length x width x depth). The photoreactor was made of stainless steel except for one face where a window of 30 cm², made of borosilicate glass with low iron content, was placed for photocatalyst illumination, provided by two UVA (Philips TL-15W/05) fluorescent lamps with a maximum emission at 365 nm wavelength. A gas mixture of TCE and air was prepared using gas cylinder of TCE/N₂ (Air Liquide, 500 ppm) and compressed air free of water and CO₂. Flow rate, pressure, temperature, UV radiation and relative humidity were controlled by automated equipment using electronic mass flow controllers and automated valves (Process Integral Development Eng&Tech S.L.). UV irradiation and water vapour content were measured using specific sensors, made of GaAsP photodiode in the former and a polymer sensing element in the later. TCE concentration was fixed to 90 ppm, and the total gas flow varied between 200-400 ml·min⁻¹ corresponding to gas hourly space velocity (GHSV) between 5000-10000 h⁻¹, (residence times between 0.74 s and 0.37s). The study of the influence of the relative humidity (0-90 %) on the photocatalytic activity was performed at 90 ppm TCE and 200 ml min⁻¹ total flow. The gas composition was monitored continuously using a FTIR Thermo-Nicolet 5700 spectrometer, provided with a temperature controller multiple

reflection gas cell (optical path 2 m) maintained at 110° C. IR spectra of 64 scans at a resolution of 2 cm⁻¹ were collected. The analysis of the reaction products was performed by following the evolution of the representative vibration bands of the desired molecules at the following wavenumber: TCE (965-903 cm⁻¹), CO₂ (2435-2233 cm⁻¹), COCl₂ (1873-1780 cm⁻¹), CO (2231-2027 cm⁻¹), HCl (2885-2662 cm⁻¹), DCAC-dichloroacetylchloride (1114-1037 cm⁻¹). The actual concentration of TCE, CO₂ and COCl₂ was evaluated against calibration mixtures provided by Air Liquid.

3. Results and discussion

3.1 Characterization of the TiO₂ films

The synthesis of the TiO₂ sols were optimised to obtain transparent and stable sols according to previous results [36]. AcAc-sols displayed a yellowish colour; meanwhile AcOH-sols were colourless. The synthesis of TiO₂ with F-127 and AcOH was ruled out because unstable sols were obtained in a wide range of compositions.

The crystallite size was estimated using Scherrer's equation from the GXRD peak broadening analysis (Table 1). In all the case, TiO₂-anatase was the only crystal phase observed. The addition of surfactants as pore generating agents inhibited the growth of crystallites as well as the aggregation of the primary particles as reported by Choi [37]. Thus, reference material and TiO₂-AcAc-PEG presented similar values of crystalline domain size of 40 and 42 nm, while the coatings prepared from sols with surfactants present a smaller crystalline domain size between 25 and 30 nm. The bands corresponding to C-H bonds vibrations (1550, 1450, 1350 and 1140 cm⁻¹ [38,39]), C=C or C=O vibrations around 1650 and 1710 cm⁻¹ and those at 2930 and 2870 cm⁻¹, associated to asymmetric and symmetric vibrations of CH₂ group, were not detected by FTIR spectroscopy, suggesting the elimination of most of the organic phase. Only a band at 435 cm⁻¹ appears, assigned to crystallisation of TiO₂ in anatase phase [40] in agreement with GXRD results.

Environmental ellipsometric porosimetry (EEP) was used to study the structural characteristics of the porous coatings. Figure 1 shows the adsorption-desorption isotherms of TiO₂-AcAc-Brij 58 and TiO₂-AcAc-PEG obtained by EEP. The first coating presented a typical isotherm of a well-developed mesoporous material. A hysteresis loop between the adsorption and desorption branches was observed. The sharp drop on the desorption branch could be associated to mesoporous constrictions at the boundaries domains and/or smaller pores in the titania walls [41]. The pore size distribution from adsorption and desorption branches were 11 and 8 nm with a pore volume of 27% vol. For TiO₂ coating with PEG, the isotherm obtained is characteristic of a low porous material in the mesoporous range. In this case, pore size of 10 nm and pore volume of 4 % was obtained.

Table 1 summarises the properties obtained by ellipsometric measurements (refraction index, pore volume, pore size, specific surface area and exposed surface) for all the coatings. The incorporation of surfactants in the synthesis route leads to thicker layers and lower refractive indexes than the reference materials. For TiO₂-AcAc and TiO₂-AcAc-PEG coatings, the refractive index lightly changed from 2.11 to 2.09 suggesting that the coatings did not present porous in the mesoporous range. For the rest of compositions, lower refractive indexes were obtained, associated with higher pore volumes. The characteristic of porosity is related to the properties of the surfactant. Thus, the porosity and the pore size increased as a function of the hydrophobic tail length of the surfactant and with the surfactant concentration. In this case, the concentration was adjusted to obtain a similar pore size independent of the type of surfactant. Consequently similar high porosity (~30 %) and pore size around 11 nm were obtained to TiO₂-AcAc-F-127 and TiO₂-AcOH/AcAc-Brij58 coatings.

In the case of TiO₂-AcOH-Brij58 multilayer coatings, the thickness and the refractive index increased with the number of coatings. The successive heat treatments between layers provoked the partial collapse of the porosity. In this case, the pore size decreased from 11 to 5 nm while pore volume was reduced from 32 to 23 %.

3.2 Photocatalytic results

The photocatalytic performance of TiO₂ thin films samples synthesised using different pore generating agents and modifier ligands was evaluated in the TCE photo-oxidation reaction, using 90 ppm of TCE and residence times between 0.74 s to 0.37 s. Moreover the effect of the film thickness, and therefore the TiO₂ content, was studied. Finally experiments varying the relative humidity of the gas stream were performed to analyse the partial oxidation products distribution in the presence of water vapour.

3.2.1 Influence of the synthesis route and TiO₂ loading

The photocatalytic oxidation of TCE at gas hourly space velocities between 5,000 and 10,000 h⁻¹ for dense samples and for those prepared with PEG, F-127 and Brij 58 is represented in Figure 2. TCE conversion and the formation of CO₂ and COCl₂ are represented in Figures 2a, 2b and 2c respectively as a function of the ratio between total

flow and illuminated sample area (F/A). As expected, TCE conversion decreased with the total flow. The photocatalytic activity was clearly influenced by the incorporation of surfactants in the sol synthesis. The TCE conversion increased according to the following sequence: $\text{AcAc} < \text{AcAc-F-127} < \text{AcAc-PEG} \leq \text{AcAc-Brij-58}$. The $\text{TiO}_2\text{-AcAc}$ coating showed significantly lower degradation of TCE likely associated to its dense structure. The incorporation of surfactants resulted in an important improvement of the photocatalytic activity mainly due to the porous structure of the films.

$\text{TiO}_2\text{-AcAc-Brij58}$ and $\text{TiO}_2\text{-PEG}$ coatings exhibited conversions 30% and 27 % higher than $\text{TiO}_2\text{-AcAc}$ reference material. Although the refractive index of $\text{TiO}_2\text{-PEG}$ coating is quite higher, it is suggested that PEG induces the appearance of an open porosity that sharply increases the hydrophilicity, as proved by the decrease of the contact angle, enhanced the adsorption capacity and thus, the photocatalytic activity. $\text{TiO}_2\text{-AcAc-Brij58}$ coating presents the best efficiency. The low contact angle indicates that the hydrophilic surface facilitates the adsorption of the contaminants improving the photocatalytic activity [37,42]. During the heat treatment and elimination of the surfactant, the inorganic phase likely mimics the textural properties of the surfactant, modifying the hydrophilic/hydrophobic pore surfaces and, therefore the photocatalytic performance of the coatings.

The main reaction products detected in the reaction outlet were CO_2 and COCl_2 (Figure 2.b and 2.c). As previously reported, CO, DCAC (dichloroacetylchloride) and HCl were also detected in the outlet gas stream in minor amounts [43], [44] (data not shown). The expected behaviour was observed and the signals for all reaction product decrease with the total gas flow. The photoactive materials that showed the fastest reaction rates were the ones that presented higher amounts of CO_2 and COCl_2 . The data related to $\text{TiO}_2\text{-AcAc-F127}$ indicated that the TCE photodegradation is high due to the formation of DCAC, explaining the lower CO_2 and COCl_2 amounts (see section 3.2.2).

The influence of the complexing agent on the photocatalytic degradation of TCE is observed in Figure 3. The TCE conversion along with TCE, CO_2 and COCl_2 concentration in the outlet are shown in this figure. The better performance of samples prepared with acetic acid is clearly observed, increasing the TCE conversion around 20

%. Both materials present similar refraction index (around 2.1) and similar contact angle.

The different behaviour could be associated to the modification of the textural properties. Moreover, according to XRD results, acetic acid favours the formation larger TiO₂-anatase crystals and this feature seems to play an important role in the photocatalytic performance.

In order to optimize the effective use of photons by TiO₂, samples with different number of layers were prepared. The results obtained with samples synthesised with acetic acid and Brij 58, the ones that showed the best photocatalytic activity results, is shown in Figure 4. A remarkable increase of the TCE conversion when the layer thickness changed from 160 to 240 nm, especially at a lower contact time, was observed. Nevertheless, the addition of a third layer increased the thickness up to 360 nm but did not produce a significant change in the activity. Since an intermediate treatment of 350°C/1h was performed after the deposition of each layer, an important reduction of porosity must be considered (Table 1) [45]. Consecutive heat-treatments likely collapsed the structure with the subsequent densification of the films. UV radiation penetrates only to a limited length and the diffusion of TCE molecules from the gas phase to the photocatalyst active sites is possibly inhibited by the increasing number of layers and the densification of the coating. Thus, the optimum thickness of the TiO₂ layer for maximum efficiency was set around 250 nm.

3.2.2 Effect of the relative humidity

Since vapour water is a common molecule present on the polluted gas streams, the effect of the relative humidity in the photocatalytic degradation of TCE was studied. Values of TCE degradation and reaction products concentration were taken at steady state conditions, in order to avoid the effect of irradiance and temperature during the warming up of the lamps. Examples of the FTIR spectra at different relative humidity for AcOH-Brij 58 (250 nm) are shown in Figure 5a. The ones corresponding to the 78 % water vapour content was not included for the sake of clarity. Trichloroethylene presented a characteristic band centred at 960 cm⁻¹. In the absence of water vapour, the presence of CO₂ (2,349 cm⁻¹), CO (2,144 cm⁻¹), phosgene (1,827 cm⁻¹) DCAC (1,076 cm⁻¹) and HCl (2,885 cm⁻¹) was appreciated. But the addition of water vapour leads to

the appearance of strong bands between 4000-3400 cm⁻¹ and 2100-1200 cm⁻¹ overlapping with those of CO, COCl₂, DCAC and HCl. The signal corresponding to water was subtracted from the original spectrum (Figure 5.b.). The intensity of the COCl₂ band kept constant within 0 % to 50 % RH but decreased significantly at 78% RH. Thus, a relationship between the CO₂/COCl₂ ratio and the water vapour content was observed.

TCE conversions as well as CO₂ and COCl₂ quantities at steady state conditions are shown in Figure 6 for the different photocatalysts. The results corroborate the effects observed in the absence of water. Coatings prepared from sols with AcOH, dense or porous, presented better photocatalytic activity than those deposited from sols with acetyl acetone. Moreover, the increase of the porosity by the addition of surfactants improved the photocatalytic properties of the TiO₂ thin films even in the presence of high quantities of water vapour. The incorporation of water vapour at contents above 50 % led to a drastic decrease of the photocatalytic activity and consequently to lower CO₂ and COCl₂ formation. This was explained through the TCE and H₂O competition for the same active sites. Figure 7 shows the adsorption isotherm of the AcOH-Brij-58 coating obtained by spectral ellipsometry compared to the evolution of the TCE conversion. At low RH, V_{ads}/V_{film} and TCE conversion changed very slowly. Above 50 % RH, V_{ads}/V_{film} sharply increased, associated to the filling of the pores with molecular water. As a consequence, the exposed surface decreased and therefore, TCE conversion began to fall. When the pores were practically full, condensation of water took place and TCE absorption was impeded because the surface suffered a violent decrease. This result is in line with the photocatalytic behaviour described above.

It is important to notice that TCE conversion was not modified within relative humidity range between 0-50% but, on the contrary, mineralization was promoted. Considering that the amount of COCl₂ is constant in this RH range, the main reaction pathway at this condition was the direct decomposition of TCE into CO₂ according to eq. 1.

Nevertheless, others side reactions must be taking into consideration to justify the behaviour of COCl_2 . One possibility could be the direct oxidation of TCE (Eq. 2) but with a lower reaction rate than in the absence of water vapour in the stream.

In the case of DCAC formation (data not shown) a progressive decrease with water vapour content was observed. These results seem to indicate that the decomposition of DCAC into COCl_2 could be a side reaction pathway and a source of COCl_2 according to Blake et al [30] [43] (Eq. 3-4). Thus, the net balance for COCl_2 was close to zero, and apparently no differences in the COCl_2 concentration were appreciated.

Our results showed that the incorporation of hydroxyl groups from water vapour increases the TCE reaction rate for Eq.1 but did not favour hydrolysis of COCl_2 at the operating conditions selected as some authors have suggested [30][31][32]. In spite of the formation of undesired products even in the presence of water vapour, increasing the residence time or including an adsorbent bed to promote the hydrolysis reaction [30] could be possible strategies to minimise the concentration of non desirable reaction compounds.

Conclusions

The incorporation of surfactants as pore generating agents resulted in titania coatings with lower crystal size, refractive index, and higher pore volume. The presence of mesoporosity reduced the internal mass transfer limitations increasing the photocatalytic behaviour compared to dense films. In this respect, the best results were obtained with TiO_2 -AcOH-Brij58 coatings. The studies on the influence of the complexing agent showed better photocatalytic behaviour for coatings prepared from acetic acid containing sols respecting to those synthesised with acetyl acetone.

Finally, the effect of the relative humidity (RH) in the photocatalytic degradation of TCE showed that the direct TCE oxidation pathway was favoured in the presence of water vapour. The quantification of the different reaction products have to be carefully analysed. Although a general overview of the spectra seems to indicate that the COCl_2 signal disappearance, the subtraction of the water signal showed the formation of COCl_2 . The concentration of COCl_2 did not changed with water vapour content between 0-50% R.H, suggesting that the hydrolysis reaction did not take place at the reaction conditions selected.

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Table(s)

Composition	e (nm)	n (700nm) ± 0.05	Contact angle (°)	Density	Volume pore (%) ±5%	Pore size(nm) ± 10%	Ss(m ² /cm ³) ± 10%	Ss(m ² /g) ± 10%	Surface exposed per cm ² /sample (cm ²) ± 10%	Crystal size ± 10%
TiO ₂ -AcAc	170	2.11	50	3.66	-----	-----	-----	-----	-----	40
TiO ₂ -AcOH	225	2.15	57	3.74	-----	-----	-----	-----	-----	45
TiO ₂ -AcAc-PEG	180	2.09	32	3.63	4	10	8	2	0.7	42
TiO ₂ -AcAc- F127	200	1.75	53	2.78	28	10	55	20	7	25
TiO ₂ -AcAc-Brij58	250	1.77	38	2.80	27	11	43	15	5	33
TiO ₂ -AcOH-Brij58	170 (1 layer)	1.70	32	2.64	32	11	74	28	13	29
	250 (2 layers)	1.80	63	2.90	27	6	93	32	24	28
	360 (3 layers)	1.84	65	3.02	23	5	95	32	34	27

Figure 1. Adsorption-desorption isotherms for TiO₂-AcAc-Brij58- (■ adsorption, □ desorption) and TiO₂-AcAc-PEG coatings (● adsorption,○ desorption).

Figure 2. Photocatalytic activity results obtained for dense and porous TiO_2 thin films with two layers prepared with acetylacetone and different surfactants: AcAc-dense(◆,◇), AcAc-Brij 58 (■,□), AcAc-PEG(●,○), AcAc-F127(▲,△).

Figure 3. Effect of the complexing agent on the TCE conversion and main reaction products for dense TiO_2 films: AcOH-dense (●,○), AcAc-dense (◆,◇).

Figure 4. Influence of thin film thickness in the photodegradation of TCE for samples prepared AcOH-Brij 58: AcOH-Brij 58-1 (■, □), AcOH-Brij 58-2 (▲, △), AcOH-Brij 58-3 (●, ○).

Figure 5. a) FTIR spectra collected at steady state conditions for porous TiO₂ films AcOH-Brij 58 with two layers at different relative humidity content. b) Subtraction spectra. Operating conditions: total flow: 200 ml min⁻¹, [TCE] = 90 ppm, R.H. = 0-80 %.

Figure 6. Variation of the photocatalytic efficiency and main reaction products with the relative humidity for samples: AcOH-Brij58 (▲,△), AcAc-Brij 58 (■, □), AcOH-dense (●,○), AcAc-dense (◆,◇).

Figure 7. Evolution of the V_{ads}/V_{film} (O) and TCE conversion (▲) with the relative humidity for TiO_2 -AcOH-Brij58 sample.

Photocatalytic performance on TiO_2 thin films for TCE abatement
Increase of the photocatalytic activity by effect of the pore generating agent.
Influence of the relative humidity on the mineralization.
Formation of COCl_2 even at low water partial pressure.

Supplementary Material

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