

OPTICAL DENSITY AND PHOTONIC EFFICIENCY OF SILICA-SUPPORTED TiO₂ PHOTOCATALYSTS

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Abstract

Over the last years, many research groups have developed supported TiO₂-based materials in order to improve the engineering applications of photocatalytic technologies. However, not many attempts have been made to evaluate the optical behaviour of these materials. This work focuses on the study of the photonic efficiencies of silica-supported TiO₂ photocatalysts following the photodegradation of dichloroacetic acid (DCA) as model compound. Catalysts with different types of silica support and titania loadings were tested and their activity was found to be in correlation with the results of the clusters size distribution of the TiO₂ nanocrystals. The photonic efficiency of the supported photocatalysts depends extremely on the optical density of the solid suspensions. Influence of the textural properties of the support and the titania loading on the optical density as well as on the photonic efficiency of the materials are discussed. The dependence of the absorption of radiation by the suspension on the catalyst concentration is also analyzed.

Keywords: Photocatalysis, photonic efficiency, optical density, supported TiO₂, dichloroacetic acid

1. Introduction

TiO₂ photocatalysis has been shown as an environmental-friendly technology for the detoxification of industrial effluents. It has been shown that a large number of chemical pollutants are susceptible of being oxidized through heterogeneous photocatalytic processes (Ollis and Al-Ekabi, 1993; Blake, 1994a, 1994b, 1996, 1999, 2001; Hoffmann, 1995; Schiavello, 1997; Herrmann, 1999; Alfano *et al.*, 2000). However, the commercial application of this method for the treatment of aqueous solutions is limited by both the recovery of the catalyst after the reaction and the economical feasibility of photocatalytic processes, conditioned by the efficiency in the use of the radiation. On this basis, many researchers have developed supported photocatalysts with suitable recovery and optimal light absorption properties (Pozzo *et al.*, 1997; Byrne *et al.* 1998).

The results reported in the literature confirm a higher activity of powdered TiO₂ compared with supported systems for most photocatalytic reactions. However, the need for down-streams processes to remove the catalyst is a strong motivation for the search of highly active supported photocatalysts. On the other hand, the use of a support can introduce diffusional restrictions to the mass transport of the pollutants (Chen *et al.* 2001) and hindrances to the light absorption by the semiconductor, thus reducing the overall photonic efficiency. For that reason, besides the conventional requirements of a support for heterogeneous catalysts, the materials used as supports for photocatalytic purposes must also fulfill stringent optical properties such as transparency to UV-A light, in order to achieve high photonic efficiencies and to minimize the energy consumption required for the illumination.

Despite the large number of supported TiO₂ photocatalysts reported in the last years, few attempts have been made to evaluate the optical behavior of these materials in terms of photonic efficiencies or quantum yields, optical parameters standardized by the IUPAC (Serpone and Salinaro, 1999; Salinaro *et al.* 1999). It is important to note that these parameters are absolutely required for the rigorous design and scaling-up of photocatalytic reactors in order to accomplish a commercial application of photocatalytic technologies (Curcó *et al.*, 2002; Sagawe *et al.* 2003a, 2003b).

The goal of this work is to report the results obtained during the evaluation of the photonic efficiencies of several supported photocatalysts recently developed (van Grieken *et al.*, 2002) and to compare them with those obtained employing commercially available Degussa P25 powder samples. The degradation of dichloroacetic acid (DCA) has been chosen as the model reaction, due to the presence of this compound in the biological degradation pathway of a large number of chlorinated hydrocarbons and due to the fact that the

photocatalytic degradation of DCA has been studied extensively evincing that a single electron/hole pair suffices for its complete oxidation. The influence of different variables such as titania loading, type of silica support and catalyst concentration is discussed. One important conclusion of the work is that an unbiased comparison of the photoactivity of supported photocatalysts is not an easy task, because similar optical properties and semiconductor contents could not simultaneously achieved.

2. Materials and Methods

2.1. Catalyst synthesis and characterization

The synthesis procedure of the silica-supported TiO₂ photocatalysts has been reported elsewhere (van Grieken *et al.*, 2002). Nanocrystalline clusters of TiO₂ were obtained through a sol-gel method, i.e., by the condensation of the required amount of titanium tetraisopropoxide inside the porous structure of the silica support. Different types of mesoporous silica materials have been used: an amorphous commercial SiO₂ (Grace Sylopol 2104, GrSiO₂) with a wide pore size distribution and the so-called SBA-15 silicas, mesostructured materials with well defined pore sizes. The characterization of the samples shows differences in the textural properties and in the TiO₂ crystal size depending on the TiO₂ loading and the silica type (see table 1). More details about the synthesis, characterization and photoactivity of these materials are given elsewhere (van Grieken *et al.*, 2002; Aguado *et al.*, 2002; Lopez-Muñoz *et al.*, 2005).

Table 1. Physical properties of the supported TiO₂ photocatalysts.

Photocatalyst	BET surface (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	BJH average pore size (nm)	XRD average crystal size (nm)
GrSiO ₂	317	1.59	19.1	-
20% TiO ₂ /GrSiO ₂	299	1.16	17.1	6.8
40% TiO ₂ /GrSiO ₂	246	0.94	17.5	8.0
60% TiO ₂ /GrSiO ₂	179	0.67	17.3	12.2
SBA-15	640	0.96	6.3	-
20% TiO ₂ /SBA-15	532	0.33	6.0	6.2
40% TiO ₂ /SBA-15	442	0.32	5.9	6.7
60% TiO ₂ /SBA-15	349	0.18	5.8	6.8
SBA-15-TMB	601	1.62	12.4	-
20% TiO ₂ /SBA-15-TMB	517	1.40	11.1	6.4

2.2. Photocatalytic degradation test

Photodegradation experiments were carried out using a lamp field photoreactor with $64 \times 110 \text{ cm}^2$ of illuminated surface, covered with a light homogenizer of UV-A transparent glass and four perpendicular reflectors in order to obtain a frame of diffuse and homogeneous light (see figure 1). The emission spectra of the lamps (Phillips Cleo-R UV-A fluorescent lamps) are mainly centered in the 300-400 nm range. The photoreactor consisted of seven rectangular tubes (500x61x13 mm) made of polymethylmethacrylate (Plexiglas®, Röhm GmbH, Darmstadt). Each tube was filled with 200 ml of the reaction suspension ten minutes after switching on the lamps, to ensure constant light emission. Both outer tubes were not used for reactions to avoid side-effects in the irradiation of the catalyst. Stirring and aeration was achieved by air bubbling through perforations in the bottom of each reactor tube. The incident photon flux measured by a Dr. Hönle UV-A sensitive photometer in the irradiated side of the photoreactor was 20 W m^{-2} , equivalent to $6.0 \cdot 10^{-5} \text{ Einstein m}^{-2} \text{ s}^{-1}$ as calculated for 365 nm wavelength radiation.

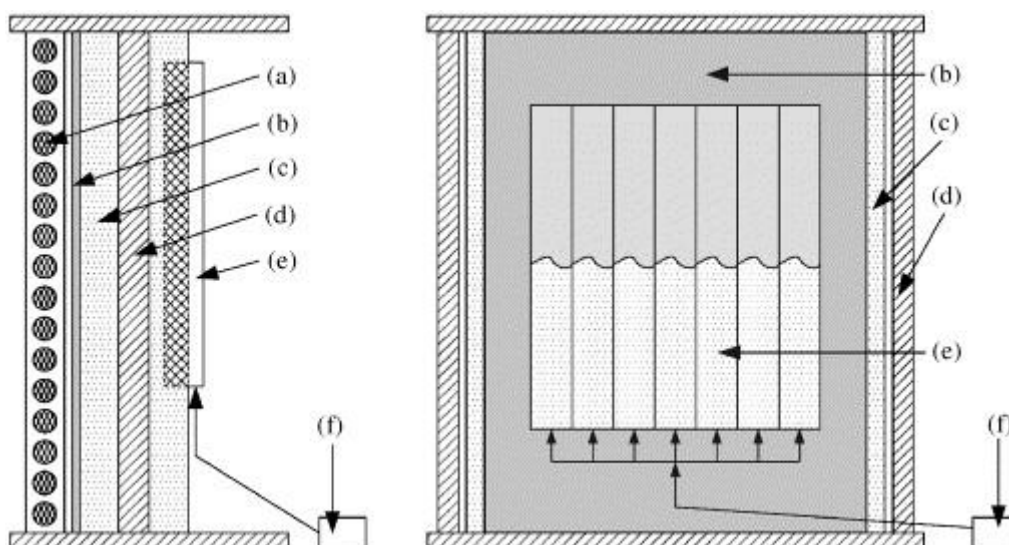


Figure 1. Schematic of the experimental setup: lateral view (left) and front view (right). (a) Fluorescent lamps (illuminating field), (b) homogenizer, (c) reflector, (d) supporting frame, (e) photoreactor, (f) air sparging unit.

The reaction suspensions consisted of 1 mM DCA in aqueous solution and the amount of catalyst to obtain the required TiO_2 concentration. The initial pH value was set to the

desired value (3, 7 or 10 depending on the desired reaction conditions) by addition of sodium hydroxide or nitric acid solutions, respectively. Samples were taken periodically to follow the degradation by chemical analysis after centrifugation. The geometry of the reactor assures the independence of the irradiation conditions during the successive withdrawal of solution, with a fixed relation between volume and irradiated surface area. The degree of the DCA photomineralization was determined by measuring the total organic carbon (TOC) concentration remaining in the clear solution by using a Shimadzu TOC-5000 analyzer. According to the accepted mechanism of DCA photocatalytic degradation (Ollis *et al.*, 1984; Bahnemann *et al.*, 2002), the TOC analysis provides the information of the remaining amount of reactant due to the absence of any stable intermediates during the total mineralization process.

The initial photonic efficiencies were calculated as $\xi = r_{DCA}^0 \text{ (mol l}^{-1} \text{ s}^{-1}) / I^0 \text{ (Einstein l}^{-1} \text{ s}^{-1})$, where r_{DCA}^0 is the initial reaction rate as extrapolated from the DCA degradation profile and I^0 is the incident photon flow per volumetric unit ($I^0 = 4.64 \cdot 10^{-6} \text{ Einstein l}^{-1} \text{ s}^{-1}$) determined by UV-A radiometric measurements. Consequently, the calculated values of ξ are averaged on the wavelength spectrum of the lamp emission, centered in the range 300 – 400 nm.

3. Results and Discussion

3.1. Influence of the SiO₂ support

Preliminary experiments were carried out at pH = 3 and 0.5 g l⁻¹ of TiO₂, in order to compare the influence of the different silica supports at constant 20 wt% loading of titania. Figure 2 illustrates the TOC removal achieved with each supported photocatalyst as compared with the unsupported Degussa P25 commercial TiO₂. The initial photonic efficiency calculated for every catalyst is reported in Table 2. It can be seen that the activity shown by the Degussa P25 TiO₂ powder is higher than the value observed with all of the supported catalysts. Among the latter, the material based on SBA-15 silica shows the highest activity as compared with the catalysts based on amorphous silica and SBA-15 modified with trimethylbenzene (TMB), SBA-15-TMB. TMB addition during the synthesis of SBA-15 silica produces an increase in the average pore size of the material due to its swelling agent nature (van Grieken *et al.*, 2002).

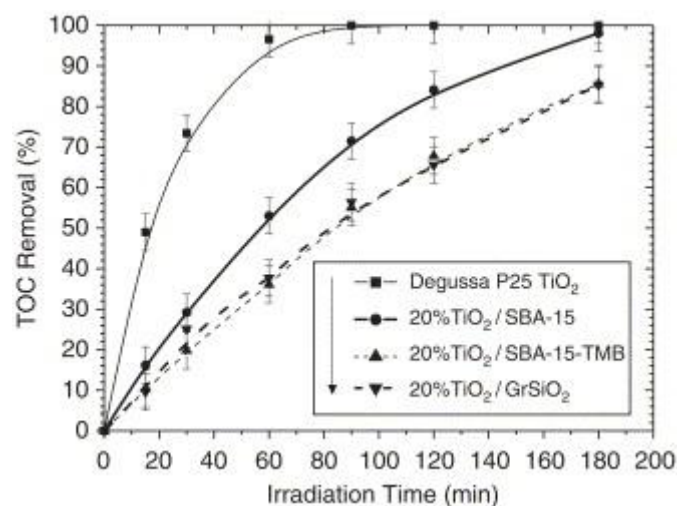


Figure 2. TOC removal during the photocatalytic degradation of 1 mM DCA ($C_{\text{Catal}} = 0.5 \text{ g TiO}_2 \cdot \text{l}^{-1}$; $I^0 = 4.64 \cdot 10^{-6} \text{ Einstein} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$; pH = 3; T = 25°C).

Table 2. Photonic efficiencies ($\text{mol}_{\text{DCA}} \text{ Einstein}^{-1}$) of the supported photocatalysts at different pH values.

	pH value		
	3	7	12
Degussa P25 TiO ₂	0.080	0.059	0.017
20% TiO ₂ /SBA-15	0.031	0.004	0.002
20% TiO ₂ /SBA-15-TMB	0.026	0.012	0.004
20% TiO ₂ /GrSiO ₂	0.021	0.008	0.003

Similar results have been previously obtained for the photooxidation of cyanides (van Grieken *et al.*, 2002). The lower activity of the supported catalysts as compared with powdered TiO₂ can either be explained in terms of a lower intrinsic activity of the TiO₂ particles or by the existence of transport restrictions (of chemicals or photons) due to the support. Concerning the higher activity of the TiO₂/SBA-15 photocatalyst, this fact has been explained in terms of the well-defined TiO₂ crystal size distribution obtained by using SBA-15 silica as support (López-Muñoz *et al.*, 2005) in comparison with the amorphous structure of the commercial silica or the too wide pore size of the SBA-15-TMB silica.

The optical properties of the suspensions were studied by the measurement of the transmitted photon flux. Figure 3 shows the comparison between the initial photonic efficiency determined for the DCA degradation at pH 3 and the UV-A transmittance of the

catalyst suspension placed inside the reactor. It is obvious that large differences of the UV-A transmittance were obtained depending on the catalyst. Whereas for Degussa P25 there is a complete absorption of the radiation under the employed reaction conditions, the absorption of the supported catalyst suspensions can be increased with higher catalyst concentration or by using a thicker reactor plate, thus probably improving their photoactivity.

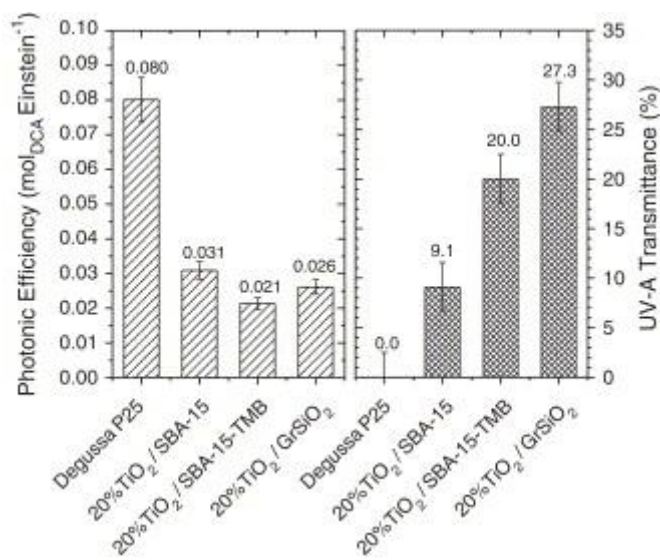
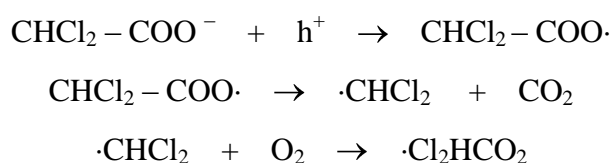
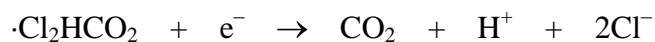


Figure 3. Photonic efficiency for DCA photodegradation and UV-A transmittance of Degussa P25 and TiO₂ supported on different silica materials ($C_{\text{Catal}} = 0.5 \text{ g TiO}_2 \cdot \text{l}^{-1}$; $I^0 = 4.64 \cdot 10^{-6} \text{ Einsteinl} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$; pH = 3; T = 25°C).

Regarding the influence of the initial pH of the solution on the photonic efficiency, the study of the DCA photodegradation was carried out at initial pH values of 3, 7 and 10. It must be noticed that these are initial values and that the pH was not controlled during the reaction. Consequently, a decrease of the suspensions pH was noticed as the mineralization of DCA proceeds, especially when the initial pH was 7. The results shown in Table 2 confirm the dependence of the photonic efficiency reported previously (Lindner *et al.*, 1997). According to these authors, the photocatalytic degradation of DCA is a photo-Kolbe process that takes place through the following reactions:





Bahnemann *et al.* (1997) reported that the initial degradation step occurs with the valence band holes as the main oxidizing species. This process requires the DCA molecules to be adsorbed on the TiO₂ surface. Taking into account that DCA is almost totally dissociated in the tested pH range (pK_a = 1.29), the interaction should be maximum in acid media, where the TiO₂ surface is positively charged.

From Table 2 it can be seen that the initial photonic efficiency of the catalyst Degussa P25 increases as the initial pH value decreases. In addition to that, the dependence of the activity on the pH of the solution observed for the supported photocatalysts shows the same trend as that obtained for the Degussa P25 TiO₂ powder. Moreover, the initial reduction of the DCA concentration in solution due to the adsorption equilibrium prior to the beginning of the reaction is found to be negligible in all cases, including experiments with P25. Consequently, despite the higher surface area of the supported photocatalysts, no evidence of a significant adsorption of DCA on the silica surface has been found. This is readily explained by the fact that the SiO₂ surface is negatively charged over the entire pH-regime studied here thus preventing a significant adsorption of the anionic DCA molecule. These results suggest that there is no change in the mechanism of the DCA photocatalytic degradation resulting from the presence of the silica support.

3.2. Influence of TiO₂ loading

Figure 4 shows the results obtained for the initial photonic efficiencies measured for the DCA degradation and the change of UV-A transmittance with increasing TiO₂ loadings on SBA-15 and amorphous silica. It can be seen that a slightly higher activity for the DCA photooxidation is obtained with SBA-15 based materials as compared with amorphous silica based materials containing similar TiO₂ loadings. Additionally, it is interesting to note that the activity results of the amorphous silica based materials are almost independent on the TiO₂ loading. On the other hand, for the SBA-15 based materials, there is a maximum in activity at 40 wt% of TiO₂.

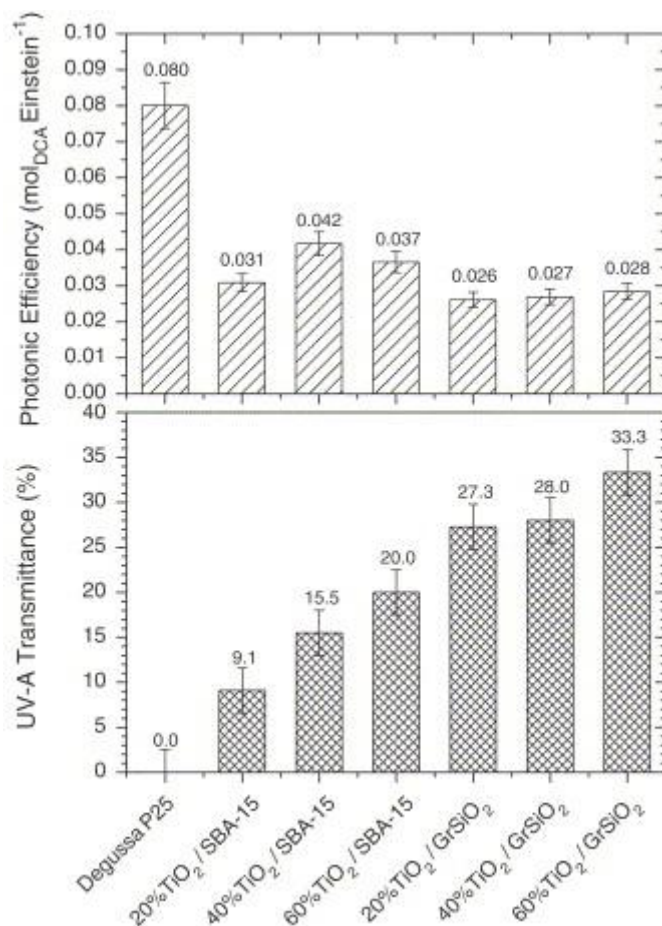


Figure 4. Influence of the titania loading on the initial photonic efficiency for DCA photodegradation and on the UV-A transmittance of the different catalyst suspensions ($C_{\text{Catal}} = 0.5 \text{ g TiO}_2 \cdot \text{l}^{-1}$; $I^0 = 4.64 \cdot 10^{-6} \text{ Einstein} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$; pH = 3; T = 25°C).

Concerning the UV-A transmittance results shown in Figure 4, since the TiO₂ concentration and the optical path are the same for all the experiments, a higher UV-A transmittance is due to a lower optical density of the material. It should be noticed that the optical density of the catalysts decreases as the loading of TiO₂ increases.

The analysis of the data does not show a correlation between the UV-A transmittance of every catalyst suspension and the photonic efficiency value. Whereas for the amorphous silica, the activity is, as expected, independent on the optical density, the rather weak maximum in the activity of the catalysts 40%TiO₂/SBA-15 cannot be related with the transmittance of the suspensions. It is important to notice that the TiO₂ crystal size and the intrinsic activity of the semiconductor in the SBA-15 supported materials is independent upon the TiO₂ loading (van Grieken *et al.* 2002). Taking into account all these considerations, the activity of the samples apparently does not only depend upon the intrinsic TiO₂ activity and the optical density but also upon the diffusion rates into the structure of the different supports.

In summary, the higher activity of the 40%TiO₂/SBA-15 catalysts could probably be due to a combination between a higher concentration of the active phase within the solid (increasing the absorption to scattering ratio of the radiation) and the lower diffusion rate in the highly-occupied channels of the 60%/SBA-15 photocatalyst.

3.3. Influence of catalyst concentration and optical density

In order to clarify the influence of the TiO₂ concentration and the optical density on the photonic efficiency for the DCA degradation, further studies have been performed varying the catalyst concentration. Figure 5 shows the results obtained with the different 20 wt% TiO₂ supported catalyst and with Degussa P25 TiO₂. Once again it is obvious that the photonic efficiency for Degussa P25 TiO₂ powder is higher than that obtained for the supported catalysts in the tested range of TiO₂ concentration (0.1 – 2.0 g l⁻¹). However, it is worth mentioning that whereas the catalyst Degussa P25 reaches at a concentration of 0.1 g l⁻¹ of TiO₂ 80% of its maximum activity, the supported materials increase their activities up to four times at higher concentrations of TiO₂. Consequently, differences in activity between Degussa P25 and the supported materials are reduced by increasing the TiO₂ concentration.

Taking into account the values of UV-A transmittance for each catalyst suspension shown in Figure 5, the results could be explained in terms of the amount of radiation absorbed by the suspension of the catalysts. For Degussa P25, radiation extinction is complete at a TiO₂ concentration of 0.5 g·l⁻¹. This factor leads to a negligible increase in activity at higher TiO₂ concentration values. On the other side, the optical density of the 20%TiO₂/SBA-15-TMB and 20%TiO₂/GrSiO₂ suspensions is increased and thus the activity is improved as the TiO₂ concentration increases. By contrast, the activity of the material 20%TiO₂/SBA-15 is not significantly increased at TiO₂ concentrations higher than 0.5 g·l⁻¹, because of the higher optical density shown by this support.

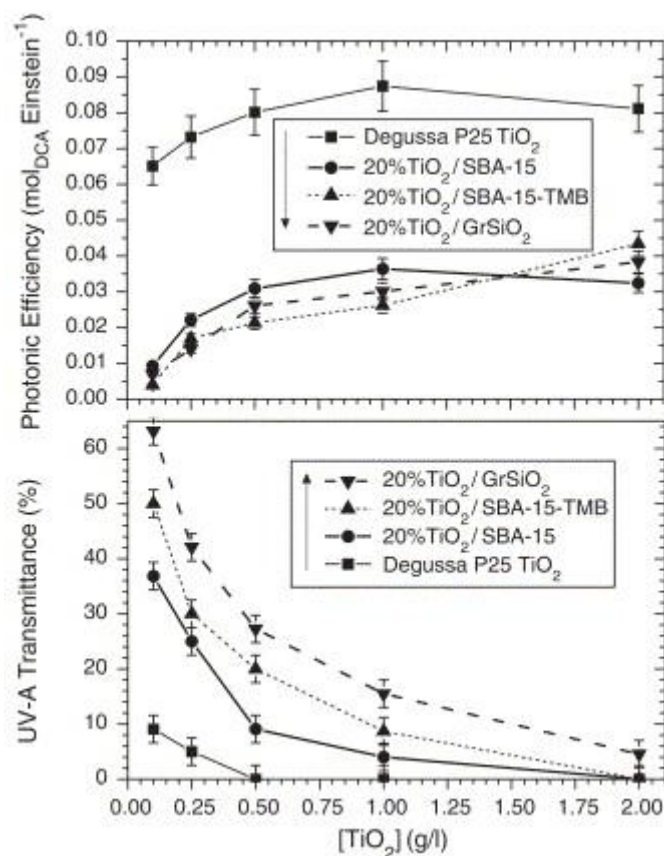


Figure 5. Influence of the TiO₂ concentration on the initial photonic efficiency for DCA photodegradation and on the UV-A transmittance of the different catalyst suspensions ($I^0 = 4.64 \cdot 10^{-6} \text{ Einstein} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$; pH = 3; T = 25°C).

Concerning the TiO₂ loading, Figure 6 shows the dependence of both the photonic efficiency and the UV-A transmittance on the catalyst concentration for catalysts supported on amorphous silica with different TiO₂ loadings. In this case, differences in activity and optical density are not pronounced. For catalyst concentrations above 0.5 g·l⁻¹ of TiO₂, a slightly increase in the photonic efficiency is achieved by increasing the TiO₂ loading of the material. Based on the characterization data shown in table 1, it seems unlikely that differences in the intrinsic activity of the TiO₂ crystals or in the diffusion rate for the mass transport of the pollutant inside the porous structure of the support are responsible for the higher photonic efficiency of the materials as the TiO₂ loading increases. Therefore the optical properties of the materials are supposed to be the main factor affecting the activity of these supported catalysts. The UV-A transmittance data show that differences in the optical density of the materials are not sufficient to explain the higher photonic efficiency upon the increasing TiO₂ loadings. Taking into account that a higher TiO₂ loading requires less amount of silica particles for the same semiconductor content, the improvements in the optical

behavior could be produced by an increase in the radiation absorption to scattering ratio. This conclusion is sustained by considering that only the semiconductor content produces the radiation absorption whereas the support particles act as scattering centers.

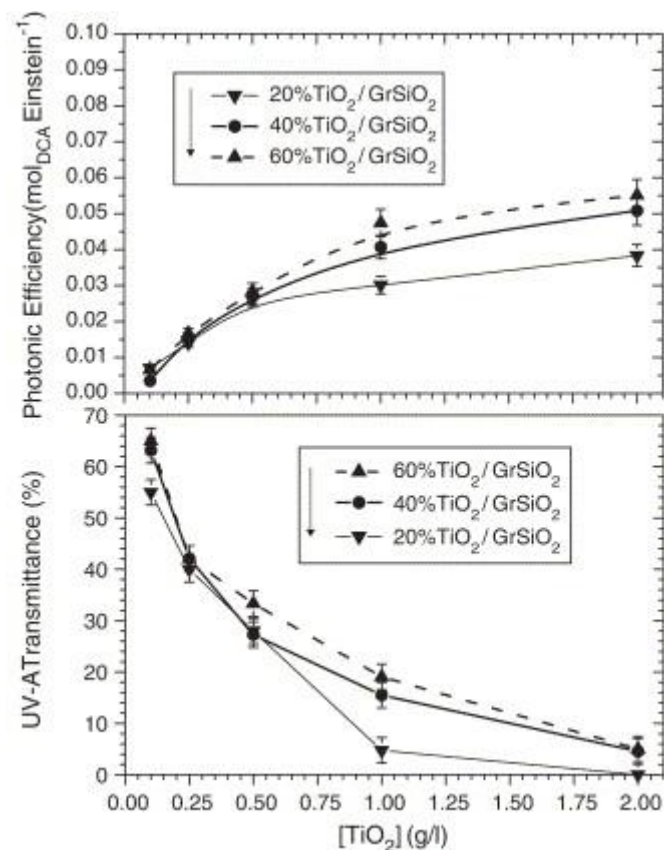


Figure 6. Influence of the TiO₂ concentration and TiO₂ loading over amorphous silica in the initial photonic efficiency for DCA photodegradation and UV-A transmittance of the different catalyst suspensions ($I^0 = 4.64 \cdot 10^{-6}$ Einstein \cdot l⁻¹·s⁻¹; pH = 3; T = 25°C).

Regarding the catalysts supported on SBA-15 silica, Figure 7 shows the influence of the catalyst concentration on the photonic efficiencies for DCA photodegradation for different TiO₂ loadings. It is obvious that the activity of the materials is almost independent of the TiO₂ loading at low catalysts concentrations. However, as the amount of catalyst increases, differences in activity become more significant and for 2.0 g·l⁻¹ of TiO₂ the photonic efficiency of the catalyst 40%TiO₂/SBA-15 is twice as high as the value observed with the 20%TiO₂/SBA-15 material. Figure 7 also shows that the dependence of the UV-A transmittance on the catalyst concentration for these SBA-15 supported photocatalysts is not significant.

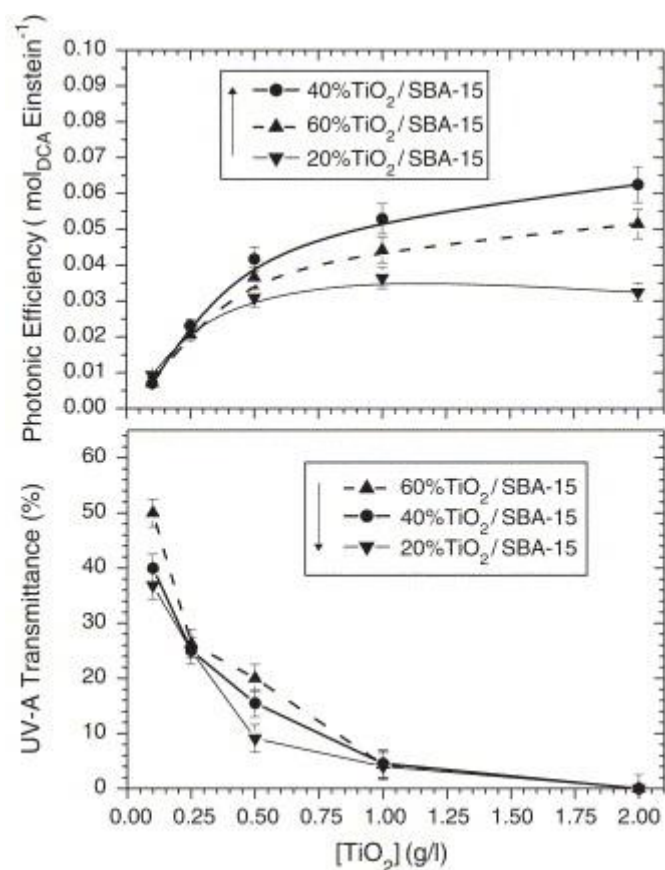


Figure 7. Influence of the TiO₂ concentration and the TiO₂ loading over SBA-15 silica on the initial photonic efficiency for the DCA photodegradation and the UV-A transmittance of the different catalyst suspensions ($I^0 = 4.64 \cdot 10^{-6}$ Einstein \cdot l⁻¹·s⁻¹ ; pH = 3; T = 25°C).

In summary, we can conclude that the higher optical density of the SBA-15 silica in comparison with the amorphous silica could not totally explain the higher activity of all the SBA-15 based photocatalysts as compared with the amorphous silica based materials. In addition, the narrower crystal size distribution achieved by using this mesostructured material seems to have an important effect.

Concerning the TiO₂ loading, it can be concluded that, generally speaking, an increase in the TiO₂ content of the material leads to higher photonic efficiencies at constant TiO₂ concentration due to the reduction in the scattering effects achieved by the use of less particles of the silica support. However, by using SBA-15 silica as support this beneficial effect at high TiO₂ loading is counteracted by an increase in the diffusional problems, thus leading to the fact that the catalyst 60%TiO₂/SBA-15 is less photocatalytically active than the 40%TiO₂/SBA-15 material.

4. Conclusions

It is important to point out that an unbiased comparison of the photoactivity of supported photocatalysts is not an easy task. Due to different scattering properties of the different catalysts preparation, the use of the same amount of light-absorbing semiconductor material cannot guarantee a correct evaluation of the photonic efficiencies. On the other hand, the use of different catalyst concentrations to ensure similar absorption of the incoming radiation within the reactor also fails to perform the comparison properly due to the different semiconductor content. These facts show the high importance of both the catalytic and the optical properties for the design of an optimal photoreactor.

Based upon our results, the photocatalyst 40%TiO₂/SBA-15 shows the maximum activity of all tested materials, independently on the catalyst concentration and therefore the transmittance of the suspension. This fact could imply the existence of an optimal choice of the support and the TiO₂ loading in order to obtain an adequate TiO₂ activity limiting the detrimental effect of the radiation scattering caused by the silica particles and the diffusional restrictions inside the porous catalyst structure.

Acknowledgements

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