Catalysis Today 151 (2010) 77–83

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Influence of photocatalytic paint components on the photoactivity of P25 towards NO abatement

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ARTICLE INFO

Article history:
Available online 4 March 2010

Keywords:
P25
NO
Photocatalysis
Paint components

ABSTRACT

The present work studies the effect of the components of a photocatalytic paint towards the photooxidation of NO. It was used a vinyl high quality exterior paint, modified with photocatalyst P25. NO conversion and selectivity towards nitrate and nitrite were obtained in an experimental photocatalytic reactor that implements essentially the standard ISO 22197-1:2007(E).

It is concluded that the paint matrix plays an important role on the photocatalytic activity: pigmentary TiO_2 absorbs competitively the UV light, being the most critical component affecting the photocatalytic activity; extenders, such as $CaCO_3$, impair the photoactivity, especially when water is involved in mixing the paint components; organic components mostly affect the performance of the paint during a transient period time of *ca.* 100–250 h.

1. Introduction

Air pollution has been calling the attention of the public in general [1]. Amongst numerous air pollutants, hazardous gases for human health are of particular concern, mainly in urban and industrial areas.

Presently, more than a half of the population in developed countries lives in highly dense traffic cities. Such way of living exposes people to toxic gases like carbon monoxide and nitrogen oxides ($NO + NO_2$). End of pipe technologies developed over the last decades have been particularly important to decrease the emission of hazardous gases to the atmosphere. However, some gases are still present in the atmosphere above their legal limits; NO_x, mainly produced by vehicles, is one of such examples. NO_x is above the legal limits established by the European Commission (2008/50/EC) not only in big cities, but also even in small cities with relative low traffic such as Guimarães (Portugal), Patras and Volos (Greece), among others [2,3]. It is therefore necessary to improve and develop new de-pollution technologies.

Photocatalysis is an attractive technology for de-pollution proposes because it uses solar radiation and works at ambient temperatures and at typical low airborne concentrations [4,5]. In a simple way, photocatalysis can be described as a redox process that uses a catalyst activated by photonic energy (photocatalyst).

Photocatalysts have been incorporated into construction materials so they can act as de-polluting agents. They have been incorporated into cement/mortars pavements [e.g. 6,7], coatings [8–12], among others. Maggos et al. [9], for instance, reported a NO photoabatement of *ca.* 40–80% in a canyon pilot street under real weather conditions using mortar panels. Bygott et al. [11] conducted a field trial in London, close to a children playground, where an area of 300 m^2 of walls was painted with a silicate-based paint loaded with 7.5 wt.% of photocatalytic TiO_2. It was reported a daily abatement of *ca.* 4.5 g of NO_x from about 10,000 m^3 of air around the school playground [11].

In order to be commercially attractive, a photocatalytic paint should exhibit a high photoactivity while preventing its own degradation. However, typical photocatalysts processes involving hydroxyl radicals are generally non-selective and strategies for minimizing paint photodegradation must be developed. At the same time, paint components can impair photoactivity concerning the abatement of target pollutants. This can be due to several factors such as blockage of radiation and/or blockage of the gas pollutants itself towards the photocatalyst, electron–hole external recombination or preferential photooxidation of organics present in the paint.

In a previous work by the authors, various commercially available photocatalytic TiO_2 materials were incorporated in an exterior water-based paint [12]. In this study it was noticed a strong influence of the paint components on the NO photooxidation [12]. Paint film incorporating the photocatalyst P25 (Evonik) was, among those tested, the only one requiring a harsher activation procedure to become promptly active. In this way, this

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doi:10.1016/j.cattod.2010.01.057

work aims to study the influence of paint components on the photoactivity of P25.

2. Experimental

2.1. Photocatalytic films

The paint formulation used in the present work is based on an exterior water-based vinyl paint by CIN (Portugal). This paint formulation was modified and half of the pigmentary TiO_2 was replaced by P25 (producing a photocatalytic paint hereafter referred as reference paint – denoted as RP#).

Paint components are typically divided according to their functionality both in the paint in-can and in the final film produced. In the present study paint components were divided according to their physical state and supply form. Therefore paint components were here divided in powder components – pigmentary and photocatalytic TiO_2, extenders and powder thickener – and non-powder or water-dispersed components (hereafter referred as non-powder organic components, for simplicity) – binder (resin) and additives such as thickener, dispersing agents and coalescent.

For evaluating the role of each paint component in the photoactivity of the paint, a series of experiments with increasing number of components was performed – see Table 1. For simplicity, whenever the films are formed by just powder components, they are called powder pressed films (denoted as PP#); the others are called pseudo-paint films (denoted as PsP#). The mass proportion of each component in the final paint was mostly kept constant in the powder and pseudo-paint films.

The powder mixtures were obtained by hand-shaking for 5 min. The powder mixtures were then evenly poured over an aluminium slab and pressed at *ca.* 5 bar for 7 min; the film was then tested for NO photoactivity as described below.

In the case of PP5 (Table 1) the powder mixture was obtained stirring 10 g of the powder mixture used in PP4 into 50 cm^3 of distilled water applying 300 rpm for 30 min followed by sonication for 5 min (Hielscher UIP1000hd, at 90% of amplitude). The slurry was then deposited over a glass plate and dried for 1 day at lab conditions and 1 more day at 50 °C (temperature already higher than the typical maximum a paint usually face). It was then powdered and the powder applied in an aluminium slab, as described before.

In the case of the pseudo-paint films, the powder and non-powder organic components were mixed in a 100 cm^3 vessel with 50 cm^3 distilled water, applying 300 rpm for 30 min. Wet films were produced with the help of a drawn down bar over the aluminium slab and let to dry for 1 day at lab conditions, producing therefore the pseudo-paint films.

All films have an area of *ca.* 10 cm × 5 cm. PP# and PsP#/RP# films have approximately 0.5 mm thickness (estimated using a micrometer) and 60 μm dry thickness (estimated by SEM images), respectively. The initial composition of the pseudo-paint films and their rheology yield different P25 loads in the film. For the case of pseudo and reference paint experiments, the fraction of volatile substances present in each non-powder organic component and the amount of water added for stirring were considered, along with the film weight, to estimate the final P25 load (weight of P25 per area of film) as reported in Table 1.

UV/Vis diffuse reflectance analysis of the films were made using a Perkin Elmer lambda 750 spectrophotometer equipped with a 60 mm integrating sphere and Spectralon® as reflectance standard.

2.2. Experimental setup

The aluminium slabs above referred used to support the testing films were introduced in the down part of the interior of the photoreactor, sketched in Fig. 1. The photoreactor has a borosilicate window (overall light transmittance of 90% over 330 nm) at the top face, above which is placed a UV lamp system (*Vilbert Lourmat* – BLB 365 nm, 2 × 6 W lamps). These units were assembled inside a thermostatic cabinet for temperature control. The setup comprehends also a feed system and a NO_x analyser (*Thermo Electron* 42C). The feed is ensured by a set of mass flow meters and one controller (Hi-Tech *Bronkhorts*) and the corre-

Table 1

Weight percentage of paint components in the film used in each experiment, load of P25 and content of powders and non-powder organic components (dry basis).

Component paint functionality	Description	Weight percentage in dry film basis (wt.%)											
		Powder pressed films						Pseudo-paint films					Reference paint film
		Run PP0	Run PP1	Run PP2	Run PP3	Run PP4	Run PP5[a]	Run PsP6	Run PsP7	Run PsP8	Run PsP9	Run PsP10	Run RP11
Powders													
Photocatalyst	Photo-TiO_2 P25	100.00	25.44	25.44	25.44	25.43	25.43	25.40	25.34	25.34	24.93	18.28	17.45
Extender	$CaCO_3$	–	74.56	–	–	1.63	1.63	1.60	1.59	1.60	1.56	1.12	1.02
Extender	$BaSO_4$	–	–	74.56	–	–	–	–	–	–	–	–	–
Extender	Silicates	–	–	–		46.93	46.93	46.89	46.78	46.66	45.86	33.57	32.56
Pigment	Pigmentary TiO_2	–	–	–	74.56	25.18	25.18	25.16	25.10	25.04	24.60	18.01	17.45
Additive	Powder thickener	–	–	–		0.83	0.83	0.83	0.84	0.83	0.82	0.60	0.58
Non-powder organics													
Extender pigment	Opaque polymeric particles	–	–	–	–	–	–	–	–	–	–	5.11	4.69
Additive	Biocides	–	–	–	–	–	–	–	–	0.41	0.02	–	0.24
Additive	Antifoam	–	–	–	–	–	–	0.12	0.12	0.12	0.13	–	0.08
Additive	Amine	–	–	–	–	–	–	–	0.23	–	0.29	–	0.16
Additive	Dispersing agent	–	–	–	–	–	–	–	–	–	1.79	–	1.26
Additive	Coalescent	–	–	–	–	–	–	–	–	–	–	3.34	4.10
Additive	Thickener	–	–	–	–	–	–	–	–	–	–	–	0.53
Binder	Resin	–	–	–	–	–	–	–	–	–	–	19.97	19.88
	$Load_{P25}$ ($mg\,cm^{-2}$)	13.5	13.9	13.6	13.4	9.7	14.5	2.6	2.6	3.1	6.1	1.8	2.3
	Powders (wt.%)	100.00	100.00	100.00	100.00	100.00	100.00	99.87	99.64	99.47	97.77	71.57	69.05
	Non-powder organics (wt.%)	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.36	0.53	2.23	28.43	30.95

[a] Equivalent to run PP4 but sonicated in a slurry, dried and powdered in mortar (see Section 2.1).

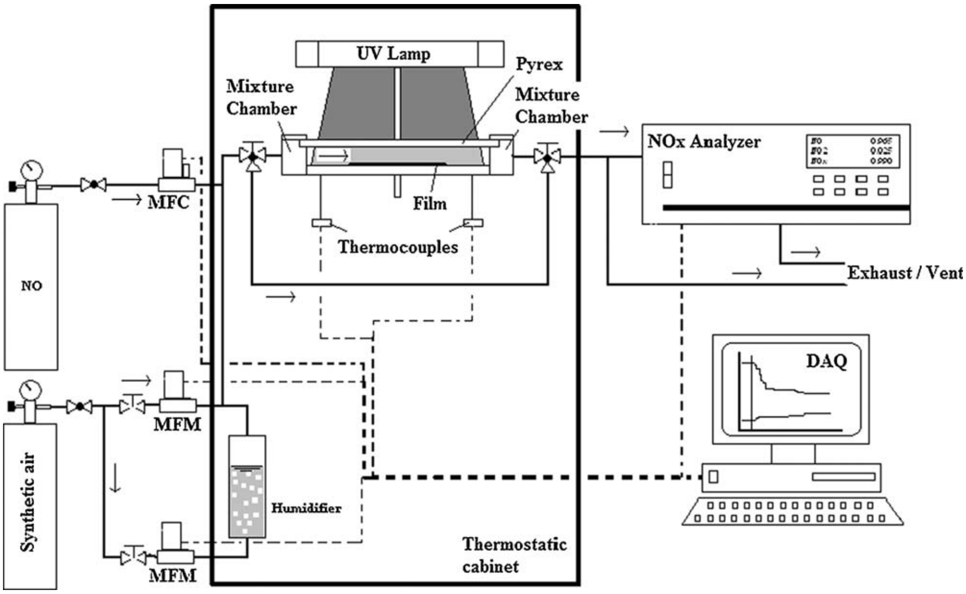

Fig. 1. Sketch of the experimental setup used for the photocatalytic tests (arrows represent the gas flow direction).

sponding relative humidity is adjusted by mixing dry and water-saturated synthetic air streams (the latter obtained allowing the gas to bubble through a water column – referred as humidifier, Fig. 1).

The photoactivity was assessed by means of NO conversion (Eq. (1)) and selectivity towards ionic species (Eq. (2)), i.e. nitrate and nitrite ions.

$$X_{NO} = \left(\frac{C_{NO}^{in} - C_{NO}^{out}}{C_{NO}^{in}}\right) \times 100 \quad (1)$$

$$S = \left(1 - \frac{C_{NO_2}^{out}}{C_{NO}^{in} - C_{NO}^{out}}\right) \times 100 \quad (2)$$

In these equations C_{NO} and C_{NO_2} stand for the concentration of NO and NO_2, respectively, while the superscripts *in* and *out* refer to the inlet and outlet streams of the reactor, respectively.

The operating conditions used were the following: 50% relative humidity (RH), 25 °C, 7 W m^{-2} of irradiance and total feed flow rate of 0.7 L$_N$ min^{-1} containing 1 ppmv of NO. Prior to the photocatalytic tests, the films were let to activate for 5 h in the same operating conditions but in the absence of NO. This procedure follows roughly the standard ISO 22197-1:2007(E). For the case of RP, a harsher activation was required (similar to the one above referred but with 90% RH, 30 W m^{-2} and for 24 h). The steady state was considered to be achieved whenever NO conversion and selectivity do not vary more than ±2.5 percentage points for 5 h, in the case of powder pressed films, and 50 h, in the case of pseudo paint and reference paint films.

3. Results and discussion

3.1. UV/Vis diffuse reflectance

The light that reaches a film can be reflected, absorbed or transmitted. According to the chemical and physical properties of the films, the contribution of each of these three phenomena may vary. Fig. 2 presents the diffuse reflectance of powder pressed (PP) films tested in the photoreactor, in which transmittance of radiation is negligible, as discussed below.

P25 absorbs light up to the wavelength of 415 nm. However, it is known that the efficiency of the photocatalyst to absorb light decays near to the longest wavelength that it can absorb [5]; accordingly, the reflectance analysis of P25 PP film exhibits a sigmoid-like curve with no significant reflection up to 320 nm (Fig. 2). The reflectance intensity starts then to increase up to the 415 nm wavelength, the minimum energy able to excite electrons in rutile crystal form of P25 (values above 100% are related to the higher reflectance of the powder film compared to the reference material, Spectralon^{TM}).

The spectrum obtained with pigmentary TiO_2 reveals an increase in reflection with the wavelength, again with a sigmoid-shape, particularly in the range 360–450 nm. The low reflection of this material at wavelengths lower than 360 nm arises from the ability of light absorption by TiO_2 (rutile crystalline form).

P25 behaves similarly to pigmentary TiO_2, but the reflectance in the UV region is generally higher. For this difference accounts several properties of the two materials, namely: the particle diameter (25 nm *vs.* 0.36 μm, respectively) and the crystal structure (80% anatase and 20% rutile for P25 and pure rutile for pigmentary TiO_2). Pigmentary TiO_2 has also a surface treatment of alumina and amorphous silica (5.5 wt.%) for minimizing the photocatalytic activity, which otherwise would degrade the paint.

The UV/Vis diffuse reflectance analysis shows that extenders $CaCO_3$ and $BaSO_4$ have a high reflection in the wavelength range analysed (Fig. 2). The spectra of $CaCO_3$ PP films are mostly independent of the support used (B – black, or W – white), indicating a negligible transmittance of these films. This effect was observed for all films tested, indicating that they are optically thick (i.e. their corresponding optical thickness is lower than the film thickness).

When mixing $CaCO_3$ or $BaSO_4$ with P25 (experiments PP1 and PP2, Table 1), films reveal similar spectra as pure P25 (Fig. 2). Reflection spectrum of the PP3 film (P25 + pigmentary TiO_2) lies in general between those of the pure components, but in the wavelength region of concern for photocatalysis (majority of irradiance promoted by the UV lamp system is in between 330 nm and 380 nm), reflectance lies closer to the one of pigmentary TiO_2. Such fact highlights the competitive absorption of photons by both components of this mixture.

Diffuse reflectance of film PP4 (see Table 1 and Fig. 2) reveals a higher UV reflectance than pigmentary TiO_2, which is consistent with the presence of P25; the spectrum of PP4 lies between the one of pigmentary TiO_2 and that of P25.

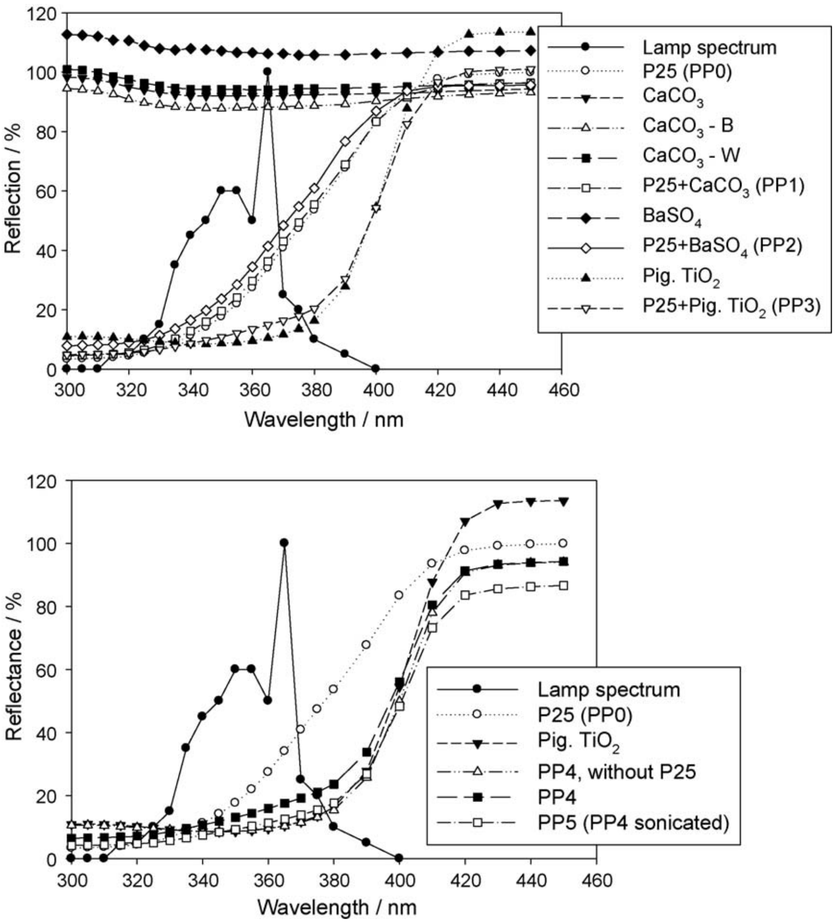

Fig. 2. Reflectance of pure powder films of P25, $CaCO_3$, $BaSO_4$, pigmentary TiO_2 and films tested in the photoreactor (Table 1); it was used an aluminium support for powder deposition except for $CaCO_3$ – B (black support – Leneta test charts) and $CaCO_3$ – W (white support – Leneta test charts).

Analysis of pure extenders was impossible to perform due to lack of powder cohesion.

Film PP5 shows a lower reflectance compared to PP4, particularly up from 340 nm, being more similar to the spectra of pigmentary TiO_2 in the UV region, while revealing the lowest reflection in visible region.

3.2. Photoactivity of powder pressed (PP) films

Fig. 3 shows the NO conversion and selectivity histories on three different powder pressed films of P25. It can be seen that the steady state conversion and selectivity towards nitrate and nitrite were reached after *ca.* 5 h, *ca.* 80% and 45%, respectively. Fig. 3 also shows that tests performed with different P25 films show good repeatability.

Tests performed with powder films of pure P25 (experiment PP0) with different thicknesses (and therefore different loads of P25) have shown no differences in either diffuse reflectance (data not shown) or photoactivity at steady state (Fig. 4). This allows concluding that only a fraction of the P25 in PP0 films becomes photoactive. Consequently, it is not totally possible to establish a direct correlation between photocatalyst load and photoactivity of the film.

Contrarily to the load, photoactivity of the powder film P25 is particularly affected by the film length, which is related to the NO contact time in the photoreactor. It can be seen that not only the conversion is smaller, but also it seems that the selectivity becomes smaller (Fig. 4). Such fact highlights once again that photocatalyst load is not the unique parameter playing a role, as the 6 cm × 5 cm film has a higher load as one of the 10 cm × 5 cm films and a lower conversion.

Fig. 5 presents the photocatalytic results of P25 mixed separately with $CaCO_3$, $BaSO_4$ and pigmentary TiO_2 (experiments PP1–PP3, respectively, cf. Table 1). The formers are extenders typically used in paints while the later is the most typical opacifier in the visible light region of the electromagnetic spectrum used in paint industry. Among all, only $BaSO_4$ does not enter in the

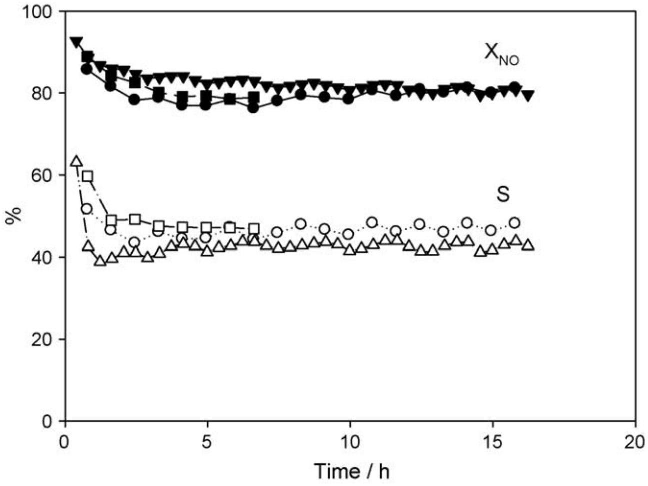

Fig. 3. Conversion (full symbols) and selectivity (empty symbols) histories on 3 different powder pressed films of pure P25 (experiment PP0).

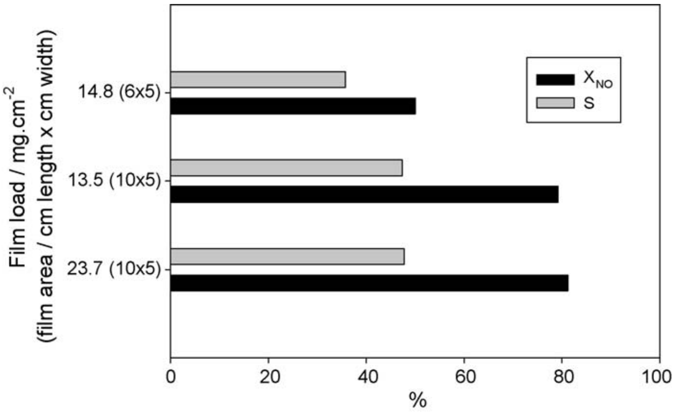

Fig. 4. Steady state conversion and selectivity on PP0 films with different loads and areas of P25: 14.8(6 × 5) – 14.8 mg cm^{-2} and 6 cm × 5 cm (length × width); 13.5(10 × 5) – 13.5 mg cm^{-2} and 10 cm × 5 cm and 23.7(10 × 5) – 23.7 mg cm^{-2} and 10 cm × 5 cm.

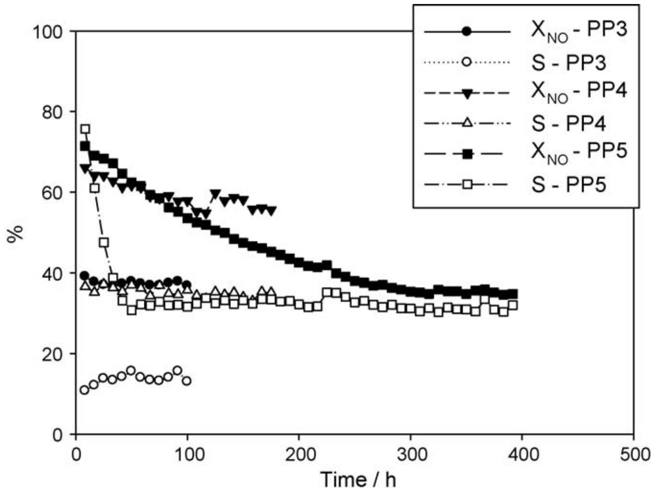

Fig. 6. Conversion (full symbols) and selectivity (empty symbols) history for experiments PP3–PP5.

reference paint formulation used herein. However, as it is a usual paint component, it was decided to use it for comparing with $CaCO_3$ in terms of the film photoactivity. NO steady state conversion on films containing $CaCO_3$ and $BaSO_4$ are similar, *ca.* 55%. The weight percentage of P25 in these films was 25% (cf. Table 1), thus explaining the smaller NO conversion when compared to the one obtained with the PP0 film (pure P25 – X_{NO} = 80%).

Films made with $CaCO_3$ and $BaSO_4$ (PP1 and PP2) show also a similar NO conversion history (Fig. 5). The lower NO steady state conversion obtained with PP3 (*ca.* 40%) should be due to the competitive light absorption between pigmentary TiO_2 and P25, as discussed before.

Regarding selectivity, literature commonly assumes that $CaCO_3$ reacts with the nitrate produced from the photooxidation of NO_x originating $Ca(NO_3)_2$, thus cleaning the photocatalyst surface [9,11]. This could explain the higher selectivity attained when mixing P25 with $CaCO_3$ (experiment PP1, Fig. 5).

Fig. 6 presents the NO conversion and selectivity on films PP4 and PP5 (conversion and selectivity obtained on film PP3 are reprinted for convenience). Film PP4 contains all powder components used in the formulation of the reference paint; basically, 66 wt.% of pigmentary TiO_2 present in PP3 has been replaced by extenders and powder thickener (cf. Table 1). The lower pigmentary TiO_2 concentration on PP4 should result in less competitive absorption of UV light and then on higher NO conversion compared to PP3. PP5 has the same composition as PP4 but the powder components were mixed in an aqueous suspension followed by sonication, drying, powdering and application over the aluminium slab, following the same procedure as for PP4. Despite the similarities between the two experiments, it was observed a significant decrease in the steady state NO conversion (from *ca.* 55% to 35%). Powder paint components used for preparing films PP4 and PP5 are minerals and thickener (see Table 1). Water should dissolve chemical species that stick on the photocatalyst surface impairing its photoactivity at steady state. It was also observed a reflectance decrease, indicating that a partial surface coverage of the photocatalyst occurs.

It is worth noting the increase on the transient period observed for experiments on films PP1–PP5 compared to film PP0, revealing an interference of the powder components.

3.3. Photoactivity of pseudo-paint (PsP) films

Figs. 7–10 show the NO conversion and selectivity histories on pseudo-paint films PsP6–PsP10 and on RP11. The non-powder

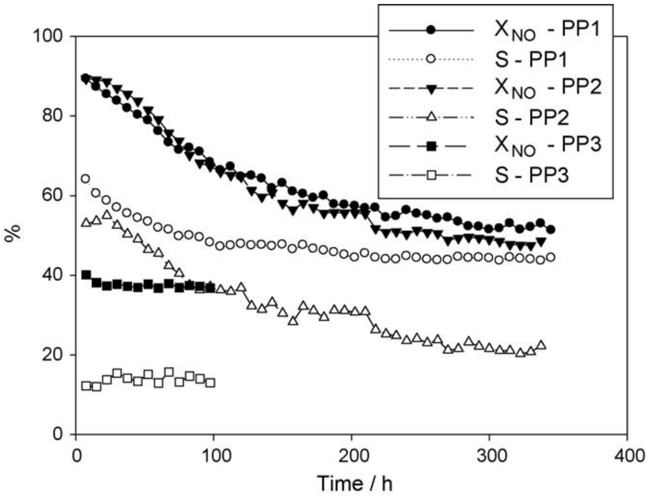

Fig. 5. Conversion (full symbols) and selectivity (empty symbols) history for experiments PP1–PP3.

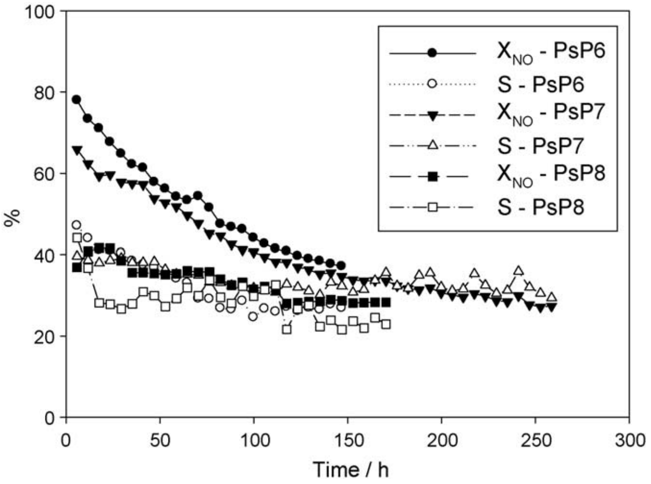

Fig. 7. Conversion (full symbols) and selectivity (empty symbols) history of experiments PsP6–PsP8.

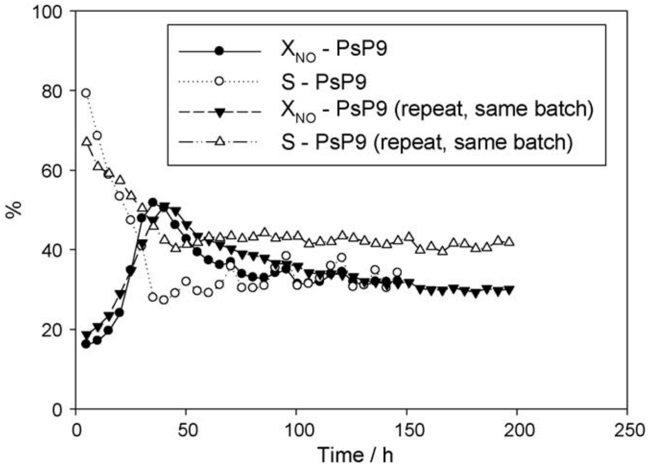

Fig. 8. Conversion (full symbols) and selectivity (empty symbols) history of experiment PsP9, employing fresh and 6 months in-can pseudo-paint.

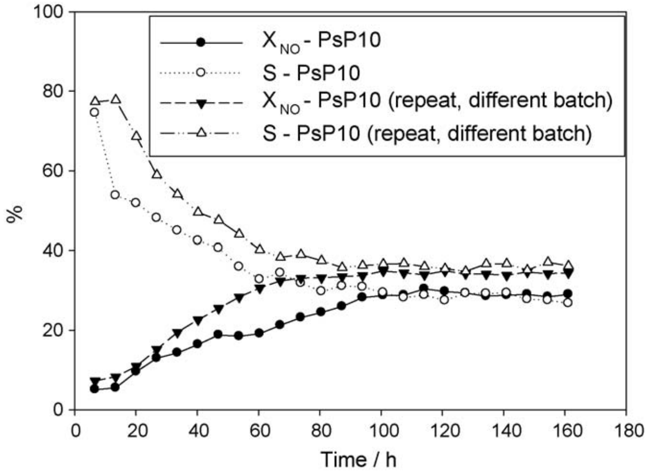

Fig. 9. Conversion (full symbols) and selectivity (empty symbols) history of experiment PsP10, using pseudo-paints produced from two different batches.

organic paint components were added step by step (cf. Table 1) and the photoactivity of the corresponding pseudo-paint films evaluated. First of all, a slurry was made with all powder components. To this slurry it was added and mixed antifoam (PsP6), antifoam and amine (PsP7), antifoam and biocides (PsP8), antifoam, amine, biocides and dispersing agents (PsP9) and antifoam, opaque polymeric particles, resin and coalescent (PsP10). Fig. 7 presents the NO conversion and selectivity histories obtained for experiments PsP6–PsP8. Although the load of P25 is higher for the case of PsP8, the initial NO conversion is lower than for PsP6 and PsP7. This might arise from the stronger detrimental influence of the biocides on the photoactivity but also from the presence of a greater amount of organic *vs.* powder components. In fact, the initial NO conversion decreases with the amount of organic components in the formulation (cf. Table 1). However, steady state conversion and selectivity values are nearly the same for these experiments and also for experiment PP5 (Figs. 6 and 7), *ca.* 30%, which may indicate that the surface of P25 is free of these organics (and products of reaction) at this stage.

PsP6 was performed in order to compare the influence of the antifoam in the transient behaviour in comparison to antifoam + amine (PsP7) and antifoam + biocides (PsP8), being therefore a reference for both tests. Fig. 7 evidences that PsP6 shows a similar transient behaviour as PsP7, indicating a major effect of the antifoam compared to the amine one, the former one present in smaller concentration (Table 1). Comparing PsP6 with PsP8, one can refer the greater impairment by the biocides during the transient period. However, the higher amount of biocides can be here playing an important role.

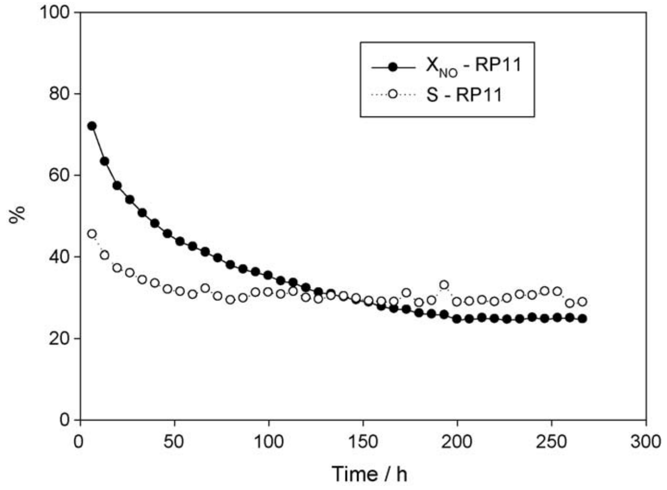

Fig. 10. Conversion (full symbols) and selectivity (empty symbols) history of experiment RP11, after harsher activation.

Similar tests performed with fresh PsP9 exhibited a low initial NO conversion, Fig. 8. Comparing with experiments PsP6–PsP8 (Fig. 7), it becomes apparent that again such fact should arise from the higher organic content and namely from dispersing agents (see Table 1). However, the steady state conversion is again *ca.* 30%. Experiment PsP9 was repeated with the pseudo-paint after its rest in-can for about 6 months (Fig. 8), producing close steady state results. This indicates also the good stability of the formulation.

Steady state conversion and selectivity obtained with PsP10 films were also *ca.* 30% (Fig. 9), which is in line with the results obtained for PP5 to PsP9. For PsP10, the initial conversion was the lowest of all experiments and, as referred above, such fact should arise from the highest content in organic components (cf. Table 1 and Figs. 7–9). Repeatability assessment made to different films from different batches of PsP10 produce similar results, especially at the steady state (Fig. 9).

In line with this, the reference paint (which has the maximum content of non-powder organic components, Table 1) does not show any photoactivity after the normal activation protocol. The ratio of the pigment volume concentration (PVC) to the critical PVC [13] is 2.1 for PsP9 and 1.2 for PsP10 and RP11. Consequently, there is a larger porosity and lower coverage of P25 by non-powder organic components in PsP9 film (therefore higher initial activity) compared to PsP10 and RP11. Compared to PsP10, RP11 contains more only the organic additives that account only for *ca.* 2.5 wt.%. However, PsP10 showed initial photoactivity while RP11 did not; it was necessary a harsher activation procedure (see Section 2.2) to make it photoactive, Fig. 10. Consequently, the lowest initial photoactivity of RP11 points out to a synergetic hiding effect of the paint components towards the photocatalyst obtained after all components being present. After the harsher activation protocol the steady state NO conversion obtained is similar to the one obtained for all PsP films, *ca.* 30% (Fig. 10).

4. Conclusions

Photocatalytic powder pressed and pseudo-paint films were produced and tested towards NO abatement. Paint components (powder and non-powder organic compounds) were progressively added, giving rise to more complex films that ended with the reference photocatalytic paint. The photoactivity of each film was assessed and the interference of each paint component in P25 photoactivity was evaluated.

The load of P25 photocatalyst explains only partially the different photoactivity of the films produced, as the composition of the film itself influences the larger or shorter penetration depth of light through the film and therefore the real active load (photoactivated photocatalyst weight *vs*. total weight of photocatalyst). When $CaCO_3$ was mixed with P25 alone (25 wt.% of P25), it was observed an improvement of selectivity towards more oxidized species (nitrate and nitrite). On the other hand, the film containing pigmentary TiO_2 has shown the worst photoactivity of all, which is due to the competitive absorption of photons in the UV region.

The production of a slurry of distilled water with the powder components deeply interfered with the photoactivity of P25. Such interaction must arise from the dissolution of species with consequent attachment to the surface of P25, impairing its photoactivity (experiment PP5).

Although the amount of organic paint components (films PsP6 to RP11) plays a major role on initial NO conversion, steady state photoactivity is mostly independent of this amount, tending to the same NO conversion of *ca*. 30%, whatever the species initially present (dispersing agents, resin, antifoam, antifoam plus amine, etc). Such fact should be related to the oxidation of organic species initially wrapping the photo-TiO_2 particles, which after being oxidized allow the NO reaction to proceed freely.

The NO conversion and selectivity histories on films produced from different batches were reproducible. The reference paint showed no photoactivity after being submitted to the normal activation procedure and needed to be activated under hasher conditions to produce conversion and selectivity values in line with experiments PsP6–PsP10. It is suggested that there should be a synergetic effect when all paint components are present in the formulation, that wrap more closely the photo-TiO_2 particles leading to no initial photoactivity.

Acknowledgments

The authors acknowledge financial support by the Portuguese Foundation for Science and Technology (FCT) through the project POCI/EQU/60366/2004 and the PhD grant of César Águia (SFRH/BD/23263/2005). Joana Ângelo acknowledges LEPAE for her research grant. The authors acknowledge *Evonik* for the supply of P25, and *CIN SA* for the paint formulation and corresponding raw materials.

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