Studying TiO$_2$ coatings on silica-covered glass by O$_2$ photosorption measurements and FTIR–ATR spectrometry Correlation with the self-cleaning efficacy

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Abstract

Self-cleaning coatings on glass plates covered with a thin silica barrier layer were formed from anatase nanoparticles mixed with Ti and Si organic salts, and subsequent calcination. UV irradiation of these coatings exposed to O$_2$ produced either a gradual increase or decrease in O$_2$ pressure P (1–120 Pa). For each coating the initial P value, P_{sat}, separating the domains of a net photoadsorption or a net photodesorption was regarded as characterizing the O$_2$ photosorption capacity. P_{sat} was found to be correlated to the self-cleaning efficacy evaluated by optically following the removal rate of an organic layer issued from hexadecanoic acid sprayed on the coating. The unfavorable role of SiO$_2$ (used to better anchor the coating) with respect to electron transfer between O$_2$ and the UV-irradiated coatings is discussed, taking into account the fact that an FTIR–ATR study showed the existence of Si–O–Ti bonds in the coatings.
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1. Introduction

Glass is a very widely employed industrial material. Its main sectors of use are housing and transportation. In most cases, periodical cleaning is required to maintain its optical properties, such as transparency and visual aspect, which can be costly, particularly when the accessibility to the glass surfaces is difficult (towers, roofs, etc.). Therefore there is a need for self-cleaning glass. A TiO$_2$ thin coating deposited onto the glass covered by a silica barrier layer has been shown to be effective in this regard owing to the photocatalytic destruction of organic dirt as a result of UV solar irradiation (see for example [1]).

Previous studies in our laboratory [2,3] have shown that TiO$_2$-coated glass samples similar to those examined here had a self-cleaning efficacy that appeared to be sufficient. This efficacy was assessed by spraying a thin layer of an organic compound representative of soiling. A fatty acid (hexadecanoic or palmitic acid (PA) [2]) and a polycyclic aromatic hydrocarbon (fluoranthene [3]) were used because these types of compounds are, in particular, important com-

ponents of suspended solid particles in the troposphere. The glass plates thus covered with an organic film were irradiated under conditions simulating solar light in the UV-A spectral region. Dissolution of the organic film with several solvents after various irradiation times and subsequent analysis of the solutions allowed us to measure the elimination rate of the deposited organic compound, to determine the nature of the degradation intermediate products (about 40 were identified in both cases), and to quantitate some of these products. Degradation pathways were deduced from these results. Additionally, quantitative measurements of volatile organic products (C$_1$–C$_6$ carbonyls) emitted during the removal of the organic film were utilized to evaluate the potential effect on air quality if the self-cleaning glass was employed indoors. About 20% of the organic carbon contained in hexadecanoic acid [2] or in fluoranthene [3] was transformed into these volatile carbonyls. This percentage was lower than that found when fluoranthene—which is photosensitive in the UV-A spectral region—was sprayed onto glass without the TiO$_2$-coating; moreover, in this latter case, the irradiated organic layer became and remained yellowish [3]. For a layer of photoinsensitive hexadecanoic acid, a simple calculation showed that volatile carbonyls cannot be emitted in quantities high enough to significantly change their usual concentration in indoor air [2]. On the basis

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of these results, it seems possible to conclude that the use of this type of self-cleaning glass in confined atmospheres not only does not impair the air quality but can improve it.

Here we report characterizations of the TiO_2 coatings on glass by O_2 photosorption measurements and by FTIR–ATR spectrometry. Correlations with the self-cleaning efficacy are also presented. The main purpose was to determine the effect of the presence of silica in the binder employed to improve the anchoring of the TiO_2 nanoparticles on the thin silica barrier layer covering the glass. As interaction of O_2 with TiO_2 is essential in photocatalytic oxidation we thought of interest to study the photosorption of O_2. Its knowledge enables one to obtain information which offers the advantage of being independent of any other reactant.

2. Experimental

2.1. Coating

The industrial glass was covered by Saint-Gobain [4] with a thin silica barrier layer whose object was to hinder the TiO_2 photocatalytic activity from being decreased by sodium ions migrating from the glass during the thermal treatment used to better fix the coating [1]. The coating was made of TiO_2 nanoparticles and an inorganic binder. The TiO_2 nanoparticles were synthesized by Rhodia via thermohydrolysis of Ti salts in acidic medium. Calcination of the sol at 373 K produced particles of anatase (90%) and no rutile. The elementary crystallite size was 7.0 ± 0.5 nm and the average diameter of the lentil-shape particles was 40 nm. Their volumic mass of 2.8 g cm^{-3} compared with 3.85 g cm^{-3} for an anatase single crystal was indicative of a high porosity. These nanoparticles were mixed in appropriate proportions with organic salts of Ti and Si dissolved in ethanol+1, 2-ethanediol [5]. According to the Saint-Gobain procedure [4], the mixture was poured into a cell, whose vertical walls (one or several) were constituted by the glass plates to be coated, and was withdrawn at a constant rate. The film thus deposited was subsequently calcined, the maximum temperature being 773 or 823 K. For the four samples studied, the mass of coating was comprised between 0.17 and 0.20 g m^{-2} of glass, the mass ratio of the TiO_2 nanoparticles to the binder was always 1:1, the weight percent of TiO_2 in the binder with respect to SiO_2 was varied from 14 to 75 (Table 1).

Table 1
Data about the coatings

Weight percent[a] of TiO_2 in the binder	Coating amount per glass area (g m^{-2})
75	0.20
50	0.17
25	0.18
14	0.17

[a] With respect to SiO_2.

2.2. O_2 photosorption measurements

For the measurements of O_2 photosorption, the glass plate (5 cm × 3 cm × 4 mm) was introduced into a specially designed Pyrex glass cell with an optical window allowing UV irradiation. The aperture permitting the glass plate introduction was closed by means of a metallic flange and a Viton O-ring. The cell was connected to a vacuum system including a Pfeiffer Duo 2.5 rotatory pump and an Edwards BRV 10 oil diffusion pump enabling one to achieve a residual pressure of 10^{-5} to 10^{-6} Pa. This system was also linked to a cylinder containing O_2 whose pressure was measured with a Datametrics Dresser barocel sensor.

Irradiation was provided by a Philips HPK 125 W high pressure mercury lamp through a 2 cm thick circulating-water cuvette and the cell optical window transmitting wavelengths >300 nm. If one takes into account the TiO_2 absorption, the Hg lines able to activate TiO_2 were those at 313 and 365.5 nm. The radiant power at the glass plate level was estimated, by use of a UDT 21 A power meter, to be ca. 40 mW cm^{-2}.

Before each experiment, the coated-glass sample was irradiated under 1.3×10^5 Pa of O_2 for 15 h to photocatalytically oxidize the adsorbed/deposited organic compounds, and the cell was evacuated in the dark to a residual pressure <0.01 Pa. The O_2 pressure desired for the photosorption experiment was then introduced in the dark.

2.3. FTIR–ATR study

A Perkin Elmer Spectrum One spectrometer equipped with a universal attenuated total reflection (ATR) accessory was used. The incident IR beam through the composite Zn Se/diamond crystal has a limited penetration depth into the sample pressed against this crystal, so that it allows one to characterize preponderantly the sample surface, that is in the present case the glass coating.

2.4. Palmitic (hexadecanoic) acid (PA) test

As mentioned in Section 1, the self-cleaning efficacy had been estimated in our laboratory by following via gas chromatography analysis the kinetic disappearance of PA sprayed onto the glass coating [2]. In the test to which we refer in this paper this disappearance was determined by Saint-Gobain by measuring the ratio of the diffuse transmission to the total transmission of the glass and equating this ratio to a layer thickness of PA. This optical measurement is faster than the chemical analysis and better corresponds to the cleaning process, since in fact it does not refer to PA only but also to its degradation intermediate products remaining on the coating and accordingly susceptible to modifying the optical properties.
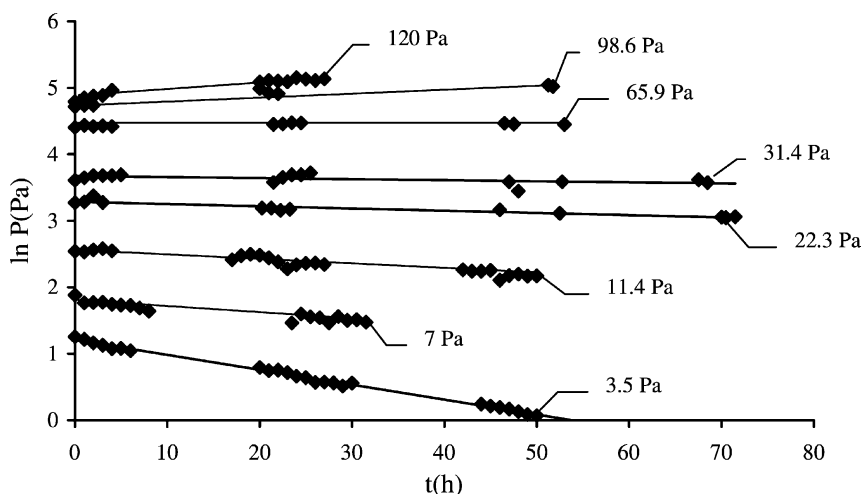
Fig. 1. Variations in the logarithm of the O_2 pressure as a function of the irradiation time over the coating containing 75 wt.% of TiO_2 in the binder (cf. Table 1) for the initial pressures indicated.

3. Results and discussion

3.1. O_2 photosorption

The O_2 initial pressure P_0 corresponded to the adsorption equilibrium in the dark. This equilibrium was reached within 1–4 h for the P_0 range investigated, that is 1–120 Pa. Upon irradiation a gradual decrease or increase in the O_2 pressure P was observed. We recorded P over 25–75 h depending on the extent of its variations. In a plot of $\ln P$ against the irradiation time t the experimental points were found to be satisfactorily aligned (Fig. 1), i.e. $\ln(P/P_0) = kt$, a positive k reflecting a net photoadsorption and a negative k a net photodesorption. Differentiating this experimental relationship leads to $dP/dt = kP$; in other words, the photosorption was found to be a first-order phenomenon with respect to P over the P range studied. This relationship also means that recording P over a few hours is sufficient to determine the value of k; durations as long as those mentioned above (25–75 h) were used only to ascertain the relationship and it will not be necessary to reach such durations in regular experiments.

The P_0 value for which the sign of k changes corresponds to the saturation of the surface by oxygen species under the irradiation conditions used; it is denoted as P_{sat} (Fig. 2). It can be regarded as reflecting the O_2 adsorption capacity of the coating. The higher P_{sat} is, the higher the O_2 adsorption capacity under irradiation. Note that photoproduced electrons induce oxygen adsorption on being captured by O_2, forming $O_2^{\bullet-}$ and possibly $O^{\bullet-}$ adsorbed/surface species, while photoproduced holes induce oxygen desorption on being captured by these radical-anions.

Fig. 3 shows a plot of P_{sat} as a function of $\Gamma_{TiO_2,b}$ the mass of TiO_2 in the binder per area unit of glass plate (the mass of TiO_2 introduced into the coating in the form of nanoparticles was kept nearly constant as can be derived from the amount of coating per glass area (Table 1)

and the nanoparticles/binder 1:1 mass ratio). P_{sat} increased slightly on going from $\Gamma_{TiO_2,b} = 1.2$ to $2.2\,\mu g\,cm^{-2}$, but much more markedly for the higher $\Gamma_{TiO_2,b}$ values (4.2 and $7.5\,\mu g\,cm^{-2}$). This increase is not unexpected since insulating silica, used in place of titania in the binder, can both forbid or restrict the accessibility of O_2 to TiO_2 by encapsulation and favor the confinement of photogenerated electrons in the individual TiO_2 nanoparticles to which O_2 can access, thereby potentially increasing the recombination rate of these electrons. By contrast, electrons photogenerated in the TiO_2 nanoparticles can migrate into the semiconducting TiO_2 binder and be captured by O_2 adsorbed on it.

P_{sat} was also determined for the TiO_2 nanoparticles used in the coating preparation. For that, these nanoparticles were dried and as uniformly as possible spread onto the glass plate covered with the silica barrier layer. The variations in P as a function of P_0 were measured as for the normally coated glass plates. In that case P_{sat} was found to be about 2.5 Pa,
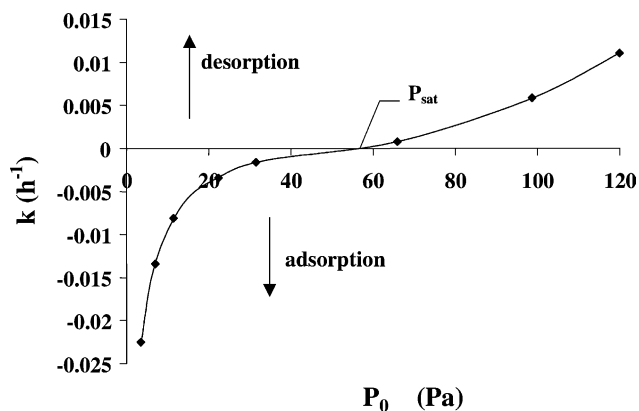

Fig. 2. Slopes of the straight lines ($\ln P = kt + \ln P_0$) of Fig. 1 against the initial O_2 pressure P_0. P_{sat} is the P_0 value above which a net photodesorption was observed for this coating.
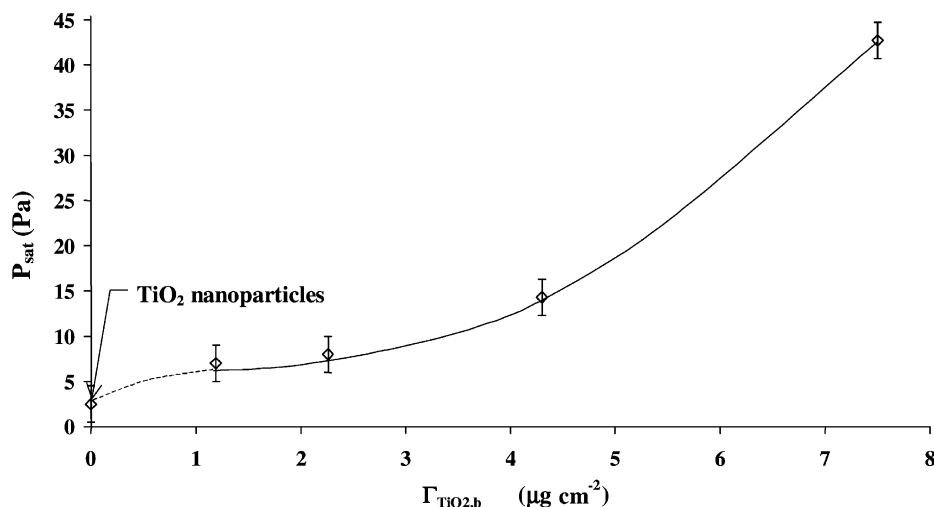
Fig. 3. Values of P_{sat} depending on the mass of TiO_2 in the binder per glass area for the samples of Table 1. The P_{sat} value obtained for a uniform layer of the TiO_2 nanoparticles used in the coatings is also shown.

that is lower than for the coatings irrespective of the silica fraction in the binder (Fig. 3). Although the dispersion of the UV light by the spread nanoparticles or by the coatings probably differs, this markedly smaller O_2 adsorption capacity in the absence of any binder is indicative both of an electron transfer from the TiO_2 nanoparticles to TiO_2 binder and of a higher amount of adsorbed O_2 on TiO_2 binder than on TiO_2 nanoparticles. This increase in adsorbed O_2 is not unexpected since scanning electron micrographs [2] showed the binder to be amorphous, which points to a high surface area and hence a high adsorption capacity. The amorphous character of TiO_2 binder also suggests a higher density in structural defects with respect to TiO_2 nanoparticles and therefore a higher recombination rate of charges photogenerated in the TiO_2 binder. Consequently, we think that the main reason for the increase in the O_2 adsorption capacity due to the TiO_2 binder (Fig. 3) is not dominantly caused by the creation of electron–hole pairs in this part of the coating, but by transfer of electrons from the TiO_2 nanoparticles to the TiO_2 binder and subsequently to O_2 adsorbed on it.

3.2. Correlation O_2 adsorption capacity—self-cleaning efficacy

As indicated in Section 2, the self-cleaning efficacy was equated to the removal rate r_{PA} of a palmitic acid layer and accordingly expressed in layer thickness unit per time unit. Fig. 4 shows that r_{PA} and P_{sat} are correlated. In more detail, r_{PA} is roughly proportional to P_{sat} for the three samples containing between 14 and 50 wt.% of TiO_2 in the binder with respect to SiO_2, the increase in this percentage having a greater effect on r_{PA} than on P_{sat}. By contrast, when this percentage increases from 50 to 75, the augmentation in r_{PA} is smaller than that in P_{sat}. To explain this slope change in the r_{PA}–P_{sat} plot (Fig. 4) the removal rate of the organic de-

posit initially constituted of palmitic acid can be regarded as limited by the amount of adsorbed oxygen species and/or the quantity of available holes (which increases with increasing electron capture) for the samples with the lowest weight percent of TiO_2 in the binder, since both types of entities can be involved in the oxidation of the organic deposit. For TiO_2 in the binder >50 wt.%—that is the highest O_2 adsorption capacity—these quantities would have reached such values that their relative influence on the organic deposit removal rate becomes less important.

3.3. FTIR–ATR study of the coatings

We also addressed the question about whether the preparation of the coating created Si–O–Ti bonds along with the Ti–O–Ti and Si–O–Si bonds. The Si–O–Ti bonds have a characteristic absorption band in the 910–960 cm^{-1} spectral region [6–8]. To search for this band we used an ATR device which allowed us to avoid or minimize the contribution of the silica barrier layer to the infrared spectrum of the coating which also contained silica.

Fig. 5 shows the spectra obtained. For the two highest contents of silica in the binder, a band at ca. 960 cm^{-1} is clearly visible. Computerized deconvolution also indicates a weak absorption around 960 cm^{-1} for the two other coatings containing Si, and its absence for a specially prepared coating without Si. Also, a 960 cm^{-1} band was found to be present in the spectrum of the powder obtained by mulling the binder containing 86 wt.% of SiO_2 which had been calcined under the conditions used to elaborate the coatings.

As proposed in Ref. [7], the relative density of the Si–O–Ti bonds with respect to the Si–O–Si bonds was determined by the use of the expression

$$D = \left(\frac{I_{Si-O-Ti}}{I_{Si-O-Si}} \right) \left(\frac{x_{Si}}{x_{Ti}} \right)$$
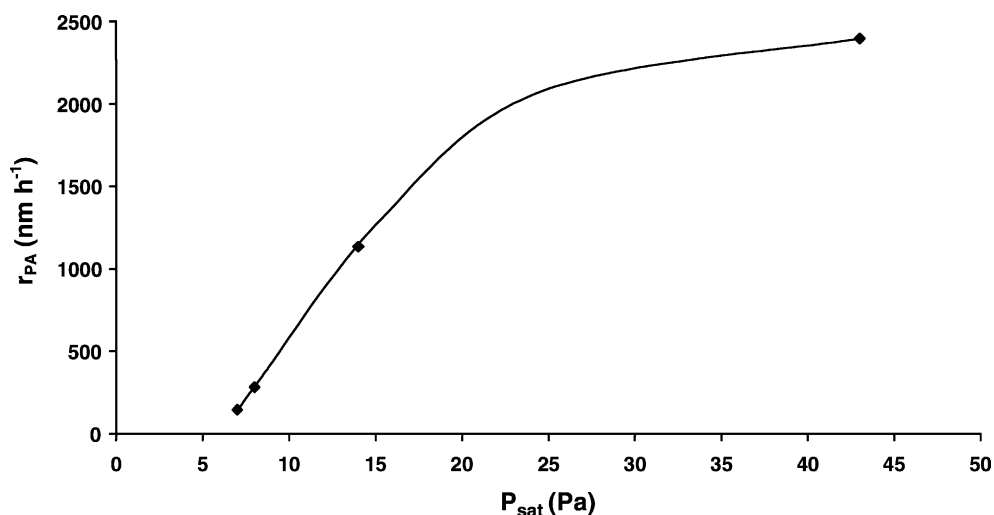
Fig. 4. Correlation between the self-cleaning efficacy, as expressed by the removal rate of a palmitic acid layer (see text), and P_{sat} reflecting the O_2 adsorption capacity under the UV irradiation used for the samples containing 14, 25, 50, and 75 wt.% of TiO_2 in the binder (from left to right).

where I is the intensity of the band corresponding to the bonds shown in the subscript, viz. the band at ca. 960 or 1210 cm^{-1}, and x_{Si} and x_{Ti} are the molar fractions of, respectively, Si or Ti in the binder. In Fig. 6, D is plotted against the mole percent of TiO_2 in a mixed TiO_2–SiO_2 powder [7] and in the binder of the coatings we examined. Both curves display the same pattern; however, for the lowest TiO_2 contents, the preparation mode of the coatings produced relatively less Si–O–Ti bonds than the sol–gel method used by the authors of Ref. [7]. Nevertheless, for the coatings with the two highest x_{Si}, D attains high values (Fig. 6) showing an important mixing between the Si and Ti atoms in the binder. Furthermore, with the reservation of a low accuracy on D for the two smallest x_{Si}, $\ln D$ appears to be roughly

inversely proportional to $\ln P_{sat}$ or, similarly, to $\ln r_{PA}$ since P_{sat} and r_{PA} are correlated (Fig. 7).

The possibility that silica shields the TiO_2 nanoparticles from the gas phase and/or isolates the TiO_2 nanoparticles from one another as we hypothesized to explain the gradual decrease in P_{sat} and r_{PA} for increasing x_{Si} is thus supported and explicated by the FTIR–ATR study. This study shows the creation of Si–O–Ti bonds during the coating preparation by use of TiO_2 nanoparticles and a Si organic derivative [4,5]. Previous studies [9–11] have shown a Ti electron affinity in Si–O–Ti bonds higher than in Ti–O–Ti bonds in agreement with the difference in electronegativity between Si and Ti. Consequently, the electrons photoproduced in TiO_2 nanoparticles might be trapped at the interface with
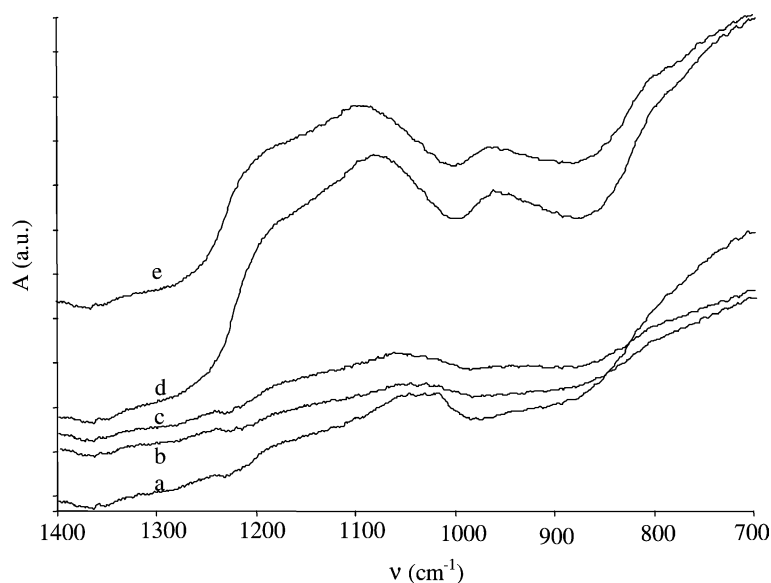

Fig. 5. FTIR–ATR spectra of the coatings containing 0 wt.% (a), 25 wt.% (b), 50 wt.% (c), 75 wt.% (d) and 86 wt.% (e) SiO_2 in the binder.
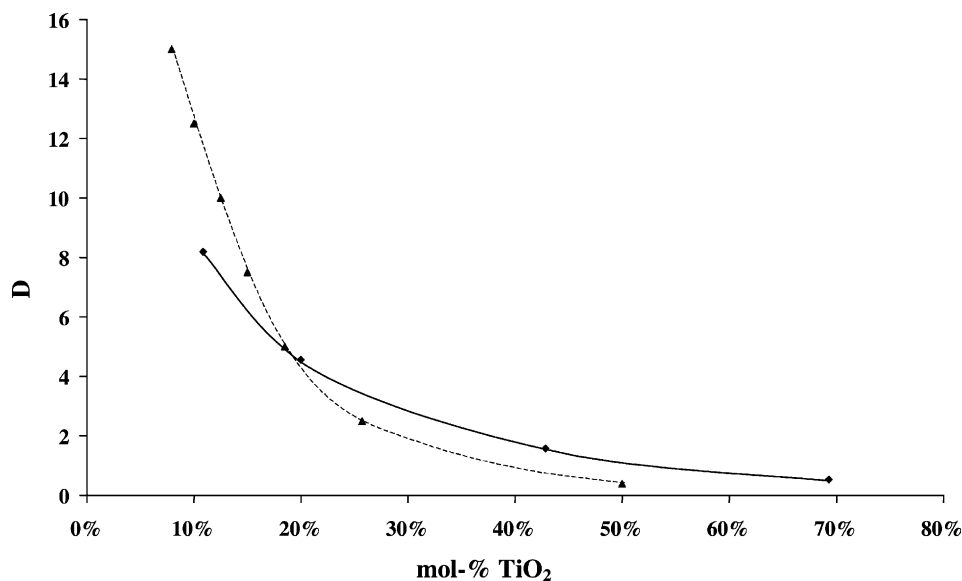
Fig. 6. Variations in the relative density of Si–O–Ti bonds as a function of the mole percent of TiO_2 in the coating (solid line) or in the SiO_2–TiO_2 mixed oxide [7] (dotted line).
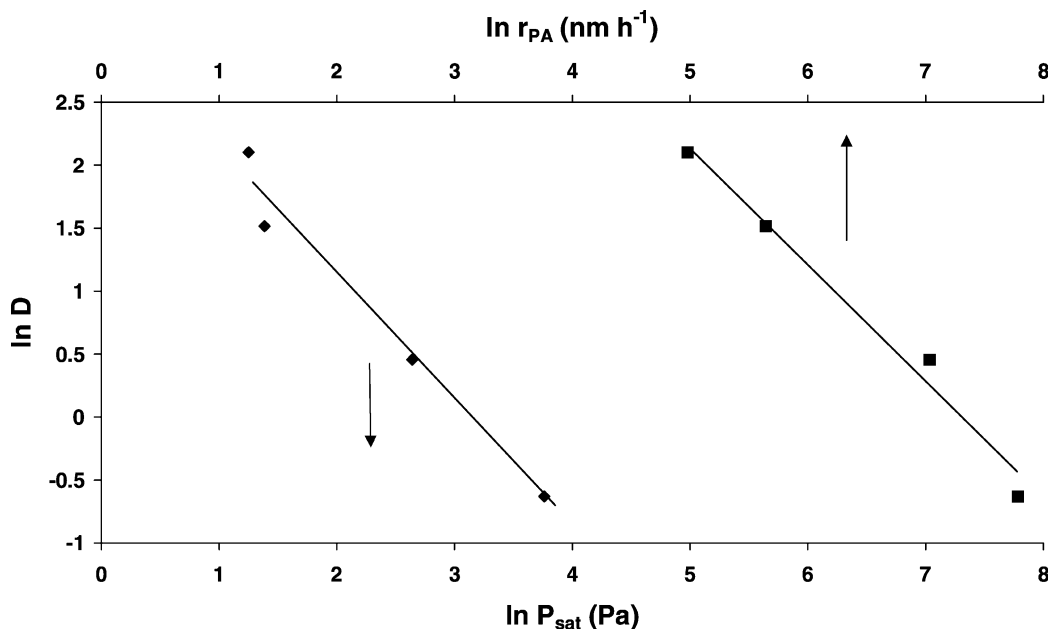

Fig. 7. The log–log plots of the relative density of Si–O–Ti bonds in the coatings vs. P_{sat} or r_{PA}.

the binder rich in Si–O–Ti bonds and hence be less easily transferred to O_2, which would account for the decrease in P_{sat} for increasing Si contents.

4. Conclusion

This study reveals that the use of a Si organic salt and subsequent calcination to anchor TiO_2 nanoparticles cre-

ates Si–O–Ti bonds. The relative density in these bonds with respect to the Si–O–Si bonds is detrimental to the coating self-cleaning efficacy (while it increases the adhesion forces between the coating and the solid substrate). We suggest that this effect might stem from deep trapping of photoproduced electrons at the Ti cations of the Si–O–Ti bonds resulting in a less easy electron capture by O_2. In parallel, we have shown that the higher the TiO_2 fraction in the binder, the higher the O_2 initial pressure P_0

at which a net photodesorption is observed for the coatings previously exposed to various P_0 in the dark. Consequently, the use of TiO_2 as a binder increases the O_2 amount adsorbed on the coating under UV irradiation and hence the self-cleaning efficacy. This is tentatively attributed to the transfer of photoproduced electrons from the TiO_2 nanoparticles to the amorphous TiO_2 binder where they are captured by larger quantities of adsorbed O_2. Unlike SiO_2, TiO_2 in the binder cannot cause the above-mentioned electron trapping, and as a semiconductor allows the migration of electrons within the coating. These interpretations provide a basis that may help to optimize the proportions of TiO_2 nanoparticles and Ti and Si organic derivatives used to elaborate these types of coatings [4,5]. They also indicate that the challenge is to find a binder based on a semiconductor oxide whose metallic element has an electronegativity close to that of Ti, with the additional requirement that, compared with TiO_2, this semiconductor oxide must possess better binding properties with the silica barrier layer covering the glass.

Acknowledgements

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