

Photocatalytic activity for exposed building materials

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Abstract

Photocatalysis is a very promising method to face most of the problems connected with the increasing environmental pollution. Titanium dioxide in its anatase crystallographic phase is the most investigated photocatalytic material and results to be perfectly compatible with silicate body mixes. The possibility to obtain photocatalytic heavy clays materials, to be used for outdoor applications, such as roof tiles, floor tile and outdoor covering tiles, could represent an important goal.

In the present work, several titania powders and a titania nanosuspension were added to a body mix used for heavy clay products and the influence of their morphological characteristics on the photoactivity of the fired materials was studied.

The titania powders, characterised by the aid of SEM, X-ray diffraction analysis and surface area measurements, BET, presented particles with different aspect ratio and size, ranging from micrometric to nanoparticles. Besides, the nanosuspension was characterised by FEG, TEM, DLS and XRD on the dried suspension. The photocatalytic activity was assessed in aqueous mixtures, by analysing the degradation of an organic dye with a spectrophotometer.

The results were explained taking into account the anatase to rutile phase transformation and its possible reaction, during sintering, with the starting raw materials.

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1. Introduction

Titanium dioxide is extensively utilized in many applications of everyday life, i.e. as white pigment in the painting, food and cosmetic industries. In the last years the interest has grown also for its use as photocatalytic material to oxidize various organic compounds.^{1,2} Indeed, the potential applications of heterogeneous photocatalysis with TiO₂ are very important. For instance, the production of photocatalytically active building materials, containing TiO₂, would allow to have self-cleaning and self-sterilizing surfaces that, in addition, might degrade several organic contaminants in the surrounding environment. Outdoor and indoor pollution could be in this way reduced by a “passive” utilization of the building materials, with consequent important beneficial effects on the relative safety problems

(e.g. sick building syndrome or reduction of car NO_x pollution). Other peculiar positive features of heterogeneous photocatalysis with TiO₂ are: the reactions take place at mild operating conditions (low level of solar or artificial illumination, room temperature and atmospheric pressure); no chemical additive is necessary; the possible intermediates of the reactions are not dangerous or at least less dangerous than the original pollutant;³ even very recalcitrant and persistent pollutants can be degraded.⁴ Besides, TiO₂ is a relatively low-cost product and it is non toxic. However, the characteristics, that TiO₂ must possess to “effectively” activate these reactions, are generally different from those which are required for its traditional and well known utilization as a pigment. In fact, according to the literature on this topic, different factors seem to affect the photocatalytic properties of titania, namely: phase composition, level of crystallinity, crystallite size, surface properties.⁵ These properties are affected by the production techniques and by the preparative conditions. So, the research should be directed on the investigation and on the desired properties of TiO₂ for this specific

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application and the techniques that would allow to get these properties.

Recent studies^{6,7} underline as nanocrystallinity of titania is of particular relevance to enhance the photocatalytic activity, due to the fact that it favours the diffusion on the surface of free electron and holes, and limits their recombination through charge carrier trapping. The TiO₂ crystalline phase is relevant as well, since it has been observed that anatase, or at least a mixture composed mainly by anatase, appears to be much more active with respect to brookite and rutile, the other two crystalline modifications of TiO₂.

These aspects have been considered in general for the utilization of titania as powders or as immobilized films on different supports. In spite of the large number of investigations on these systems, there are relatively few scientific works that analyze the problems related to the manufacturing of ceramic materials which contain in the bulk or on the surface the TiO₂. Actually, for photocatalytically active building materials, such as ceramic tiles, with the photocatalyst powders dispersed in the inert matrix or on the surface, additional peculiar problems must be taken into account, such as the necessity that the photocatalytic properties of TiO₂ are not destroyed or reduced, during the production of the material, and the requisite that the photocatalyst is present in zones where both the organic compounds and a sufficient amount of UV-light are available during the utilization of the material.

In the present paper, TiO₂ is used to produce photocatalytically active ceramic samples by adopting some original techniques. The materials are characterised with different analysis and the results are discussed in order to investigate the factors which influence the photocatalytic activity with the aim to develop a technology which gives a good photocatalytic activity and is, at the same time, compatible with the ceramic processing.

2. Experimental procedures

2.1. Materials

Four different kinds of TiO₂ powders, commercially available, named A, B, C and D, together with a titania nanosuspension as well, noted as E, were used as photocatalysts. The mineralogical characterisation of the powders was carried out by X-ray powder diffraction analysis, XRPD, by using a Philips PW 3830 instrument, with Cu K $\alpha_{1,2}$ radiation (15–95° 2 θ range, 0.02° 2 θ s⁻¹ step-scan and 9 s/step). Rietveld crystal structure refinements were performed using GSAS-EXPGUI software.^{8,9} The initial atomic parameters of anatase were taken from Sanchez et al.,¹⁰ the rutile ones from Gonshoren and Feld.¹¹

Moreover, the average crystal size of each titania powder was calculated measuring the broadening of the X-ray reflections, from selected FWHM values, using the Scherrer formula, with Warren's correction for instrumental broadening¹²:

$$t = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where t is the linear dimension of particle, k is the Scherrer constant (0.9), λ is the wavelength of the incident X-rays, θ is the Bragg's angle and β is the sample line broadening (FWHM) that was calculated using LaB₆ (NIST SRM 660a) as line broadening standard:

$$\beta^2 = \beta_M^2 - \beta_S^2 \quad (2)$$

where β_M is the measured FWHM, β_S the instrumental contribution on the total FWHM.

The relative amounts of anatase and rutile in the TiO₂ powders were calculated by using the Spurr–Myers equation¹³ via XRD patterns (10–70° 2 θ range, 0.02° 2 θ s⁻¹ step-scan and 1 s/step).

The powders morphology was analysed by SEM (Zeiss EVO 40, D) equipped with an energy dispersion X-ray attachment, EDS, (Inca, Oxford Instruments, UK) and the surface area was determined by using the BET (Brunauer Emmet Teller) method (Flowsorb II 2300 Micromeritics, USA), with N₂ as adsorbate gas.

The results of the characterisation of the titania powders are reported in Fig. 1 and Table 1. Even if powder A contains a very small amount of rutile phase, its morphology results to be very similar to that of powder B, containing 100% of anatase. Both the powders present similar surface area values and rounded single particles, of dimension in the range of 96–140 nm. Powder C is characterised by the presence of larger platelet-like shaped particles, each particle contains several smaller crystallites. Powder D, nanometrically sized, contains a not negligible amount of rutile and it is characterised by a very high surface area value. All the powders were strongly agglomerated.

The titania nanosuspension, E, was synthesized by high temperature hydrolysis of metal alcoxides in a coordinating solvent. It is completely crystallised in the anatase phase and the nanoparticles are dispersed (7 wt.%) in DEG medium. The particles morphology was characterised by means of FEG (Zeiss Supra 40, D) and TEM (JEOL JEM 2010, J). The mineralogical phase was determined by XRD on the dried suspension; its crystallite size (~20 nm), being nanoparticles in suspension, was measured by DLS (Malvern Instrument, Zetasizer Nano ZS, UK). Its main characteristics are summarized in Table 1 and the particles morphology is shown in Fig. 2.

The starting ceramic matrix, denoted S, was a clay body mix, used for the production of roofing tiles. Its chemical analysis and mineralogical composition are reported in Table 2.

The titania powders were added to the clay body mix, in two percentages, 2.5 wt.% and 7.5 wt.%. The preparation of the samples followed two different procedures.

In the first one, named bulk addition, the titania powders were mixed with the clay, in water (55 wt.%), using an overhead stirrer, a soft mixing apparatus. After 1 h of mixing, the suspension was dried in oven at 105 °C, overnight. In order to obtain powders suitable for shaping, the resulting cakes were crushed and sieved to pass at 125 μ m screen. The test specimens, discs of 4.0 cm in diameter, were prepared by uniaxially pressing at 30 MPa the powders, containing 6 wt.% of water.

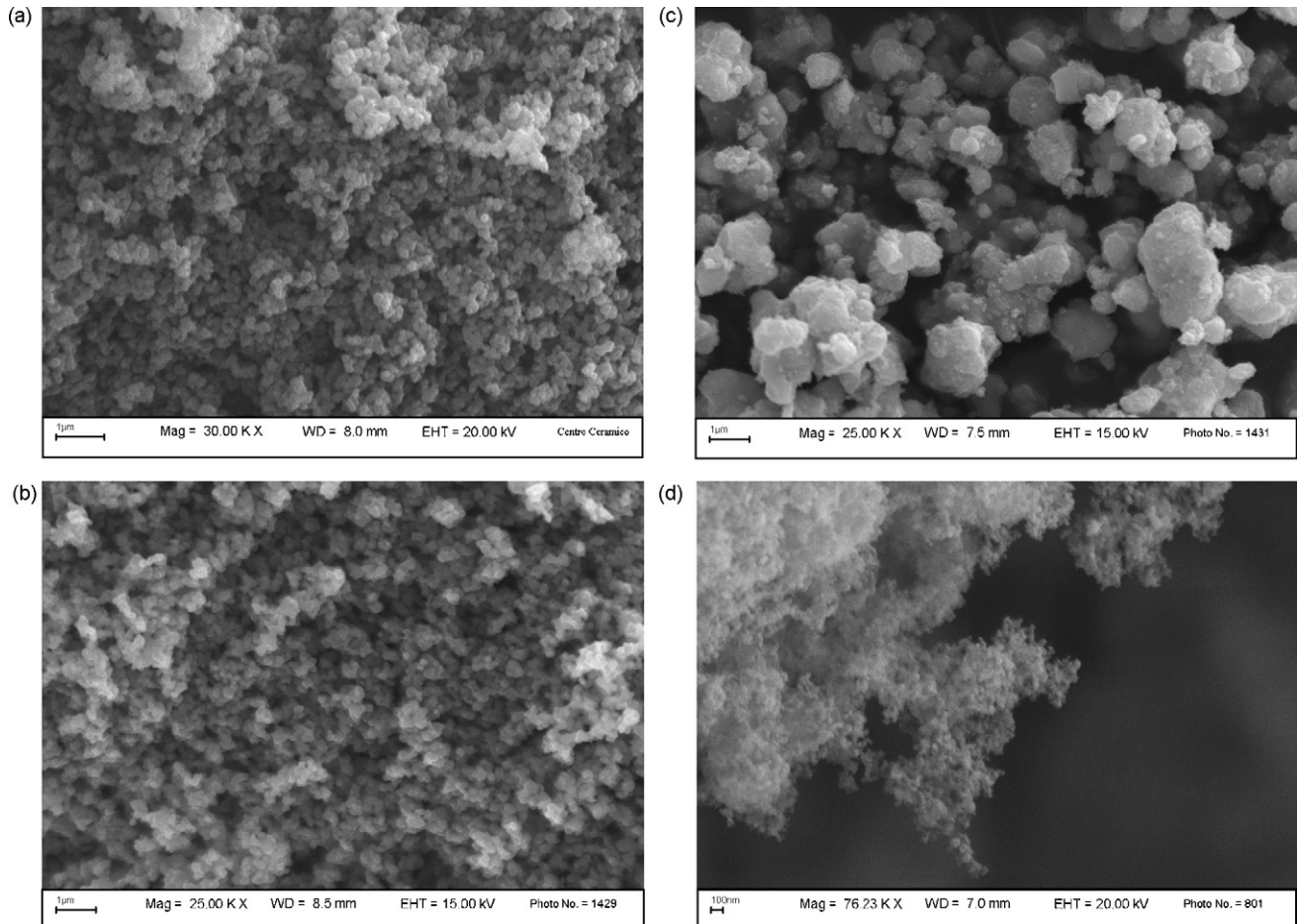


Fig. 1. SEM micrographs of the tested titania powders: (a) powder A, (b) powder B, (c) powder C, (d) powder D.

The second procedure, named spray addition, foresaw the preparation of the same mixtures, containing the clay and the two percentages of titania, 2.5 wt.% and 7.5 wt.%, in form of slip with 60 wt.% of distilled water, and mixed with a high shear mixer (Silverson L4R, USA) for 1 min, with the aim to destroy the titania agglomerates. 0.4 g of the mixed slip, was sprayed over the S green pressed disc surfaces, previously humidified (3.0 wt.% of distilled water). 0.4 g of the nanosuspension, E, both as it is and diluted, to have 2.5 wt.% of TiO₂, was directly sprayed over the S green humidified discs.

All samples, with and without titania, were sintered in a laboratory muffled furnace at three maximum temperatures 900, 950 and 1000 °C. The heating rate, from room temperature to 600 °C, was of 60 °C/h, with a holding time of 2 h. From 600 °C to the

maximum firing temperature, the heating rate was 40 °C/h, with 4 h of soaking time, then natural cooling to room temperature was used.

The sintering behaviour of the fired specimens was evaluated on the basis of their linear shrinkage and water absorption, determined according to the Standard EN ISO 10545–3.

A thorough analysis of the morphology and crystalline phases of the titania particles embedded in the ceramic matrix was carried out by the use of the SEM-EDS and XRD.

2.2. Photocatalytic test

The photocatalytic activity of the prepared samples was evaluated in liquid phase by monitoring the degra-

Table 1
Physical and mineralogical characteristics of the tested titania powders and nanosuspension

Sample	Anatase cell parameter		Anatase (wt.%)	Rutile (wt.%)	S _{BET} (m ² /g)	Crystallite size (nm)	
	a (Å)	c (Å)				Anatase	Rutile
A	3.7850(1)	9.5144(2)	97.7(1)	2.3(3)	9.6	140	^a
B	3.7858 (1)	9.5177(2)	100	–	8.9	96	–
C	3.7841(1)	9.5240(3)	100	–	17.0	55	–
D	3.7887(2)	9.5149(6)	84.9(1)	15.1(4)	50.0	23	35
E			100	–		20	–

^a The amount of rutile resulted to be too low for a reliable measure.

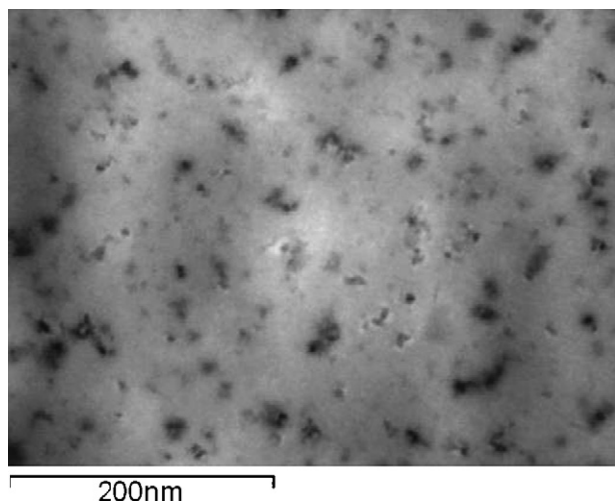


Fig. 2. FEG micrograph of the titania nanosuspension, E.

dation of a solution of indigo carmine, IC.¹⁴ The tests were performed at room temperature in a photocatalytic reactor containing a water solution of the dye, at the initial concentration of 1 ppm. The light source was a 9 W blacklight fluorescent lamp (Philips PL-S 9W/08/2P, NL), having $\lambda_{\max} = 370$ nm and placed upon the sample. The light intensity, that reached the surface of the sample, was of 11 W/m^2 , value measured in the range of wavelengths 315–380 nm.

In order to mix the solution thoroughly, a recirculation pump was operating into the vessel. The reactor was covered with a pyrex glass, to avoid the evaporation of the solution.

The evolution of the IC concentration was analyzed by measuring, with a spectrophotometer (Uvikon 923, F), the absorbance at a wavelength at 610 nm. The extent of IC photocatalytic degradation, η ,¹⁵ is evaluated as:

$$\eta\% = \frac{C_0 - C_S}{C_0} \times 100 \quad (3)$$

where C_0 is the initial IC concentration and C_S is the concentration after a certain UV irradiation time.

Table 2

Chemical analysis and mineralogical composition of the starting raw material used as ceramic matrix

Chemical analysis		Mineralogical composition
Elements	%	
L.O.I.	14.48	Quartz
CO ₂	9.30	Calcite
SiO ₂	48.27	Albite
Al ₂ O ₃	12.03	Illite
TiO ₂	0.66	(Mg, Fe)-chlorite
Fe ₂ O ₃	6.37	Muscovite
CaO	11.86	Kaolinite
MgO	3.28	k-Feldspar
K ₂ O	1.77	Smectitic interlayer minerals
Na ₂ O	0.72	
CaCO ₃	21.20	

The samples, for the measure of the IC concentration, were taken from the reacting system at fixed intervals for a total irradiation time of 30 h.

3. Results and discussion

The addition of TiO₂, in both percentages and techniques, has not modified the sintering behaviour of the fired specimens, in respect to the standard S, fired at the three different temperatures. The linear shrinkage values are all in the range 1.50–1.70%, whereas the water absorption values are included in the range 18–20%, for the whole sets of samples.

In Figs. 3 and 4, the photodecomposition efficiency, η , as a function of the irradiation time for all the samples, fired at the different temperatures, is reported.

For the bulk type samples fired at 900 °C, a significant increase in η is observed when 2.5 wt.% of the titania powders is added (Fig. 3a), by comparing the results with the standard S. The sprayed samples (Fig. 3b) present a stronger photodecomposition efficiency, reaching, after 30 h, ~92% with powder B. Even powder A, that in the bulk samples showed a very weak photoactivity, when sprayed increases its performances. This behaviour is essentially due to the more efficient destruction of the titania agglomerates, reached with the high shear mixer, and to the addition technique. In this way, a larger number of titania particles and as a consequence, photocatalytically active sites, are present on the surface, enabling the oxidation of the organic compound. The SE sample shows photodecomposition efficiency slightly lower than the best performing sample, SB, but it is still in the trend of SC and SD.

The presence of a larger amount of titania, 7.5 wt.% (Fig. 3c and d) both in the bulk and sprayed type samples, causes higher values of η , favouring the photodecomposition, even if the increase is not directly proportional to the amount of the photocatalyst. Again, the highest values of η are obtained with the sprayed samples: after 30 h of irradiation, SD completely destroys the organic compound, while samples SB and SC reach values very close to the full photodecomposition.

The photocatalytic activity of the samples treated with the nanosuspension (Fig. 3d) is comparable with the activity of samples sprayed with 7.5 wt.% TiO₂, even if the titania amount in DEG is slightly lower, 7 wt.%. Apart that, its photoactivity at 900 °C is still appreciable, but lower than the one of samples SB, SC and SD.

The increasing of the firing temperature, 950 °C, causes a remarkable decrease of the photoactivity of the bulk samples (Fig. 4a and c). For the sprayed samples, the decrease of η is less evident, with 7.5 wt.% of added titania, about the 80% of IC photodecomposition is reached after 30 h of irradiation and the nanosuspension keeps aligned to this trend, even if its photoactivity is slightly lower (Fig. 4b and d).

When fired at 1000 °C, no samples acted as a photocatalyst.

The mineralogical analysis of the phase transformations occurring in the samples, during the firing steps, allowed to clarify the different behaviours found.

In Fig. 5, the quantitative anatase–rutile phase transformation, taking place in the tested titania powders fired with the

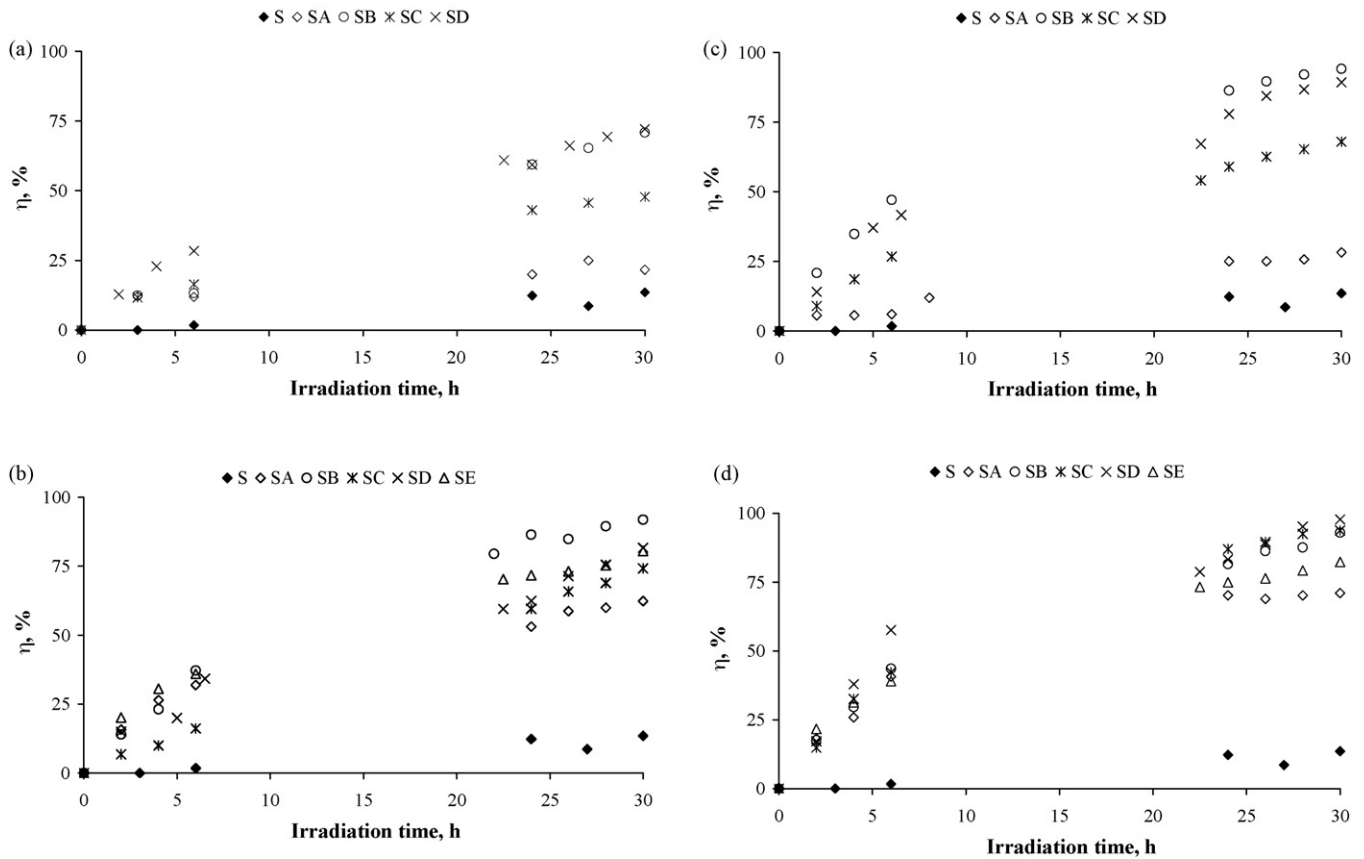


Fig. 3. Photodecomposition efficiency, η , as a function of the irradiation time, for the samples fired at 900 °C: (a) and (c) bulk type, (b) and (d) sprayed type.

same thermal cycle adopted for the ceramic samples, is reported. For the powders A, B and C, the phase transformation from anatase to rutile begins at 950 °C. At 1000 °C, it is completed only for powder C, in A and B, the rutile amount is still about 90 and 14 wt.%, respectively. A completely different behaviour is observed for powder D, that, already at 900 °C, presents only rutile. These results are in agreement with the ones reported in literature, for which the anatase–rutile transformation is promoted by high surface area values, which encourage the nucleation–growth phenomenon.¹⁶ In the present study, this is particularly evident for powder D, that, having 50.0 m²/g of surface area, at 900 °C is completely transformed in rutile.

The mineralogical composition of the standard S, sintered at 900 °C and 950 °C, shows the presence of quartz, clinopyroxenes, plagioclase, gehlenite, and pseudobrookite, with traces of hematite. At 1000 °C, both gehlenite and hematite disappear.¹⁷ When the titania powders are added, SA, SB and SC present a similar mineralogical composition, Table 3. At 900 °C, together with the phases present in the standard, only anatase is revealed. At 950 °C, a mixture of anatase and rutile is present and, in addition, the CaO, remaining from the decomposition of the calcite present in the original raw material, reacts with the titania to form perovskite. In this way, the amount of free titania, acting as photocatalyst, is strongly reduced and, part of that is in its rutile form, characterised by considerably increased crystallite size. All that is able to explain the lower photoactivity shown by the titania added samples when fired at 950 °C.

The titania crystal phase, present in the ceramic sample fired at 1000 °C, is only rutile. In addition, the strong increase in perovskite and pseudobrookite amount, found in the ceramic samples, due to a further reaction of TiO₂ with the CaO and Fe₂O₃ respectively, drastically reduces the amount of free titania, in this way no photocatalytic activity is presented by the ceramic samples.

By increasing the amount of titania, from 2.5 to 7.5 wt.%, even if the mineralogical transformations and reactions are always the same, the larger amount of free TiO₂ is able to explain the higher photoactivity shown by the samples.

Table 3

Mineralogical composition of the samples containing titania fired at different conditions

Crystalline phase	900 °C		950 °C		1000 °C	
	SA, SB, SC	SD	SA, SB, SC	SD	SA, SB, SC	SD
Quartz	●	●	●	●	●	●
Clinopyroxenes	●	●	●	●	●	●
Plagioclase	●	●	●	●	●	●
Gehlenite	●	●	●	●	–	–
Anatase	●	–	●	–	–	–
Rutile	–	●	●	●	●	●
Pseudobrookite	–	–	–	–	●	●
Hematite	●	–	–	–	–	–
Perovskite	–	–	●	●	●	●

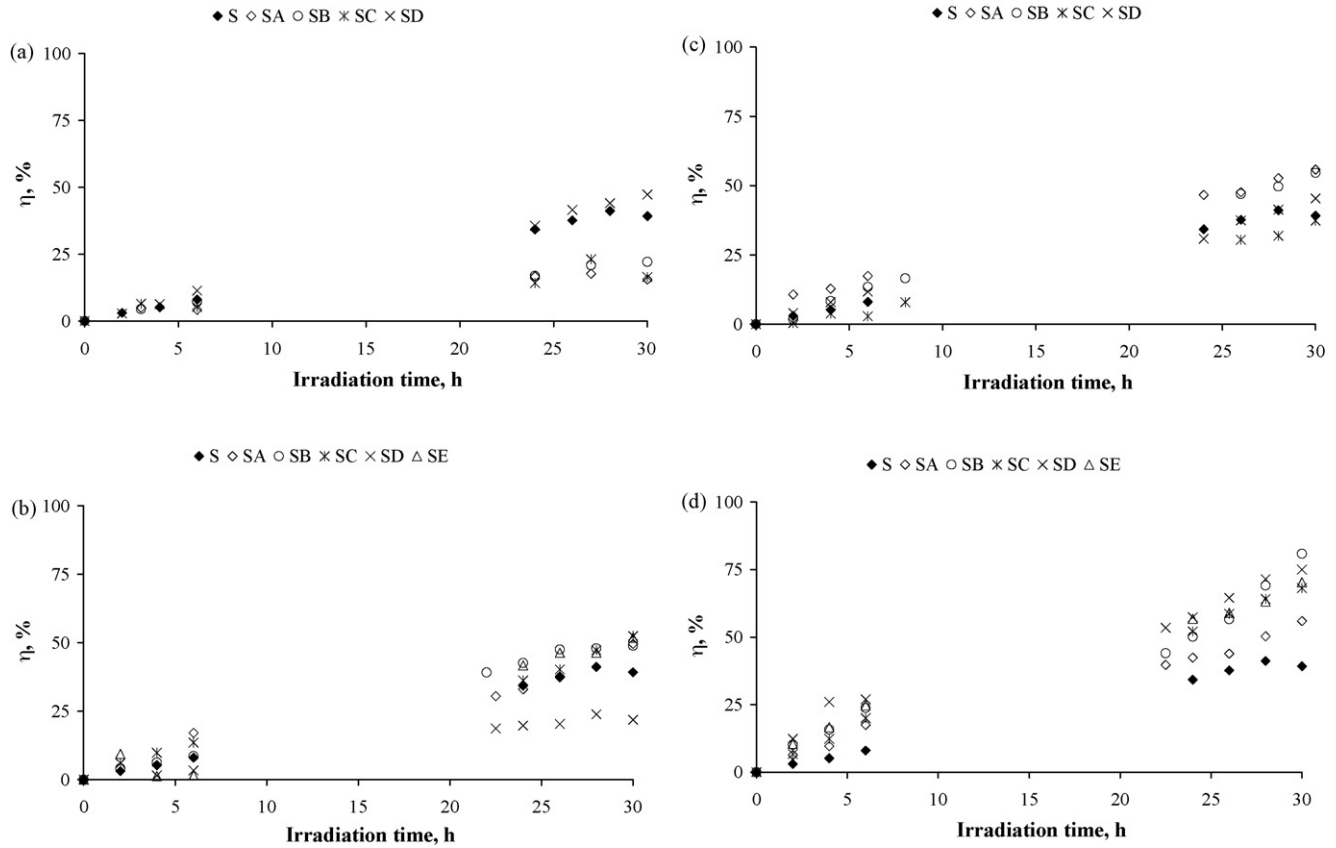


Fig. 4. Photodecomposition efficiency, η , as a function of the irradiation time, for the samples fired at 950 °C: (a) and (c) bulk type, (b) and (d) sprayed type.

Microstructural observation of the fired ceramic samples pointed out as in the bulk type samples, large agglomerates of the original titania powders are always still visible (Fig. 6), according to the softer mixing action used during their preparation.

The surface of the sprayed type samples shows the presence of titania particles rather well dispersed (Fig. 7a and b). The stronger mixing action allowed to better destroy the original titania agglomerates. So, a larger number of titania single particles or agglomerates, of very reduced dimension, are available on the surface of the samples, allowing best photocatalytic performances.

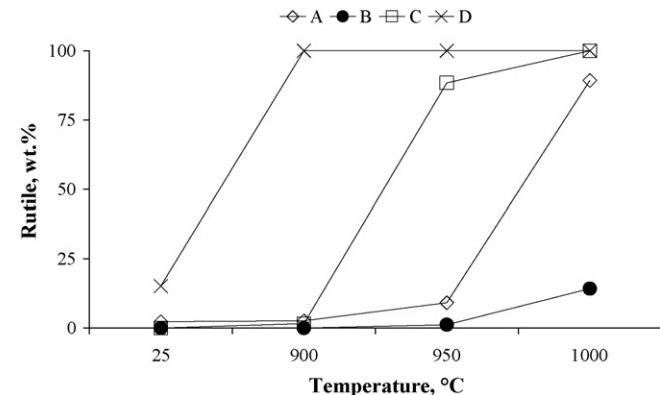


Fig. 5. Quantitative anatase–rutile phase transformation of the tested TiO₂ powders as a function of the firing temperature.

The titania of the samples sprayed with the nanosuspension, fired at 900 °C, is in both its anatase and rutile phase, with an amount of anatase higher than rutile. When the same sample is fired at 950 °C, an opposite trend is revealed, with a rutile amount higher than anatase. The photocatalytic activity of these samples is quite the same, having, of course, a better photoactivity the sample fired at the lower temperature.

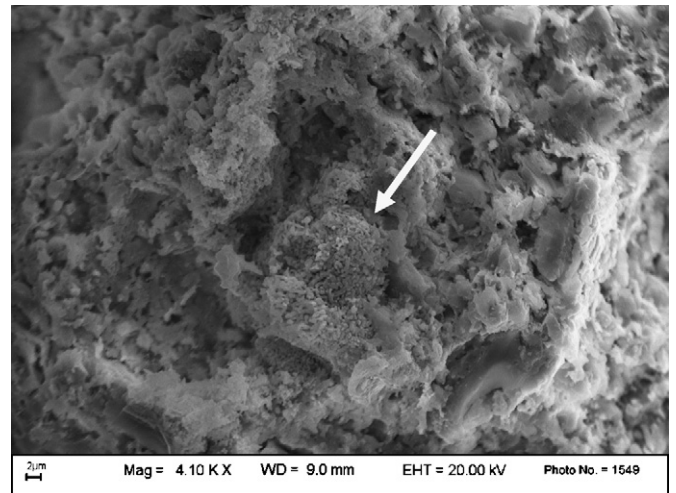


Fig. 6. SEM micrograph of the surface of the sample SA 7.5, bulk type and fired at 900 °C, the arrow points the presence of a titania agglomerate.

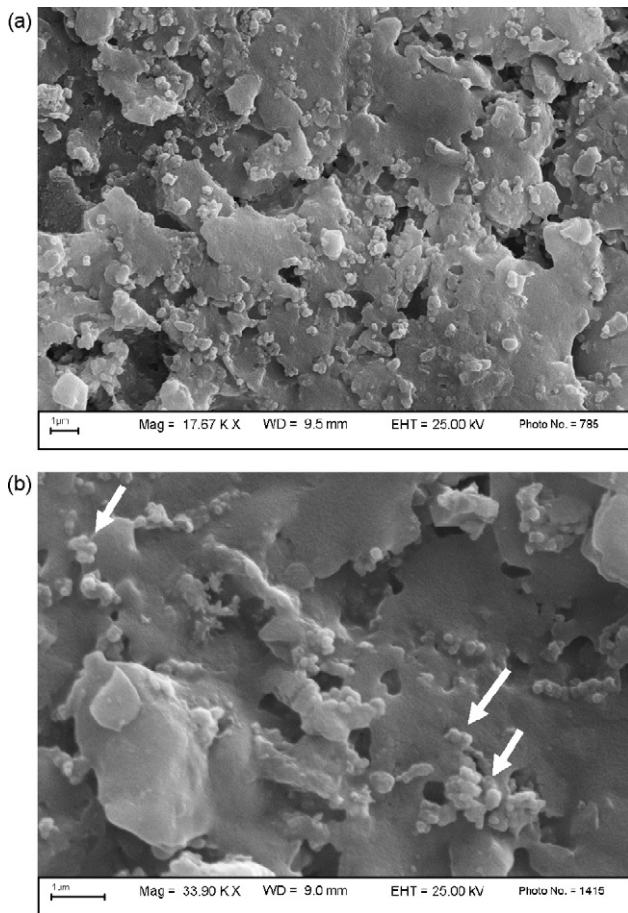


Fig. 7. SEM micrograph of (a) surface of the sample SA 7.5, sprayed type and fired at 900 °C. The round lighter particles are titania; (b) enlargement of the previous micrograph in which the morphology of the single titania particles are better evidenced.

The results obtained allow to underline the strong effect of the particle size of titania powder on the photocatalytic activity. In particular, the nanopowder D, even if completely transformed in rutile, already at the lowest temperature tested, 900 °C, is able to give better performances to the corresponding ceramic samples, SD, in comparison with the results obtained with the addition of titania powders with larger particle size and in the anatase phase, i.e. powder A. Many authors underline as titania, in its anatase phase, is more efficient as photocatalyst than rutile,^{18–22} due to the larger energy band gap ($E_G = 3.23$ eV for anatase, $E_G = 3.02$ eV for rutile) and to its higher hole-trapping ability.²³ For others researchers,²⁴ all that depends by the fact that, in the rutile phase, the recombination of electron-hole produced by UV-light irradiation occurs more rapidly on the surface of the particles and the amount of reactants and hydroxides linked onto the particle surface is smaller than that of the anatase phase. More recent studies^{25,26} emphasize as the photocatalytic activity of titania catalyst is more strongly dependent on its surface area, porosity and morphological aspects, than on its crystalline phase. For these reasons, several studies report, as nanorutile powders with acicular shape show performances similar or even higher than anatase powders.^{27–29} Although, in the present study, titania particles are embedded in a ceramic matrix, the results obtained

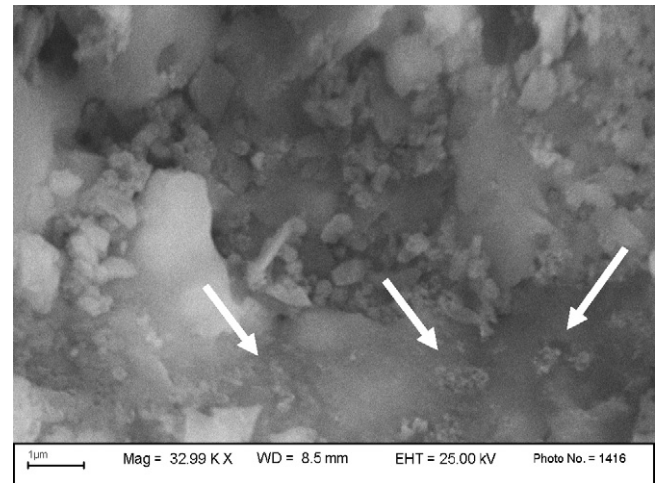


Fig. 8. SEM micrograph of SD 7.5 sprayed type sample surface fired at 900 °C. The lighter arrows underline the presence of titania nanoparticles, in its rutile form.

with powder D are very similar to the published ones.^{27,28} The SEM observation of the surface of the SD samples underlines as the titania particles retain their extremely reduced dimension, in the range 60–100 nm, also after the firing of the ceramic samples (Fig. 8). In this way, the fine rutile particles are able to act as photocatalyst even better than anatase.

4. Conclusions

Several titania powders and a nanosuspension, characterised by different physical and mineralogical characteristics, were used to produce photocatalytically active silicatic based ceramics samples. The photocatalytic activity was evaluated by following the degradation of an organic compound, indigo carmine, in aqueous medium under UV radiation.

The results underline as it is possible to obtain titania added heavy clay ceramics with photocatalytic activity, by using a rather simple processing procedure. The ceramic samples, sprayed with a slip containing 7.5 wt.% of titania powder and fired at 900 °C, presents the best photoactivity, with a complete photo-decomposition of the organic compound. Higher firing temperatures favour both phase transformation (anatase to rutile) and reactions among titania and the iron and calcium oxides (formation of pseudobrookite and perovskite). These factors may be considered responsible of the decreasing photodecomposition extent.

Concerning the photocatalytic activity, titania particle size seems to have a more relevant role than its crystalline phase. The tested powder D, at 900 °C, even if completely transformed in rutile, gives, to the ceramic samples which is added to, the best performances, due to its nanosized dimension.

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