Photocatalytic cement: influence of TiO_2 particle size on photocatalytic performances

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Abstract
The present work addresses the influence of titania (TiO_2) particle size on the self-cleaning and depollution performances of photocatalytic white cement. Degradation of Rhodamine B (RhB), a red dye used to assess self-cleaning performances of concretes containing TiO_2, as well as oxidation of gaseous nitrogen oxides (NOx), atmospheric pollutants responsible for acid rains and photochemical smog, are investigated using two commercial titania samples in cement and mortar specimens: a microsized, m-TiO_2 (average particle size 153.7 nm ± 48.1 nm) and a nanosized, n-TiO_2 (average particle size 18.4 nm ± 5.0 nm). Experimental data on photocatalytic performances are discussed in relation to the chemical environment of cement and impacts on applications in structural concrete.

1. Introduction

Applications of TiO_2 photocatalysts to construction materials began towards the end of the 1980s. Redox reactions on the photocatalyst surface [1], promoted by sunlight (or in general, weak U.V. light), drive the oxidation of environmental pollutants. The photo-induced surface hydrophilicity [2] enhances this self-cleaning effect by mobilising dirt and stains through rainwater soaking between the adsorbed substance and the TiO_2 surface. Examples of TiO_2 – cementitious binders for enhanced aesthetic durability are included in many European, North American and North African structures [3].

The pollution mitigation effect provided by TiO_2 in concretes is mainly achieved by oxidation of atmospheric nitrogen oxides (NOx) to nitrates (NO_3^-). NOx represents the total concentration of nitric oxide (NO) and nitrogen dioxide (NO_2) [4]. Amongst the most used technologies for NOx remediation (combustions modifications, dry processes and wet processes), photocatalytic oxidation (PCO) has become a valid alternative as confirmed by the large number of literature produced [5, 6] in recent years and the increasing number of commercial products available on the market. These products are essentially paints or cements containing photoactive TiO_2 [7], photocatalytic pavement blocks [8], filters and membranes for indoor/outdoor air purifications, etc... A considerable advantage of PCO over other technologies is that the catalyst can be supported on conventional structures and requires only light, atmospheric oxygen and water.

2. Experimental

2.1 TiO_2 samples

Throughout this study, two commercially available titanias: *m-*TiO_2 (microsized) and *n-*TiO_2 (nanosized), both 100% anatase, have been tested. Samples have been fully characterised in another paper of the same authors [9] and results obtained are grouped in Table 1.

Sample	**Crystalline Phase**	**Band Gap**	**S_{BET}**	**BJH Φ_{pore}**	**Particle size**		
					TEM	**XRD**	**BET**
		eV	***m^2g^{-1}***	***Å***	***nm***	***nm***	***nm***
m-TiO_2	100% Anatase	3.29±0.02	8.7	> 500	153.7±48.1	–	177.6
n-TiO_2	100% Anatase	3.34±0.02	78.9	79.6	18.4±5.0	16.6±2.0	19.5

Table 1 – TiO_2 physical characterisation data.

2.2 Aesthetic durability, self-cleaning performances (RhB test)

Two sets of photocatalytic cement pastes were prepared, one for each of the two commercial TiO_2 products. The TiO_2 and white Portland cement (CEM I 52.5 R) powders were dry mixed in the mass ratio 3.5:96.5. 20g of the mixture was subsequently hydrated with 8g of distilled water (water : solid mixture ratio, w/s = 0.4). A third set (control) was prepared without photocatalyst. After mixing, pastes were cast in 42 mm diameter x 5 mm height moulds and let harden (with no cover) for one day at room temperature and 80.5 % relative humidity (over a saturated solution of $(NH_4)_2SO_4$). Six cement discs were produced for each set. After one day of curing, all samples were coated with 20µl of aqueous RhB solution (1.0 g l^{-1}). The coating area was approximately 1.2 cm^2. All three sets were subsequently irradiated with a UVItec LI-208.m lamp (2 tubes 8W each, main wavelength 312nm) and reflectance measurements were performed after various illumination times using a StellarNet EPP2000 Spectrometer.

2.3 Depollution, NOx oxidation

Mortar samples for the NOx oxidation test have been prepared according to the procedure described in the European Standard ISO 679 [10]. In this case mortars were cast in 9 cm diameter x 1 cm thickness plastic Petri dishes. Three sets of twelve mortar discs each were produced: one with m-TiO_2, one with n-TiO_2 and one without photocatalyst as a control.

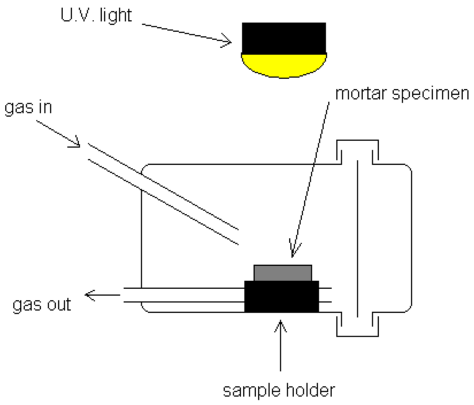

Figure 1 – Photocatalytic reactor for NOx oxidation.

Samples were cured for seven days at room temperature in sealed plastic bags and further seven days at room temperature and 60 % of relative humidity. NOx oxidation experiments have been carried out in a continuous gas flow reactor equipped with a chemiluminescence analyser according to the Italian Standard UNI 11247 [11]. The photocatalytic reactor consists of a Pyrex glass chamber having a total volume of 3.58 l where the specimen under testing can be located on the bottom part supported by a proper sample holder. The gas inlet tube allows the air/NOx mixture to flow directly onto the specimen upper surface whilst the gas outlet tube is positioned underneath the sample holder. The system is kept at room temperature. U.V. light is provided by an OSRAM ULTRAVITALUX lamp having a main emission in the U.V.-A field distributed around a maximum intensity wavelength of about 365 nm. The lamp – sample distance was set to achieve on the upper sample surface an average irradiance of 20 ± 1 W m^{-2}. A schematic diagram of the photocatalytic reactor equipped with the U.V. lamp is illustrated in Figure 1. Experiments were carried out at an inlet NO concentrations of 600 ppb in air with a ratio NO/NO_2 equal to 2 at three different flow rates: 3 l min^{-1}, 2 l min^{-1} and 1.5 l min^{-1}.

3. Results and Discussion

3.1 Aesthetic durability, self-cleaning performances (RhB test)

The degradation of colour of RhB was quantitatively measured by light absorption as a function of wavelength by reflecting light from the cement surface on which the dye is deposited (U.V.-vis Diffuse Reflectance Spectroscopy). Figures 2 shows the spectra obtained. The peak area of the main absorption centred on 541.5 nm is indicative of the concentration of the dye molecule and it can be observed that under illumination, the area reduces as a function of time, i.e. the dye molecule degrades. It can be noted that there is also degradation of colour in samples which do not contain photocatalyst and this highlights an important source of misrepresentation of catalyst efficiency where controls are not used. The loss of colour by photolytic degradation of the dye is quite common, in fact this effect is observed as coloured fabrics are bleached in sunlight. However, even by taking account of this effect, it can be shown that there is an enhanced degradation of colour in the presence of photocatalyst [9]. This proves the self-cleaning effect of cement surfaces if TiO_2 is present in the structure. Figure 2 shows that m-TiO_2 performs better than n-TiO_2. This is quite surprising because according to the BET specific surface areas, 8.7 m^2 g^{-1} for m-TiO_2 and 78.9 m^2 g^{-1} for n-TiO_2, and particle sizes, about 150 nm for m-TiO_2 and about 18 nm for n-TiO_2, the latter is expected to exhibit much higher activities due to higher surface area for adsorption of the RhB and much lower electron – hole recombination in the particles volume.

3.2 Depollution, NOx oxidation

Figures 3(a), 3(b) and 3(c), show the nitric oxide, NO, concentration profiles obtained during the NOx oxidation test at three different flow rates and under illumination. In each graph trends obtained with photocatalytic cement mortars (either with m-TiO_2 or n-TiO_2) are compared to trends exhibited by TiO_2-free white cement mortars. The flat character of profiles where TiO_2 is not present indicates very low impact on NO oxidation by the cement environment itself. Trends also suggest that the lower the flow rate (i.e. the higher the average gas residence time) the lower the NO pseudo steady state concentration (concentration at 90 minutes), hence the higher the conversion. The NO pseudo steady conversion versus flow rate is reported in Figure 3(d). A comparison between photocatalytic activities of mortars containing either m-TiO_2 or n-TiO_2 suggests that n-TiO_2 generally performs better than m-TiO_2. In this case, results are in agreement with what is expected on the basis of the different specific surface areas of the two TiO_2 powders. Note however that surface areas failed to explain the higher activity towards RhB degradation exhibited by samples containing m-TiO_2.

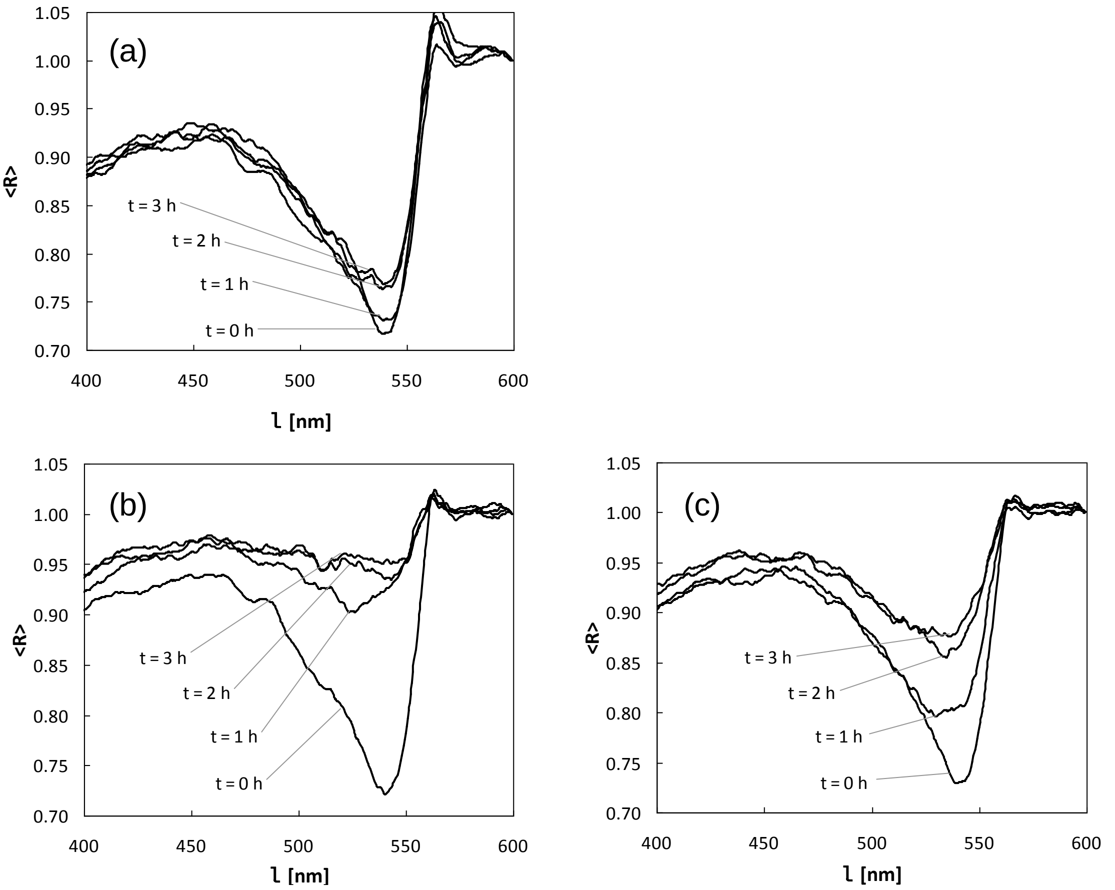

Figure 2 – Diffuse reflectance spectra at various illumination times for white cement paste (a) without photocatalyst, (b) with m-TiO_2, and (c) with n-TiO_2.

3.3 TiO_2 dispersion in hardened cement: a particle aggregation model

In an attempt to understand the different activities exhibited by m- and n-TiO_2 towards RhB and NOx, a surface chemistry approach has been adopted [12]. Coupling surface chemical analyses, ζ-potential and surface charge densities profiles with sedimentation experiments in simulated cement pore solutions, have shown that in conditions of high pH and in the presence of non-indifferent electrolytes (e.g. Ca^{2+}) at high ionic activities (a typical cement environment), both m- and n- TiO_2 particles exhibit tendency to surface overcharging and aggregation due to ion-ion correlation phenomena[12-15]. This has been reported similarly for C-S-H particles [16] and because C-S-H is the principle binder in Portland cement pastes, explains the setting behaviour of cements. The structure of particle clusters due to enhanced agglomeration in cement is however very different if comparing m-TiO_2 with n-TiO_2 [12]. m-TiO_2 agglomerates are smaller, with bigger pores and better dispersed than n-TiO_2 ones [12]. On the basis of such experimental evidence, photocatalytic activities can be interpreted in terms of *available surface area* in the hardened structure rather than B.E.T. specific surface area of titania in powder form. Large molecules like RhB, with an average molecular diameter of about 1.6 nm [17], can penetrate only with difficulty the interior of a n-TiO_2 cluster (pore size around 8 nm), but readily can access m-TiO_2 clusters (see Table 1). Moreover, RhB does not penetrate inside the cement pore structure. The smaller and better dispersed m-TiO_2 clusters on the surface of the specimens offer a higher *available* surface area for adsorption and consequent reaction of big molecules like Rhodamine B than the bigger and poorly dispersed n-TiO_2 agglomerates. On the other hand, gaseous NOx has much smaller dimensions, 100 pm – 200 pm [18], and can easily penetrate *both* m-TiO_2 and n-TiO_2 clusters, accessing a higher surface area in both catalyst types; the higher *available* specific surface area of n-TiO_2 corresponds to the higher NOx degradation on this catalyst.

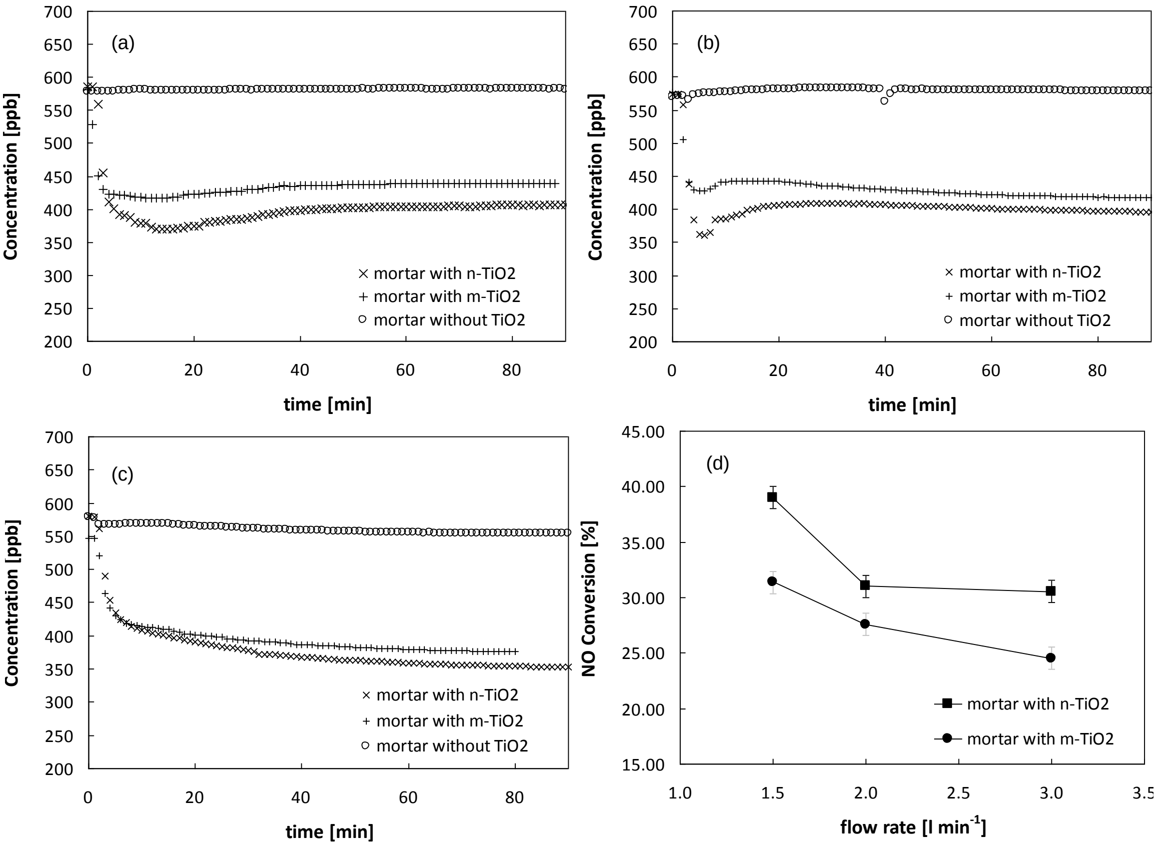

Figure 3 – NO concentration profiles at: (a) 3 l min^{-1}, (b) 2 l min^{-1}, (c) 1.5 l min^{-1}. (d) NO conversion versus flow rate.

4. Conclusions

The study has linked photocatalytic performances to TiO_2 surface/colloidal chemistry and structure of TiO_2 clusters in cement. TiO_2 primary and secondary particle size, dispersion and agglomerate porosity in cement define accessible surface area. Big particle agglomerate pores, small and highly dispersed agglomerates of m-TiO_2 offer a higher *available* surface area for adsorption and reaction of big molecules like RhB which hardly penetrate n-TiO_2 particle agglomerate pores. On the other hand, very small molecules like nitrogen oxides which can easily penetrate into n-TiO_2 agglomerate pores too, are better degraded by n-TiO_2. Indeed in this case, dispersion and agglomerates porosity are not crucial; the available surface area is most likely to be due to the specific surface area determined by primary particle size. These data provide a useful guideline for engineering photocatalytic concretes: where self-cleaning is the main purpose titania samples like m-TiO_2 are preferred to smaller primary particle size titania like n-TiO_2 that conversely are recommended where enhanced depollution properties need to be targeted.

5. Acknowledgment

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