Novel Photocatalytic Paint towards NO Deep Oxidation

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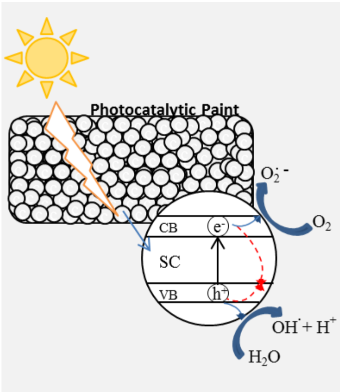

Photocatalysis with titanium dioxide (TiO_2) is a promising approach for photoabatement of pollutants such as nitrogen oxides (NO_x). Bearing in mind outdoor applications, the photocatalysts have to be supported in specific substrates and constructive elements such as tiles, cement mortars or paints are a possibility. Mortars and paint coatings are actually the most used building materials for photoabatement of pollutants. In the present work, a composite photocatalyst of TiO_2/graphene was prepared and studied concerning NO deep oxidation. The performance of this photocatalyst was compared with P25 from Evonik and PC500 from Cristal. Three photocatalytic paints loaded with these photocatalysts were formulated and compared. TiO_2/graphene photocatalyst presented the highest photocatalytic activity concerning NO deep oxidation.

Introduction

Air pollutants were recently recognized to be associated to deaths related to heart disease, stroke, chronic obstructive pulmonary disease and lung cancer than though before. The United Nations considered recently that air pollution is the "single largest environmental health risk", responsible for ca. 3.7 million premature deaths per year. In the past years, a significant legislative effort has been done in Europe and in other regions to improve the quality of air[1, 2]. Photocatalysis with titanium dioxide is being considered for end of pipe treatments since it can decompose a large spectrum of contaminants without additional chemicals and using a relative low-cost, stable and environmentally neutral material[3-5]. Titanium dioxide semiconductor absorbs photons with energy higher than its band gap when irradiated by sun and injects electrons from the valence to the conduction band, creating electron-hole pairs. The holes are responsible for the formation of $OH^{\bullet}$ radicals, which serve as intermediate for the oxidation of organic contaminants[6], while the excited electrons originate superoxide radicals $O_2^{\bullet -}$ that serve as intermediate in the redox reactions during the organic contaminants degradation. TiO_2 is considered an almost ideal photocatalyst, exhibiting several desirable properties. However, this semiconductor has two main drawbacks: it does not absorb visible light and it is a nanoparticulated powder that may bring risks to the human health. So, a new kind of photocatalyst composite is being considered made of graphene decorated with TiO_2 nanoparticles[7]. This composite presents several advantages over bare TiO_2: it has a smaller band gap with better charge separation properties (less recombination) and titania nanoparticles are chemically bonded to the graphene platelets, which makes them harmless for humans.

Concerning the immobilization of the composite photocatalyst TiO_2/graphene, it can be loaded in an especially prepared paint for NO photo-abatement. Photocatalytic paints are interesting supports for photocatalysts, presenting two main features: i) they can be applied in different constructive elements such as streets, buildings or tunnels and ii) they display a porous 3D structure where TiO_2 nanoparticles are available for photocatalysis up to the paint film optic thickness, ca. 100 µm[3]. A photocatalytic paint coating has a very large interfacial area available for photocatalysis, originating very photoactive surfaces to degrade pollutants.

In the present work, TiO_2/graphene photocatalyst was prepared and NO abatement assessed in a photoreactor following approximately standard ISO 22197-1:2007 (E).

Experimental

TiO_2/graphene photocatalyst was prepared as described elsewhere[8]. For hosting the photocatalyst it was selected a commercial exterior water-based paint (vinyl paint), later optimised for maximizing the photocatalytic activity. This paint has high porosity due to a pigment volume concentration (PVC) slightly above the critical value (CPVC), thus allowing the easy access of the pollutant to the photocatalyst. A brief description of this paint composition can be found elsewhere[9].

NO degradation tests were performed using an experimental setup based on standard ISO 22197-1:2007. It consists of four main sections: i) feed, ii) photoreactor, iii) NOx quantification and iv) computer monitoring/control – Figure 1. For these tests the powder catalysts were compressed in aluminium slabs to form a 2 x 2 cm^2 layer of ca. 0.5 mm thick. The photocatalytic paints were applied in the same substrates forming a layer with a thickness of 200 μm.

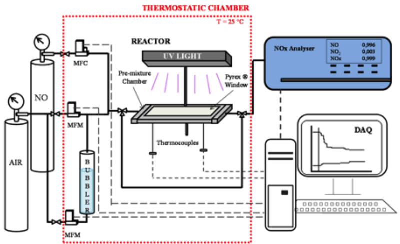

Figure 1. Sketch of the experimental setup used for the photocatalytic tests.

Results and discussion

The photocatalytic activity of TiO_2/graphene, P25 and PC500 photocatalysts towards the NO abatement was assessed in the experimental setup shown in figure 1.

The correspondent results are shown in Figure 2, from which is possible to conclude that the composite photocatalyst presents the best NO conversion. This test allowed also to assess the good stability of the composite during a 150 h experiment – Figure 3. Nevertheless, the photocatalytic activity of PC500 is also very high and so the great advantage of using TiO_2 composite is its reduced bandgap, ca. 2.95 eV (corresponding to a wavelength of 421 nm). Indeed, the composite photocatalyst showed a decrease in the bandgap when compared with P25 and PC500, opening the opportunity of using this photocatalyst under visible light. The band gap of photocatalysts were obtained from Tauc equation, using the diffuse reflectance spectra; the bandgap values for all tested photocatalysts are presented in Table 1[10].

Table 1. Photocatalyst bandgap

Photocatalyst	Bandgap / eV
TiO2/Graphene	2.95
PC500	3.20
P25	3.05/3.16

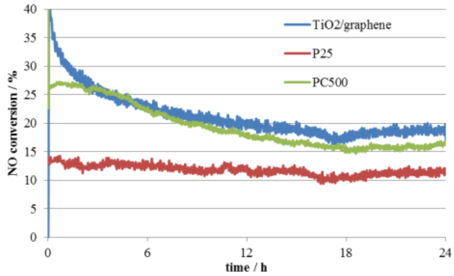

Figure 2. NO conversion histories for commercial photocatalysts (PC500 and P25) and composite photocatalyst (TiO_2/graphene) in powder pressed films.

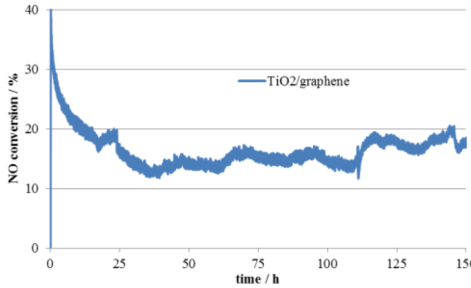

Figure 3. Stability of composite photocatalyst (TiO_2/graphene) in powder pressed films for NO conversion.

A previous work showed that the best performing stand-alone catalyst was not the best performing in a photocatalytic paint, suggesting that the interaction between the paint matrix and TiO_2 plays an important role on the correspondent photoactivity[11]. One of the major components on the formulation of a paint is titanium dioxide, which gives opacity to the paint. The so-called pigmentary TiO_2 is made of coated rutile microparticles, where the coating is used for preventing the paint degradation. Indeed, for preparing photocatalytic paints the formulation needs to be modified to remove all pigmentary TiO_2, which acts as a blocking agent for the solar radiation resulting in low levels of NO conversion, and, instead, incorporate photocatalytic titanium dioxide (anatase). Since the maximum photocatalytic TiO_2 content that can be incorporated is ~12 wt.%, the remaining content of pigmentary TiO_2 has to be replaced by extenders, which is actually beneficial for the photoactivity of the paint film. Calcium carbonate was selected as extender since it is a cheap material, more transparent to the UV light than the pigmentary TiO_2 and it reacts with nitrate compounds producing calcium nitrates; these are easily washed off from the paint surface. Indeed, NO conversion is favoured when using calcium carbonate since it assists removing the reaction products nitrates and nitrites[12].

The optimized photocatalyst content incorporated in the present formulated paints was 9 wt.%.

The photocatalytic activity tests of the paint films are currently being obtained.

Conclusion

A TiO_2/graphene photocatalyst was prepared and its photocatalytic activity assessed in a photoreactor according to standard ISO 22197-1:2007 (E). This test also allowed to evaluate the stability of the photocatalyst. The photocatalytic activity of the TiO_2 composite was then compared with two commercial photocatalysts: P25 and PC500. The TiO_2/graphene photocatalyst showed the highest photocatalytic activity for NO degradation in powder pressed film with a very good stability and it has a reduced bandgap, enabling its usage under visible light conditions.

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