



## Photocatalytic NO<sub>x</sub> abatement: The role of the material supporting the TiO<sub>2</sub> active layer

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### ABSTRACT

The importance of the choice of a suitable substrate as supporting material for photoactive TiO<sub>2</sub>, either in the form of powders or thin films or in photoactive paints, is frequently disregarded. In this paper four different supports (stainless steel, sand-blasted stainless steel, Teflon and glass) are object of investigation. The final aim is to verify the presence of interactions between the photocatalyst (AEROXIDE® TiO<sub>2</sub> P25 by Evonik Degussa Corporation) and the support, directly involved in the photocatalytic activity in the NO<sub>x</sub> abatement. The characterization results have been correlated with the photoactivity of the different samples. In particular, a coating of about 6–9 μm seems to allow a photocatalytic result free from any positive or negative interference with the supporting material, therefore giving reliable results about the photoactivity of the TiO<sub>2</sub> under investigation.

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### 1. Introduction

Nitrogen oxides (NO<sub>x</sub>), are one of the major air pollutants and are often used as reference pollutant in the gas phase. In fact, they can be effectively removed by photocatalytic oxidation on titanium dioxide [1]. As reported in many papers of the recent literature, the development of photocatalytic systems based on TiO<sub>2</sub> is essential for the design of highly efficient photocatalytic materials for environmental purification. In particular, the possibility of preparing TiO<sub>2</sub>-based powders or thin films with tailored features, pure or doped with foreign ions, is one of the main targets of the present and future investigations [2,3].

However, the experimental set-up and the procedures employed to perform the photocatalytic tests have not yet been adequately assessed in literature. When operating in the liquid phase, slurry reactors, consisting in the catalysts dispersed in the liquid medium, are commonly used. When photocatalytic materials are tested in gas reactions, many different kinds of reactor are reported. Few examples from the most recent literature on NO<sub>x</sub> photocatalytic degradation include: a gas-tight acrylic flow reactor equipped with a Pyrex window containing the pressed photocatalyst [4]; a photoactive sample coated on a glass plate placed into a quartz reactor [5]; a fixed-bed reactor [6]; a glass holder plate set in the center of a reactor [7]; a glass substrate coated with the film

placed in the center of an acrylic container [8], and so on and so forth. The experimental procedure and set-up according to the ISO 22197-1 standard test [9] should also be mentioned. In this case the photocatalyst coats a Teflon holder inside the reactor and TiO<sub>2</sub> is often mixed with a support, whose choice is usually not motivated.

Thus, it is difficult to select the best reaction set-up. Furthermore, when powders, paints or thin films of TiO<sub>2</sub> are tested, it is necessary to find a suitable "sample holder" to keep samples under the UV or solar lamp irradiation during the test.

Very few papers are present in the literature highlighting the possible interference of the holder on the photocatalytic properties of the material. In particular Yu and Zhao [10] showed the behavior of transparent anatase TiO<sub>2</sub> nanometer thin films prepared on soda-lime glass, fused quartz, and soda-lime glass precoated with a SiO<sub>2</sub> layer. The diffusion of sodium and calcium ions from the soda-lime glass into the nascent TiO<sub>2</sub> films was found to be detrimental to the photocatalytic activity of the resulting TiO<sub>2</sub> films. The authors concluded that when the thickness of the SiO<sub>2</sub> layer on the soda lime glass was 0.3 mm or greater, diffusion of sodium and calcium ions was prevented and the photocatalytic activity of TiO<sub>2</sub> films was enhanced.

Chen et al. [11] proposed a rational approach in determining the effect of mass transfer and catalyst layer thickness during photocatalytic reactions. An ideal thickness of 5 μm was reported.

In the present paper the effects of different substrates employed as supporting materials are investigated. The TiO<sub>2</sub> photocatalyst (AEROXIDE® TiO<sub>2</sub> P25 by Evonik Degussa Corporation) was deposited on the surface of four fixed-sized supporting plates

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(glass, Teflon, steel and sand-blasted steel) in order to verify the existence of interactions between the photoactive powder and the supporting material. Ideally, this latter should only hold the powder during the reaction test and have no influence on photoactivity.

The results show a strong dependence of photoactivity on both the thickness of the P25 layer and the kind of supporting material, with a large decrease of the NO<sub>x</sub> photodegradation in gas phase when a single TiO<sub>2</sub> layer is deposited on glass. A three times thicker layer leads to the final result of total NO<sub>x</sub> removal after 90 min in all cases. However, by comparing the initial (30 min) pseudo-first order rate constants of NO<sub>x</sub> abatement, a slight difference among the titania-coated supports is still present.

## 2. Experimental

### 2.1. Samples preparation

The commercial TiO<sub>2</sub> powder, AEROXIDE® TiO<sub>2</sub> P25 by Evonik Degussa Corporation (called P25 henceforth – anatase–rutile composite, specific surface area 50 m<sup>2</sup> g<sup>-1</sup>) was used as photocatalyst. Four different supports were chosen: a Teflon lamina (T), a simple glass lamina (G), a stainless steel lamina, employed either as received (SS) or after sand-blasting and etching in 10% oxalic acid for 1 h (BS). All the laminas had a geometric area of 40 cm<sup>2</sup> (rectangular shape, 20 cm × 2 cm).

The TiO<sub>2</sub> powder was first suspended in 2-propanol (50 ml) so obtaining a homogeneous suspension and then deposited by drop casting onto one side of the laminas. The solvent was simply evaporated at room temperature without any further treatment.

Two different series of samples were prepared. The first one consisted in a thin TiO<sub>2</sub> layer obtained with a single coating of 0.015 g of pure P25 (labeled as M, standing for monolayer and followed by the substrate abbreviation). The second series consisted in a thicker layer, obtained by overlapping three TiO<sub>2</sub> coatings, each containing 0.050 g of pure P25 (labeled as T, standing for triple layers, followed by the substrate abbreviation).

The mechanical stability of powdered TiO<sub>2</sub> was not checked systematically, because this is out of the scope of the present paper. The support, in fact, should only act as holder for the photocatalytic powders and allow the test of their activity in the gas phase avoiding the use of a fixed-bed set-up.

### 2.2. Samples characterization

The photocatalytic samples were characterized by XPS and Contact Angle measurements, and by metallographic microscope and profilometer analyses.

XPS measurements were performed in an M-Probe Instrument (SSI) equipped with a monochromatic Al-Kα source (1486.6 eV) with a spot size of 200 μm × 750 μm and a pass energy of 25 eV, providing a resolution of 0.74 eV. Using a monochromatic source, an electron flood gun was adopted to compensate the buildup of positive charge on the insulator samples during the analyses: a value of 10 eV was selected to perform the measurements. For all samples, the C1s peak at 284.6 eV was taken as internal reference. The accuracy of the reported binding energies (BE) can be estimated to be ±0.2 eV. The quantitative data were accurately checked and reproduced several times (at least 10 times for each sample). In the present study, the attention was focused on the binding energies of the Ti 2p region.

Contact angle measurements with water were performed to check the wetting and adhesion properties of the photocatalytic layer. The instrument adopted is a Data Physics OCA 150 equipped with a SCA20 version 2.3.9. build 46 software. The reported results were determined as average of four different lecture points.

Measurements were performed on both the uncoated and coated materials.

A metallographic microscope (Nikon Eclipse MA200) was used to investigate the TiO<sub>2</sub>-coated and uncoated surface of the supports so to verify the homogeneity of the photoactive layer.

Measurements of both the surface profiles and the layers thickness were performed on all M and T samples by non-contacting laser profilometry (3D laser profilometer, UBMMicrofocus Compact, NanoFocus AG, Germany).

### 2.3. Photocatalytic testing

Each photocatalyst, immobilized on the support as already described, was placed into a Pyrex reactor (volume of 20 L) and irradiated with an halogenide lamp (Jelosil, model HG500) emitting in the 340–400 nm wavelength range (20 W cm<sup>-2</sup>, photon flux 2.4 × 10<sup>-5</sup> E dm<sup>-3</sup> s<sup>-1</sup>, determined by actinometry), with a nominal power of 500 W, at room temperature [12,13]. The relative humidity was kept constant at 50% in all of the runs. Air and NO<sub>x</sub> gas streams were mixed to obtain the desired concentration (1 ppm NO<sub>x</sub>), and sent to the photoreactor. The concentrations of the photodegradation products, NO and NO<sub>2</sub>, were continuously monitored by an on-line chemiluminescence analyzer (TeledyneInstruments M200E).

Blank tests in the dark and experiments in the absence of photocatalyst were performed to assess the extent of NO<sub>x</sub> adsorption on the TiO<sub>2</sub> layer (ca. 10% after 120 min) and direct photolysis (<5% after 150 min).

## 3. Results and discussion

Fig. 1 shows the metallographic microscope images of TiO<sub>2</sub>-M samples. The presence of the TiO<sub>2</sub> thin layer can be appreciated together with its good homogeneity on all the supports, except for M.BS. In this case small areas of the metallic support are not completely covered by the photoactive material, probably due to the excessive roughness of the surface of the support. As expected, all T samples show a complete and homogeneous support coverage.

A more detailed analysis was achieved through layer thickness measurements by profilometry. All M samples show a TiO<sub>2</sub> layer of 1.5–2 μm (average value) with a maximum thickness value equal to 3 μm, while all T samples show an average thickness value of 5–6 μm, with a maximum of 9 μm.

Contact angle measurements highlight the different behavior of the materials in terms of surface hydrophilicity/hydrophobicity properties. Images from bare and monolayer samples are reported in Fig. 2.

A comparison between the results obtained for the bare and coated materials, supported on different substrates, provided information about the surface properties of the native materials and the ones induced by the presence of the TiO<sub>2</sub> layer. In particular, the strong hydrophilicity of the glass support (Fig. 2a1) is maintained also in the presence of the TiO<sub>2</sub> layer (Fig. 2b1). On the contrary, stainless steel (as received or sand-blasted, Fig. 2a2 and a3, respectively) and Teflon (Fig. 2a4) show hydrophobic characteristics that radically turn to hydrophilicity when the TiO<sub>2</sub> coating is added. Average contact angle values (from Young equation) for both M and T samples are reported in Table 1. It can be observed that the presence of even a single TiO<sub>2</sub> layer is able to alter the surface properties of the chosen support.

The effect of the support properties on the TiO<sub>2</sub> surface layer was also evidenced by XPS analysis. Our examination was mainly focused both on the survey analysis, which revealed the absence of any contaminant on all the studied samples, and the binding energies (BE) of the Ti 2p region. The XPS spectrum of the pure

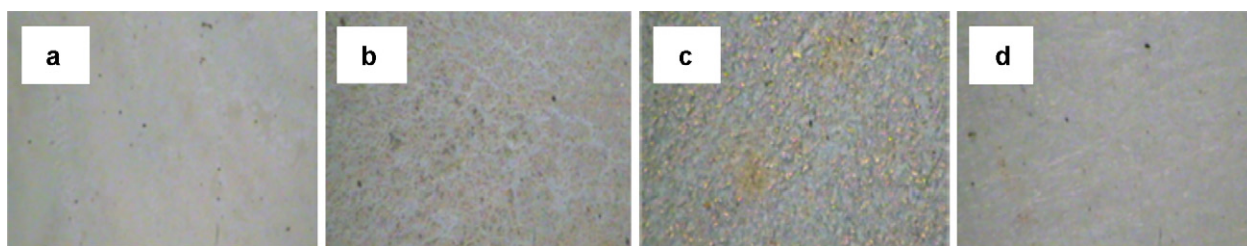


Fig. 1. Metallographic microscope images of the supports with one layer of TiO<sub>2</sub> P25: (a) glass; (b) steel; (c) blasted steel; and (d) Teflon.

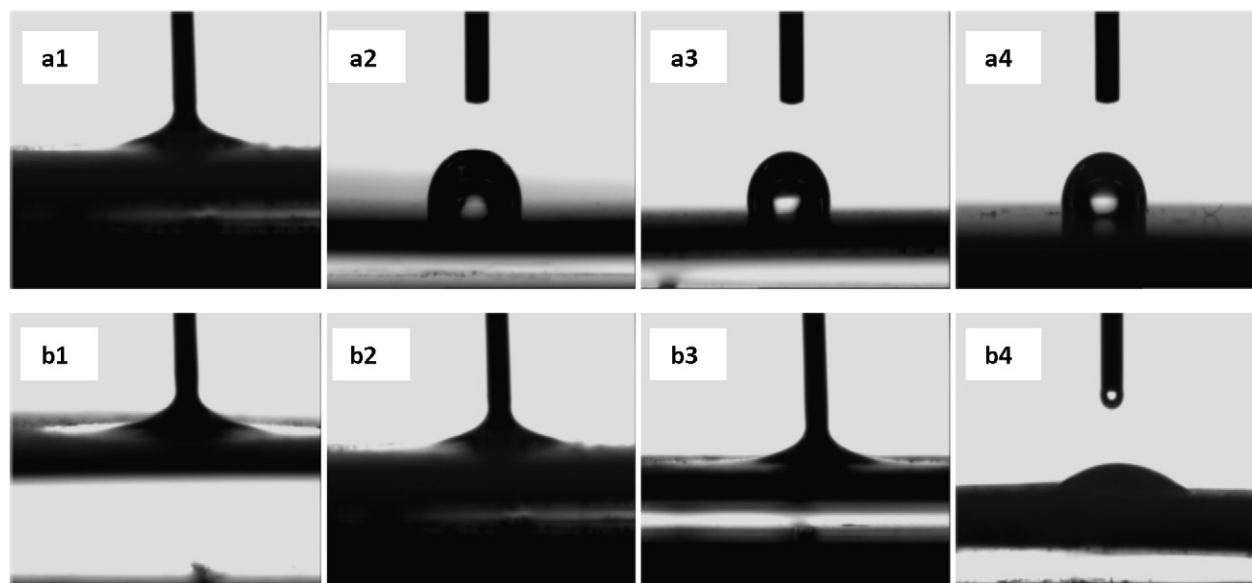


Fig. 2. Contact angle measurements for bare and M-samples: (a) glass; (b) steel; (c) blasted steel; (d) Teflon.

TiO<sub>2</sub> powder (P25) shows the classical Ti 2p doublet with the main peak (Ti 2p<sub>3/2</sub>) at 458.5 eV as already reported many times in the literature [14] (Fig. 3a). The same BE value ( $\pm 0.2$  eV) was obtained for all the T laminas and for the two M samples immobilized on steel.

Completely different spectra were registered for the M.G and M.T samples, i.e. for TiO<sub>2</sub> monolayers deposited on glass or Teflon. In both cases the Ti 2p doublet is characterized by a very complex shape, possibly fitted by more than one component. More in detail (Fig. 3b and c), both M.T and M.G show a second peak at lower BE as a Ti<sup>4δ-</sup> and at higher BE as Ti<sup>4δ+</sup>, respectively. The modification of the Ti 2p region can only be ascribed by an unexpected interaction between the photoactive powder and the two supporting materials. In fact, no other ions were present on the samples surface, as verified by the XPS survey analyses, and no thermal or chemical treatments that could have altered the P25 chemical structure were performed after the deposition of the TiO<sub>2</sub> films.

This interaction is probably the reason to which is to ascribe the different performance of the M samples in the gas phase NO<sub>x</sub> photocatalytic abatement (Fig. 4).

**Table 1**  
Mean contact angle values. Measurements performed with water.

	Glass	Stainless steel	Sand-blasted steel	Teflon
Uncoated sample	n.d.	102.7°	100.3°	112.5°
M sample	n.d.	n.d.	n.d.	31.9°
T sample	n.d.	n.d.	n.d.	27.0

n.d., not definable.

The NO<sub>x</sub> concentration is the sum of the NO and NO<sub>2</sub> concentrations; the general mechanism of photodegradation of NO<sub>x</sub> implies the oxidation of the nitric monoxide to nitric or nitrous acid by the reactive species at the TiO<sub>2</sub> surface. All the samples resulted in a very efficient photodegradation of the NO<sub>x</sub>, giving a very similar trend and the achievement of a quasi-plateau after 90 min. Complete NO<sub>x</sub> abatement and 90% NO<sub>x</sub> degradation was attained only in the case of BS and SS, respectively. As all the M-supporting materials were coated with the same amount of P25 (0.015 g), the better performance of the sand-blasted sample might be explained by possible backscattering phenomena due to the roughness of the support.

Less satisfactory results were obtained for both M.T and M.G, where only 78% and 58% photocatalytic NO<sub>x</sub> abatement was respectively obtained at the end of the test (150 min). For photocatalytic coatings applied on the glass substrate, a similar result was already reported by Bertron et al. [15]: the authors observed a decrease of the process efficiency attributable to the deactivation of the photocatalyst. Analogous results of support-depending photoactivity were obtained using nanometer thin films prepared via the sol-gel method on soda-lime glass, fused quartz, and soda-lime glass precoated with a SiO<sub>2</sub> layer [10] and with photocatalytic films deposited on quartz, soda lime glass, and SiO<sub>2</sub>-coated substrates, via the spray pyrolysis method [16].

In the case of our samples, an explanation is provided by the partial variation of the Ti binding energy, as evidenced by XPS measurements (Fig. 3). It is well-known that the photocatalytic activity of TiO<sub>2</sub> may be directly correlated to the presence of Ti<sup>4+</sup> ions, giving rise to the 458.6  $\pm$  0.2 eV XPS peak [14]. In the present case, both TiO<sub>2</sub> samples supported on Teflon and glass showed one shoulder

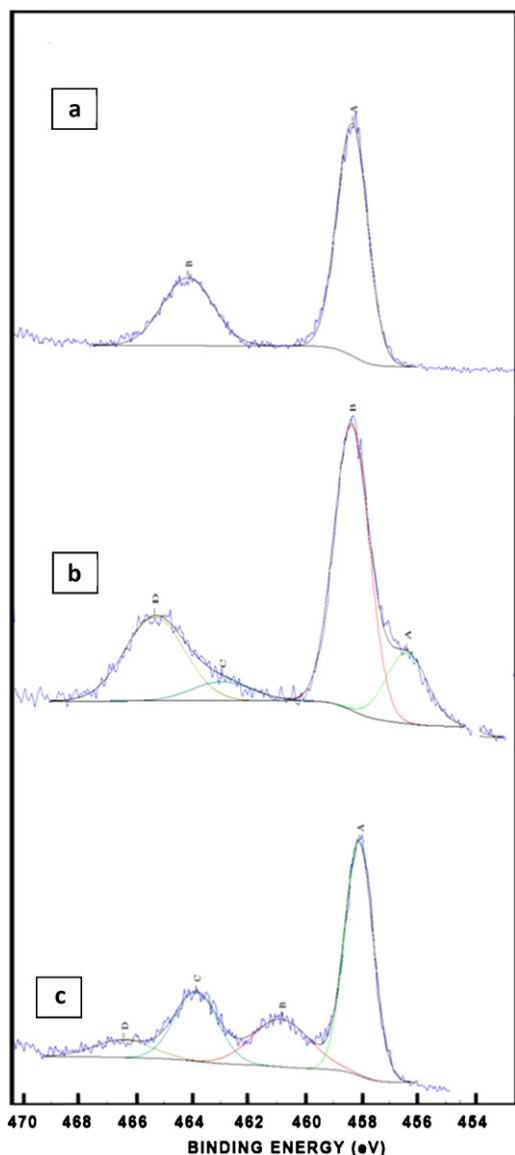


Fig. 3. XPS Ti 2p region: (a) pure P25; (b) M.Teflon sample; and (c) M.glass sample.

in the main Ti 2p<sub>3/2</sub> peak (Fig. 3), due to the probable interaction between the photocatalytic crystallites and the lamina surface, as previously mentioned. In particular, M.T exhibits a new XPS component at lower BE (456.6 eV), similar to the BE usually attributed to Ti(III) [17]. Hence, to hypothesize a reduction of part of the Ti(IV) by the simple deposition of the P25 powder on the Teflon lamina is in this case impossible. The shift of the BE can indeed be ascribed to an interaction of the Ti crystallites with the electron-rich surface of the supporting material (due to the presence of the F-atoms). This new BE component is about 23% of the whole Ti species, according to the fitting of the Ti 2p<sub>3/2</sub>, therefore in good agreement with the observed loss of photocatalytic activity (22%).

The XPS spectrum of M.G is characterized by an extra component at higher BE (460.4 eV, 30% of the whole Ti signal), not completely consistent with the 43% of the decrease of the photoactivity. An interaction between titania nanofilms and the glass substrates was already observed through XPS measurements by Guo-Jun and Zhi-Ming [18], who mainly investigated the shape of the Si 2p region. These authors observed two Si components: one at higher BE (103.5–104.0 eV) assigned to Si–O–Si bonds, and the lower BE peak (102.1–102.3 eV) ascribed to Ti–O–Si bonds [19]. Ti

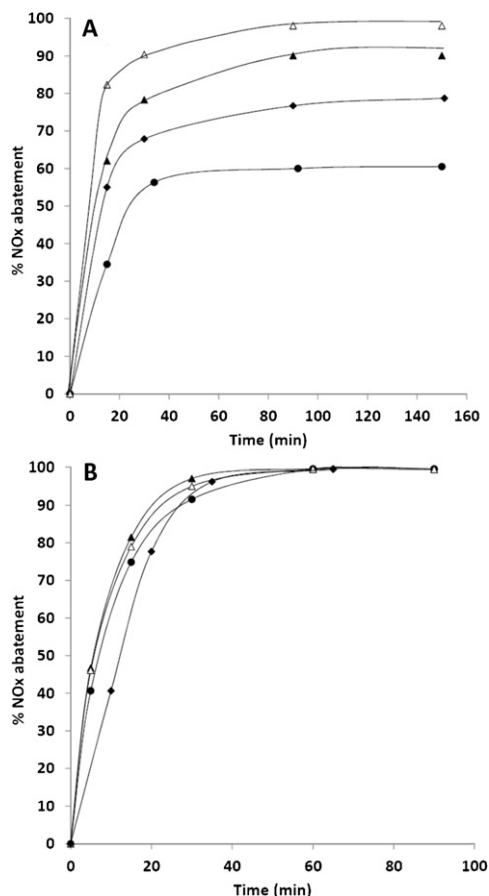


Fig. 4. Gas-phase NO<sub>x</sub> photodegradation. For all samples: [NO<sub>x</sub>]<sup>0</sup> 1 ppm, T=30 °C, relative humidity = 50%. (A) M.samples, (B) T.samples. Supports symbols: (●) glass, (◆) Teflon, (▲) steel, and (△) sand-blasted steel.

atoms seemed to increase the electron density around the Si atoms and enhanced the shielding effect on them; therefore, the BE of Si 2p in Ti–O–Si bonds was lower than that in Si–O–Si bonds and consequently the BE of Ti 2p was higher, as confirmed by Wang et al. [20].

The XPS spectra of all the T samples evidenced no alterations of the Ti 2p region, showing the classical Ti 2p doublet, as usually shown by P25 and, with these samples, the full degradation of the pollutant was obtained in 90 min (100% NO<sub>x</sub> abatement, Fig. 4b).

In order to produce a further comparison among the tested samples, first order rate constants were calculated from the experimental data relative to the first 30 min of irradiation, as reported elsewhere [13]. The data are displayed in Table 2. Besides the expected differences in the NO<sub>x</sub> abatement rates for the different M samples, it was also possible to appreciate different values of the rate constants for the T samples. These latter follow in fact the same trend observed for M.coatings. Thus, P25 thicker layers still interact with the supporting substrate and this causes alterations in the material photoactivity, although only the external fraction of the material, exposed to radiation, acts as photocatalyst.

Table 2  
Initial (30 min) pseudo-first order rate constants for M and T samples in the case of NO<sub>x</sub> degradation in gas phase.

Support	M_sample $k^{30} \times 10^2$ (min <sup>-1</sup> )	T_sample $k^{30} \times 10^2$ (min <sup>-1</sup> )
Glass	2.46 ± 0.6	7.10 ± 0.2
Teflon	3.86 ± 0.6	8.22 ± 0.1
Stainless steel	5.02 ± 0.2	9.01 ± 0.1
Sand-blasted steel	7.66 ± 0.3	10.00 ± 0.2

#### 4. Conclusions

The choice of a suitable support to test the photoactivity of TiO<sub>2</sub> in powders, thin films or formulated in paints turned out to be not a minor detail in order to achieve satisfactory photocatalytic test results. In the present paper commercial P25 was deposited on four different supporting plates (stainless steel, sand-blasted stainless steel, Teflon and glass).

For very thin TiO<sub>2</sub> films or deposits (in the range of 3 μm), the photoactive material was affected by interactions with the support bringing to an alteration of the photocatalytic performance in the NO<sub>x</sub> abatement in the gas phase. In particular, the outcome of this study showed that glass and Teflon supports should be avoided due to a very strong interaction that might occur with the photocatalytic crystallites. In fact, this provoked an important decrease of the material photoactivity in the photodegradation of the pollutants in the gas phase.

On the other hand, steel, better if sand-blasted, turned out to be a good support, even if specific interactions with the tested photocatalytic material cannot be discarded also in this case. The positive role of the steel in the photocatalytic activity may be ascribable to its conductive properties. These might in fact have improved the charge separation between the excited electrons and the positive holes, thus enhancing the photocatalytic process.

A triple layer coating higher than 6 μm seems to lead to photocatalytic tests free from any positive or negative interference with the supporting materials, therefore giving reliable results about the photoactivity of the TiO<sub>2</sub> under investigation.

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