Visible light TiO$_2$ photocatalysts assessment for air decontamination

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**A B S T R A C T**

Different visible light responses of commercial TiO$_2$ photocatalysts are assessed for their application in air decontamination. To do that the modified TiO$_2$ catalysts were immobilized on borosilicate glass plates according to a dip coating method. Then, the photocatalytic performance of these plates was evaluated in a continuous gas flat plate photo reactor irradiated with visible light lamps using two representative air pollutants: nitrogen oxide and acetaldehyde. Working under visible light, the modified TiO$_2$ catalysts were compared by means of efficiency parameters: the true quantum efficiency, which relates the moles of degraded pollutant with the moles of the absorbed photons, and the apparent photonic efficiency, which relates the moles of degraded pollutant with the moles of incident photons. Also, the photocatalytic pollutants degradation by immobilized modified TiO$_2$ could be related with their optical properties, finding a clear correlation between them. These results are useful to decide which TiO$_2$ will be more efficient for a full scale air decontamination process under visible light illumination.

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1. **Introduction**

Heterogeneous photocatalysis represents an emerging environmental control option for the efficient removal of chemical pollutants that can be applied for water and air purification (Hoffmann et al., 1995). One of the limitations of this technology is that normal TiO$_2$ can only be activated by UV radiation (280–400 nm) that represents 4% of the total energy of the sun; meanwhile the visible light constitutes 45% of the solar radiation. On the other hand, the UV radiation amounts to only 0.001–0.05 W/m$^2$ in indoor lighting (Kuo et al., 2007). To extend the use of photocatalysis to visible light region, it is necessary to prolong TiO$_2$ radiation absorption to wavelengths corresponding to visible spectrum (400–700 nm). So far, several modification methods of photocatalyst to amplify its absorption spectrum to visible radiation have been investigated and therefore, the applicability of heterogeneous photocatalysis has been extended (Banerjee et al., 2014; Chatterjee and Dasgupta, 2005; Daghiri et al., 2013; Kisch and Maceyk, 2002). Several commercial types of modified TiO$_2$ can be already found in the market for indoor visible light applications.

There are various types of modified TiO$_2$ active under visible light and different methods to perform the modification process. A first method is the treatment of TiO$_2$ with reductive hydrogen plasma (Van Durme et al., 2007). TiO$_2$ can also be sensitized by adsorbed dyes and semiconductors having lower band-gaps and more cathodic conduction bands (Demeester et al., 2005). A third method is the TiO$_2$ doping with...
transition metals such as Fe, Cu, Co, Ni, Cr, V, Mn, Mo, Nb, W, Ru, Pt and Au (He et al., 2010). Finally, an alternative approach is the doping with non-metal anions, like nitrogen (Jo and Shin, 2010), carbon (Kuo et al., 2007) or sulphur (Nishijima et al., 2007).

In many studies employing modified TiO₂ with visible light absorption, the photocatalytic degradation of several volatile organic compounds (VOCs) and inorganic gases has been studied: nitrogen oxides (Yu and Brouwers, 2009; Lin et al., 2006; Nakamura et al., 2000), 2-propanol (Ihara et al., 2001), toluene (Fuertes et al., 2001; Ihara et al., 2001; Kubacka et al., 2009; Van Durme et al., 2007), acetaldehyde (Asahi et al., 2001; Iketani et al., 2004; Nishijima et al., 2007; Sakthivel and Kisch, 2003a, 2003b), acetone (Ihara et al., 2003), benzene (Sakthivel and Kisch, 2003a,b), carbon monoxide (Sakthivel and Kisch, 2003a,b), trichloroethylene (Demeestere et al., 2005; Jo and Yang, 2010), dimethyl sulphide (Demeestere et al., 2005) and dimethyl disulphide (Jo and Shin, 2010), methyl-tertiary butyl ether (Jo and Yang, 2010), acetic acid (Nishijima et al., 2007), and formic acid (Nishijima et al., 2007).

In the present work, different visible light absorption TiO₂ commercially available catalysts, one doped with carbon, another doped with nitrogen and two photocatalytic solutions ready to use, are studied. The carbon doping introduces new states close to the valence band edge of TiO₂ narrowing the photocatalyst band gap. In addition, carbonaceous species at the surface of the photocatalyst facilitates the absorption in the visible wavelengths as well as the high surface area of the doped TiO₂ promotes the adsorption of pollutants. Nitrogen doped titania could have either substitutional or interstitial N atoms in the TiO₂ matrix, resulting in a visible light response due to the electron transition from the localized N orbital to the conduction band or to the surface adsorbed O₂. One of the employed solutions is made of silver modified TiO₂. The noble metal doping increases the separation of photogenerated charge carriers and reduces the recombination rate of photoinduced electron–hole pair.

Two representative air pollutants are employed to assess the photocatalytic performance under visible light of the modified TiO₂ mentioned above: (i) NO as an inorganic contaminant and (ii) acetaldehyde as a simple structured organic pollutant. The nitrogen oxides (NOₓ) are the generic term for a group of highly reactive gases, most of them emitted to air in the form of nitric oxide (NO) and nitrogen dioxide (NO₂). They are mainly formed in combustion processes and cause a wide variety of health and environmental impacts. The NOₓ compounds are responsible for tropospheric ozone and urban smog through photochemical reactions with hydrocarbons. Furthermore, NOₓ together with SO₂ (sulfur dioxide and sulfur trioxide) is the major contributor to the “acid rain”. On the other hand, acetaldehyde is one of toxic, irritant, and probable carcinogen VOC contaminant in indoor and outdoor environments. It is also a result of: (i) combustion processes, such as vehicle exhaust, tobacco smoke, and wood burning, and (ii) sources in homes including building materials, like laminate, linoleum, wooden varnished, and cork/pine flooring, plastic water based and matt emulsions paints, wooden, particleboard, plywood and chipboard furniture (Missia et al., 2010).

The photocatalysts were immobilized on borosilicate glass plates according to a dip coating method. The optical properties of the immobilized samples were determined in order to correlate the visible light absorption with the de-polluting capability. The performance of these systems was evaluated calculating the photonic and the quantum efficiencies, that correlate the contaminant reaction rate with the incident radiation flux and the absorbed radiation by the catalysts, respectively. The main objective of this work is to determine which photocatalyst will present the best pollution abating ability in a full scale application under visible light conditions.

### Table 1 – Prepared samples and main characteristics.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Type of catalyst</th>
<th>Number of layers</th>
<th>Glass surface</th>
<th>Suspension pH</th>
<th>Specific load (g cm⁻²) × 10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-C-1 L</td>
<td>Carbon doped TiO₂ powder</td>
<td>1</td>
<td>Smooth</td>
<td>6</td>
<td>3.75</td>
</tr>
<tr>
<td>TiO₂-C-4 L</td>
<td></td>
<td>4</td>
<td>Smooth</td>
<td>6</td>
<td>8.02</td>
</tr>
<tr>
<td>TiO₂-C-1 L-S</td>
<td></td>
<td>1</td>
<td>Sandblasted</td>
<td>1</td>
<td>1.06</td>
</tr>
<tr>
<td>TiO₂-C-4 L-S</td>
<td></td>
<td>4</td>
<td>Sandblasted</td>
<td>1</td>
<td>2.34</td>
</tr>
<tr>
<td>TiO₂-N-1 L</td>
<td>Nitrogen doped TiO₂ powder</td>
<td>1</td>
<td>Smooth</td>
<td>6</td>
<td>2.12</td>
</tr>
<tr>
<td>TiO₂-N-4 L</td>
<td></td>
<td>4</td>
<td>Smooth</td>
<td>6</td>
<td>4.43</td>
</tr>
<tr>
<td>TiO₂-N-1 L-S</td>
<td></td>
<td>1</td>
<td>Sandblasted</td>
<td>1</td>
<td>0.965</td>
</tr>
<tr>
<td>TiO₂-N-4 L-S</td>
<td></td>
<td>4</td>
<td>Sandblasted</td>
<td>1</td>
<td>1.53</td>
</tr>
<tr>
<td>TiO₂-Ag-Sol-4 L</td>
<td>Silver modified TiO₂ solution</td>
<td>4</td>
<td>Smooth</td>
<td>–</td>
<td>0.280</td>
</tr>
<tr>
<td>TiO₂-Sol-4 L</td>
<td>Visible light response modified TiO₂ solution</td>
<td>4</td>
<td>Smooth</td>
<td>–</td>
<td>0.501</td>
</tr>
</tbody>
</table>

2. Experimental

2.1. Sample preparation

Four types of visible light photocatalysts were acquired from the marked: a powder doped with carbon, a powder doped with nitrogen and two liquid solutions ready to use for coatings. The measured BET area for the Carbon and Nitrogen doped TiO₂ powders were 251 m² g⁻¹ and 34 m² g⁻¹ respectively.

The immobilization of the TiO₂ powders and liquid suspensions was carried out according to a dip coating procedure on borosilicate glass plates. The TiO₂ powders load in deionized water to prepare the coating was 75 g L⁻¹. For every dip coating cycle, the glass piece was dried at 110 °C for 2 h and calcined at 500 °C for 2 h, repeating this procedure four times. Additionally, in order to increase the adhesion between the TiO₂ particles and glass, especially for employing the carbon doped catalyst, some plates were sandblasted. On the other hand, as the TiO₂ suspensions at natural pH precipitate quite fast, different suspensions at different pHs adjusted with nitric acid and sodium hydroxide were prepared, finding that the suspension at pH 1 for both TiO₂ powders were the most stable. Table 1 summarizes all prepared sample and the corresponding deposited photocatalyst mass per unit area. The given sample names are TiO₂-m-nL or TiO₂-m-nL-S, where m refers
to the agent that modifies the TiO₂, n is the number of layers (L) of the immobilized sample, and S means sandblasted glass.

In order to assess the stability of the prepared samples, the coatings made with TiO₂-C and TiO₂-N were flushed with water, observing only a mass decreased of the films on the smooth glasses.

2.2. Optical properties

The optical properties of the immobilized TiO₂ on the glass plate were determined as a function of wavelength between 300 and 600 nm in an Optronic OL Series 750 spectroradiometer equipped with an OL 740-70 integrating sphere reflectance attachment coated with polytetrafluorethylene (PTFE). To evaluate the fraction of energy absorbed (A) by the TiO₂ film, the spectral diffuse reflectance and the spectral diffuse transmittance of the coated glass were experimentally determined according to the schematic representation made in Fig. 1 (Zacarías et al., 2012).

2.3. Photocatalytic performance

The photocatalytic performance of the prepared samples was studied with the degradation of two air contaminants, one inorganic and another one organic, in to some extent quite similar experimental setups. Some operating conditions stated in the ISO standards 22197-1 and 22197-2 (ISO, 2007, 2011) for nitrogen oxide and acetaldehyde degradation

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**Fig. 1** – Integrating sphere configuration (a) Diffuse reflectance measurement. (b) Diffuse transmittance measurement.

**Fig. 2** – Experimental setup. (a) NO degradation, and (b) acetaldehyde degradation.
respectively were followed. For the degradation of the inorganic compound (nitrogen oxide), the applied experimental device is composed of a planar reactor cell housing the photocatalytic plate sample, a suitable visible light source, an online chemiluminescent NOx analyzer and an appropriate gas supply (Fig. 2(a) (Ballari et al., 2010). The chemiluminescence method uses the reaction of NO with O3 generating excited NO2* molecules that return to the ground state emitting chemiluminescence in the range of 600–3000 nm. The light intensity is proportional to the concentration of NO molecules. On the other hand, a deoxidation converter changes the NO2 to NO, which is then measured. In other words, the NO2 concentration can be obtained by the difference between: (i) the NOx (NO + NO2) concentration measured when the sample gas is directed through a converter and (ii) the NO concentration measured when the gas is not run through the converter.

For the degradation of the organic pollutant (acetaldehyde) a continuous planar photoreactor with similar dimensions to the previous one was also employed, with the difference that here the glass pieces with the immobilized TiO2 were irradiated on both sides of the photoreactor to improve the photocatalytic degradation of the pollutant. The photocatalytic reactor was fed by acetaldehyde gas stabilized in nitrogen and irradiated with fluorescence visible light lamps (Fig. 2(b)). The outlet and inlet contaminant concentration from the reactor was analyzed employing a gas chromatograph with a FID detector performing a direct injection of the gas sample.

Table 2 shows the main characteristics, dimensions and operating conditions of the experimental setup that were employed to carry out the NO and acetaldehyde photocatalytic degradation experiments.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Nitrogen oxide</th>
<th>Acetaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Length</td>
<td>20 cm</td>
<td>20 cm</td>
</tr>
<tr>
<td>Width</td>
<td>10 cm</td>
<td>10 cm</td>
</tr>
<tr>
<td>Height</td>
<td>0.3 cm</td>
<td>0.2 cm each side</td>
</tr>
<tr>
<td>Volume</td>
<td>60 cm³</td>
<td>40 cm³ each side</td>
</tr>
<tr>
<td>Photocat. sample</td>
<td>Length</td>
<td>20 cm</td>
</tr>
<tr>
<td>Width</td>
<td>10 cm</td>
<td>10 cm</td>
</tr>
<tr>
<td>Visible lamps</td>
<td>Input power</td>
<td>Philips master TLD 865 × 3</td>
</tr>
<tr>
<td></td>
<td>Emission Wavelength</td>
<td>GE F4TS/CW × 14</td>
</tr>
<tr>
<td>Flow rate</td>
<td>3 L min⁻¹</td>
<td>1 L min⁻¹</td>
</tr>
<tr>
<td>Temperature</td>
<td>20–23 °C</td>
<td>21–24 °C</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>Irradiance flux</td>
<td>10 W m⁻²</td>
<td>64 W m⁻² each side</td>
</tr>
<tr>
<td>Inlet pollutant concentration</td>
<td>1 ppm</td>
<td>5 ppm</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Optical properties

The results of the diffuse transmittance and reflectance measurements of the prepared samples on the smooth glasses (\(T_{\text{TiO}_2-g \text{TiO}_2}\) and \(R_{\text{TiO}_2-g \text{TiO}_2}\) respectively) can be found in Fig. 3. Fig. 4 shows the optical measurements for the sandblasted samples for 1 and 4 layers.

The radiation absorption fraction (\(A\)) of the immobilized photocatalyst can be calculated from the measured values of diffuse reflectance (\(R\)) and diffuse transmittance (\(T\)) of the borosilicate glass alone and coated with TiO2 on both sides.

Fig. 3 – Experimental optical properties of smooth coated glass. (a) Diffuse transmittance, and (b) diffuse reflectance.

To do that, a radiative flux balance is applied in each layer of Fig. 5 according to (Edwards, 1977; Siegel and Howell, 2002):

\[
q_{m-1} = T_n q_n + R_n q_{m-1} \quad n = 1, 2, 3 \tag{1}
\]

or:

\[
q_m = R_m q_m + T_m q_{m-1} \quad n = 1, 2, 3 \tag{2}
\]
where $T_n$ and $R_n$ are the diffuse transmittance and reflectance of the $n^{th}$ layer respectively, $q_n^+$ and $q_n^−$ are the net radiation flux going into and out from the $n^{th}$ layer respectively.

Also, considering that:

$$T_{\text{TiO}_2, \text{g}, \lambda} = \frac{q_3}{q_5}$$  \hspace{1cm} (3)

$$R_{\text{TiO}_2, \text{g}, \lambda} = \frac{q_7}{q_5}$$  \hspace{1cm} (4)

and $R_3 = R_5 = R_{\text{TiO}_2}, R_2 = R_7 = T_3 = T_{\text{TiO}_2}$, and $T_2 = T_5$, the following expressions for the optical properties of the TiO$_2$ film can be derived (see Appendix A):

$$R_{\text{TiO}_2} = \frac{R_{\text{TiO}_2, \lambda}T_3 - T_{\text{TiO}_2, \lambda}R_4}{T_{\text{TiO}_2, \lambda}R_7 - T_{\text{TiO}_2, \lambda}R_5 + T_7}$$ \hspace{1cm} (5)

$$T_{\text{TiO}_2} = \sqrt{\frac{R_{\text{TiO}_2, \lambda}R_7 - R_{\text{TiO}_2, \lambda}R_5 + T_{\text{TiO}_2, \lambda}R_4}{R_8 + (T_{\text{TiO}_2, \lambda}R_7 - R_{\text{TiO}_2, \lambda}R_5)}}$$ \hspace{1cm} (6)

where $R_5$, $R_{\text{TiO}_2, \lambda}$, $T_5$, and $R_{\text{TiO}_2, \lambda}$ are the experimental diffuse reflectance and transmittance of the borosilicate glass and the coated glass on both side with TiO$_2$, respectively.

Fig. 4 – Experimental optical properties of sandblasted coated glass. (a) Diffuse transmittance, and (b) diffuse reflectance.

Fig. 5 – Schematic representation of the immobilized TiO$_2$ on glass during the optical properties measurements.

Then, the absorption radiation fraction can be calculated as follows (Siegel and Howell, 2002):

$$A_{\text{TiO}_2} = 1 - R_{\text{TiO}_2} - T_{\text{TiO}_2}$$ \hspace{1cm} (7)

The calculated absorption fraction for the different tested samples together with the spectral emission distribution of the employed lamps can be found in Figs. 6 and 7 for the coatings on the smooth and sandblasting glasses respectively.

As it can be observed in Fig. 6, the fraction of energy absorbed by the commercial photocatalytic solutions is significantly lower than the TiO$_2$ powders absorption. On the other hand, the TiO$_2$ doped with carbon and 4 layers presents better radiation absorption on both smooth (Fig. 6) and sandblasted (Fig. 7) glasses. However, comparing the results in Figs. 6 and 7 for TiO$_2$-C and TiO$_2$-N samples and 4 layers, the sandblasting samples prepared with a TiO$_2$ suspension at pH equal to 1 present a significantly lower radiation absorption capability than the samples prepared on smooth glass with a natural pH suspension. This last is due to the TiO$_2$ suspension prepared at pH1 presents smaller particle agglomerates and a less amount of catalyst deposited on the sandblasted glass (see Table 1).

In average, the TiO$_2$-C absorbed 32% and 20% more radiation than the TiO$_2$-N for the smooth and sandblasted samples respectively.

Fig. 6 – Spectral fraction of energy absorbed by the immobilized TiO$_2$ on smooth glass and the spectral emission distribution of the Philips lamps.
Fig. 7 – Spectral fraction of energy absorbed by the immobilized TiO₂ on sandblasted glass and the spectral emission distribution of the GE lamps.

3.2. Nitrogen oxide degradation

The photocatalytic oxidation of NOₓ mixtures is reported in several publications (Devalhasdin et al., 2003; Shelimov et al., 2008; Wang et al., 2007). All of them proposed the NO decomposition to NO₂, and then NO₂ to HNO₂ through the hydroxyl radical attack generated during the photocatalyst activation stage. For the reacting system applied here, fed with NO, NO₂ generation was observed as a reaction intermediate. As a result, the NOₓ (NO + NO₂) concentration is higher than the NO concentration at the reactor outlet.

The NO and NO₂ conversions for all samples on smooth glasses are reported in Table 3 and calculated according to:

$$X_i[\%] = \frac{C_{i\text{in},i} - C_{i\text{out},i}}{C_{i\text{in},i}} \times 100$$  \hspace{1cm} (8)

where i indicates NO or NOₓ (NO + NO₂), and Cᵢᵢ and Cᵢᵢ are the reactor inlet and outlet concentration, respectively.

The samples prepared with the two commercial photocatalytic solutions did not show a significant NO₂ reduction (less than 2%). So, these samples were not considered for further analysis.

Fig. 8 shows the total NOₓ and NO concentration during the test for the carbon and nitrogen doped TiO₂ immobilized on the smooth glasses. Clearly, the carbon doped TiO₂ has shown a better photocatalytic performance for the NOₓ degradation than the nitrogen doped TiO₂ powder. Meanwhile the total NO₂ conversion by the TiO₂-C was about 18%, the TiO₂-N presented only 6% of NO₂ degradation (Table 3).

In Table 4, three parameters related with the photocatalytic performance of the samples are reported. The first one is the average reaction rate in the photoreactor, calculated as:

$$\langle r_i \rangle_R = \frac{Q(C_{i\text{in},i} - C_{i\text{out},i})}{A_{\text{meas}}}$$  \hspace{1cm} (9)

where Q is the gas flow rate in the photoreactor and Aₘₑₐₛ is the catalytic interfacial area. The calculated average reaction rate can be assumed free of external and internal mass transport limitations according to Appendix B.

The second parameter, the apparent photonic efficiency, is calculated as (Imoberdorf et al., 2007; Passalía et al., 2013; Muñoz Batista et al., 2014):

$$\eta_{p,i} = \frac{\langle r_i \rangle_R}{\sum_i q_{\text{wall}} \lambda}$$  \hspace{1cm} (10)

where \(\sum_i q_{\text{wall}} \lambda\) is the total incident radiation flux on the catalytic wall expressed in Einstein m⁻² s⁻¹.

Finally, in order to incorporate the effect of the effectively absorbed radiation by the catalyst, the true quantum efficiency is calculated according to Eq. (11) (Imoberdorf et al., 2007; Passalía et al., 2013; Muñoz Batista et al., 2014) and summarized in Table 4.

$$\eta_{q,i} = \frac{\langle r_i \rangle_R}{\sum_i A_{\text{TiO}_2,i} q_{\text{wall}} \lambda} = \frac{\langle r_i \rangle_R}{\sum_i A_{\text{TiO}_2,i} (E_{\lambda,i}/E_{\text{wall}}) q_{\text{wall}} \lambda}$$  \hspace{1cm} (11)

The values of the parameters reported in Table 4 follow the same trend than the NO and NO₂ conversion reported in Table 3 for both samples. However, the difference between the quantum efficiencies of TiO₂-N and TiO₂-C samples is clearly less important since the TiO₂-N catalyst absorbs less radiation than the TiO₂-C. Meanwhile the NO₂ conversion, reaction rate and photonic efficiency for the TiO₂-N sample are about 70% lower than the TiO₂-C ones, the quantum efficiency is only 50% lower.

3.3. Acetaldehyde degradation

The global reaction pathway of the acetaldehyde photocatalytic degradation can be assumed as follows (Sauer and Ollis, 1996):

Acetaldehyde → Formaldehyde → FormicAcid → CO₂  \hspace{1cm} (12)

However, in the studied system only trace amounts of formaldehyde were detected and no formic acid was present (within the detection limit of 0.2 ppm for the developed analytical method).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>X_SCO</th>
<th>X_NOₓ</th>
<th>X_Aacet</th>
<th>X_Min_Aacet</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-C-4L</td>
<td>65.31</td>
<td>18.47</td>
<td>97.88</td>
<td>89.13</td>
</tr>
<tr>
<td>TiO₂-C-4L-S</td>
<td>-</td>
<td>-</td>
<td>77.67</td>
<td>70.53</td>
</tr>
<tr>
<td>TiO₂-N-4L</td>
<td>10.75</td>
<td>6.13</td>
<td>88.09</td>
<td>83.00</td>
</tr>
<tr>
<td>TiO₂-N-4L-S</td>
<td>-</td>
<td>-</td>
<td>51.06</td>
<td>44.67</td>
</tr>
<tr>
<td>TiO₂-Ag-Sol-4L</td>
<td>1.88</td>
<td>1.12</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂-Sol-4L</td>
<td>1.76</td>
<td>0.58</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
The degradation of acetaldehyde by the samples prepared on smooth or sandblasted glasses with the carbon and nitrogen doped TiO$_2$ can be compared in Fig. 9. For this contaminant, again the degradation by samples prepared with the commercial photocatalytic solutions is neglected compared with the carbon and nitrogen doped TiO$_2$.

In addition to the experimental results shown in Fig. 9, extra and longer tests were performed employing the sandblasted samples in order to evaluate the catalysts deactivation. After more than 10 h of reaction, the acetaldehyde degradation remained nearly constant.

Table 3 also reports the acetaldehyde conversion calculated according to Eq. (8) (with $i=\text{Acet}$) as well as the acetaldehyde total oxidation or mineralization ($X_{\text{Min,Acet}}$) that takes into account the formation of intermediates, calculated as:

$$X_{\text{Min,Acet}}[\%] = \frac{C_{\text{in,Acet}} - C_{\text{out,Acet}} - C_{\text{out,Form}}}{C_{\text{in,Acet}}} \times 100$$  \hspace{1cm} (13)

where $C_{\text{out,Form}}$ is the concentration of the formed formaldehyde at the reactor outlet.

Table 5 shows the acetaldehyde average reaction rates, and the apparent photonic and true quantum efficiencies.

Employing this contaminant, again the best de-pollution capability is observed for the TiO$_2$-C deposited on smooth glass, reaching almost 100% of conversion (Table 3). In this reaction system, two new samples prepared on sandblasted glasses and employing TiO$_2$-C and TiO$_2$-N powders suspension at pH 1 were tested. As discussed before, the amount of catalyst on this support was smaller, leading to a lower radiation absorption and therefore to a reduced acetaldehyde conversion.

In the same way that for the NO$_x$ pollutant, the acetaldehyde conversion, reaction rate and photonic efficiency present the same trend if all samples are compared. However, the true quantum efficiency for the TiO$_2$-C-4 sample decreases significantly and its value becomes lower than for the rest of the samples. This last result is because an almost complete conversion was reached for the organic contaminant under the used operating conditions. In other words, as the acetaldehyde is consumed before is getting out of the reactor, for the TiO$_2$-C sample on smooth glass the effective catalyst reacting area is lower. Notice that for the calculation of the reaction rate the same area of 10 x 20 cm$^2$ was taken into account for all samples; consequently, the average reaction rate for TiO$_2$-C catalyst was underestimated leading to a lower quantum efficiency value.

Comparing the two reacting systems, the acetaldehyde conversion and reaction rate are significantly higher than the NO$_x$ conversion using the smooth glass support. However, the acetaldehyde degradation for the nitrogen doped TiO$_2$ is exceeding the NO$_x$ degradation by only a factor of 1.7 and 1.9 considering the apparent photonic and true quantum efficiencies respectively. On the contrary, for the case of the carbon doped TiO$_2$, the apparent photonic and true quantum efficiencies for the NO$_x$ degradation is 1.6 and 1.5 respectively higher than for the acetaldehyde degradation due to, as mentioned before, the reaction rate for this sample was undervalued.

Anyhow, the true quantum and apparent photonic efficiencies for both reacting systems become more comparable than the respective reaction rates and conversions since the incident radiation flux in the acetaldehyde reacting system is higher than for the NO$_x$ degradation.

A correlation between the obtained results for the photocatalytic performance and the fraction of energy absorbed by the immobilized TiO$_2$ powders can be observed. At the same time that the TiO$_2$-C absorbs about 32% more energy than TiO$_2$-N on smooth borosilicate glass, it could convert 66% more NO$_x$. On the other hand, using the sandblasted glasses, TiO$_2$-C also absorbs 20% more radiation than TiO$_2$-N and could degrade 37% more acetaldehyde. One of the reasons of the better performance of TiO$_2$-C can be attributed to its higher specific surface. However, it is worth to mention that other photocatalyst characteristics not studied here can influence its performance.

### Table 4: Average reaction rate, apparent photonic and true quantum efficiencies for nitrogen oxide degradation.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>($\frac{r_{\text{NO}<em>2}}{r</em>{\text{NO}_2}}$) $\times 10^3$ mol m$^{-2}$ s$^{-1}$</th>
<th>($\frac{r_{\text{NO}<em>x}}{r</em>{\text{NO}_x}}$) $\times 10^3$ mol m$^{-2}$ s$^{-1}$</th>
<th>$\eta_{\text{phot,NO}} \times 10^3$</th>
<th>$\eta_{\text{phot,NO}_x} \times 10^3$</th>
<th>$\eta_{\text{phot,NO}} \times 10^3$</th>
<th>$\eta_{\text{phot,NO}_x} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-C-4 L</td>
<td>7.28</td>
<td>2.06</td>
<td>1.64</td>
<td>0.46</td>
<td>5.36</td>
<td>1.52</td>
</tr>
<tr>
<td>TiO$_2$-N-4 L</td>
<td>1.20</td>
<td>0.68</td>
<td>0.27</td>
<td>0.15</td>
<td>1.28</td>
<td>0.73</td>
</tr>
</tbody>
</table>

### Table 5: Average reaction rate, apparent photonic and true quantum efficiencies for acetaldehyde degradation.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>($\frac{r_{\text{Acet}}}{r_{\text{Acet}}}$) $\times 10^3$ mol m$^{-2}$ s$^{-1}$</th>
<th>($\frac{r_{\text{Min,Acet}}}{r_{\text{Min,Acet}}}$) $\times 10^3$ mol m$^{-2}$ s$^{-1}$</th>
<th>$\eta_{\text{phot,Aacet}} \times 10^3$</th>
<th>$\eta_{\text{phot,Min,Acet}} \times 10^3$</th>
<th>$\eta_{\text{phot,Aacet}} \times 10^3$</th>
<th>$\eta_{\text{phot,Min,Acet}} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-C-4 L</td>
<td>9.10</td>
<td>8.28</td>
<td>0.31</td>
<td>0.28</td>
<td>1.11</td>
<td>1.01</td>
</tr>
<tr>
<td>TiO$_2$-C-4 L</td>
<td>7.22</td>
<td>6.56</td>
<td>0.25</td>
<td>0.22</td>
<td>1.74</td>
<td>1.58</td>
</tr>
<tr>
<td>TiO$_2$-N-4 L</td>
<td>8.19</td>
<td>7.71</td>
<td>0.36</td>
<td>0.26</td>
<td>1.49</td>
<td>1.40</td>
</tr>
<tr>
<td>TiO$_2$-N-4 L</td>
<td>4.75</td>
<td>4.15</td>
<td>0.01</td>
<td>0.14</td>
<td>1.56</td>
<td>1.36</td>
</tr>
</tbody>
</table>
4. Conclusions

The performance of different commercial modified TiO2 photocatalysts was assessed under visible light for their application for air decontamination. Two representative air pollutants, nitrogen oxide and acetaldehyde, were successfully degraded for two of the four catalyst tested, the carbon and nitrogen doped TiO2 powders.

The radiation absorption fraction of the immobilized catalysts was calculated from a radiation flux balance model and using the experimental values of diffuse reflectance and diffuse transmittance measurements.

The de-polluting performance of the selected catalysts for both inorganic and organic reacting systems was evaluated calculating the apparent photonic and the true quantum efficiencies. A correlation between the photocatalytic pollutants degradation and the immobilized TiO2 optical properties was also found. These results are useful to appraise which TiO2 will be more efficient for a full scale air decontamination process under indoor conditions. Particularly, under the tested operating conditions employed in the present work, the carbon modified photocatalyst promises a better performance for a real application.

Acknowledgements

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Appendix A. Appendix A

According to Eq. (1), it can be written:

\[ q_5 = T_q q_5 + R_q q_5 = T_{\text{NO}_2} q_5 \] (A.1)

\[ q_1 = T_q q_1 + R_q q_1 = T_{\text{NO}_2} q_1 + R_{\text{NO}_2} q_1 \] (A.2)

Then, considering a system conformed by only one layer (layer 1), \( q_1 \) can be expressed according to:

\[ q_1 = R_{\text{NO}_2} q_1 = R_{\text{NO}_2} q_1 \] (A.3)

Replacing Eq. (A.3) into Eq. (A.2) and vice versa, the following expressions can be obtained respectively:

\[ q_1 = \frac{T_q q_1}{1 - R_q T_{\text{NO}_2}} \] (A.4)

Also expressing \( q_2 \) according to Eq. (1):

\[ q_2 = T_3 q_3 + R_3 q_3 = T_{\text{NO}_2} + R_{\text{NO}_2} q_2 \] (A.6)

Now, considering a system conformed by two layers (layers 1 and 2) the out coming flux \( q_2 \) can be expressed according to:

\[ q_2 = R_{1.2} q_2 = R_{\text{NO}_2} q_2 \] (A.7)

In the same way as before, the following expression for \( q_3 \) and \( q_1 \) can be derived:

\[ q_3 = \frac{T_{\text{NO}_2}}{1 - R_{\text{NO}_2} R_{\text{NO}_2}} \] (A.8)

\[ q_2 = \frac{R_{\text{NO}_2} g T_{\text{NO}_2}}{1 - R_{\text{NO}_2} R_{\text{NO}_2} g} \] (A.9)

Replacing Eq. (A.8) into Eq. (A.4):

\[ q_1 = \frac{T_q T_{\text{NO}_2}}{(1 - R_q R_{\text{NO}_2})(1 - R_{\text{NO}_2} R_{\text{NO}_2} g)} \] (A.10)

Replacing Eq. (A.10) into Eq. (A.1):

\[ q_0 = \frac{T_q T_{\text{NO}_2}^2}{(1 - R_q R_{\text{NO}_2})(1 - R_{\text{NO}_2} R_{\text{NO}_2} g)} \] (A.11)

Now considering the global transmittance of the three layer system composed by TiO2, glass and TiO2:

\[ q_0 = T_{1.2.3} q_3 = T_{\text{NO}_2} q_3 \] (A.12)

Then, substituting Eq. (A.11) into Eq. (A.12), one can write:

\[ T_{\text{NO}_2} q_3 = \frac{T_q T_{\text{NO}_2}^2}{(1 - R_q R_{\text{NO}_2})(1 - R_{\text{NO}_2} R_{\text{NO}_2} g)} \] (A.13)

Performing a radiation flux balance in the third layer, according to Eq. (2) we obtain:

\[ q_3 = R_{3} q_3 + T_3 q_3 = R_{\text{NO}_2} q_3 + T_{\text{NO}_2} q_3 \] (A.14)

Replacing Eq. (A.9) into Eq. (A.14):

\[ q_3 = R_{\text{NO}_2} + \frac{R_{\text{NO}_2} g T_{\text{NO}_2}^2}{1 - R_{\text{NO}_2} R_{\text{NO}_2} g} \] (A.15)

Now considering the reflectance of the whole system:

\[ q_3 = R_{1.2.3} q_3 = R_{\text{NO}_2} \] (A.16)

Substituting Eq. (A.15) into Eq. (A.16):

\[ R_{\text{NO}_2} = R_{\text{NO}_2} + \frac{R_{\text{NO}_2} g T_{\text{NO}_2}^2}{1 - R_{\text{NO}_2} R_{\text{NO}_2} g} \] (A.17)
Table B1 – Estimation of internal and external mass transfer modulus.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Internal mass transfer modulus</th>
<th>External mass transfer modulus</th>
<th>Nitrogen oxides</th>
<th>Acetaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2-C-4 L</td>
<td>5.03 × 10^{-6}</td>
<td>3.95 × 10^{-2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2-C-4 L-S</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2-N L</td>
<td>4.42 × 10^{-7}</td>
<td>1.23 × 10^{-2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2-N L-S</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By symmetry, applying the same procedure for a two layers system (conformed by TiO2 and glass) an equivalent expression for the global reflectance can be obtained:

\[
R_{\text{TiO}_2 \text{glass}} = R_g + \frac{R_{\text{TiO}_2} T_g^2}{1 - R_{\text{TiO}_2} R_g} \quad \text{(A.18)}
\]

Then, replacing Eq. (A.18) into Eq. (A.13) and into Eq. (A.17), we have:

\[
T_{\text{TiO}_2 \text{glass}} = \frac{T_g^2 T_{\text{TiO}_2}}{1 - R_{\text{TiO}_2} (1 - R_{\text{TiO}_2} T_g (1 - R_{\text{TiO}_2} R_g)))} \quad \text{(A.19)}
\]

\[
R_{\text{TiO}_2 \text{glass}} = R_{\text{glass}} + \frac{T_{\text{TiO}_2} T_g^2 (R_g + (R_{\text{TiO}_2} T_g^2) (1 - R_{\text{TiO}_2} R_g)))}{1 - R_{\text{TiO}_2} (1 - R_{\text{TiO}_2} R_g))} \quad \text{(A.20)}
\]

From Eqs. (A.19) and (A.20) the transmittance and reflectance of the TiO2 film \((T_{\text{TiO}_2}, R_{\text{TiO}_2})\) can be solved as a function of the experimental values of transmittance and reflectance of the three layer system \((T_{\text{TiO}_2 \text{glass}}, R_{\text{TiO}_2 \text{glass}})\) and of the glass \((T_g, R_g)\), obtaining Eqs. (5) and (6).

**Appendix B. Appendix B**

The influences of internal mass transfer can be assessed by using the modified Weisz–Prater Criterion, assuming a pseudo-first order reaction rate (Missen et al., 1999):

\[
\frac{(r_i/e)^2}{D_C C_{\text{cis}}} < 0.5 \quad \text{(B.1)}
\]

where \((r_i/e)\) is the average reaction rate calculated according to Eq. (9), “e” the photocatalytic film thickness, \(C_{\text{cis}}\) the contaminant concentration on the catalytic surface, and \(D_e\) the effective diffusion coefficient.

The thickness of the deposited photocatalyst can be estimated as follows:

\[
e = \frac{m_t}{A_{\text{surf}} \epsilon (1 - \phi)} \quad \text{(B.2)}
\]

where \(m_t\) is the deposited catalyst mass, \(\rho_t\) the solid catalyst density, and \(\phi\) the porosity of the catalytic film.

The effective diffusion coefficient is defined as:

\[
D_e = \frac{D \phi}{r} \quad \text{(B.3)}
\]

where \(r\) is the tortuosity and \(D\) is the global diffusion coefficient:

\[
D = \frac{1}{((1/D_{\text{air}}) + (1/D_b))} \quad \text{(B.4)}
\]

In Eq. (B.4), \(D_{\text{air}}\) is the molecular diffusion coefficient of the i contaminant in air and \(D_b\) is the Knudsen diffusion coefficient:

\[
D_b = 9700 \phi \left( \frac{T}{M_i} \right)^{1/2} \quad \text{(B.5)}
\]

where \(\phi\) is the porous ratio, \(T\) is the temperature and \(M_i\) is the molecular weight of the i compound.

On the other hand, the external mass transport limitations can be neglected when the average reaction rate is much slower than the interfacial mass transfer (Walter et al., 2005):

\[
\frac{(r_i/R)^2}{k_{\text{e}} L_C / D_{\text{air}}} < 0.1 \quad \text{(B.6)}
\]

where \(k_{\text{e}}\) is the external mass transfer coefficient that can be calculated from:

\[
S_h = k_{\text{e}} L_C / D_{\text{air}} \quad \text{(B.7)}
\]

Shah and London (1974) proposed that for slits with one exchanging side, the Sherwood number \(S_h\) can be taken as equal to 5. The characteristic length \(L_c\) of this system can be assumed equal to the hydraulic diameter of the photoreactor.

Results of the external and internal modulus (Eqs. (B.1) and (B.6)) are shown in Table B1 for the two contaminants and the different samples employed in this work. According to the adopted criteria, both the external and internal mass transfer limitations can be safely neglected.

**References**


