Photocatalytic Nb₂O₅-doped TiO₂ nanoparticles for glazed ceramic tiles

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Abstract

TiO₂ nanoparticles are currently used as coating for self-cleaning building products. In order to achieve high self-cleaning efficiency for outdoor applications, it is important that titania is present as anatase phase. Moreover, it is desirable that the particle sizes are in nano-range, so that a large enough surface area is available for enhanced catalytic performance. In this work, TiO₂ nanoparticles doped with 0 to 5 mol% Nb₂O₅ were synthesized by co-precipitation. Nb₂O₅ postponed the anatase to rutile transformation of TiO₂ by about 200 °C, such that after calcination at 700 °C, no rutile was detected for 5 mol% Nb₂O₅-doped TiO₂, while undoped TiO₂ presented 90 wt.% of the rutile phase. A systematic decreasing on crystallite size and increasing

on **specific surface area** of TiO_2 were observed with higher concentration of Nb_2O_5 dopant. Photocatalytic activity of anatase polymorph was measured by the decomposition rate of methylene blue under ultraviolet and daylight illumination and compared to commercial standard catalyst (P25). The results showed enhanced catalysis under UV and visible light for Nb_2O_5 -doped TiO_2 as compared to pure TiO_2 . In addition, 5 mol% Nb_2O_5 -doped TiO_2 presented higher photocatalytic activity than P25 under visible light. The enhanced performance was attributed to surface chemistry change associated with a slight shift in the band gap.

Keywords: titanium dioxide, rutile, anatase, photocatalysis, niobium oxide, ceramic tiles.

1. Introduction

Oxide photocatalysts have been intensively investigated for applications in air and water remediation, self-cleaning and self-sterilizing surfaces. Among different photocatalytic materials, titanium dioxide (TiO_2) is by far the most attractive choice due to its high chemical stability, environmental inertness, and relative low cost [1-3]. One of the most emergent applications of TiO_2 is on glazed ceramic tiles [4-6]. The most common deposition techniques of TiO_2 on tile surfaces are roller printing [4], ink jet printing [4], spraying [5-7] and dip coating [8]. Ceramic tiles have received particular attention in the last years regarding innovative applications and manufacturing processes, such as reduced thickness products [9,10], digital decoration [11] and antimicrobial activity [12,13], which aggregate value to those building materials.

When a TiO_2 photocatalyst site absorbs a photon with energy equal to or greater than its band-gap, an electron-hole pair is generated; subsequently, the pair is split into a free electron and a free hole [1]. The photogenerated electron/hole pair promotes the reduction and oxidation of species adsorbed at the surface of the semiconductor and induces oxidative degradation of

species in solution through radical reactions [14]. Therefore, when TiO_2 is irradiated with UV-light, it can decompose organic dyes such as methylene blue (MB) [15, 16], alizarin S [17, 18], crocein orange G [17], methyl red [17, 19], and congo red [17, 20]. MB is commercially employed in textile, leather and paper industries, and it is one of the most used dyes for measurement of photocatalytic activity. Since dye-containing wastewater can block both sunlight penetration and oxygen dissolution, which are essential for aquatic life, there is considerable interest in treating these colored effluents before discharging them to water bodies [21]. Furthermore, discoloration of MB dye as a model pollutant is most often used for testing of materials with self-cleaning properties [5, 6, 22].

The optimization of TiO_2 performance as photocatalyst is an active research field given the above mentioned industrial relevance. This entails understanding the dependences of the catalytic behavior on the system chemistry, structure and microstructure. TiO_2 has three main polymorphs: rutile, anatase and brookite. Among those, anatase presents generally the highest activity, which is improved from high crystallinity and surface area [23-25], although a mix of anatase and rutile can improve photoactivity in some cases [26-29]. Kordoult *et al.* [30] have studied the photodegradation of two representative azo-dyes, one acidic (Orange G) and one basic (Yellow 28) for different anatase-rutile ratios. For both azo-dyes they have showed that the increasing of rutile percentage decreases the photoactivity ratio.

Several dopants have been used to postpone the anatase-to-rutile transformation (ART) while simultaneously changing physical-chemistry of the surface of TiO_2 in order to increase its photocatalytic performance. For instance, rare-earth-doped TiO_2 has led to increased photocatalytic activity under visible light as compared to pure titanium dioxide [31-33]. Transition metals have also improved activity by reducing the recombination of photogenerated

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4 electrons and holes [34-36]. Non-metal doped TiO₂ has shown improvement on absorption and
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6 photocatalytic activity in the visible light region [37, 38].
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9 Niobium has been considered a promising candidate for enhanced catalysis of titania
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11 [39]. The ionic radius of Nb⁵⁺ (0.64 Å) is only slightly larger than Ti⁴⁺ (0.605 Å). Thus, Nb⁵⁺ can
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13 form solid solution in the lattice of TiO₂. To compensate the excess charge of Nb⁵⁺ in
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15 substitution to Ti⁴⁺, one Ti cation vacancy may be created per 4 Nb introduced. Alternatively, the
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17 stoichiometric reduction of Ti⁴⁺ to Ti³⁺ may also occur depending on preparation conditions,
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19 which will introduce shallow donor levels below the conduction band (CB) edge of TiO₂ [40,
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21 41]. The electronic transition from valence band (VB) to these donor levels will be excited by the
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23 visible light and therefore render the Nb-doped TiO₂ photocatalyst to be visible light responsive,
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25 such as nonstoichiometric TiO₂ [42].
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31 Nb₂O₅-doped titania has been shown to have higher photocatalytic activity for the
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33 degradation of diquat dibromide monohydrate under UV-light as compared to pure TiO₂ [43].
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35 Photocatalytic oxidation of 4-chlorophenol and iodide as well as the photoreduction of
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37 hexavalent chromate (Cr⁶⁺) have been studied by Nb-TiO₂ catalysts, which presented enhanced
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39 photocatalysis under visible light [44].
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43 In this work, the temperature of the anatase to rutile phase transition as a function of
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45 Nb₂O₅-doping concentration was studied in titania nanoparticles prepared by coprecipitation in
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47 order to enhance anatase stability. The presence of anatase or anatase/rutile mixed phases at the
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49 700 to 800°C would allow the use of titania powder as a coating in glazed ceramic tiles,
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51 particularly for those processes which include a second firing stage at this temperature range for
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53 decoration purposes.
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2. Experimental procedure

2.1. Sample preparation

TiO₂ nanoparticles containing 0, 0.5, 1, 2, and 5 mol% Nb₂O₅ were synthesized by co-precipitation. The respective compositions were named 0NbTi, 0.5NbTi, 1NbTi, 2NbTi and 5NbTi. Titanium (IV) isopropoxide (TTIP, Sigma-Aldrich, ≥97%) and niobium butoxide (NB, Sigma-Aldrich, 99%) were used as Ti and Nb precursors, respectively. TTIP and NB were mixed for 10 min and they have visually formed a homogeneous solution. No partially pre-hydrolyzed was observed in this step. Thus, the solution was added dropwise into an ammonium hydroxide solution (NH₄OH, 5M, Fisher Scientific) under vigorous stirring. The colloidal suspension was centrifuged at 3000 rpm for 5 min to separate the nanopowder from the liquid. The powder was then washed three times (in water, water/ethanol 1:1 in volume, and ethanol, respectively). The samples were dried at 90 °C for 72 h and ground with a pestle and mortar. The calcination procedure was performed in a box furnace (Lindberg/Blue M) at different times and temperatures (450-900 °C). For the photocatalytic experiments, calcination temperatures that lead to anatase-only with maximum specific surface area were selected for each composition, i.e. 450 °C for 0NbTi, 2NbTi and 5NbTi; and 500 °C for 0.5NbTi and 1NbTi.

2.2. Characterization of powders

Powder X-ray Diffraction (XRD) patterns were obtained using a Bruker AXD D8 Advance diffractometer (Bruker AXS, Madison, WI) with CuK α radiation, and $\lambda = 1.5406$ Å, operated at 40 kV and 40 mA. Data were collected in the range 20°-90° (2-theta) and the pattern profile fitting was performed using the Jade 6.1 (MDI) software to determine crystal structure, phase purity, and crystallite size. Specific surface area measurements were carried out using the

Brunauer, Emmett, and Teller (BET) method with nitrogen gas adsorption (Micromeritics Gemini VII). Thermogravimetry results have showed that significant mass changes can only be observed up to 400 °C; hence, this temperature was selected for degassing prior to BET experiment (Micromeritics VacPrep 061, sample degassing system). Surface morphology and particle size distribution were analyzed by High Resolution Transmission Electron Microscopy (HRTEM; Jeol JEM 2500SE with 200 keV). The absorption studies were carried out by UV-visible spectrophotometer (Evolution 220, Thermo Scientific). The UV-vis absorption spectra were recorded in the wavelength range 300-800 nm. The values of the energy band gap were determined applying Kubelka-Munk phenomenological theory assuming the indirect band gap [45].

2.3. Photocatalytic activity

The photocatalytic activity of the prepared nanoparticles was assessed in liquid-solid media monitoring the degradation of the organic dye methylene blue (MB, Sigma-Aldrich) under UV and visible light. Commercial titania photocatalytic powder (Degussa, Evonik P25, Aeroxide TiO₂) was used as reference for comparison. P25 has been used as a reference photocatalyst due to high levels of activity in many reaction systems as reported in the literature [46].

The tests were performed at room temperature, in a cylindrical photocatalytic reactor (86 mm in diameter) containing an aqueous solution of the dye (0.3 L), at an initial concentration of 10 µmol. The concentration of the photocatalyst in the slurry was normalized by surface area (6 m²) and by weight (50 mg). Table 1 shows the amount of powder used in the photocatalytic experiment for each sample. In order to mix the solution thoroughly, the slurry was magnetically stirred throughout the reaction. The reactor was designed following the guidelines of the

international standard ISO 10678 [47]. The distance between the lamp and the slurry was ~8.5 cm to obtain $10 \text{ W}\cdot\text{m}^{-2}$ intensity in the middle of the solution measured by radiometer (General UV513AB, Digital UV AB Light Meter). UV-light (GE black light F15) and visible light (GE daylight F15) sources were used.

Along the experiments, the photocatalytic degradation of MB was monitored by sampling about 3 mL of the slurry from the reactor, at regular time intervals (up to 7 h). Before turning the lamps on, the suspensions with the photocatalyst were stirred in the dark for 10 min. The powders were separated from the suspension by centrifugation, and then the MB concentration in the liquid was determined by measuring the absorbance in a spectrometer (PerkinElmer precisely, Lambda 750 UV/VIS Spectrometer) at a wavelength of 664 nm, using distilled water as reference.

3. Results and discussion

3.1. Structural characterization of Nb_2O_5 -doped TiO_2

The prepared Nb_2O_5 -doped TiO_2 powders were analyzed by XRD to verify the purity, crystallinity and phase(s) of samples calcined at different temperatures (450-900 °C). The powder XRD patterns of doped and undoped samples are shown in Fig. 1. At 450 and 500 °C most samples presented single anatase phase (JCPDS card n. 71-1167), showing broad peaks typical of nanosized crystallites. A small amount of brookite (JCPDS card n. 76-1937) is observed in 1NbTi, 2NbTi and 5NbTi samples calcined at 450 °C, 500 °C and 600 °C. The existence of brookite in the samples can be identified by the diffraction peaks at 30.7° (211, reflection). Co-existence of anatase and brookite frequently occurs in water-based synthesis, but the photocatalytic activity, which is primarily responsible for the anatase phase, has been

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4 reported to be unaffected by it [48]. The diffraction peaks at 25.3°, 37.8°, 48°, 53.9° and 55° can
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6 be indexed to the (101), (004), (200), (105) and (211) reflections of anatase TiO₂. The presence
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8 of rutile phase (JCPDS card n. 86-0147) was detected only at temperatures above 600 °C. The
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10 diffraction peaks at 27.4°, 36.2°, 41.3°, 54.4° and 69.1° can be indexed to the (110), (101), (111),
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12 (211) and (112) reflections of rutile TiO₂.
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16 Fig. 2 shows a compilation of rutile weight percentage determined from XRD patterns as
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18 a function of temperature of calcination. It is observed that the stability of anatase phase is
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20 enhanced with increasing Nb₂O₅ concentration. At 600 °C, the rutile percentage of 0NbTi,
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22 0.5NbTi and 1NbTi is 48.4 %, 19 % and 6.8 %, respectively. On the other hand, 2NbTi and
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24 5NbTi did not show any transformation at this point. At 700 °C, just 5NbTi presents pure anatase
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26 phase. Other compositions have shown anatase-rutile mixture. The trend shown in Fig. 2
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28 suggests that Nb₂O₅-doping can stabilize the anatase phase and postpone the phase transition to
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30 rutile. The ART delaying can be attributed to the formation of strong Nb-O-Ti bonds, which
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32 inhibit the movement of surface Ti atoms required to initiate the phase transformation [49]. The
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34 mobility of oxygen vacancies also influences the phase transformation rate, because they act as
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36 nucleation sites for the anatase to rutile transition [40]. This is expected to be decreased with
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38 increasing Nb content due to its higher valence (+5) substituting (+4) titanium sites.
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46 At 800 °C, 0NbTi has shown pure rutile phase, while the doped samples presented
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48 anatase-rutile mixed phases in different fraction weights, following the trend observed at 600 and
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50 700 °C. Thus, the postponing of anatase-rutile phase transition by Nb₂O₅-doping may allow the
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52 use of TiO₂ as a high efficient photocatalyst material in systems that require higher processing
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54 temperatures. At 900 °C, all compositions have completely transformed to rutile. However,
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5NbTi presents the titanium niobium oxide phase (TiNb_2O_7 – monoclinic, JCPDS card n. 39-1407) in addition to the rutile phase.

Traversa *et al* [50] have studied Nb-doped- TiO_2 and Ta-doped- TiO_2 nano-sized powders to use at thick-film gas sensors for atmospheric pollutant monitoring. In their work, the presence of Nb (5 at% and 10 at%) has postponed the ART by about 200 °C, which agrees with this work. However, in Traversa's work the transition from anatase to rutile started at ~50 °C higher than what reported here, even for pure TiO_2 . This difference may be attributed to the synthesis method, which was sol-gel, but also to the presence of agglomerates (solid-solid interfaces) that has been proven to affect the anatase-rutile transition [51].

Atanacio *et al.* [52] have showed that niobium has a potential to segregate on the surface of TiO_2 under oxidizing conditions. Moreover, the segregation-induced enrichment of the surface in niobium results in the formation of a TiNb_2O_7 -type surface structure. The observation of TiNb_2O_7 phase at 800 and 900 °C for the 5 mol% Nb_2O_5 -doping suggests that niobium is segregated on the surface of TiO_2 . However, the second phase remains undetectable for samples annealed at low temperature possibly because of a lack of crystallinity associated with very small grain sizes that would not provide enough coherent scattering in XRD [53]. Higher temperatures increase the crystallite size of the TiNb_2O_7 phase, making it visible.

Table 1 shows a list of the powders tested for photocatalysis selected among those in which no rutile or second phases are observed. P25 was included as a reference. Crystallite size, specific surface area and the amount of powder were used as input data to provide ~6 m² of reactive surface. The samples with 0.5 and 1 mol% Nb_2O_5 -doped TiO_2 were calcined at 500 °C for 5 h instead of 450 °C for 7 h in order to reach S_A values close to those of pure TiO_2 . The BET

S_A values found for 0NbTi, 0.5NbTi and 1NbTi were 92.5 ± 0.6 , 85.6 ± 0.5 and $92.9 \pm 0.5 \text{ m}^2 \cdot \text{g}^{-1}$ respectively.

For 2NbTi and 5NbTi, the values increased to 125.4 ± 0.6 and $168.9 \pm 0.6 \text{ m}^2 \cdot \text{g}^{-1}$, respectively. The increase at the specific surface area for 2NbTi and 5NbTi when compared to pure TiO_2 is due to the lower crystallite sizes. The anatase crystallite sizes, as determined by XRD for samples calcined at 450°C for 7 h were 9.6 ± 0.5 , 7.1 ± 0.2 and $6.0 \pm 0.3 \text{ nm}$ for 0NbTi, 2NbTi and 5NbTi respectively. This systematic decrease suggests that Nb_2O_5 -doping is stabilizing TiO_2 nanopowder and consequently helping to postpone the ART. The Nb^{5+} radius is slightly larger than the Ti^{4+} radius and this means that Nb^{5+} induces a slight stress in the titania lattice, which may hinder the growth of the TiO_2 crystallites [54]. Moreover, Guidi *et al.* [55] suggested that the main mechanism for nucleation of rutile in doped TiO_2 samples was a slow surface nucleation, which also prevented conspicuous grain growth, and ascribed such inhibitions to a decrease in the ionic oxygen mobility. The powders calcined at 500°C for 5 h presented crystallite sizes as 10.9 ± 0.5 and $9.0 \pm 0.3 \text{ nm}$ for 0.5NbTi and 1NbTi, respectively. These powders did not follow the trend showed for 0NbTi, 2NbTi and 5NbTi, because they were calcined at different times and temperatures. For comparison purposes, P25 was also characterized. The BET S_A of P25 ($54.1 \pm 0.5 \text{ m}^2 \cdot \text{g}^{-1}$) is smaller than those values of any Nb_2O_5 -doped- TiO_2 or pure TiO_2 used for photocatalytic activity in this work. P25 presented 81.1 anatase and 18.9 wt% rutile and crystallite sizes of 22 ± 1 and $38 \pm 8 \text{ nm}$ for anatase and rutile, respectively.

Figures 3(a) and (b) show HRTEM images for 0NbTi and 5NbTi calcined at 450°C for 7 h. The particles are relatively isotropic and the estimated sizes are in the range of those obtained from XRD analysis. Powder agglomeration is also observed, which is usual in nanoparticles.

Figures 3(c) and (d) show the size distribution of 0NbTi and 5NbTi obtained from ~150 nanoparticles for both compositions. The average grain sizes determined by TEM is consistent with the values determined by XRD. The histograms show a tendency to a skewed distribution. However, 0NbTi has presented a right skewed distribution, presenting less powder above the average and 5NbTi has presented a left skewed distribution, with less powder below the mean. The decreasing on the grain size for doped samples can be attributed to the surface segregation of dopants. The hypothesis is that the presence of niobium pentoxide on the surface of TiO₂ can both affect the driving forces for particle growth and act as pinning agents limiting the growth rate. This behavior has been also observed for chromium-doped SnO₂ [56].

Figures 4 (a), (b) and (c) show UV-vis absorbance spectra and Kubelka-Munk plots of pure TiO₂ (0NbTi), 5 mol% Nb₂O₅-doped-TiO₂ (5NbTi) and P25 respectively. The results show that Nb₂O₅ decreases the optical indirect band gap of titania from 3.20 to 3.07 eV for pure TiO₂ and 5NbTi, respectively. These results suggest that Nb₂O₅ extend the absorbance of TiO₂ to the visible light. Hence, the photocatalytic activity is expected to increase under visible light as the band gap is reduced and then produce more electron-hole pairs under visible light. The literature presents some controversies about the influence of Nb₂O₅ on the band gap. Castro *et al.* [43] have shown no difference in the band gap of pure TiO₂ and Nb-doped TiO₂. However, Yang *et al.* [39] found a reduced band gap for Nb-doped TiO₂ porous microspheres. Those divergences can be attributed to the particle morphology and/or distribution of Nb₂O₅ on TiO₂, since those powders were prepared by different synthesis methods. The smaller band gap of 5 mol% Nb₂O₅-doped TiO₂ suggests that Nb₂O₅ dopants modify the CB of TiO₂ by downshifting the CB edge, probably through the mixing of Nb_{4d} and Ti_{3d} states [40, 57]. For comparison purpose, the P25 indirect band gap was also calculated and the value found was 3.05 eV, which agrees with the

value found in the literature [58]. The narrower band gap for P25 is attributed to the presence of rutile as a mixed phase [58].

3.2. Photocatalytic activity

The oxidized and reduced forms of MB have different absorption bands in the UV-Vis spectrum. Therefore, the progress of discoloration or decomposition can be monitored by measuring the decrease in absorption of MB on UV-Visible spectrum at a λ_{max} of 664 nm. The evaluation of photocatalytic activities of Nb₂O₅-doped TiO₂ powders comparing to undoped TiO₂ and P25 under UV-light and visible light is shown in Figures 5 and 6, respectively.

Light exposure in the absence of the photocatalysts did not result in the photocatalytic discoloration of MB. It is observed from Fig. 5a that the degradation of MB under UV light increases for Nb₂O₅-doped samples compared to undoped titania. For 0.5 mol% Nb₂O₅-doped TiO₂, MB degradation is slightly higher than that for non-doped TiO₂. The photocatalytic performance was similar for TiO₂ powders with Nb₂O₅ concentrations between 1-5 mol%. However, it was higher than 0.5 mol% Nb₂O₅-doped and undoped TiO₂. P25 showed the highest photocatalytic activity under UV-light. This has been reported in the literature to be associated with the small fraction of rutile in the sample, although there are still some controversies. The hypothesis is that the co-presence of anatase and rutile crystallites induces the high level of photocatalytic activity; the transfer of photoexcited electrons and positive holes between interconnecting anatase and rutile particles would enhance charge separation and improve the efficiency of utilization of electron-hole pairs [59]. However, Ohtani *et al.* [46], after investigating structural and photocatalytic properties of a mixture of anatase and rutile particles

corresponding to the components of P25, found that anatase, rutile and amorphous phases behave independently without any interaction.

The large specific surface area is beneficial to absorb more light, which could offer more adsorption sites and photocatalytic reaction centers [39]. Therefore, to minimize the influence of the specific surface area on the photocatalytic activity, the photocatalyst powders were normalized in order to get the same total surface area (6 m^2) (Fig. 5a and 6a) and the same sample weight (50 mg) (Fig. 5b and 6b). The amount of powders for Fig. 5a and 6a varies according to the specific surface area of each material and it is shown in Table 1. The 0.5NbTi and 1NbTi powders were calcined at 500°C for 5 h in order to get similar specific surface area as pure TiO_2 and minimize any improvement of doping samples by the surface area. Hence, 0NbTi and 1NbTi have presented similar specific surface area ($92.5 \pm 0.1 \text{ m}^2 \cdot \text{g}^{-1}$ and $92.9 \pm 0.5 \text{ m}^2 \cdot \text{g}^{-1}$, respectively). However, 1NbTi has presented higher photocatalytic activity comparing to 0NbTi, showing that the improvement on the photocatalytic activity is due to the Nb_2O_5 -doping.

Figure 5b compares the MB degradation under UV-light of 0NbTi, 5NbTi and P25 with the same catalyst concentration, normalized by weight. It can be observed that 5NbTi and P25 have a better performance comparing to the 0NbTi. On the other hand, 5NbTi and P25 have similar behavior showing total MB degradation by 2.5 h. It can also be observed that for 1 and 1.5 h 5NbTi has presented higher performance, suggesting a slightly faster kinetics of degradation.

Hirano and Matsushima [60], have prepared Nb-doped- TiO_2 (0-10 mol%) using hydrothermal method in three different conditions, in the absence and presence of urea and aqueous ammonia. They have studied the MB degradation of 50 mg of catalyst suspended in 100 mL of MB. In their best result 10 mol% Nb_2O_5 -doped- TiO_2 completely degraded MB after 5 h.

In the present work we have used 50 mg of 5 mol% Nb₂O₅-doped-TiO₂ suspended in 300 mL of MB and after 2.5 h the dye was completely degraded under UV-light. The different performance between the present work can be attributed to the different dilution, but also specific nanoparticle morphologies, since Hirano and Matsushima used a different synthesis method and different precursors.

The photocatalytic activity under visible light (Figures 6a and b) shows slower degradation kinetics, but a more pronounced effect of the dopant in the overall catalytic performance of the TiO₂ nanoparticles. In Fig. 6a, where the powders were normalized by surface area, the best performance was found for 5NbTi. At the first hour of the experiment, 5NbTi has presented higher photocatalytic activity than P25. From 2-7 hours, the behaviors were similar between the two. The improvement on photocatalytic activity of Nb₂O₅-doped TiO₂ can be attributed to the increase of the absorption under visible light and decrease of the band gap comparing to pure TiO₂ [39, 61]. Even though 5NbTi and P25 have presented similar photocatalytic degradation of MB for the same surface area, the amount of powder used for 5NbTi was around three times less than P25. The quantity of powder used for 5NbTi was 35.5 mg and for P25 was 111 mg. Fig. 6b shows the photoactivity of 0NbTi, 5NbTi and P25 with the catalyst normalized by weight (50 mg). In this case, 5NbTi has presented considerable higher activity when compared to P25 and 0NbTi. Note that P25 had moderate degradation behavior due to the limited content of powder.

The poorer behavior of the catalysts under visible light can be attributed to the photosensitized type of the reaction, where MB dye molecule is photoexcited instead of the photocatalyst. In this kind of process, an electron is transported from the photoexcited MB to the conduction band of the photocatalyst and reacts, e.g., with an O₂ molecule, which is an electron

scavenger, and a superoxide radical is created. These radicals can further react towards complete decomposition of MB. It seems that even a very small overlap of the adsorption spectra of MB and the applied irradiation is sufficient to drive the photosensitized type of reaction.

The present observation is consistent with the fact that Nb₂O₅ itself shows high photocatalytic decomposition of methylene blue, especially for Nb₂O₅ nanorods which present high surface acidity [62]. As previously mentioned, Nb⁵⁺ is expected to form solid solution into the lattice of TiO₂ because the ionic radius of Nb⁵⁺ is only slightly larger than Ti⁴⁺. Once Nb⁵⁺ is introduced into the lattice of TiO₂, the compensation of the excess charge of Nb⁵⁺ in substitution to Ti⁴⁺ can be explained by two mechanisms. A first possibility is if one Ti⁴⁺ cation vacancy is created for every 4 Nb⁵⁺ cations (Eq. (2)). Another option is reduction of Ti⁴⁺ to Ti³⁺ for every Nb⁵⁺ incorporated (Eq. (3)) [39, 56, 63, 64], where O²⁻ is oxidized (the equations are expressed in classical Kröger-Vink notation).

From the thermodynamic point of view, equation (3) is more favorable since reduction is less energetic than vacancy formation. Hence, Ti³⁺ would produce isolated states in the forbidden gap exhibiting visible light absorption and enhancing the photocatalytic property of TiO₂-based photocatalyst [65]. Moreover, the presence of active Ti³⁺ sites on the surface could serve as sites for trapping photogenerated electrons that could effectively inhibit the recombination of the photoinduced electrons and holes [66].

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4 Yang *et al.* [39] have shown by photoluminescence (PL) emission spectra of Nb-doped
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6 TiO₂ microspheres that Nb-doped samples can have better charge separation. Nb-doping
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8 introduces shallow donor levels below the CB edge, which can act as electron traps to retard
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10 electron-hole recombination. Thus, the lifetime of photogenerated electrons and holes can be
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12 increased, which is beneficial to enhancing the photocatalytic efficiency.
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19 **4. Conclusions**

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21 TiO₂ coating on glazed ceramic tiles with good photocatalytic or self-cleaning performance
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23 requires starting TiO₂ nanoparticles with an enhanced performance. In the present work, Nb₂O₅-
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25 doped TiO₂ nanopowder was successfully synthesized by co-precipitation with Nb₂O₅
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27 concentrations of 0-5 mol%. The anatase phase of TiO₂ was found to be stable up to 700 °C for
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29 doped samples, and thereon, initiation of rutile phase formation was observed. Nevertheless, up
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31 to 44.3 wt% anatase is present after calcination at 800 °C for 5% mol Nb₂O₅-doped TiO₂, while
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33 for non-doped TiO₂ the ART is complete at the same temperature. The crystallite sizes decrease
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35 and the specific surface area increases with the increasing of doping concentration calcined at the
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37 same temperature. All Nb-doped samples have presented higher photocatalytic activity by
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39 degradation of methylene blue than pure TiO₂ synthesized at the same condition under UV and
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41 visible light. The powders containing 5 mol% Nb₂O₅-doped TiO₂ presented similar photoactivity
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43 under UV-light and higher photoactivity than P25 under visible light, with the benefit of having
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45 very small crystallite sizes, making it more suitable for glazed ceramic coatings.
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Figures Captions

Figure 1. XRD patterns of Nb₂O₅-doped TiO₂ (0-5 mol%) calcined at 450-900 °C. a) 450 °C, b) 500 °C, c) 600 °C, d) 700 °C, e) 800 °C and f) 900 °C. (A-anatase; R-rutile; * TiNb₂O₇).

Figure 2. Rutile weight percentage as a function of the calcination temperature for Nb₂O₅-doped and non-doped TiO₂. Complementary percentage is anatase.

Figure 3. HRTEM of pure TiO₂ (a) and TiO₂ containing 5 mol% Nb₂O₅ (b), and grain size distribution of pure and doped powder, (c) and (d) respectively.

Figure 4. UV-vis absorbance spectra and Kubelka-Munk plots for: a) pure TiO₂ (0NbTi), b) 5 mol% Nb₂O₅-doped-TiO₂ (5NbTi) and c) P25.

Figure 5. Photocatalytic decomposition of MB under UV-light of Nb-doped and non-doped titania. a) Amount of catalyst normalized by surface area: it was dissolved 6 m² of the catalyst into 0.3 L of the MB solution. The amount of powders varies according to the specific surface area of each material, which is shown in Table 1. b) Amount of catalyst normalized by weight: it was dissolved 0.05 g of the catalyst into 0.3 L of the MB solution, which gives a catalyst concentration of 0.17 g·L⁻¹.

Figure 6. Photocatalytic decomposition of MB under visible-light of Nb-doped and non-doped titania. a) Amount of catalyst normalized by surface area: it was dissolved 6 m² of the catalyst into 0.3 L of the MB solution. The amount of powders varies according to the specific surface

area of each material, which is shown in Table 1. b) Amount of catalyst normalized by weight: it was dissolved 0.05 g of the catalyst into 0.3 L of the MB solution, which gives a catalyst concentration of $0.17 \text{ g}\cdot\text{L}^{-1}$.

Table 1. Nb₂O₅-doped TiO₂ and P25 characterization (crystallite sizes, specific surface areas and amount of powder used for photocatalytic activity).

Sample	Calcination temperature (°C)	Calcination time (h)	Anatase (wt%)	Anatase crystallite size (nm)	Rutile (wt%)	Rutile crystallite size (nm)	Specific surface area (m ² ·g ⁻¹)	Amount of powder (mg)*
0NbTi	450	7	100	9.6±0.5	0	---	92.5±0.6	64.86
0.5NbTi	500	5	100	10.9±0.5	0	---	85.6±0.5	70.09
1NbTi	500	5	100	9.0±0.3	0	---	92.9±0.5	64.61
2NbTi	450	7	100	7.1±0.2	0	---	125.4±0.6	47.86
5NbTi	450	7	100	6.0±0.3	0	---	168.9±0.6	35.52
P25	---	---	81.1	22±1	18.9	38±8	54.1±0.5	110.93

* referring to ~6 m²

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