Preparation of nanostructured TiO₂ films with high catalytic activity and their 3D spatial distribution of anatase and rutile phases

M. T. Colomer^{1,*} and A. del Campo¹

¹ Instituto de Cerámica y Vidrio (CSIC), c/Kelsen n° 5, 28049 Madrid, Spain

Received: 23 January 2019

Accepted: 19 March 2019

Published online:
1 April 2019

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ABSTRACT

In this study, a facile, cheap, scalable, and environmentally friendly method has been developed to prepare nanostructured TiO₂ coatings with a high catalytic activity. In addition, a protocol to characterize the prepared films in order to obtain consistent results between their texture, their structure, their microstructure, and their catalytic behavior has been established. For that, two types of TiO₂ coatings have been fabricated by applying once TiO₂ aqueous suspensions, prepared from commercial nanopowders, by immersion followed by an adequate thermal treatment. The first type of films is constituted by coatings with anatase as single phase, and the second one by films with a rutile molar fraction of $X_R = 0.07 \pm 0.02$, determined from grazing incidence X-ray diffraction (GI-XRD) data. High spatial resolution chemical imaging, obtained by confocal Raman microscopy (CRM), of the surface and of the cross section for the films showed a good distribution of rutile without any segregation of this phase. Furthermore, high resolution electron microscopy (HREM) confirmed the presence of anatase/rutile biphasic domains in those areas in which both phases were previously found together by CRM. In addition, the catalytic data fit to a first-order kinetic model with high catalytic reaction constants (k'), especially when rutile is present. Furthermore, consistent results have been found in this study between the textural, structural, and microstructural studied features with the catalytic properties for the prepared TiO₂ films.

Introduction

TiO₂ has attracted particular attention owing to its exceptional properties, such as low cost, high chemical inertness, non-toxicity, biocompatibility, etc. [1, 2]. For those reasons, titania is one of the most

widely used ceramic materials for different applications such as pigment [3], photovoltaic material [4], photocatalyst [5, 6], hydrogen and oxygen sensor [7, 8], waveguide [9], etc. In addition, TiO₂ could be used as a proton exchange membrane for electrochemical devices [10, 11].

Address correspondence to E-mail: tcolomer@icv.csic.es

As it is well known, the photocatalytic performance of titanium oxide is strongly dependent on several parameters including heat treatment conditions, crystalline phases, particle size, specific surface area, coating surface hydroxylation, the amount and binding strength of the bonded water, or other adsorbed species on the surface of the coating or morphology of the coating particles [12–15]. A key factor observed in the previous research has been the maintenance of the largest amount of anatase in the films because of its superior photocatalytic performance compared to that of rutile [16–18]. However, the lack of a good correlation between photocatalytic activity and anatase content has been reported in the literature [19–27]. This unsuitable correlation was, in part, attributed to the fact that the amount of anatase phase determined by XRD does not suitably represent the amount of anatase onto the surface of the coatings. Furthermore, when TiO_2 films were prepared from commercial submicronic or nanoparticle water-based suspensions, and deposited by atmospheric plasma (APS) or high velocity oxy-fuel spraying (HVOF), heterogeneities in the obtained films, such as rutile segregation, were found [19–27]. Nowadays, it is widely recognized that the mixed phase of TiO_2 is beneficial to reduce the recombination of photogenerated electrons and holes, as long as there is assembly between both phases, which results in an increment of the photocatalytic activity due to the synergic effect in mixed-phase materials. For that reason, the study of the phase junction of anatase/rutile has attracted considerable attention [28–33].

In order to prepare TiO_2 coatings in which no segregation of rutile is produced, and anatase/rutile heterojunctions are present and well distributed, and therefore with an appropriate catalytic activity, a facile, cheap, and scalable protocol should be developed. Furthermore, a suitable protocol of characterization should be established in order to obtain consistent results between anatase and rutile contents, their location, and the presence of anatase/rutile junctions in the prepared films with their catalytic behavior. For that, in this study nanostructured TiO_2 films were prepared by immersion applying the aqueous-based suspensions obtained from commercial anatase nanopowders once onto ZrSiO_4 substrates. In addition, the protocol of characterization included GI-XRD that allows us to determine the rutile and anatase amounts with a penetration, in this case, of about 400 nm, and CRM imaging of the surface and of

the cross section for the films, using the fingerprint of TiO_2 in Raman and the high spatial resolution in the sub-micro-scale. Furthermore, HREM technique was applied to confirm the presence of the anatase/rutile phase junction. Near anatase/rutile transition temperatures were selected for the calcination of the as-prepared films in order to avoid a high increase in the crystallite size and thus, a high decrease of the specific surface area for the films during the calcination treatment. Then, a low content of rutile will be achieved which is, in addition, adequate to check if with the established protocol consistent results are obtained.

Experimental procedure

Characterization of as-received commercial nanopowders

The crystal size (d_{XRD}) of the commercial powders was calculated using the Scherrer's equation after the corresponding correction for the instrumental broadening. The evolution of the crystalline phases were identified by high-temperature X-ray diffraction (HT-XRD) (X'Pert PRO Panalytical, Netherlands) from 25 to 1000 °C (heating ramp of 2 °C/min and delay time of 2 s). The nanopowders were placed within an Al_2O_3 holder. The scans were performed with the detector operating in snapshot mode for 60 s with its window being opened at $12^\circ 2\theta$ to register simultaneously the angular range 20° – $32^\circ 2\theta$.

The as-received powders were examined by field-emission gun scanning electron microscopy (FEG-SEM) and also by TEM/SAED/XEDS analyses. The average dimensions of the nanoparticles were determined by quantitative image analysis of TEM micrographs using in the calculations at least 200 different and well-resolved nanoparticles. The crystalline phases of the powder samples were identified from the positions and intensities of the diffracted peaks using the ICDD database powder diffraction (<http://www.icdd.com/>). The solved structures used in the study to carry out the quantification were obtained from ICDD PDF 4 database of inorganic structures.

Preparation of the suspensions and the films and textural characterization of the coatings

Suspensions were prepared to a solids content of 30 vol% using as deflocculant a commercial polyacrylic

acid-based electrolyte DURAMAX™ D-3005 (Rohm & Haas, USA) in a 0.2 wt% (with respect to the TiO₂ total mass). The suspensions were prepared with 5-min sonication to deagglomerate the nanopowder, followed by 3-min sonication after the dispersant addition, and kept in agitation using an orbital shaker for 45 min to allow the complete adsorption of deflocculant on the nanopowder surface. Then, the particle size distribution of the nanoparticles was determined by dynamic light scattering (DLS) (Zetasizer Nano ZS, Malvern S, UK). The agglomerate particle size of the suspensions measured by DLS and the agglomeration factor (F_{ag}) calculated according to Staiger et al. [34] was 118 ± 9 nm and 3.5, respectively.

The coatings were obtained by applying the suspension once by dip-coating on ZrSiO₄ substrates at room temperature using a withdrawal rate of 20 cm.min⁻¹ controlled by a DY 30 controller (Adamel Lomarghy, France). The coated substrates were dried at 100 °C overnight and finally, heat treated at 670 or 690 °C in air for 30 min, with a heating and a cooling rate of 2 °C min⁻¹.

The specific surface area (SSA) was determined by N₂ adsorption–desorption determined using the single-point BET method (Monosorb Surface Area Analyser, MS-13, Quantachrome Co., USA) of sheets from the films after they were scratched off the substrate.

Structural and microstructural characterization of the coatings

The crystalline structure of the films was first, identified by standard X-ray diffraction (XRD). The XRD patterns were collected (D8 Advance, Bruker AXS, Karlsruhe, Germany) at room temperature in a zero-background holder using CuK α incident radiation in the step-scanning mode over the angular range 20°–80° 2 θ with step width of 0.02° 2 θ and counting time of 3 s per step. Second, GI-XRD technique using a Bruker D8 automated advance diffractometer (Germany) with an incident angle of 0.5° (Panalytical, Empyrean, Pixel3D detector), using CuK α radiation at a step of 0.02°(2 θ)/3 s from 20° to 80° and performed with the detector operating in snapshot mode, was performed. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. Phase identification was performed with the aid of the PDF2 database.

The anatase fraction was calculated from GI-XRD data using the equation:

$$X_A = 1/[1 + 2.18(A_R/A_A)] \pm 2\% \quad (1)$$

where X_A is the molar fraction of anatase, and A_A and A_R are the total areas of the peaks of the X-ray intensities of the anatase and rutile strongest peaks, (101) and (110), respectively [35].

The penetration depth values (t) have been calculated using the following equation:

$$t = \sin(i)/\mu \quad (2)$$

where i is the incidence angle, and μ is the X-ray mass absorption coefficient for TiO₂ [36]. Thus, penetration depths probed by 0.5° in GI-XRD can be estimated as 420 nm.

Raman spectra and images were recorded by means of a CRM WITec Alpha 300 RA (Ulm, Germany) using a Nd:YAG laser of 532 nm wavelength at 1 mW output power, through a 100 × objective (N.A.: 0.95) and two different gratings of 600 and 1800 grooves/line. Micro (μ)-Raman imaging spectroscopy was performed point by point each 100 nm with a piezodriven stage and an optical fiber of 25 μ m in diameter as pinhole to guarantee a spatial resolution less than 300 nm. The spectra obtained by Raman measurements and Raman cartography were computed with Witec Project Plus software with baseline correction of the spectra.

The spectra were taken directly on the surface and on the cross section of the films. For the latter analysis, the films were previously sectioned transversely with a diamond slitting wheel in a precision cutting saw, embedded into an epoxy-resin and polished first with 3, second 2, and finally, 1 μ m diamond paste.

The following Raman modes were used as references to identify the different titania phases (the most intense vibrations are underlined):

- Anatase [37]: 144 ($E_{g,1}$), 197 ($E_{g,2}$), 397 ($B_{1g,1}$), 513 (A_{1g}), 519 ($B_{1g,2}$), and 639 ($E_{g,3}$) cm⁻¹. The 513 and 519 cm⁻¹ bands can be only resolved at low temperature (73 K).
- Rutile [37]: 143 (B_{1g}), 235, 449 (E_g), 610 (A_{1g}), and 826 (B_{2g}) cm⁻¹.
- Brookite [38]: 128 (A_g), 153 (A_g), 247 (A_g), 322 (B_{1g}), and 636 (A_g) cm⁻¹.

The microstructure of the surface and the cross section of the films were studied by FEG-SEM-XEDS

(S-4700 type I, Hitachi, Japan) at 20 kV. For the observation of the cross sections of the films, they were also sectioned transversely with a diamond slitting wheel in a precision cutting saw, embedded into an epoxy-resin and polished as it is described above. In order to demonstrate the existence of the anatase–rutile phase junction in our films, they were cut as thin plates using a diamond saw and thinned by ion milling, then deposited on the Cu grid. After that, they were subjected to HREM imaging. These observations were conducted at 200 keV (JEM-2100F, JEOL, Tokyo, Japan). The image processing was done using the ImageJ 1.45 software (Wayne Rasband, NIH, Bethesda, Maryland, USA), utilizing the standard diffraction lines of the tetragonal TiO_2 -anatase phase (JCPDS- 89-4921) and of the tetragonal TiO_2 -rutile phase (JCPDS-021-1276).

Photocatalytic activity of the coatings

TiO_2 coatings were used as photocatalysts to decompose the methylene blue (MB) in water under $\lambda = 370$ nm UV irradiation with an intensity of 2.5 mW/cm^2 . The films were immersed in a beaker containing 25 ml of a 5 ppm MB aqueous solution in contact with the catalytic film to determine the degradation under UV light. After every 1 h of UV light exposure, 3 ml of the testing solution was sampled and then subjected to UV–Vis spectroscopy (Perkin Elmer precisely Lambda 950, USA) using as a reference the maximum intensity of the band at 664 nm, which is the most intense. The solution was stirred before sampling. A bared substrate was tested as a blank sample to determine the influence of UV radiation in MB concentration decrease by photolysis. The blank substrate exhibited no significant degradation after the UV irradiation.

Results and discussion

Characterization of the as-received commercial nanopowders

The average crystal size (d_{XRD}) of the as-prepared powder calculated from the Scherrer's equation was 35.2 ± 0.1 nm, and the average particle size observed by TEM was 31.3 ± 0.2 nm. Both values are in good agreement each other. In addition, the specific surface area determined using the single-point BET method

was $46 \pm 3 \text{ m}^2/\text{g}$, and the average particle size value (d_{BET}), calculated from specific surface area measurements, was 34 ± 1 nm, both previously reported [39].

The XRD patterns of the as-received commercial powder as a function of temperature are shown in Fig. 1a. It can be noted that the XRD pattern at room temperature corresponds to the anatase phase as unique phase and is highly crystalline (PDF card 89-4921). The appearance of an additional peak indexed as being the 110 peak ($2\theta = 27.525^\circ$) of rutile is firstly observed at 600°C as a very small peak (Fig. 1b) and clearly observed at 700°C (Fig. 1a). From 800°C onwards, the 101-anatase peak (25.425°) completely disappears. When the calcination temperature increases the peaks for both phases are narrower and sharper, i.e., their resolution is higher, as it is expected, due to a higher crystallinity. From

Figure 1 **a** XRTD patterns of the as-received Inframat[®] Advanced Materials[™] (USA) powder in situ at different temperatures, as indicated. Peak assignments are included: the anatase phase is labeled *a* and the rutile phase is labeled *r*. **b** XRD pattern of the Inframat[®] Advanced Materials[™] (USA) powder heated in situ at 600°C . Peak assignments are included: the anatase phase is labeled *a* and the rutile phase is labeled *r*.

those results, and taking into account that the evolution of the anatase/rutile transition is retarded in films, temperatures of 670 and 690 °C for 30 min were selected for the calcination of our films in order to keep high values of specific surface area, and to provoke in the latter case (690 °C) a small range of anatase to rutile phase transformation.

Microstructural observations made by FEG-SEM at different magnifications for the commercial anatase-TiO₂ powder (Fig. 2a,b) show that the powders were spray dried before commercialization, i.e., they are constituted by spherical granules, being in the size range of ~ 4 µm to 50 µm. When the as-prepared powders were used to prepare the suspensions, the

Figure 2 FEG-SEM images of as-received Inframat® Advanced Materials™ (USA) commercial anatase powders obtained at different magnifications.

particle size distribution of the nanoparticles was determined to be ~ 118 nm by DLS, as it is mentioned above. Finally, primary particles in the range of ~ 20 to 40 nm were observed by TEM (Fig. 3).

Textural, structural, microstructural, and catalytic characterization of the coatings

Textural characterization

The standard XRD patterns of the films exhibited peaks of the substrate that overlap with those of the films and accurate analysis could not be performed (not shown here). There must be taken into account that the penetration of XRD is in this case about 20 microns. For that reason, GI-XRD was used in our analysis.

The average crystal size (d_{XRD}) of anatase calculated by Scherrer's equation from GI-XRD data was 53.0 ± 0.1 and 58.1 ± 0.1 nm, for the films calcined at 670 and 690 °C, respectively. In addition, the average crystal size (d_{XRD}) of rutile was 61.0 ± 0.1 nm in the films calcined at 690 °C. The specific surface area (SSA) was 30 ± 3 and 26 ± 3 m²/g for the films after calcination at 670 and 690 °C, respectively. Furthermore, the average particle size calculated from the SSA (d_{BET}) was 52 ± 1 nm and 60 ± 1 nm, respectively.

Figure 3 Representative bright field TEM micrograph of the as-received Inframat® Advanced Materials™ (USA) commercial anatase powders.

Structural characterization

The diffraction patterns of coatings calcined at 670 and 690 °C for 30 min from 2θ range of 20°–80° obtained by GI-XRD can be observed in Fig. 4a, b, respectively. The peaks associated with the lattice planes of the tetragonal TiO_2 -anatase phase (JCPDS-89-4921) were identified in both types of coatings. In addition, in the films calcined at 690 °C for 30 min a peak at $2\theta = 27.375^\circ$, associated with the (110) lattice plane of the tetragonal TiO_2 -rutile phase (JCPDS-021-1276), was also clearly identified. Furthermore, in the latter coatings a molar fraction $X_A = 0.93 \pm 0.02$ of anatase and a molar fraction $X_R = 0.07 \pm 0.02$ of rutile were found, according to Eq. (1).

Figure 5 shows representative microstructures of the surface for the calcined coatings observed by FEG-SEM. Similar microstructures are obtained for both films. The morphology of both types of coatings is very similar showing uniform and defect-free microstructures with rounded grains. Gray and dark areas represent titania and pores, respectively. The pores can be attributed to intergranular porosity, and their size corresponds to mesoporosity.

Figure 6 shows the microstructure after polishing of the cross section for a film calcined at 690 °C. It can be observed that the coating is well-bonded to the substrate since any crack can be detected at the substrate/coating interface. In fact, a clean and uniform interface between the film and the substrate is observed. A similar microstructure is observed for the coating calcined at 670 °C. The layer thickness

Figure 4 GI-XRD patterns of the films after calcination at 670 (a) and at 690 °C for 30 min (b), respectively. Peak assignments are included: the anatase phase is labeled a and the rutile phase is labeled r.

Figure 5 Representative FEG-SEM images of the top surface microstructures of the films calcined at a 670 and b 690 °C for 30 min, respectively.

was estimated by FEG-SEM, and in all cases thicknesses of about 8 μm were determined.

Confocal Raman studies

The anatase phase is characterized by the tetragonal space group $D4h(I41/amd)$ containing two formula units per primitive unit cell [40]. From the group analysis, there are six Raman active modes, $A_{1g} + 2B_{1g} + 3E_g$ and three infrared active modes, $A_{2u} + 2E_u$.

A detail of the average Raman spectra taken directly on the surface of the films (Fig. 7) reveal that the anatase is the only phase present regardless of the

Figure 6 FEG-SEM image of a representative cross section of a polished TiO₂ coating calcined at 690 °C for 30 min.

Figure 7 Detail of two confocal Raman spectra taken directly on an area of the surface of the films calcined at **a** 670 (blue line) and **b** 690 °C (red line), respectively.

calcination temperature (Fig. 7a, b). Five Raman bands at 143 ($E_{g,1}$), 198 ($E_{g,2}$), 398 ($B_{1g,1}$), 517 ($B_{1g,2}$), and 640 ($E_{g,3}$) cm^{-1} that correspond to the anatase phase are observed for the calcined films at 670 °C. Similar values were observed for the bands of the films calcined at 690 °C. These Raman modes are detected at similar frequencies compared to bulk anatase TiO₂ in previous studies [37, 41, 42]. These results are inconsistent with those obtained by GI-XRD since by the latter technique rutile is detected for the films calcined at 690 °C. However, when another area of the film calcined at 690 °C was analyzed by CRM, a band of rutile was observed in addition to those of anatase. Figure 8 shows a detail

Figure 8 Detail of two confocal Raman spectra taken on the surface of the films calcined at **a** 670 (blue line) and **b** 690 °C (red line) for 30 min, respectively.

of the confocal Raman spectra taken on the surface of the films calcined at **a**) 670 (blue line) and **b**) 690 °C (red line) for 30 min, respectively. Figure 8b shows the region of the Raman spectrum, for the films calcined at 690 °C, in which the band at 448 cm^{-1} (E_g) assigned to rutile is clearly detected [37]. These results are then consistent with those obtained by GI-XRD. Due to the low content of rutile many areas of the surface of each film should be analyzed in order to achieve coherent results with those obtained by GI-XRD.

Although the presence of anatase and rutile plays an important role in the catalytic activity of TiO₂ films, their distribution is a key factor. Segregation of rutile has been previously reported in cases in which other procedures have been used to prepare TiO₂ films, giving rise to coatings with low k' values [21–27]. Then, the determination of the 3D chemical analysis distribution is essential in this type of materials. In this study, the anatase and rutile distribution has been assessed by CRM for both the surface and for the cross section of the films, as it is indicated in the experimental section. This technique is suitable for chemical mapping based on Raman spectroscopy, allowing the determination of anatase and rutile phase distribution with a resolution of about $200 \times 200 \times 600 \text{ nm}^3$ [43].

As an example, an optical micrograph of the polished cross section for a film calcined at 690 °C, its chemical Raman mapping, and typical Raman spectra registered at different spots located at different depths of the film are shown in Fig. 9a–c, respectively. The mapping (Fig. 9b) was recorded at the

Figure 9 **a** Optical micrograph of the polished cross section for a film calcined at 690 °C for 30 min. **b** Chemical Raman mapping of the cross section recorded at the area included in the red square indicated in **a**. The surface of the film is located on the left of both, the optical micrograph and the Raman mapping picture. Different colors in the mapping picture indicate a different ratio between the areas of the bands at 448 (rutile) and 398 cm^{-1} (anatase) at each point. Black color is associated with areas with pure anatase and

the other colors correspond to relative areas with variable rutile content with the concentration corresponding to the shade indicated in the scale. **c** Confocal Raman spectra registered at the points indicated with numbers from 1 to 4 in Fig. 9b. The raw spectra are shown in red and fits of the spectra to Lorentzian fashion mode in black. Peak assignments are included: anatase phase is labeled *a* and rutile phase is labeled *r*.

region included in the red square indicated in Fig. 9a and was based on the ratio of the areas for the bands at 398 (anatase) and 448 cm^{-1} (rutile), respectively. The color code of the mapping in Fig. 9b shows the ratio of rutile with respect to anatase in each spot. The scale indicates that the maximum ratio found between areas was 0.15 and the minimum was 0. Black color is associated with regions with pure anatase and the other colors correspond to regions with variable rutile content. The different colors create images reflecting the actual distribution of both polymorphs in the TiO_2 film with a concentration that corresponds to the shade indicated in the scale. Representative spots where CRM analyses were carried out are indicated by numbers in the picture (Fig. 9b). A good distribution of rutile without any segregation is observed, unlike previous studies in

which the films were prepared from commercial nanoparticle suspensions and deposited by APS [22] or HVOF [23]. That segregation hampers the catalytic activity of those coatings which presented catalytic reaction constants quite low unlike those obtained in this study (see next section). Similar results were obtained for all the other analyzed points and regions in the films. For samples calcined at 670 °C only anatase phase is detected by CRM for both, at the surface and at the cross section of the films. The mapping of those coatings is not shown here because a completely black picture is obtained. These results are again consistent with those obtained by GI-XRD.

High resolution electron microscopy

Several interfaces between anatase and rutile surfaces with low-index, such as (110)_r/(101)_a or (100)_r/(100)_a, were identified as stable structures of a mixed-phase anatase/rutile [44]. Both interfaces were observed in those areas where both anatase and rutile were previously found together by CRM. Figure 10 shows by way of example a HREM image of a thin plate of an area from the surface for a coating calcined at 690 °C for 30 min and previously analyzed by CRM. The existence of a lattice spacing of 0.325 nm, which corresponds to (110) plane of the rutile lattice and in addition, the lattice spacing of a neighbor nanoparticle of 0.352 nm, which corresponds to the (101) facet of the anatase lattice can be observed. It confirms the existence of an interfacial crossing zone between anatase and rutile in those films. The presence of these interfacial crossing areas is crucial for the fast electron transfer and slow charge recombination under irradiation [32, 45]. As it is mentioned above, when the anatase/rutile phase junctions are present, rapid electron and hole transfer processes seem to take place from rutile to anatase, decreasing the recombination and producing the generation of photocatalytic “hot spots” in the mixed-phase materials [45, 46].

Figure 10 Bright-field HREM image of an area of a thin plate of the surface of a TiO₂ coating calcined at 690 °C for 30 min and previously analyzed by CRM.

Photocatalytic activity

Finally, the photocatalytic activity of the coatings was determined by measuring the degradation of MB dye in an aqueous solution, as it is mentioned above.

The variation in MB concentration with time can be represented by Langmuir–Hinshelwood first-order kinetic equation, which is applied to low concentrations [47]:

$$d[C]/dt = -k'[C] \quad (3)$$

After integration, Eq. (3) gives:

$$\ln[C]/[C_0] = -k't \quad (4)$$

where [C] is the MB concentration in ppm at a given irradiation time, C_0 is the initial concentration of MB, t is the irradiation time in hours, and k' is the constant of photocatalytic activity in hours⁻¹. Therefore, the plot of $\ln([C_0]/[C])$ versus t is a straight line whose coordinate in the origin and slope are 0 and k' , respectively.

Figure 11 shows the variation of $\ln([C_0]/[C])$ with irradiation time for the studied films. The rate constants (k') and correlation coefficients (r^2) determined by the Langmuir–Hinshelwood first-order kinetic equation [47] for both coatings are indicated in Table 1. The change in MB concentration as a function of time fits very well with the Langmuir–Hinshelwood first-order kinetic equation, which is applied to low concentrations [47]. As it can be observed in Table 1, the k' values for the films in which rutile and anatase/rutile junction is present

Figure 11 Variation of $\ln([C_0]/[C])$ as a function of irradiation time (t) for the film with anatase as a single phase (a) and for the film containing rutile with anatase/rutile junctions (b).

Table 1 Anatase fraction and photocatalytic reaction constants with the corresponding correlation coefficients for the calcined films

Calcination temperature of the film (°C)	Anatase fraction $\pm 2\%$	Rate constant ($10^{-2} k'$, h^{-1})	r^2
670	100	21.0	0.996
690	93	28.9	0.997

(films calcined at 690 °C) are 1.4 times higher than those without rutile. If we compare other previous ones, the k' rate constants show that the photocatalytic activity for the degradation of MB of the films prepared in this study are higher (in the range of 1.2 and up to 4.5 times) than those prepared in previous studies [15, 22, 48]. Although, the comparison of the k' values for the coatings obtained by sol-gel, APS, and immersion should be carried out with caution because the anatase and rutile contents, microstructure and, more important, the thickness of these types of coatings are different. For films prepared by APS, the best value of k' was found to be $17.1 \times 10^{-2} (\text{h}^{-1})$. Those films were prepared from commercial TiO_2 suspensions (AERODISP 740X, Evonik Degussa GmbH, Germany) [22]. For commercial TiO_2 coatings prepared by sol-gel techniques (X-clean PK 3033 P, Nano-X GmbH, Germany) and calcined at 400 °C the best value of k' was only $5.98 \pm 0.95 \times 10^{-2} (\text{h}^{-1})$ [22, 48]. Then, the lower k' values could be attributed to heterogeneities in those films, in particular to the rutile segregation at the bottom of the films, then anatase/rutile phase junction could be located only at the bottom of the films which is not favorable for the catalytic activity of those coatings. In this study, the values of k' were also determined after immersion in water of the films obtaining values of 11.8 and $18.8 \times 10^{-2}, \text{h}^{-1}$ for the films calcined at 670 and 690 °C, respectively, which are still high.

In summary, the high spatial resolution chemical imaging and the specificity of the Raman technique in the localization of both rutile and anatase are crucial in the study of photocatalytic TiO_2 films. This technique when the surface and the cross sections of the films are analyzed allows us to determine the distribution of phases present to determine if rutile is segregated or not and then, to correlate the photocatalytic activity, not only with the anatase and rutile

contents obtained from the GI-XRD measurements, but also with their distribution. In addition, HREM is also essential for establishing the presence of anatase/rutile phase junctions since it seems to be a key factor determinant of the photochemical properties for the films. Our results showed that the films heat treated at 690 °C with a rutile/anatase ratio of $X_R/X_A = 0.07 \pm 0.02/0.93 \pm 0.02$ according to the GI-XRD patterns present the best photocatalytic activity.

Conclusions

Two types of nanostructured crack-free TiO_2 films, that contain anatase as unique phase or contain both, anatase and rutile phases, have been fabricated by applying once a TiO_2 aqueous suspension by dip-coating onto ZrSiO_4 substrates followed by an adequate thermal treatment. GI-XRD patterns and CRM spectra indicate that the films are constituted by anatase as single phase when the films were calcined at 670 °C for 30 min, meanwhile the films calcined at 690 °C for 30 min present $X_A = 0.93 \pm 0.02$ and $X_R = 0.07 \pm 0.02$ molar fractions of anatase and rutile contents, respectively. In addition, CRM shows a good distribution of rutile on the surface and on the cross section of the films without any segregation. The existence of anatase/rutile junctions is determined by HREM at the spots where both phases were previously detected together by CRM. Moreover, the experimental catalytic data fit to a first-order kinetic model and high catalytic reaction constants (k') were obtained, especially when rutile and then anatase/rutile junctions are present. Furthermore, consistent results have been found in this study between the textural, structural and microstructural studied features with the catalytic properties for the prepared TiO_2 films.

Acknowledgements

This work was supported by MINECO (Government of Spain) and Feder Funds under Grant no. MAT2016-78700-R. The authors are also grateful to Mrs. C. Díaz-Dorado for her help in the preparation of FEG-SEM, TEM, and HREM pictures.

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