Yttrium deposition on mesoporous TiO₂: textural design and UV decolourization of organic dyes

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Abstract. This study discusses about the photochemical, topological and textural properties of yttrium-doped titanium dioxide (TiO₂) photocatalysts. The mesoporous yttrium-doped TiO₂ substrates prepared in this research work operate efficiently *via* low-cost commercial 13-W UV lamps. A quantity of 2 wt% yttrium deposition on TiO₂ accelerates methyl orange UV decolourization kinetics. When Y content increases to 8 wt%, besides anatase, rutile is formed from 600°C. The Y₂Ti₂O₇ photoinactive compound emerges at 800°C. The P-123 surfactant mesopore templating treatment of TiO₂ xerogels (when concurrent with the sol–gel Y-doping of Ti alkoxides) features the following two correlated phenomena: (i) The surface area increases while the access to the inner porosity of the substrate becomes much easier, so that a larger portion of the surface is made accessible to the dye molecules as well as to the yttrium dopant; (ii) the inclusion of tubular instead of ink-bottle pores facilitates the transport of organic species in and out of the pore structure. The most active mesoporous substrate resulted to be made of 2 wt% Y; contrastingly, when Y=8 wt%, photoinactivity arose because of Y₂Ti₂O₇ formation. The involvement of P123 was not the sole factor influencing the efficiency of TiO₂ mesoporous photocatalysts. There were additional key factors, such as the surging of co-ordination and nucleophilic species, during the dye photodegradation process, which were also induced by the presence of Y species on the surface of these substrates.

Keywords. Y³⁺ deposition; mesoporous TiO₂; dye UV decolourization; Y₂Ti₂O₇ photoinactive; P123 sol–gel nanomorphology; low-cost 13-W UV lamp.

1. Introduction

Titanium dioxide (TiO₂) plays a major role over a wide variety of applications in modern materials technology, which extend from ceramics and pigments to gas sensors and catalytic devices.^{1–4} TiO₂ is present in nature in three different crystal arrangements, known as anatase, rutile and brookite. In all of these structures, each titanium atom is bonded to six oxygen atoms, each one of these joined, in turn, to three titanium ions, with all Ti–O bonds being equally long. Depending on the precise experimental conditions,⁵ the type of synthesis method, and the presence of selected ionic impurities, the anatase form is stable to temperatures ranging from 500 to 950°C. It is (from the point of view of certain applications, mainly in the field of catalysis) the most interesting phase.⁶ Besides, it is well known that when M_xO_y metal oxides are intimately mixed with ionic impurities (i.e., dopants), their physical and chemical properties are drastically altered.^{7–9} Therefore, a detailed study of the varied important effects that temperature exerts over the

anatase–rutile transformation in metal-doped TiO₂ substrates is of utmost importance. The so-called sol–gel technique¹⁰ is a useful method of choice for introducing easily and efficiently (while still in the liquid phase, when oligomeric species are still growing in size) any type of impurity, which after gelation becomes quite homogeneously trapped within or deposited on the M_xO_y network.

The electronic structure of most lanthanides corresponds to [Xe]6s²4f^{*n*} (*n* = 0–14); La, Sc and Y technically being d-block elements. Another common property of these metallic elements is their propensity to exhibit a +3 oxidation state.¹¹ The deposition of yttrium onto the TiO₂ lattice favours the formation of surface oxygen vacancies.^{12–15} The amount of dopant added is important in order to control the number of surface oxygen vacancies created, something that directly affects the photocatalytic activity.

Previous studies on the possible incorporation of Y³⁺ into the TiO₂ network have recognized several possible outcomes. In the first place, Y dopants cannot be structurally incorporated but bound at the TiO₂ surface.¹⁶ The reason for which Y³⁺ is not substituting Ti⁴⁺ in TiO₂ nanoparticles is the difference in the size of Y³⁺ (0.089–0.11 nm) and Ti⁴⁺ ions (0.5–0.68 nm).¹⁷ Also, because of Yttrium, the

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anatase-to-rutile transformation does not take place below 600°C. Moreover, EXAFS data analysis renders Y-O bonds of length (0.23 nm), a nearly 20% mismatch with the Ti-O bond lengths in the nanoparticles (0.192 and 0.196 nm).¹⁸ Additionally, the characteristic X-ray diffraction (XRD) peaks of Y₂O₃ are not detected thus indicating that, if present, individual clusters of this phase should be smaller than ~1 nm. Furthermore, the Y-O bond length (~0.23 nm) is larger than that of bulk Y₂O₃ (0.22749 nm).¹⁹ Then, it can be concluded that yttrium impurities are mostly present as individual, oxygen-co-ordinated atoms on the titania surface (i.e., as YO₆ groups) and also that about 15% of the surface oxygen sites are bound to Y.

Till date, the state of the art concerning the production and performance of TiO₂ photocatalysts doped with Y³⁺ ions involves the following discoveries:^{20–22}

1. The 4f electron structure of yttrium provides strong adsorption sites for the capture of organic molecules on the surface of Y³⁺-doped TiO₂ substrates, thus facilitating the reduction of such molecules by the electrons liberated after UV irradiation.
2. Besides, Y³⁺ doping inhibits the rapid recombination of photogenerated electrons and hole pairs.
3. Textural parameters of TiO₂ substrates, such as the specific surface area, total pore volume and mean pore width, greatly influence the performance of photocatalysts of this sort. It is also likely that the pore shape plays a crucial role as the main surface transport mechanisms (adsorption, desorption and displacement) of bulky organic molecules (such as azo dyes) are greatly affected by the geometry of the voids existing in a pore network. It is not the same for a chemical species to be steadily transported along a cylindrical tube as across a pore network made of narrow entrances interconnected to wide bulges. This last assertion is suggested by the shape of the N₂ sorption isotherms developed on the assorted substrates.
4. Nearly a total methyl orange (MO) photodegradation usually occurs after UV irradiation times of about 60–70 min under 300-W UV lamps.

In this work, pristine- and Y³⁺-doped TiO₂ samples were prepared by a simple sol-gel method, and the photocatalytic activities of the resulting substrates were evaluated by monitoring the degradation of a methyl orange solution. It was found that Y³⁺-TiO₂ mesoporous samples exhibited excellent photocatalytic activity for the degradation of methyl orange. The factors influencing both the optical absorption property and photocatalytic activity of pristine- and Y³⁺-doped TiO₂ mesoporous materials are discussed.

First, TiO₂ sols were synthesized, and subsequently either 2 or 8 wt% of Y³⁺ was added as impurity, in the absence of Pluronic P-123 surfactant; the complementary preparation was also performed when 2 or 8 wt% of Y³⁺ was added together with the P123 templating surfactant. The catalytic activity of xerogels containing 2 wt% Y³⁺ was found

to be substantially higher than that originating from those substrates holding 8 wt% Y³⁺. The reason is explained in section 3.8. Consequently, the synthesis of catalytically active mesoporous TiO₂ samples was performed mainly by focussing on a concentration of 2 wt% Y³⁺ either in the presence or absence of P123.

2. Experimental

2.1 Synthesis of materials

Yttrium nitrate, Y(NO₃)₃, and titanium tetraisopropyl alkoxide, Ti(i-OPr)₄, were employed as precursors of Y³⁺-doped TiO₂ samples (supplied by Aldrich). The hydrolysis rate of the Ti alkoxide was controlled by the addition of acetylacetone (acac)²³ and HNO₃. Pluronic P123, a surfactant triblock copolymer of formula (EO)₂₀(PO)₇₀(EO)₂₀, where EO=ethylene oxide and PO=propylene oxide) with an average molar mass (M_{av} = 5800 Da), was purchased from BASF.

A mixture of 5.6 ml (0.075 mol) of isopropyl alcohol, 1 ml (0.0125 mol) of acac and 0.9 ml HNO₃, 1×10^{-2} M was added to the doping solution containing the appropriate amount of Y³⁺ to obtain the desired 2 and 8 wt% Y³⁺. A blank (pristine) TiO₂ sol-gel material was synthesized under the same reactant composition but without doping Y³⁺ ions; this material was later used as a blank catalyst during MO decolourization experiments. After stirring this mixture for 1 h, 3.8 ml (0.0125 mol) of Ti(i-OPr)₄ was slowly added. A yellow-red solution was eventually formed. Stirring was maintained for 5 h (in order to complete alkoxide hydrolysis). Afterward, at ambient temperature, the beaker was covered with plastic paraffin film until the solution gelled. The ensuing gel was dried for 72 h at 100°C, and, finally, annealed in air for 2 h at 200, 400, 600 and 800°C, respectively. The samples were labelled as Ti2Y and Ti8Y, the digit representing the dopant concentration of either 2 or 8 wt% of Y³⁺, respectively; in turn, the materials prepared in the presence of P123 surfactant were labelled as M2Y (M standing for the increased mesoporous character of the sample containing 2 wt% Y³⁺) and MTi (for the mesoporous blank TiO₂ catalyst having no Y³⁺). The M2Y sample was prepared in the same manner as the Ti2Y material, but still including the proper amount of P123 (1.8 g) surfactant template in the initial solution in order to obtain a mesoporous substrate.

2.2 Characterization techniques

The produced pristine- or Y³⁺-doped TiO₂ samples were characterized by XRD in a Siemens D-500 diffractometer system employing a CuK α radiation with a 0.017° step size. A Horiba Jobin-Yvon model T64000 Excell FT-Raman spectrometer, equipped with an Ar 514.5 nm laser, an X100 objective, and a 10 mW head beam laser, working at 6 accumulations per 10 s was used to determine the corresponding

Raman spectra of the samples. The UV-diffuse reflectance technique was used to ascertain the optical properties of the materials *via* a Cary-300 spectrometer. TGA–DTA thermal analyses were performed by means of a NETZSCH STA 449 instrument, which helped identify the different decomposition stages that follow the obtained materials as function of temperature. The heating speed was set at $10^{\circ}\text{C min}^{-1}$ under air with a flow rate of 100 ml min^{-1} . Infrared spectra were recorded in a Varian FTIR 640 spectrometer with a resolution of 4 cm^{-1} . The texture and surface morphology of the materials were observed by using a scanning electron microscope (SEM) Stereoscan S360 system. The textural properties of the diverse substrates were calculated from N_2 adsorption–desorption isotherms at 76 K (N_2 boiling point at Mexico City's altitude) measured in an automatic Quantachrome 1L-C instrument. Finally, the photocatalytic activity of the materials was evaluated by monitoring the photodecomposition of MO in aqueous solution under two 13-W UV irradiation lamps, displaying an emission maximum at 364 nm. Therefore, in order to monitor the kinetic degradation of MO by Y-doped TiO_2 substrates, it was chosen the most intense UV–visible (UV–vis) band of the dye molecule which appears at 464 nm. The optical absorption of the dye solution was measured by means of a UV–vis Cary-300 spectrophotometer by using deionized water as the reference signal.

3. Results and discussion

3.1 Thermal analysis

The DTA–TGA analyses results for the Ti2Y and Ti8Y samples are presented in figure 1a and b. For sample Ti2Y, TGA renders a total weight loss at 1000°C of around 43% (figure 1a); in turn, DTA provides a rather wide endothermic peak at approximately 140°C , which can be assigned to the desorption of water molecules. The exothermic peak at 250°C corresponds to the decomposition of organic solvents (isopropyl alcohol and acac) as well as to the evaporation of physisorbed water occluded in the gel. At 460°C , a small exothermic peak indicates the onset of the crystallization transition from amorphous to anatase phase.²⁴

For the Ti8Y sample (figure 1b), TGA accounts for a total weight loss of 42% at 1000°C ; as for the TGA results, a broad endothermic peak is seen at approximately 131°C and can be assigned to the loss of physically adsorbed water; in turn, the exothermic peak at 210°C is attributed to the decomposition of the organic species. A broad exothermic peak, centered at 400°C , depicts the transformation between the amorphous–crystalline forms (i.e., anatase–rutile mixture). Finally, and importantly, the broad signal centered at 620°C is due to the formation of the stoichiometric compound $\text{Y}_2\text{Ti}_2\text{O}_7$ ($\text{Y}_2\text{O}_3 \cdot 2\text{TiO}_2$).

The TGA and DTA curves of the M2Y powder, prepared and dried at room temperature, are presented in figure 1c. There, it can be observed that the TGA curve can be divided

into three main stages and that the total weight loss accounts to about 70% up to 1000°C . The first mass loss stage in M2Y takes place from room temperature to 200°C and is related

Figure 1. DTA–TGA curves of (a) Ti2Y, (b) Ti8Y and (c) M2Y powders.

to the evaporation of water and alcohol existing in the gel structure.²⁵ The second stage occurs from 200 to 400°C; this loss can be assigned to the combustion of most of the organic moieties as well as to the decomposition of P123 organic chains.²⁶ The third stage takes place from 400 to 650°C and can be due to the oxidation of carbon residues and evaporation of chemisorbed water. In turn, the DTA curve of M2Y reveals a small broad endothermic peak at around 100°C caused by the evaporation of water and alcohol from the structure. At about 380°C, an exothermic peak is observed because of further TiO₂ crystallization towards the anatase phase.

3.2 X-ray diffraction

The XRD patterns as a function of temperature are shown in figure 2 for samples Ti2y, M2y and Ti8y, respectively. for undoped TiO₂, the anatase–rutile phase transformation starts occurring at temperatures of about 400°C. Nevertheless, as it could be expected, the influence of the Y³⁺ dopant ion (in a 2 wt% proportion) on the anatase phase stability is remarkable. For the Ti2Y and M2Y materials, at 400°C, we can

clearly see anatase even at temperatures as high as 800°C. These XRD patterns witness the remarkable stability attained by this phase, given its almost exclusive presence, while the rutile phase is barely seen.

As for the Ti8Y sample, XRD shows that at 400°C the solid is still rather amorphous, but at 600°C the rutile form is becoming present, and peaks belonging to incipient rutile formation are then evident. Furthermore, at 800°C the XRD pattern shows a mixture of rutile with an almost equal amount of a new phase, which was identified as the stoichiometric compound Y₂O₃·2TiO₂. Additionally, some traces of residual anatase can still be seen.

3.3 FT-Raman

Figure 3 shows the Raman spectra of the MTi, M2Y and Ti2Y samples calcined at 400°C; the peaks appearing at 145, 396, 517 and 639 cm⁻¹ can be assigned to the E_g, B_{1g}, A_{1g} or B_{1g}, and E_g vibration modes, respectively, which are associated with the anatase phase.²⁷ The strongest mode, i.e., at 145 cm⁻¹, corresponds to the E_g mode and arises from the external vibration of the anatase structure, which indicates that

Figure 2. XRD patterns of TiO₂, Ti2Y, Ti8Y and M2Y powders, after being subjected to heat treatment at different temperatures (see the temperature label over each XRD pattern). A=anatase, R=rutile, S=stoichiometric Y₂Ti₂O₇.

an ordered long-range anatase phase has been established; in addition, no rutile phase is detected. Such conclusions are consistent with the XRD results shown in figure 2. From all this information, the idea that Y^{3+} just exists as a surface species is reinforced; otherwise, the previous Raman signals should appear shifted and widened.

3.4 SEM study

SEM micrographs of pristine Ti2Y and M2Y substrates calcined at 400°C for 2 h are shown in figure 4. Some differences of surface morphology between the surfactantless Ti2Y and mesoporous M2Y P123-templated specimens can obviously be noted from the two images.

As seen in the corresponding micrograph, the basic structure of the Ti2Y substrate consists of a collection of nanometric globules disposed in a kind of random packing; in turn, the not too evident underlying structure of the M2Y specimen

is made by scattered tubes (as successors of the P123 micelles originally present) within the globular medium (this point will be more fully addressed during the N_2 sorption textural study). In the photograph, it is possible to distinguish the constituting globules for Ti2Y.

Together with SEM, EDS mapping was also performed in order to analyse the presence of some chemical elements in the samples; from this study, it was possible to establish that yttrium was homogeneously dispersed throughout the TiO_2 surface of all incumbent samples. From this technique, it was possible to identify the presence of elements such as C, O, Ti and Y. The Y contents were found to be 2.0, 7.6 and 1.8 wt% for Ti2Y, Ti8Y and M2Y, respectively; these values indicate that the amount of $Y(NO_3)_3$ employed during the preparation of these samples was almost completely deposited on the surface of the resultant materials.

3.5 UV-vis diffuse reflectance

Figure 5 illustrates the UV-vis diffuse reflectance spectra of Ti2Y, Ti8Y, MTi and M2Y samples after thermal treatment at 400°C. A strong UV-vis absorption band in the 280–390 nm interval is observed for all samples. This band is due to the $M \leftarrow L$ charge transfer²⁸ from O^{2-} to Ti^{4+} . The bandgap can be estimated from the intercept of the slope of the rising part of the UV-vis spectrum with the wavelength abscissa axis.²⁹ The appearances of the UV-vis spectra of the samples annealed at 400°C lead to the following observations: (i) the mesoporous substrate depicts a sharper spectrum from 400 nm thereon, thus indicating the practically complete elimination of organic residues; (ii) conversely, the Ti2Y and mainly the Ti8Y samples still contain vestiges of organic matter.

3.6 FTIR analysis

Infrared spectra of the Ti2Y and Ti8Y samples (not shown here) depict common features. Nevertheless, we shall

Figure 3. Raman spectra of Ti2Y, MTi and M2Y materials.

Figure 4. SEM micrographs of (a) Ti2Y and (b) M2Y materials. The figure insets depict the EDS histogram for Ti, O and Y chemical composition on the surface of the adsorbents.

initially discuss the FTIR spectral characteristics of the Ti2Y sample. A broad band centred at 3390 cm^{-1} represents the O-H stretching vibration; this band disappears entirely at 800°C . A band at 1580 cm^{-1} is assigned to the O-H bending vibration from water and ethanol molecules that are still present in the gel. This band, is still strong even at 200°C , but disappears completely at 800°C . Two more bands, at 1530 and 1385 cm^{-1} , whose intensities decrease with temperature, indicate the bending and scissors-type vibrations of C-H bonds of the alkoxy groups of some residual alkoxide precursor. A further shallow band at 454 cm^{-1} is caused by the bending vibration of Ti-O bonds. At higher temperatures, this band shifts to lower energy regions thus increasing its intensity, which results in structural changes of the metal oxide network. In turn, the FTIR spectra of the M2Y material calcined at different temperatures provide information about surface functional groups and also allow observation of the surfactant elimination process. At 200°C , the spectra still show the existence of organic moieties proceeding from the P123 template. The bands found between 2800 – 3100 and 1250 – 1500 cm^{-1} correspond to the stretching and bending modes of C-H bonds of the surfactant (P123 tri-block copolymer) molecule,³⁰ respectively. However, after calcination at 400°C practically all P123 is removed, thus confirming the previous TGA, XRD and UV analyses.

A wide band around 3400 cm^{-1} is typical of the stretching modes of the O-H bonds from the Ti-OH groups. At approximately 1630 cm^{-1} , a band appropriate to the bending mode of the OH bond appears. The signal at 1050 cm^{-1} can be assigned to the Ti-O bond stretching mode. Finally, shallow bands at 600 and 450 cm^{-1} correspond to the O-Ti-O bending modes.

3.7 N_2 sorption

Prior to the sorption experiments, samples were subjected to a thermal treatment at 400°C for 24 h. This was made

Figure 5. UV-visible diffuse reflectance spectra of Ti2Y, Ti8Y and M2Y substrates at 400°C .

with the aim of not only counting with a surface avid to perform significant adsorption, but also to have substrates with a certain combination of anatase and rutile phases.

(a)

(b)

(c)

Figure 6. N_2 adsorption-desorption isotherms of (a) Ti2Y, (b) Ti8Y and (c) M2Y materials. ABC = adsorption boundary curve; DBC = desorption boundary curve.

N₂ adsorption–desorption isotherms of Ti2Y, Ti8Y and M2Y materials are shown in figure 6. These isotherms were measured in an automatic Quantachrome Autosorb-1LC instrument; each substrate was outgassed under vacuum provided by a combination of mechanical and turbomolecular pumps. Some of the most important textural properties³¹ of the Ti2Y, M2Y and Ti8Y substrates are listed in table 1. IUPAC Type IV isotherms,³² which are typical of mesoporous materials with H1 and H2 hysteresis loops, are depicted by the M2Y and Ti-8Y materials, respectively. In turn, the Ti-8Y sample displays an isotherm similar to an apparent IUPAC Type I isotherm; nevertheless and importantly, as it will be ascertained later, this solid is not built by micropore but by mesopore entities. Furthermore, the BET surface areas of all samples completely coincide with their external surface areas (calculated either by the *t*-plot or α_s -plot methods, see table 1). This fact also indicated the absence of micropores in all specimens.

The range of relative pressures (p/p^0) at which the H1 hysteresis loop of the M2Y isotherm occurs, i.e., $p/p^0 \in [0.5, 0.85]$ confirms the mesoporous nature of this specimen. In the case of the Ti2Y sample, while still showing a Type IV isotherm, the corresponding hysteresis loop is an H2 shape rather than an H1 hysteresis cycle.

The following observations with respect to the textural properties are useful to appraise the nature of each of these substrates. First, note that the M2Y and Ti2Y samples depict surface areas of 132 and 51.2 m² g⁻¹ and total pore volumes of 248 and 46 mm³ g⁻¹, respectively (table 1). The mean pore width, proceeding from estimations provided by the non-local functional density theory (NLDFT), as applied to cylindrical pores with respect to the adsorption boundary curve (ABC) of the hysteresis loop, indicates sizes of 7.3 (M2Y, 4.9 (Ti2Y) and 3.2 (Ti8Y) nm for the M2Y, Ti2Y and Ti8Y substrates, respectively.

Another useful information is that the NLDFT mean pore width arising from the desorption boundary curve (DBC) of the hysteresis loop accounts for sizes of 8.1 (M2Y), 4.6 (Ti2Y) and 2.6 (Ti8Y) nm, respectively. Most interestingly, the mean pore diameter calculated from the formula $d_p = 4V_p/A_{BET}$, (table 1, last column), while assuming an adsorbent made exclusively of cylindrical pores, is close to the NLDFT value for the case of the M2Y substrate (7.3 vs. 7.5 nm). The fitting between these two quantities is just fairly good for the Ti2Y (4.9 vs. 3.6 nm) and Ti8Y (3.2 vs. 2.2 nm)

specimens. This pore width agreement has to be investigated with and without the involvement of P123, during the synthesis of the M2Y and TiY xerogels.

The above data and information allow us to configure a vision of the pore structure of each material as follows:

M2Y. The addition of P123 templating surfactant to the sol–gel reaction mixture renders a substrate constituted by a large amount of quasi-cylindrical pores. This geometrical characteristic is validated by:

- (i) The evident H1 shape of the hysteresis loop: the fact that the ABC and DBC isotherms are not completely parallel to each other could mean some degree of swirling appearance along the axis of the tubular pores. However, this does not detract the texture values obtained from a completely straight cylindrical pore model.
- (ii) The very similar aspects of the pore size distributions (PSDs) depicted by both the ABC and DBC curves of the H1 hysteresis loop (figure 7a). The total surface area and total pore volume if divided by the individual cylindrical volume and area of a single pore, having the average pore width and an adjusted pore length of 1 μ m, may render a total amount of pore entities corresponding to approximately 10²⁰ g⁻¹.
- (iii) The comparable mean pore widths calculated from either the NLDFT or the $d_p = 4V_p/A_{BET}$ formula.

The action of the P123 surfactant was to coin cylindrical micelles from which cylindrical pores were created. The hexagonal (honeybee array) arrangement of these micelles that is usually seen in SBA-15 silica was not clearly observed by SEM in this TiO₂ sample (although some oval pore entrances could be detected). Even so, an irrefutable proof that these tubular aggregates existed was the very good correlation of textural properties derived from a cylindrical pore model applied to both ABC and DBC isotherms delimiting the hysteresis loop.

Ti2Y. This substrate is mesoporous in view of the Type IV isotherm and the H2 hysteresis loop that it depicts. Besides, a mean pore width of about 4.9 nm obtained from the ABC further supports this previous evidence. The reason by which the mean pore width proceeding from the DBC (4.6 nm) is not more closely matching the ABC outcome, suggests that this material consists of some wide pore cavities or chambers

Table 1. Textural properties of Ti2Y, Ti8Y and M2Y solids.

Sample	$A_{BET}/\text{m}^2 \text{ g}^{-1}$	$V_p/\text{mm}^3 \text{ g}^{-1}$	$A_{\text{ext}}/\text{m}^2 \text{ g}^{-1}$	ε	W_p/nm	d_p/nm
Ti2Y	51.2	46	51.2	0.094	4.9 abc, 4.6 dbc	3.6
Ti8Y	34.4	19	34.4	0.041	3.2 abc, 2.6 dbc	2.2
M2Y	132	248	132	0.848	7.3 abc, 8.1 dbc	7.5

A_{BET} =BET surface area; V_p =total pore volume; A_{ext} =external surface area; ε =porosity; W_p =mode pore width; d_p =mean pore diameter (cylindrical pores assumed); abc=adsorption boundary curve; dbc=desorption boundary curve.

interconnected to each other by narrow necks. This picture is consistent with the predominant H2 character of the hysteresis loop. This is because the DBC curve renders a rather sharp PSD in the interval $p/p^0 \in [0.5, 0.35]$, thus unveiling a relatively weak pore blocking effect due to the narrow throats that are interconnecting the pore cavities. The most striking evidence that the T2Y solid is suffering from a somewhat sudden vapour percolation along the DBC is the aspect of the PSD obtained from the latter isotherm (figure 7b); this curve results to be very acute if compared to that proceeding from the ABC.

Figure 7. Pore size distributions (PSD) depicted by both the ABC and DBC curves of substrates: (a) Ti2Y, (b) Ti8Y and (c) M2Y.

The above observations are consistent with the sorption characteristics that are expected from a random array of solid globules (i.e., a globular material). In these systems, pore cavities are surrounded by a number of narrower pore necks that interconnect them to fellow chambers. The sorption hysteresis loop of these solids is consistent with a IUPAC H2 shape. A prominent example of this kind of solids is porous glass. The remaining issue to remark is the narrow dispersion of the NLDFT PSD obtained from the DBC when compared to the wider NLDFT PSD proceeding from the ABC. This reinforces the idea of vapour percolation along the DBC and of a more gradual filling of the cavities with capillary condensate along the ABC.

Ti8Y. This sample displays the lowest surface area and pore volume among all specimens. The sorption isotherm resembles a IUPAC Type I shape with a very narrow hysteresis loop. The mean pore sizes (figure 7c) obtained from the ABC and DBC are relatively close to each other (3.2 vs. 2.6 nm). These values together with the narrowness of the hysteresis loop suggest that the pores of this substrate are hollow entities, which communicate straightforwardly to the outer surface of the solid. In addition, t - and α_S plots show an important linear portion at assorted p/p^0 values.

There exist three common ways to modulate the surface area and porosity of TiO₂ substrates doped with Y³⁺. The first procedure involves no other reactants than yttrium ions and titanium alkoxide. The second procedure includes the use of acetic acid in order to obtain Ti acetate species, the removal of which after thermal treatment generates mesopores. The third procedure engages the use of a mesopore templating agent, such as Pluronic P123.

3.8 Photocatalytic properties

The photocatalytic properties of the samples were evaluated by monitoring the degradation of a 15-ml sample of a MO aqueous solution (1×10^{-5} M) under UV irradiation. The mass of the solid was 20 mg. The photodegradation at room temperature shows changes in the MO absorbance after the photocatalytic reaction with Ti2Y and M2Y, respectively. The M8Y shows no activity at all.

The bands appearing at 271 and 464 nm in MO UV-vis spectra, which are cited in the literature, can be principally attributed to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the azo group ($-N=N-$) when conjugated with the phenyl rings.

The intensity of these signals was gradually reduced according to the illumination time, eventually disappearing completely after some hours. The complete degradation of MO due to the M2Y sample was achieved after 7 h. The pristine TiO₂ sample could only degrade MO up to 50%, while for the Ti2Y specimen the degradation was limited to 67% even after longer exposure times (figure 8).

The above results suggested that M2Y was the most effective to induce a more efficient photocatalytic activity of Y-TiO₂ solids for decomposition of organic compounds. The kinetics of reaction for the MO photodecomposition was obtained by plotting $\ln(A_0/A)$ vs. irradiation time, as

Figure 8. Degradation percentage of MO in contact with Ti2Y, Ti8Y, MTi and M2Y specimens.

Figure 9. MO decolouration kinetics plots of TiO₂, Ti2Y, Ti8Y, MTi and M2Y materials.

shown in figure 9. The experimental results indicate that the photocatalytic reduction of MO by all substrates follows a first-order reaction, as expressed by the equation below:³³

$$\ln\left(\frac{A_0}{A}\right) = kt, \quad (1)$$

where A_0 is the initial absorbance at the MO maximum, A is the absorbance after an irradiation time t (min), k is the reaction rate constant. The reaction rate constants for each substrate are indicated in figure 9. They follow the descending sequence: $k_{M2Y} > k_{MTi} > k_{Ti2Y} > k_{TiO2} > k_{Ti8Y}$.

According to the values of these reaction rate constants (table 2), the presence of yttrium in small doses (i.e., ≈ 2 wt %) causes faster reaction rates, irrespectively of the substrate being mesoporous or not. Still, the existence of mesopores has a positive effect, as these void entities produce a larger surface area and porosity and, consequently, a faster reaction rate compared to a substrate endowed with larger pores. It is also interesting to note that the rise in surface area is not sufficient to explain the increased activity of mesoporous TiO₂ solids. For instance, the surface area ratio between M2Y and Ti2Y is equal to 2.6, while the MO decomposition rate constants ratio of the same specimens corresponds to 3.6.

Table 2. Reaction rate constants of pristine- and yttrium-doped TiO₂ photocatalysts.

Sample	$k \times 10^3/\text{min}^{-1}$	R^2
M2Y	9.14	0.995
MTi	6.34	0.987
Ti2Y	2.88	0.994
TiO ₂	1.86	0.995
Ti8Y	4.34×10^{-2}	0.480

k = MO rate constant at 25°C; R^2 = linear correlation constant of the plots appearing in figure 9.

Thus, an additional factor (i.e., the Y³⁺ presence on the surface) is required to explain the different activities showed by the latter samples. In summary, mesoporous solids with homogeneously deposited Y³⁺ ions turn out to be the best photocatalyst among all substrates tested in this work.

In view of the information reported in three recent references with respect to MO degradation by yttrium-doped TiO₂ materials^{21,22,34} together with our own manuscript, table 3 shows the comparison of different synthesis and operational parameters as well as the results obtained.

Table 3 reveals the following:

1. In our case, the UV illumination power was provided by two 13-W low-price commercial LUMIACTION lamps (operating wavelength of 365 nm), while in the remaining works 300-W lamps were utilized.
2. Textural parameters, such as pore width and pore network topology (see further discussion below) instead of surface area or total pore volume, were revealed as crucial factors for achieving an efficient degradation of MO molecules when adsorbed from solution.
3. It is interesting to note that the TiO₂-specific surface area obtained in the presence of templating agents (i.e., Pluronic P-123, our work) resulted in values larger than the corresponding values yielded by other methods even when they involved a template-free TiO₂ synthesis.
4. With respect to the topology and morphology, pore networks obtained from the sol-gel processing of metal oxide alkoxides mostly render arrangements of globular solid particles, in which the resultant pore structures consist of a collection of wide bulges interconnected to each other by narrow throats. Therefore, the transport of molecules across the surface and along the pores of such substrates is more difficult compared to the movement of these species along straight cylindrical capillaries.
5. Likewise, it could be recognized that a stronger adsorption together with a faster degradation of organic molecules, occurs altogether when sites on the TiO₂ surface fix in a co-ordinated kind of bond to some Y³⁺ ions. The anionic regions of the MO molecule got electrostatically attracted more easily and more strongly

Table 3. Comparison of textural, kinetic and other physicochemical properties of Y^{3+} -doped TiO_2 substrates in relation to the degradation of methyl orange according to different methods of synthesis.

Paper	Wang <i>et al</i> ²¹	Niu <i>et al</i> ³⁴	Wu <i>et al</i> ²²	This work
Illumination power Watt	300 Xenon lamp	300 Hg lamp	300W Xenon lamp	Two 13-W commercial lamps
Initial MO concentration	10 mg l ⁻¹	20 mg l ⁻¹	10 mg l ⁻¹	32 mg l ⁻¹
Surface area	37.6–69	84.73–95.21	63.6	51.2–132
% Degradation time	96	99.8 Under UV irradiation for 70 min	82.6 and 81.3% 6 h	98 at 7 h
Rate constant in min ⁻¹	6×10^{-3} (pH 5.3)	—	4.8×10^{-3}	9.14×10^{-3}

to the substrate surface. Thus, the degradation of such a molecule became easier due to the production of nucleophilic species resulting from UV irradiation in an environment rich in water or oxygen.

- With respect to the rate constant related to the pseudo-first-order kinetics undertaken by the MO molecules, two considerations are pertinent to remark. The rate constant obtained by us was the largest of all; however, the initial MO concentration was also the highest of all but, as this quantity influences the value of the rate constant, it would be wise to just consider this result as a possible perspective for a better performance of our photocatalytic devices.

The shapes of N_2 sorption isotherms on Y^{3+} -doped TiO_2 xerogel samples support some of the above remarks. A Type I IUPAC hysteresis loops³² can be ascribed to the mesoporous M2Y substrate. This shape is proper of tubular arrangements of pores. In turn, the shape of the Ti_2Y material (figure 6a) indicates that, in this sample, there exists pores that fill sequentially with condensate according to their size (i.e., the boundary adsorption curve is sloping), while the boundary desorption branch, especially the PSD curve (figure 7a), shows the combination of a pore-blocking effect together with a vapour percolation threshold (i.e., these characteristics indicate the presence of narrow throats delimiting the wider interconnected pore cavities).

Additionally, we now present an opinion about the mechanism by which MO molecules can be captured from solution at surface sites on which the Y^{3+} species are initially fixed on TiO_2 substrates (figure 10). Afterward, the resultant nucleophilic species proceeding from UV irradiation, degrade the organic molecule *in situ*. At the start of the degradation process, MO molecules are electrostatically attracted to the substrate surface by a co-operative effect between the TiO_2 and the Y species deposited on it. The electrostatic attractions of these sites towards the electrodonating regions in the MO species are the reason for this selective adsorption from solution (figure 10). The TiO_2 -liberated electrons then create nucleophilic moieties (Nu), such as hydroxyl or singlet oxygen radicals,³⁵ ultimately responsible for the degradation of azo groups ($-N=N-$) in the dye molecule. However, this proposed mechanism is just an idea that requires eventual confirmation.

Figure 10. Hypothetical representation of an MO molecule coordinated to the surface of Y-doped TiO_2 mesopores. The liberation of electrons by UV illumination creates nucleophilic species (Nu), such as $Nu = \cdot O_2$, $\cdot OH$ and ^-OH , which degrade the adsorbed MO molecules.

4. Conclusions

The interplay of several physicochemical parameters resulted essential for achieving a successful design and performance of the Y-doped TiO_2 catalysts that were developed in this work. The most outstanding achievement was employing low-cost and low-energy 13-W UV lamps to accomplish an almost complete degradation of MO within a few hours. The good performance of these mesoporous Y-doped TiO_2 photocatalysts was also reflected in the accomplishment of an MO rate degradation constant that was superior to or comparable with some of the most prominent values that have already been reported in the literature.

The textural characteristics suitable for the design of effective photocatalysts include an adequate porosity, sufficient surface area and appropriate pore morphology and topology. These last characteristics were found to be satisfactorily met by the mesopore templating action of a triblock surfactant (i.e., Pluronic P-123).

The development of effective metal oxide photocatalysts for the degradation of organic compounds requires the interplay of chemical and textural properties. Once the deposition

of a rare earth species (in this case yttrium) is made on the surface of the TiO₂ substrate it is still required to

Once an efficient photocatalyst has been synthesized after the deposition of an adequate amount (e.g., 2 wt%) of yttrium, the mechanism of MO degradation by Y-doped TiO₂ mesoporous substrates seems to include the following steps:

- (i) Initially, MO molecules are deposited on the Y-doped TiO₂ surface. This is a process that corresponds to an adsorption from solution phenomenon,³⁶ which is promoted by the surface deposition of Y³⁺ ions. This process can be linked to the existence of oxygen vacancies on the TiO₂ surface. These are generated through the presence of surface Y³⁺ species acting, on the one hand, as adsorption sites for the MO molecules and, on the other, as electron providers for the effective reduction of the dye species on the surface.
- (ii) The Y-doped sites that are first occupied by MO molecules correspond to those that lie close to the outer surface of the substrate. If the innermost sites are to be occupied by the organic dye species, it is required that these molecules can effectively diffuse through the pore structure. The size of the pore also determines the steadiness of diffusion of the organic molecule.
- (iii) The creation of mesopore entities throughout the TiO₂ mass, initiated by the seeding of cylindrical micelles of the P123 surfactant, acted positively in two ways. First, the surface area attained a significant value when the solid became mesoporous. Second, the mesoporous sizes and tubular shapes of the resultant pores were very adequate for allowing the MO molecules to diffuse into the deepest profundities of the solid substrate.
- (iv) The rate of reaction for the different doped and undoped Y-TiO₂ materials followed a first-order kinetics, for which the MO degradation rate constants observed the sequence: $k_{M2Y} > k_{Ti2Y} > k_{Ti8Y}$ (i.e., the mesoporous 2 wt% Y-doped TiO₂ substrate was the most efficient, while the surfactantless 8 wt% Y-doped TiO₂ the least efficient one).

In conclusion, it should be pointed out that the objective of drilling mesopores (*via* templating surfactant species) inside the originally globular structure of TiO₂ xerogels consists not only in increasing the specific surface area, but also in facilitating the ingoing and outgoing transport of the molecules to be degraded, especially if these are bulky. It is also essential to stipulate that this study provides not a single but a conjoint overview of TiO₂ photocatalysts, synthesized under assorted conditions, and subjected to different circumstances so as to allow a deeper understanding with respect to the photodegradation of organic compounds in solution.

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