Study of the photocatalytic activity of Fe^{3+} , Cr^{3+} , La^{3+} and Eu^{3+} single-doped and co-doped TiO_2 catalysts produced by aqueous sol-gel processing

Charline Malengreux^a, Sophie L. Pirard^a, Géraldine Léonard^a, Julien G. Mahy^a, Marcus Herlitschke^{b,c,*}, Benedikt Klobes^b, Raphaël Hermann^{b,c,d}, Benoît Heinrichs^a, John R. Bartlett^{e,f}

^aDepartement of Chemical Engineering, Laboratoire Nanomatériaux, Catalyse, Electrochimie, B6a, Université de Liège, B-4000 Liège, Belgium

^bJülich Centre for Neutron Science JCNS and Peter Grünberg Institute PGI, JARA-FIT, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

^cFaculté des Sciences, Université de Liège, B-4000 Liège, Belgium

^dMaterials Science and Technology Division, Oak Ridge National Laboratory, Tennessee 37831, USA

^eSchool of Natural Sciences, University of Western Sydney, Penrith South DC, NSW 1797, Australia

^fFaculty of Science, Health, Education and Engineering, University of the Sunshine Coast, Maroochydore DC, Qld 4558, Australia

*Present address: FS-PE, Deutsches Elektronen-Synchrotron, 22607 Hamburg (Germany)

Abstract

An aqueous sol-gel process, previously developed for producing undoped and Cu^{2+} , Ni^{2+} , Zn^{2+} or Pb^{2+} doped TiO_2 photocatalysts with remarkably high photocatalytic activity without requiring any calcination step, has been adapted to produce Fe^{3+} , Cr^{3+} , La^{3+} or Eu^{3+} single-doped TiO_2 photocatalysts as well as La^{3+} - Fe^{3+} and Eu^{3+} - Fe^{3+} co-doped TiO_2 catalysts. The physicochemical properties of the obtained catalysts have been characterized using a suite of complementary techniques, including ICP-AES, XRD, UV-Vis spectroscopy, nitrogen adsorption-desorption and Fe-57 Mössbauer. The active crystalline phase is obtained without requiring any calcination step and all the different catalysts are composed of nanocrystallites of anatase with a size of 6-7 nm and a high specific surface area varying from 181 to 298 $\text{m}^2 \text{g}^{-1}$. In this study, the effect of the $\text{NO}_3:\text{Ti(IV)}$ mole ratio used to induce the peptisation reaction during the synthesis has been studied and the results revealed that this ratio can influence significantly the textural properties of the resulting catalyst.

A screening of the photocatalytic activity of the undoped and Fe^{3+} , Cr^{3+} , La^{3+} or Eu^{3+} single-doped and co-doped photocatalysts has been performed by evaluating the degradation of 4-nitrophenol under UV-Visible light (330 nm $< \lambda <$ 800 nm). This study suggests that the photocatalytic activity is significantly influenced by the dopant nature and content with an optimal dopant content being observed in the case of Fe^{3+} or La^{3+} single-doped as well as in the case of La^{3+} - Fe^{3+} and Eu^{3+} - Fe^{3+} co-doped catalysts. In the case of Cr^{3+} single-doped catalysts, a detrimental effect of the dopant on the photocatalytic degradation of 4-nitrophenol has been observed while no significant influence of the dopant has been detected in the case

of Eu^{3+} single-doped catalysts. The role of the different dopants in modulating the photocatalytic activity is discussed.

1. Introduction

Environmental pollution has become a critical issue for our society. In the case of water pollution, advanced oxidation processes (AOP) has been investigated to remove the pollutants from water [1]. Heterogeneous semiconductor photocatalysis was proven to be a promising technology for the total mineralization of most organic pollutants by using natural or artificial light [2]. The most frequently used semiconductor is titanium dioxide, TiO_2 , due to its high oxidative potential, chemical stability, availability and its relatively low price [3]. Numerous studies have been undertaken to extend the activity of the TiO_2 towards the visible range by either enlarging the range of light which can be absorbed by the catalysts or by enhancing the electron-hole separation efficiency. In recent years, the sol-gel method has become an interesting approach for the synthesis of pure and modified TiO_2 based materials with controlled nanostructures and surface properties [4-8].

Non-aqueous sol-gel processes are typically performed in organic solvents to prevent precipitation and complexing ligands are used to lower the reactivity of the titanium alkoxide, enabling the production of stable sols [5, 7, 8]. The hydrolysis and condensation reactions are followed by drying and calcination steps (450–600 °C) to remove the organic component and to crystallize either anatase or rutile. The calcination process inevitably causes a decrease in surface area at high temperature (due to sintering and crystal growth), a loss of surface hydroxyl groups, and even a phase transformation. From an industrial perspective, high temperature thermal treatments are costly and make large-scale productions difficult. It is therefore important to try to develop room temperature syntheses.

The aqueous sol-gel process is a very promising breakthrough for air and water decontamination. Aqueous sol-gel approaches have been reported by Bartlett et al. [9-11] for producing titanate-based materials in which a titania precipitate is initially produced via the rapid hydrolysis of appropriate titanium alkoxides or covalent halides followed by the addition of small quantities of mineral acid to induce a repulsive electrostatic charge on the surface of the titania crystallites. Then they have been recently extended to the development of an environmentally-friendly aqueous sol-gel process for producing undoped and Cu^{2+} , Ni^{2+} , Zn^{2+} or Pb^{2+} -doped TiO_2 bulk photocatalysts exhibiting a remarkably high photocatalytic activity without requiring any calcination step [12].

In order to induce an enhancement of the photocatalytic activity by increasing the charge carriers lifetime and/or by extending the absorbance range of the TiO_2 -based materials towards the visible range, the introduction of metal ions into the TiO_2 particles is currently considered to be a promising approach [5]. Among possible metal ions, Fe^{3+} is considered as a successful dopant due to the half-filled (d5) electronic configuration. When Fe^{3+} ions trap the photogenerated electrons, the half-filled electronic configuration is destroyed and the stability decreases. The trapped electrons can then be easily transferred to adsorbed oxygen on the

surface of titania particles and the metallic ion returns to its original d5 state. Thus, the transfer and separation of the charge carriers is possible by optimising the Fe^{3+} dopant concentration, which is believed to increase the photogenerated charge carriers lifetime. It is also known that Fe^{3+} doping influences the bandgap of the catalyst, enabling a possible extension of the activity of titania towards the visible region [13-18].

Recently, doping with metal ions such as La^{3+} , Cr^{3+} and Eu^{3+} has also received attention. Several articles relate the synthesis and the activity of TiO_2 photocatalysts doped with La^{3+} [19-21], Cr^{3+} [22, 23] and Eu^{3+} . Controversial results regarding the effect of these dopants on the photocatalytic activity of the TiO_2 catalysts have been found, but it has been reported that these dopants can influence the morphology of the final materials by modulating the properties of the colloids [14]. Co-doping of TiO_2 with two kinds of ions is a very recent development which appears to enhance the photocatalytic activity through a synergistic effect [14, 24, 25].

The first objective of the paper is to adapt the aqueous-sol gel process in order to produce Fe^{3+} , Cr^{3+} , La^{3+} or Eu^{3+} single-doped as well as $\text{La}^{3+}\text{-Fe}^{3+}$ and $\text{Eu}^{3+}\text{-Fe}^{3+}$ co-doped TiO_2 photocatalysts. The second objective is to study the relationship between the physicochemical properties of the catalysts characterized by using ICP-AES, XRD, UV-Vis spectroscopy, nitrogen adsorption-desorption and Fe-57 Mössbauer spectroscopy, and their photocatalytic activity by evaluating the degradation of 4-NP in aqueous medium under artificial light after 7 h of illumination.

2. Experimental

2.1. Preparation of undoped TiO_2 catalyst

The undoped TiO_2 catalyst was prepared according to the procedure previously described using titanium tetraisopropoxide (TTIP > 97%, Aldrich), anhydrous acetic acid (HAc, Aldrich) and nitric acid (HNO_3 , 1 M solution in reagent-grade water) as starting materials [12]. The effect of high temperature treatment on the catalyst morphology and photocatalytic activity was investigated by heating a small amount of the TiO_2 -undoped sample in air at 500°C for 3 h using a heating rate of $10^\circ\text{C min}^{-1}$, prior to testing. The resulting sample is labelled TiO_2 -Undoped-500.

2.2. Preparation of doped and co-doped TiO_2 catalysts

Several series of Fe^{3+} , Cr^{3+} , La^{3+} and Eu^{3+} single-doped TiO_2 catalysts as well as $\text{La}^{3+}\text{-Fe}^{3+}$ and $\text{Eu}^{3+}\text{-Fe}^{3+}$ co-doped TiO_2 catalysts were prepared using TTIP (> 97%, Aldrich), anhydrous acetic acid (HAc, Aldrich), nitric acid (HNO_3 , 1 M solution in reagent-grade water) and, respectively, ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.5 M solution in reagent-grade water, Merck), chromium nitrate ($[\text{Cr}(\text{H}_2\text{O})_6](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, 0.5 M solution in reagent-grade water, Merck), lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.5 M solution in reagent-grade water, Merck),

and europium nitrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.5 M solution in reagent-grade water, Alfa Aesar) as starting materials [9].

The procedure used to obtain the agglomerated titania slurry was the same as described in [12]. The required amount of nitrate solution was introduced at the beginning of the peptisation corresponding to the transformation of the agglomerated titania slurry into a well-dispersed nanoparticle sol. Two sources of nitrate are used. Initially, the required amount of nitrate solution was introduced in order to obtain different Dopant:Ti(IV) mole ratios and then, the required amount of nitric acid solution was added under vigorous stirring at 45°C in order to reach a total NO_3 :Ti(IV) mole ratio equal to 0.2 in all cases. The Dopant:Ti(IV) mole ratios are expressed in mol % to represent the amount of dopant introduced in the catalysts, as presented in Table 1.

In the case of La^{3+} - Fe^{3+} co-doped catalysts, the required amount of nitrate solution was introduced to obtain a La(III):Ti(IV) mole ratio equal to 0.5% or 1%. In each case, samples corresponding to Fe(III):La(III) mole ratios equal to 0.3, 0.6 and 1.5 were tested, leading to a total of six La^{3+} - Fe^{3+} co-doped catalysts.

To prepare Eu^{3+} - Fe^{3+} co-doped catalysts, the required amount of nitrate solution was introduced to obtain a Fe(III):Ti(IV) mole ratio equal to 0.76% for five different Eu(III):Ti(IV) mole ratios (equal to 0.1%, 0.5%, 1%, 2% and 3%Eu(III)), leading to five Eu^{3+} - Fe^{3+} co-doped catalysts. In all cases, the total NO_3 :Ti(IV) mole ratio is equal to 0.2. The co-doped catalysts are labelled as presented in Table 2.

The reactor vessel was sealed to avoid evaporation and the peptisation process was continued overnight. Translucent sols, with different colourations depending on the nature and content of dopant were obtained and finally, the resulting sols were dried in a Petri dish at room temperature in a laminar-flow hood in order to obtain xerogels.

Two supplementary series of La^{3+} single-doped and of La^{3+} - Fe^{3+} co-doped TiO_2 catalysts were produced in order to study the effect of the NO_3 :Ti(IV) mole ratio. The procedure used to obtain the agglomerated titania slurry was the same as previously described with an amount of nitrate solution calculated to obtain a total NO_3 :Ti(IV) mole ratio equal to 0.1 in all cases. In order to distinguish those catalysts a “ ’ ” is added at the end of their labels in Tables 1 and 2 [12]. It has to be noted that the pH influence was not studied in this paper because it was previously showed that acid pH, meaning smaller than 5, does not influence the crystalline size and textural properties of TiO_2 photocatalysts [26]. All syntheses in this study were performed in acid media. That is the reason why only the NO_3 :Ti(IV) mole ratio is described in this paper.

The effect of high temperature treatment on the morphology and photocatalytic activity of four catalysts (TiO_2 -La-C', TiO_2 -La-Fe-C', TiO_2 -Eu-B, TiO_2 -Eu-Fe-B) was investigated by heating the samples in air at 500°C for 3 h using a heating rate of 10°C min⁻¹, prior to testing. The resulting samples are respectively referred to as TiO_2 -La-C'-500, TiO_2 -La-Fe-C'-500, TiO_2 -Eu-B-500 and TiO_2 -Eu-Fe-B-500 in the discussion below.

Table 1: Physico-chemical properties and photocatalytic activity for the different series of single-doped catalysts compared to the TiO₂-Undoped catalyst. Measured dopant content determined by ICP-AES; $E_{g, \text{direct}}$ and $E_{g, \text{indirect}}$ values obtained by using transformed Kubelka–Munk function calculated from DR-UV-VIS measurement; S_{BET} , specific surface area obtained by BET method; V_p , liquid nitrogen volume adsorbed at the saturation pressure of nitrogen; V_{micro} , microporous volume calculated from the nitrogen adsorption isotherm by the Dubinin-Raduskevich theory; d_c , the crystallites size calculated by using the Scherrer equation; d_p , the particle size calculated by using the S_{BET} and theoretical anatase density value; $\bar{f}_{\text{norm}}$, mean normalized conversion with standard deviation σ after 7h under illumination; ^a Not applicable; ^b Not measured.

Sample	Theoretical dopant content (mol/mol)	Measured dopant content (mol/mol)	$E_{g, \text{direct}}$ (eV)	$E_{g, \text{indirect}}$ (eV)	$E_{g, \text{indirect}}$ (eV)	S_{BET} (m ² g ⁻¹)	V_p (g cm ³)	V_{micro} (g cm ³)	d_c (nm)	d_p (nm)	$\bar{f}_{\text{norm}} \pm \sigma$ (%)
TiO ₂ -Undoped	-	^a -	3.14	3.00	^a -	275	0.14	0.12	5	6	51 ± 2
TiO ₂ -Fe-A	0.15%	0.17%	3.26	2.97	^a -	268	0.12	0.11	6	6	60 ± 1
TiO ₂ -Fe-B	0.76%	0.76%	3.21	2.88	2.16	267	0.13	0.11	5	6	76 ± 2
TiO ₂ -Fe-C	1.52%	1.53%	3.12	2.75	2.16	261	0.12	0.11	4	6	60 ± 1
TiO ₂ -Fe-D	3.00%	2.90%	3.03	2.54	2.15	257	0.12	0.11	6	6	42 ± 2
TiO ₂ -Fe-E	5.00%	4.94%	2.99	2.41	2.12	230	0.10	0.09	5	7	32 ± 2
TiO ₂ -Cr-A	0.07%	0.07%	3.39	3.03	^a -	185	0.11	0.08	4	8	53 ± 2
TiO ₂ -Cr-B	0.13%	0.14%	3.40	3.04	2.15	181	0.10	0.08	5	8	47 ± 3
TiO ₂ -Cr-C	0.26%	0.26%	3.34	3.02	2.19	181	0.12	0.08	5	8	37 ± 5
TiO ₂ -Cr-D	0.51%	0.51%	3.33	2.91	2.14	209	0.11	0.09	6	7	33 ± 4
TiO ₂ -Cr-E	1.00%	0.99%	3.38	2.97	2.12	214	0.11	0.08	4	7	25 ± 2
TiO ₂ -Cr-F	2.00%	1.96%	3.33	2.88	2.14	235	0.10	0.10	5	7	10 ± 2
TiO ₂ -La-A	0.05%	0.06%	3.26	3.01	^a -	204	0.09	0.08	6	8	30 ± 3
TiO ₂ -La-B	0.25%	0.26%	3.25	3.00	^a -	^b -	^b -	^b -	7	^b -	56 ± 3
TiO ₂ -La-C	0.50%	0.51%	3.25	3.01	^a -	207	0.09	0.08	7	7	61 ± 1
TiO ₂ -La-D	1.00%	1.00%	3.24	3.00	^a -	^b -	^b -	^b -	6	^b -	55 ± 4
TiO ₂ -La-E	1.50%	1.57%	3.25	3.01	^a -	253	0.12	0.11	6	6	40 ± 2
TiO ₂ -La-A'	0.05%	0.06%	3.22	2.99	^a -	279	0.13	0.11	5	6	50 ± 2
TiO ₂ -La-B'	0.25%	0.25%	3.24	2.99	^a -	^b -	^b -	^b -	5	^b -	54 ± 3
TiO ₂ -La-C'	0.50%	0.50%	3.27	2.99	^a -	273	0.15	0.11	8	6	34 ± 1
TiO ₂ -La-C'-500	0.50%	^b -	^b -	^b -	^b -	^b -	^b -	^b -	12	^b -	38 ± 5
TiO ₂ -La-D'	1.00%	0.98%	3.26	3.01	^a -	^b -	^b -	^b -	8	^b -	40 ± 2
TiO ₂ -La-E'	1.50%	1.60%	3.25	3.01	^a -	274	0.21	0.11	9	6	39 ± 4
TiO ₂ -Eu-A	0.10%	0.10%	3.27	3.00	^a -	214	0.09	0.09	4	7	47 ± 1
TiO ₂ -Eu-B	0.50%	0.51%	3.27	2.99	^a -	^b -	^b -	^b -	6	^b -	47 ± 5
TiO ₂ -Eu-B-500	0.50%	^b -	^b -	^b -	^b -	^b -	^b -	^b -	12	^b -	40 ± 5
TiO ₂ -Eu-C	1.00%	1.00%	3.27	2.99	^a -	226	0.10	0.09	4	7	46 ± 4
TiO ₂ -Eu-D	2.00%	1.88%	3.27	2.99	^a -	^b -	^b -	^b -	5	^b -	47 ± 3
TiO ₂ -Eu-E	3.00%	2.92%	3.27	2.99	^a -	234	0.12	0.10	8	7	43 ± 3

Table 2: Physico-chemical properties and photocatalytic activity for the different series of co-doped catalysts compared to the TiO₂-Undoped catalyst.

nt content (mol _{Fe} /mol _{Ti})	Measured dopant content (mol _{La or Eu} /mol _{Ti})	(mol _{Fe} /mol _{Ti})	$E_{g, direct}$ (eV)	$E_{g, indirect, 1}$ (eV)	$E_{g, indirect, 2}$ (eV)	S_{BET} (m ² g ⁻¹)
0.15%	0.53%	0.18%	3.19	2.93	^a -	235
0.30%	0.50%	0.33%	3.23	2.93	^a -	228
0.76%	0.50%	0.76%	3.16	2.83	2.16	242
0.30%	1.03%	0.33%	3.16	2.91	2.16	232
0.61%	1.00%	0.60%	3.16	2.86	2.15	^b -
1.51%	0.99%	1.50%	3.13	2.76	2.12	202
0.15%	0.50%	0.17%	3.21	2.95	^a -	282
0.30%	0.51%	0.33%	3.19	2.89	^a -	280
0.76%	0.53%	0.77%	3.18	2.83	2.16	298
0.76%	^b -	^b -	^b -	^b -	^b -	^b -
0.30%	1.01%	0.32%	3.24	2.91	2.04	278
0.61%	1.00%	0.61%	3.23	2.93	2.12	^b -
1.51%	1.01%	1.51%	3.16	2.76	2.09	288
0.76%	0.11%	0.73%	3.17	2.76	2.10	213
0.76%	0.50%	0.74%	3.17	2.79	2.14	^b -
0.76%	^b -	^b -	^b -	^b -	^b -	^b -
0.76%	0.85%	0.75%	3.10	2.73	2.16	214
0.76%	1.87%	0.73%	3.11	2.75	2.16	^b -
0.76%	2.96%	0.71%	3.15	2.77	2.12	237

2.3.Characterization

The dopant and TiO₂ contents in the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using an Iris Advantage ThermoJarrel Ash device. For analysis, samples were prepared according to the procedure detailed in [12]. X-ray diffraction (XRD) powder patterns were recorded with a Bruker D8 diffractometer using Cu-K_α radiation, a Ni filter and operating conditions of 40 kV and 40 mA [27].

Room temperature Fe-57Mössbauer spectra were measured on a constant-acceleration spectrometer in transmission mode using a rhodium matrix cobalt-57 source [28, 29]. The spectrometer was calibrated at 295 K with a 10 μm α-Fe foil and isomer shifts reported are relative to α-Fe. Eu-151Mössbauer spectroscopy measurements were attempted but failed to reveal a measurable absorption spectrum after acquisition times in excess of one week, presumably due to the relatively small Eu concentration.

Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 after outgassing for 1 h at 120°C in order to eliminate the remaining water trapped in the dried xerogels. Textural properties were calculated from the isotherms using standard techniques [30]. The optical properties were evaluated by performing diffuse reflectance spectroscopy measurements in the 200-800 nm region with a Varian Cary 500

UV-Vis-NIR spectrophotometer, equipped with an integrating sphere (Varian External DRA-2500) and using BaSO₄ as reference. By using the Kubelka–Munk function, the direct and indirect optical band-gap values, $E_{g,direct}$ (eV) and $E_{g,indirect}$ (eV) were obtained [4].

2.4. Photocatalytic activity under UV-Visible light

The measurements of the photocatalytic degradation were carried out using the multisamples photoreactor described in Fig. 1.

Fig. 1: Experimental device for measuring photocatalytic activity under halogen-lamp illumination (Scheme based on Fig. 2 from [31]).

Six batch reactors ($V_0 = 10 \times 10^{-6} \text{ m}^3$ each) were placed at equal distances from the cylindrical halogen lamp (Philips, 200 W) inside the black box and constantly homogenized using vigorous magnetic stirring. All batch reactors were hermetically sealed to avoid evaporation, and the internal temperature was maintained at 25°C using the circulating water jacket. After treatment at 100°C for 1 h under an air in an oven, suspensions of the different catalysts in the 4-NP solution ($C_0 = 1.0 \times 10^{-4} \text{ kmol m}^{-3}$) were prepared in order to reach a concentration of 1 kg m^{-3} in each batch reactor. Dark tests were performed for each catalyst over a 7 h period to evaluate the time required to reach the adsorption–desorption equilibrium and to confirm that only the protonated form of 4-NP was present in the mixture.

After these dark tests, the reactors were irradiated over a 7 h period and the degradation of 4-NP was determined by measuring the absorbance of the solution before and after illumination at $\lambda = 317 \text{ nm}$. All sampling was performed as described previously: $2.0 \times$

10^{-6} m³ aliquots of 4-NP solution containing the catalyst in suspension were sampled in each batch reactor using a syringe and then filtered with a polypropylene 0.2 μ m filter to separate the catalyst from the 4-NP solution. All experiments were replicated three times in order to study the reproducibility of the results.

No spontaneous break down of the 4-NP after 7 h under illumination in the absence of TiO₂ [12] was detected, thus ensuring that any observed decrease in 4-NP content was due to photocatalytic degradation.

3. Results

3.1. Macroscopic observations on sols

In the case of sols doped with La³⁺ and corresponding to a NO₃:Ti(IV) mole ratio of 0.1, milky sols were obtained at the end of the peptisation step, suggesting that the TiO₂ particles had formed agglomerates that were sufficiently large to scatter visible light. No precipitation or settling was observed, confirming that the sols were still colloidal solutions. By increasing the NO₃:Ti(IV) mole ratio to 0.2, translucent sols were obtained regardless of the dopant content.

3.2. Macroscopic observations on xerogels

TiO₂-Undoped as well as TiO₂-La³⁺ and TiO₂-Eu³⁺ catalysts are white powders regardless of the dopant content. For the TiO₂-Fe³⁺ catalysts, the characteristic orange coloration due to the Fe³⁺ cation is evident while the expected dark green coloration due to the Cr³⁺ cation is observed in the case of TiO₂-Cr³⁺ catalysts. It has to be noted that for TiO₂-Cr³⁺ catalysts, after treatment at 100°C under air in an oven for 1 h, a dark yellow coloration was observed suggesting the presence of Cr(VI) species such as [CrO₄]²⁻ or [Cr₂O₇]²⁻ ions. In the case of co-doped catalysts, the expected orange coloration due to Fe³⁺ cation was observed. In all cases, the color intensity varies with the dopant content as expected.

3.3. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

The theoretical and measured dopant contents of the various samples presented in Tables 1 and 2 are comparable, which indicates that there is no loss of dopant during processing (consistent with essentially complete incorporation of the dopant in the catalyst). The reproducibility of the synthesis method, assessed by measuring the dopant content in samples obtained by replicating the synthesis procedure, is highlighted in Tables 1 and 2 by comparing the dopant contents measured in different catalysts corresponding to the same theoretical composition.

3.4.X-Ray Diffraction (XRD)

Fig. 2 illustrates the XRD patterns of TiO_2 -Undoped as well as $\text{TiO}_2\text{-Fe}^{3+}$ catalysts. It was observed that the material is composed of anatase in all cases, and that the XRD patterns are not influenced by the dopant content. No traces of rutile or brookite were observed. Similar XRD patterns were measured for the uncalcined Cr^{3+} , La^{3+} and Eu^{3+} single-doped TiO_2 catalysts as well as for the uncalcined $\text{La}^{3+}\text{-Fe}^{3+}$ and $\text{Eu}^{3+}\text{-Fe}^{3+}$ co-doped TiO_2 catalysts.

By using the Scherrer equation, the size of the crystallites, d_c , both for undoped and doped catalysts was evaluated and the calculated values are reported in Tables 1 and 2. It can be observed that the calculated crystallite sizes are around 6 nm for uncalcined catalysts and are not influenced by the nature or content of dopant as previously observed for the Cu^{2+} , Zn^{2+} , Ni^{2+} - and Pb^{2+} -doped TiO_2 catalysts [12].

In the case of calcined catalysts, the XRD patterns show that the material is still composed of anatase only. Fig. 3 compares the powder patterns of calcined and uncalcined $\text{TiO}_2\text{-La-C'}$ and $\text{TiO}_2\text{-La-C'-500}$ catalysts, as well as $\text{TiO}_2\text{-La-Fe-C'}$ and $\text{TiO}_2\text{-La-Fe-C'-500}$ catalysts. It can be observed in Fig. 3 that the patterns obtained for single-doped and co-doped samples are different, the peaks being more intense in the case of $\text{TiO}_2\text{-La}^{3+}\text{-Fe}^{3+}$ co-doped catalysts. Similar observations can be made by comparing the XRD patterns obtained for the $\text{TiO}_2\text{-Eu-B-500}$ catalysts and $\text{TiO}_2\text{-Eu-Fe-B-500}$ catalysts.

Fig. 2: XRD patterns of TiO_2 -Undoped and $\text{TiO}_2\text{-Fe}^{3+}$ compared to the reference pattern of TiO_2 -anatase (ICDD file N°. 21-1272).

Fig. 3: XRD patterns of calcined and uncalcined $\text{TiO}_2\text{-La-C'}$, $\text{TiO}_2\text{-La-C'-500}$, $\text{TiO}_2\text{-La-Fe}$ and $\text{TiO}_2\text{-La-Fe-C-500}$ catalysts compared to the reference pattern of $\text{TiO}_2\text{-anatase}$ (ICDD file N°. 21-1272).

In the case of calcined catalysts, the crystallites size, d_c , has been found to be respectively equal to 12 nm and 15 nm for $\text{TiO}_2\text{-La-C'-500}$ and $\text{TiO}_2\text{-La-Fe-C'-500}$ catalysts (which is not significantly different), as well as for both $\text{TiO}_2\text{-Eu-B-500}$ and $\text{TiO}_2\text{-Eu-Fe-B-500}$ catalysts. These values are reported in Tables 1 and 2.

A comparison of the values of d_c for the $\text{TiO}_2\text{-La-C'-500}$, $\text{TiO}_2\text{-La-Fe-C'-500}$, $\text{TiO}_2\text{-Eu-B-500}$ and $\text{TiO}_2\text{-Eu-Fe-B-500}$ calcined catalysts (12 to 15 nm) with those reported previously for the $\text{TiO}_2\text{-Undoped-500}$ and $\text{TiO}_2\text{-Zn}^{2+}\text{-500}$ calcined catalysts (33 and 44 nm, respectively [12]), indicates that the values obtained in the present study are much lower. This observation suggests that the crystal growth induced during thermal treatment is hindered by the presence of La^{3+} and Eu^{3+} dopants, as well as in the presence of $\text{La}^{3+}\text{-Fe}^{3+}$ and $\text{Eu}^{3+}\text{-Fe}^{3+}$ co-dopants. However, it appears that the presence of Fe^{3+} favours the formation of small crystallites (with a size around 12-15 nm) leading to more intense diffraction peaks, while La^{3+} and Eu^{3+} appear to hinder the crystallization. These results are in agreement with previous reports in the literature [24, 25].

3.5. Textural properties of powders

Tables 1 and 2 summarize the textural properties of the 48 catalysts prepared in this study. In all cases, the uncalcined catalysts exhibit a relatively high S_{BET} , ranging from 181 $\text{m}^2 \text{g}^{-1}$ to 298 $\text{m}^2 \text{g}^{-1}$. Different factors influencing the value of S_{BET} can be observed: (i) the nature

of the dopant; (ii) the dopant content; and (iii) the value of the $\text{NO}_3:\text{Ti(IV)}$ mole ratio used during the synthesis of the catalyst. The data in Table 1 highlight that for a series of uncalcined catalysts corresponding to a specific dopant, S_{BET} and V_{micro} appear to increase with the dopant content introduced in the TiO_2 catalyst, except in the case of the $\text{TiO}_2\text{-Fe}^{3+}$ catalysts where the S_{BET} and V_{micro} values decrease with increasing dopant content.

The isotherms measured for the 22 uncalcined catalysts corresponding to a $\text{NO}_3:\text{Ti(IV)}$ mole ratio equal to 0.2 (Table 1) always exhibit a sharp increase in the adsorbed volume at very small p/p_0 values, which is characteristic of microporous materials. As an example, Fig. 4 presents the isotherm obtained for the TiO_2 -Undoped, $\text{TiO}_2\text{-Fe-A}$, $\text{TiO}_2\text{-Fe-C}$ and $\text{TiO}_2\text{-Fe-E}$ catalysts. The absence of hysteresis at p/p_0 between 0.4 and 0.8 suggests that there are no mesopores in the catalysts [30].

Fig. 4: Nitrogen adsorption-desorption isotherms for TiO_2 -Undoped, $\text{TiO}_2\text{-Fe-A}$, $\text{TiO}_2\text{-Fe-C}$ and $\text{TiO}_2\text{-Fe-E}$ catalysts.

Fig. 5: t-plots for TiO₂-Undoped, TiO₂-Fe-A, TiO₂-Fe-C and TiO₂-Fe-E catalysts.

In order to confirm this observation, the t-plot method has been applied for each catalyst and Fig. 5 presents the t-plot derived from the isotherm obtained for the TiO₂-Undoped, TiO₂-Fe-A, TiO₂-Fe-C and TiO₂-Fe-E catalysts. These results illustrate that when a threshold value of p/p_0 is reached, the adsorption decreases, indicating that the accessible surface is reduced during subsequent nitrogen adsorption. Such t-plots presenting a downwards deviation are typical of microporous material [30].

The isotherms measured for the 11 uncalcined co-doped catalysts corresponding to a NO₃:Ti(IV) mole ratio equal to 0.2 are similar to the isotherms measured for the catalysts doped with a single cation. As already mentioned above, the sharp increase in the adsorbed volume at very small p/p_0 values as well as the absence of hysteresis p/p_0 between 0.4 and 0.8 suggests that the samples are microporous, and that no mesopores are present in the catalysts [30]. The t-plot method has been applied for each catalyst in order to confirm this observation and it has been observed that all the t-plots present a downwards deviation, typical of microporous material.

The influence of the NO₃:Ti(IV) mole ratio on the textural properties of the catalysts can be highlighted by comparing the results obtained for the two TiO₂-La³⁺ series of catalysts corresponding to the different NO₃:Ti(IV) mole ratio reported in Table 1. In the case of the TiO₂-La³⁺ catalysts, corresponding to a NO₃:Ti(IV) mole ratio equal to 0.1, it can be observed that the S_{BET} values do not appear to be correlated to the dopant content while the values of V_p increase with the dopant content.

In this case, an interesting change can be observed in the isotherms measured for these TiO₂-La³⁺ catalysts, as shown in Fig. 6. Indeed, as the dopant content increases, the

appearance of a hysteresis at p/p_0 between 0.4 and 0.8 suggests that the material contains mesopores. The t-plot method has been applied for $\text{TiO}_2\text{-La-A'}$, $\text{TiO}_2\text{-La-C'}$ and $\text{TiO}_2\text{-La-E'}$ catalysts in order to confirm this observation. Fig. 7 shows that the t-plot corresponding to the $\text{TiO}_2\text{-La-E'}$ catalyst exhibits an upwards deviation, typical of a mesoporous material. In contrast, the $\text{TiO}_2\text{-La-A'}$ and $\text{TiO}_2\text{-La-C'}$ t-plots present a downward deviation typical of microporous materials, even though a small hysteresis appears for the $\text{TiO}_2\text{-La-C'}$ catalyst.

Mesopores also appears in the case of $\text{TiO}_2\text{-La}^{3+}\text{-Fe}^{3+}$ catalysts corresponding to a $\text{NO}_3\text{:Ti(IV)}$ mole ratio equal to 0.1 when increasing the La^{3+} content but it has been observed that an increasing content of Fe^{3+} appears to hinder the appearance of the mesopores.

Fig. 6: Nitrogen adsorption-desorption isotherms for $\text{TiO}_2\text{-La-A'}$, $\text{TiO}_2\text{-La-C'}$ and $\text{TiO}_2\text{-La-E'}$ catalysts.

Fig. 7: t-plot for TiO₂-La-A', TiO₂-La-C' and TiO₂-La-E' catalysts.

The particle size, d_p , can be estimated from the measured S_{BET} values and the theoretical density of the particles ($\rho_{anatase} = 3.89 \times 10^6 \text{ g m}^{-3}$) by assuming spherical, non-porous particles:

$$\frac{d_p}{6} = \frac{1}{\rho_{anatase} S_{BET}} \quad (1)$$

Tables 1 and 2 present the results obtained for the different catalysts. The values are consistent with an apparent particle size of around 7 nm, independent of the dopant nature and content, for uncalcined catalysts.

3.6. UV-Vis diffuse reflectance (DR-UV-VIS)

Fig. 8 presents the evolution of the normalized Kubelka–Munk function $F(R_\infty)$ with wavelength, λ , for the TiO₂-Undoped catalyst compared to the TiO₂-Fe³⁺ (Fig. 8a) and TiO₂-Cr³⁺ (Fig. 8b) catalysts. The transformed Kubelka–Munk function $(F(R_\infty)h\nu)^{1/m}$ plotted as a function of the energy, $h\nu$, enables the direct band gap ($m = 1/2$) and the indirect band gap ($m = 2$) values, obtained at the intersection between the linear fit and the energy axis, to be

estimated. As an example, plots included in Fig. 8a and Fig. 8b show the evolution of the transformed Kubelka–Munk function, $(F(R_{\infty})h\nu)^2$, plotted as a function of $h\nu$ for the $\text{TiO}_2\text{-Fe}^{3+}$ and $\text{TiO}_2\text{-Cr}^{3+}$ catalysts compared to the $\text{TiO}_2\text{-Undoped}$ catalyst. By using this procedure, the values of $E_{g, \text{ direct}}$ and $E_{g, \text{ indirect}}$ can be estimated for each series of catalysts, as reported in Tables 1 and 2.

Different effect on the values of $E_{g, \text{ direct}}$ and $E_{g, \text{ indirect}}$ can be observed according to the dopant nature and content. In the case of $\text{TiO}_2\text{-Fe}^{3+}$ and $\text{TiO}_2\text{-Cr}^{3+}$ catalysts, both values of $E_{g, \text{ direct}}$ and $E_{g, \text{ indirect}}$ decrease when increasing the dopant content, suggesting a possible activation of the catalyst under UV-Visible light. For the $\text{TiO}_2\text{-Fe}^{3+}$ and $\text{TiO}_2\text{-Cr}^{3+}$ catalysts, it is important to note that a second absorbance band appears at longer wavelengths, leading to a second possible energy transition corresponding to a lower value of $E_{g, \text{ indirect}}$. For those catalysts, two values of $E_{g, \text{ indirect},1}$ and $E_{g, \text{ indirect},2}$ are presented in Table 1. In the case of $\text{TiO}_2\text{-La}^{3+}$ and $\text{TiO}_2\text{-Eu}^{3+}$ catalysts, no significant influence of the dopant content on the values of $E_{g, \text{ direct}}$ and $E_{g, \text{ indirect}}$ has been observed. In the case of $\text{TiO}_2\text{-La}^{3+}\text{-Fe}^{3+}$ and $\text{TiO}_2\text{-Eu}^{3+}\text{-Fe}^{3+}$ catalysts the values of $E_{g, \text{ direct}}$ and $E_{g, \text{ indirect}}$ are only influenced by the presence of Fe^{3+} ions in the catalysts.

A comparison between Tables 1 and 2 highlight that the value of the $\text{NO}_3\text{:Ti(IV)}$ mole ratio does not influence significantly the estimated values of $E_{g, \text{ direct}}$ and $E_{g, \text{ indirect}}$.

Fig. 8: Normalized Kubelka–Munk function $F(R_\infty)$ calculated from DR-UV-Vis spectra and transformed via the Kubelka–Munk function $(F(R_\infty)h\nu)^2$ for (a) the $\text{TiO}_2\text{-Fe}^{3+}$ and (b) the $\text{TiO}_2\text{-Cr}^{3+}$ catalysts compared to the $\text{TiO}_2\text{-Undoped}$ catalyst.

3.7. Fe-Doped TiO₂ nanoparticles

Room temperature Fe-57 Mössbauer spectra obtained for Fe doped and Eu-Fe co-doped nanoparticles are shown in Fig. 9 and 10, respectively, and the corresponding Mössbauer spectral parameters are summarized in Table 3. All Mössbauer spectra are dominated by a component with quadrupole splitting, ΔE_Q , ranging from 0.55 to 0.72 mm/s. The lines are broadened, with widths around 0.45 and 0.73 mm/s for the Fe and Eu-Fe samples, respectively. Additionally, the spectra for the Eu-Fe samples with the higher Eu content feature a 10% contribution from a singlet component centered at about 0.37 mm/s. The component I, which exhibits quadrupole splitting, is representative of substitutional Fe³⁺ in anatase TiO₂ nanoparticles, although we note that values obtained for ΔE_Q vary from 0.5 to about 1.2 mm/s in the literature [32, 33]. The second component can only be observed for Eu/Fe mol-ratios above 1 and could only be fitted using a fixed, narrow line width of 0.25 mm/s. The origin of this component remains unclear, but hematite nanoparticles can be ruled out due to the absence of any quadrupole splitting. Considering the occurrence of this component with increasing Eu content, and because Mössbauer spectroscopy is a local probe technique, one might speculate that a ternary Eu-Fe-O phase is formed with a cubic coordination for iron that yields a vanishing quadrupole splitting and thus a singlet component. The Eu₂O₃-Fe₂O₃ system has been investigated earlier by both Fe-57 and Eu-151 Mössbauer spectroscopy [34, 35]. In bulk form, the europium orthoferrite EuFeO₃ and the europium iron garnet Eu₃Fe₅O₁₂ are the most likely phases to form. Both phases exhibit a magnetic hyperfine splitting at ambient temperature [34, 35], even in nanoparticle systems obtained by ball-milling [35] with a crystallite size of 9 nm. For the latter smallest particles, a small fraction of paramagnetic iron is observed but with a rather large quadrupole splitting of ~0.9 mm/s [35]. Clearly the particles herein are much smaller as no magnetic hyperfine splitting is observed. Furthermore, the most likely origin of the small minority singlet is nanocrystalline europium orthoferrite, closely matching the reported isomer shift of 0.32 mm/s [35], because (super)paramagnetic europium iron garnet would exhibit two lines with isomer shifts of 0.13 and 0.35 mm/s [34].

Fig.9: Fe-57Mössbauerspectra ofsingle-doped TiO₂-Fe samples.

Fig. 10: Fe-57 Mössbauer spectra of Eu-Fe co-doped TiO₂ nanoparticles obtained at room temperature. For samples Eu-Fe-3-1 and Eu-Fe-2-1, spectra consist of two components which are represented by the dotted and dashed lines, respectively.

Table 3: Isomer shift, δ , quadrupole splitting, ΔE_Q , and linewidth, Γ , for differently Eu and Fe co-doped nanoparticles. Error bars are given for free fit parameters.

Sample	Component	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	Relative weight
Fe-F	I	0.39(1)	0.54(1)	0.45	1
Fe-E	I	0.37(1)	0.55(1)	0.45	1
Fe-D	I	0.37(1)	0.53(1)	0.45	1
Fe-C	I	0.30(1)	0.57(2)	0.45	1
Eu-Fe-E	I	0.30(2)	0.69(6)	0.74(9)	0.89(3)
	II	0.36(2)	-	0.25	0.11(3)
Eu-Fe-D	I	0.29(2)	0.72(3)	0.73(4)	0.91(2)
	II	0.37(2)	-	0.25	0.09(2)
Eu-Fe-C	I	0.33(2)	0.55(4)	0.72(6)	1.00

3.8. Photocatalytic activity under UV-Visible light

Adsorption tests were performed in the dark for all photocatalysts and the results showed that the measured concentration of pollutant in the solution at the end of the dark tests is not significantly different from the initial concentration. These tests confirmed that the 4-NP concentration of the solution remained constant for 7 h in the absence of illumination. The blank experiments have already established that there is no spontaneous decomposition of the 4-NP after 7 h under illumination in the absence of TiO₂. Hence, according to those results, the degradation of 4-NP measured under illumination is only due to the photocatalytic activity of the xerogels. In order to compare the activity of the different catalysts, the conversion reached after 7 h under illumination was calculated *via*:

$$f_{norm} = 1 - \frac{C}{C_0} \quad (2)$$

where C is the 4-NP concentration measured after 7 h under illumination and C_0 , the initial 4-NP concentration before illumination commenced ($C_0 = 1.0 \times 10^{-4} \text{ kmol m}^{-3}$). The conversion was normalized by using a correction factor calculated for each experiment in order to facilitate comparison between the different catalysts. This correction factor is defined as the ratio between the actual concentrations of catalyst in the solution calculated using the measured weight of catalyst used to prepare the suspension, and the theoretical value equal to 1 kg m^{-3} . The correction factors ranged from 0.96 to 1.07.

The photocatalytic experiments were replicated at least three times for each catalyst in order to facilitate statistical treatments of the measured data. The mean values of the normalized conversion, $\bar{f}_{norm}$, calculated by using the results of the replicated experiments of the photocatalytic degradation measurement in the presence of each catalyst with margins of errors equal to the standard deviation, σ , are presented in Fig. 11 and Fig. 12. It is important to note that, in contrast to the results reported in a previous study [12], the results obtained in the present paper (Fig. 11) suggest that for the Fe³⁺, Cr³⁺ and La³⁺ single-doped TiO₂ catalysts, the normalized conversion of 4-NP reached after 7 h under illumination is significantly influenced by the dopant nature and content. However, in the case of TiO₂-Eu³⁺ catalysts, the values of the standard deviation, σ , calculated from replicated experiments indicate that all the measured $\bar{f}_{norm}$ are in the same statistical population regardless of the Eu³⁺ content and thus, they cannot be discriminated.

Fig. 11: Mean normalized 4-NP conversion ($C_0 = 1.0 \times 10^{-4} \text{ kmol m}^{-3}$) with standard deviation reached after 7 h under illumination for the different single-doped catalysts (1 kg m^{-3}) compared to the TiO_2 -Undoped catalyst.

By analyzing Fig. 11 according to the dopant nature, significant differences can be observed between the series of catalysts. In the case of $\text{TiO}_2\text{-Fe}^{3+}$ catalysts, the presence of Fe^{3+} as dopant initially enhances the photocatalytic activity and then becomes detrimental to the photocatalytic activity when the dopant content increases beyond an optimum value. The presence of an optimal dopant content corresponding to a Fe(III):Ti(IV) mole ratio of 0.76% leading to a maximum conversion of the pollutant is highlighted in Fig. 11. In the case of $\text{TiO}_2\text{-Cr}^{3+}$ catalysts, a detrimental effect on the photocatalytic degradation of 4-NP has been observed. When increasing the Cr^{3+} content, the normalized conversion calculated after 7 h under illumination decreases considerably. In the case of $\text{TiO}_2\text{-La}^{3+}$ catalysts, the introduction of the dopant in the catalyst allows a slight but significant enhancement of the photocatalytic activity, with an optimum dopant content being observed for a La(III):Ti(IV) mole ratio equal to 0.5%.

In order to evaluate the influence of co-doping on the photocatalytic activity of the catalysts, Fig. 12 presents the results obtained for the $\text{TiO}_2\text{-La}^{3+}\text{-Fe}^{3+}$ catalysts corresponding to a constant La^{3+} content and varying Fe^{3+} content, together with the results obtained for the $\text{TiO}_2\text{-Eu}^{3+}\text{-Fe}^{3+}$ catalysts corresponding to a constant Fe^{3+} content and varying Eu^{3+} content. The effect of the $\text{NO}_3\text{:Ti(IV)}$ mole ratio can also be observed.

Fig. 12: Mean normalized 4-NP conversion ($C_0 = 1.0 \times 10^{-4} \text{ kmol m}^{-3}$) with standard deviation reached after 7 h under illumination for the different co-doped catalysts (1 kg m^{-3}) compared to the TiO_2 -Undoped catalyst.

In the case of a $\text{NO}_3:\text{Ti(IV)}$ mole ratio equal to 0.2 (first and second series in Fig. 12), it can be observed that the introduction of Fe^{3+} leads to a significant enhancement of the 4-NP conversion with a maximum conversion obtained in the case of a Fe(III):La(III) mole ratio equal to 0.3. For a $\text{NO}_3:\text{Ti(IV)}$ mole ratio equal to 0.1 (third and fourth series in Fig. 12), the influence of co-doping on the photocatalytic activity of the catalysts is different. Indeed, the introduction of Fe^{3+} induces an enhancement of the conversion but in this case, the optimal Fe^{3+} content is observed when the Fe(III):La(III) mole ratio is equal to 0.6 instead of 0.3. It is important to note that for the TiO_2 -La-D' catalysts and the corresponding co-doped catalysts, the conversion reached is lower than the conversion measured for the TiO_2 -Undoped catalyst. Finally, Fig. 12 shows that in the case of TiO_2 -Eu³⁺-Fe³⁺ catalysts, a significant decrease of the photocatalytic activity is observed, in particular, when the value of the Eu(III):Fe(III) mole ratio are equal to 0.1% or 0.5%.

The effect of the thermal treatment at 500°C is presented in Fig. 13. A significant reduction in the photocatalytic activity can be observed for both co-doped catalysts while the effect of the thermal treatment seems to be less important in the case of La^{3+} and Eu^{3+} single-doped catalysts.

Fig. 13: Mean normalized 4-NP conversion ($C_0 = 1.0 \times 10^{-4} \text{ kmol m}^{-3}$) with standard deviation reached after 7 h under illumination for the different calcined catalysts compared to the TiO_2 -Undoped catalyst.

It has been reported in the literature [36, 37] that the presence of intermediate species associated with the partial degradation of 4-NP can be detected by the presence of peaks corresponding to the intermediates (4-nitrocatechol, 1,2,4-benzenetriol, hydroquinone) in the UV-Vis spectrum measured between 200-500 nm after several hours under illumination. In the present study, the absence of supplementary peaks in the UV-Vis spectra measured between 200-500 nm after 7 h under illumination is consistent with the complete mineralization of the pollutant and hence, we can conclude that the photocatalysts developed here promote complete mineralization of the 4-NP.

4. Discussion

The reproducibility of the synthesis method, as well as the total incorporation of the Fe^{3+} , Cr^{3+} , Eu^{3+} and La^{3+} dopants, has been highlighted, reflecting the wide versatility of the aqueous sol-gel process.

The results of the XRD experiments performed on the uncalcined xerogels corresponding to a $\text{NO}_3:\text{Ti(IV)}$ mole ratio equal to 0.2 established that the anatase phase is obtained at near-ambient temperatures. Tables 1 and 2 highlight that for these uncalcined catalysts, the crystallite sizes, d_c , estimated by the Scherrer equation (Eq. 1) are comparable to the values of d_p estimated from S_{BET} (Eq. 3) suggesting that the xerogels are predominantly composed of nanocrystallites of anatase with essentially no amorphous phase. Nonetheless, it has demonstrated that the dopant content and nature could affect the morphology of the catalysts, in contrast to the results reported in [12].

The effect of the dopant on the morphology of the catalyst and, in particular, the appearance of mesopores for the $\text{TiO}_2\text{-La}^{3+}$ catalysts in the case of a $\text{NO}_3\text{:Ti(IV)}$ mole ratio equal to 0.1, can be explained due to a modification of the electric repulsion potential and hence, the repulsive barrier between the particles in suspension in the media during the peptisation step.

As described by Brinker and Scherer [38], the formation of a gel occurs in two step: (i) the formation of the particle of TiO_2 by hydrolysis and condensation reactions and (ii) the formation of a gel by aggregation of the particles. In the present case, the aqueous sol-gel process leads to stable sols and the final xerogels are obtained by drying of the sols at room temperature by simple evaporation of the water in a laminar-flow hood.

It can be assumed that the aggregation of two particles depends on the total interaction potential between the particles. According to the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [39, 40], the interaction between two particles in a suspension is considered to be the combination of the van der Waals attraction potential and the electric repulsion potential, neglecting short-range solvation forces. The super-position of these interactions leads to a maximum potential energy known as the barrier to aggregation. In order to agglomerate two particles, the barrier to aggregation has to be overcome.

If the barrier to aggregation is low, i.e. the sticking probability is high, the particles adhere to each other after a small number of collisions, and the adhesion is more likely to generate a random, relatively open structure. In contrast, if the barrier to aggregation is high, i.e. the sticking probability is low, many collisions are required in order to aggregate the particles, leading to a better interpenetration of the particles and hence, a more compact structure [41, 42].

A schematic representation of the catalyst composed of anatase nanocrystallites organized in a compact arrangement (pores between the crystallites < 2 nm) but maintaining a high specific surface area, S_{BET} , is proposed in Fig. 14. It illustrates the effect of a modification of the structure and packing of the anatase nanocrystallites due to a modification of the sticking probability between the particles.

Fig. 14: Schematic representation of the effect of the sticking probability on the morphology of catalyst.

The electrostatic repulsion and therefore the barrier to aggregation and sticking probability, is dependent on the concentration and charge number (Z) of the counter-ions involved into the electrical double layer formed at the surface of the charged particles. In contrast, the van der Waals attraction potential is almost independent of the concentration and charge number (Z) of counter-ions. As a consequence, the overall interactions potential is strongly influenced by the concentration and valence state of counter-ions, an increase in concentration and charge number (Z) of counter-ions leading to a reduced barrier to aggregation. When the concentration of counter-ions is high enough, the particles are likely to associate with each other leading to the formation of aggregates, which is known as flocculation [39, 40].

The nature of the charge at the surface of the particle depends among others on the point of zero charge (pzc) which has been measured at pH = 6 for TiO₂ nanoparticles in suspension [43]. The pH of the sols corresponding to the different catalysts ranges between pH = 4 and 5 suggesting that the surface of the particle is positively charged.

By analyzing the results presented in Table 1 and in Fig. 6 and Fig. 7, it is observed that each TiO₂-La³⁺ and TiO₂-La³⁺-Fe³⁺ catalyst corresponding to a NO₃:Ti(IV) mole ratio equal to 0.1 and a La(III):Ti(IV) mole ratio equal or higher than 0.5% contains mesopores. Because La³⁺ is a trivalent cation, an increasing content of La³⁺ can induce significant increase of the ionic strength of the solution, associated with a reduction of the barrier to aggregation and therefore a higher sticking probability leading to a possible flocculation of the particles. As mentioned previously, milky sols are obtained at the end of the peptisation step for those catalysts confirming the presence of agglomerates due to the flocculation of the particles, which promotes the scattering of light. For the catalysts corresponding to a NO₃:Ti(IV) mole ratio equal to 0.2, no mesopores were detected regardless of the dopant content employed in this study. In this case, translucent sols are obtained leading to purely microporous xerogels suggesting that the effect of an increasing content of La³⁺ is too weak to induce the flocculation of the particles leading to the appearance of mesopores.

The colorations observed for the different series of catalysts suggest that the dopants are in the form of hydrated ions or hydroxides, and hence we assume that this is also the case for the series of $\text{TiO}_2\text{-La}^{2+}$ and $\text{TiO}_2\text{-Eu}^{2+}$ catalysts. The absence of additional peaks or distortion of the anatase peaks in the XRD patterns measured for the different series of doped catalysts suggests that the dopants are mostly located near the surface of the TiO_2 crystallites and that no significant quantities of dopant oxide phases are produced in the samples.

The possibility of incorporating the dopant presenting a similar ionic radius to the Ti^{4+} (0.68 Å) in substitutional and /or interstitial positions in the near-surface regions of the crystallites has been discussed previously. During the peptisation step, the amorphous agglomerated titania slurry is transformed into a well-dispersed crystallized nanoparticle sol and limited dissolution/precipitation might occur at the surface of the nanoparticles, promoting the incorporation of dopants with suitable ionic radii. The values of the ionic radii of Fe^{3+} , Cr^{3+} , Eu^{3+} and La^{3+} , respectively equal to 0.64, 0.63, 0.95 and 1.16 Å, suggest that the TiO_2 crystallites can be substitutionally as well as interstitially doped with Fe^{3+} and Cr^{3+} while Eu^{3+} and La^{3+} are most likely to be found as highly dispersed metal oxide “clusters” (with a size less than 2 nm) at the surface of the TiO_2 particles. This suggestion is in agreement with results previously reported in the literature [24, 25].

Concerning the nature of iron-based nanoparticles in Fe single-doped catalysts, the component I observed by Mössbauer spectral analysis (which exhibits quadrupole splitting, Fig. 8) confirms substitutional Fe^{3+} in anatase TiO_2 nanoparticles. For $\text{Fe}^{3+}\text{-Eu}^{3+}$ co-doped catalysts, another small minority singlet component is highlighted in Fig. 10, characteristic of nanocrystalline europium orthoferrite.

Regarding the photocatalytic activity of the Fe^{3+} , Cr^{3+} , Eu^{3+} and La^{3+} single-doped and co-doped catalysts, several features depending on the dopant nature have been observed in this study.

First of all, it is important to emphasize the difference between materials described as “loaded catalysts” (in which highly dispersed species are located in the near-surface region of the TiO_2 crystallites), as opposed to “doped catalysts” (in which the metal ions are incorporated in substitutional positions within the TiO_2 crystal lattice). In the case of loaded catalysts, Di Paola et al. [13] reported that either no enhancement or a decrease in the photocatalytic activity was observed.

On the one hand, dopant such as Fe^{3+} promotes the enhancement of the photocatalytic activity, with an optimal dopant content being observed for Fe(III):Ti(IV) mole ratios equal to 0.76%. Similar behaviour can be observed for the $\text{TiO}_2\text{-La}^{3+}$ catalysts with an optimum activity corresponding to a La(III):Ti(IV) mole ratio equal to 0.5%. In the case of catalysts produced with a lower $\text{NO}_3\text{:Ti(IV)}$ mole ratio (equal to 0.1), the appearance of mesopores is detrimental for the photocatalytic activity, leading to catalysts less active than the TiO_2 -Undoped catalyst. The results also show that in the case of $\text{TiO}_2\text{-La}^{3+}\text{-Fe}^{3+}$ catalysts, the introduction of the Fe^{3+} dopant induces a general enhancement of the photocatalytic activity with an optimum being observed for a La(III):Fe(III) mole ratio equal to 0.3 or 0.6 according to the value of the $\text{NO}_3\text{:Ti(IV)}$ mole ratio (Fig. 12).

It was mentioned that the introduction of the metal ion dopant would lead to an increase in the -OH density at the surface of the catalyst, due to hydrolysis of the dopant species (M^{n+}) during peptisation and associated formation of $[M_x(OH)_y]^{(nx-y)+}$ species [12]. In the case of Fe^{3+} dopant, it is known that the hydroxylated species are particularly stable [44] and hence, this increased density of -OH groups could explain the remarkable enhancement of the photocatalytic activity observed for the Fe^{3+} single-doped catalysts. Moreover, Fe^{3+} species have been reported to be effective dopants due to the batho-chromic shift induced by the substitution of Ti^{4+} by Fe^{3+} atoms. Indeed, Fig. 8a highlights a decrease of the band gap correlated to the dopant content, suggesting that an intra-band gap level enables the absorption of visible light by the catalyst. Tables 1 and 2 also demonstrated that a batho-chromic shift appears systematically when Fe^{3+} dopant is introduced in the co-doped TiO_2 catalysts.

Another important effect of the Fe^{3+} dopant is the possibility of influencing the rate of $e^- - h^+$ recombination by acting as charge trapping site. According to the redox potential of the couple Fe^{2+}/Fe^{3+} , oxido-reduction reactions may occur in the near surface region of the particles [5, 45]. The Fe^{3+} dopant can act as acceptor which can trap photogenerated e^- and reduce the metal ion species into a lower oxidation state. The photogenerated e^- trapped into the reduced ion can then be transferred to the Ti^{4+} due to the close energy level of the Ti^{4+}/Ti^{3+} couple and lead to the production of Ti^{3+} which has been reported to enhance the photodegradation of phenol by acting as a hole trap [46]. At the same time, the reduced Fe^{2+} species can also trap photogenerated h^+ decreasing again the recombination rate of photogenerated $e^- - h^+$ species. All of these reactions lead to a higher production of radicals which enhances the photocatalytic activity. The detrimental effect of a high Fe^{3+} content has been attributed to the appearance of “short-circuiting reactions” which create a cyclic redox process without generating active radicals available for the photocatalytic degradation process [36].

Another argument proposed to explain the existence of an optimum dopant content suggests that only a limited amount of Fe^{3+} can be incorporated in substitutional positions within the TiO_2 , with excess dopant introduced during the peptisation step being simply “loaded” into the near-surface region of the TiO_2 crystallites (with essentially no impact on the photocatalytic activity).

Finally, Fe^{3+} is known to induce a photo-Fenton effect in the presence of the H_2O_2 produced into the reactive system and this reaction is believed to induce the production of more OH radicals facilitating the photodegradation of the pollutant. The photo-Fenton can be described by [47]:

Eq. (1) highlights that by photo-Fenton effect, Fe^{3+} reacts with water and light to produce $OH\bullet$ radicals which can degrade organic pollutants.

In contrast, the results of this study highlighted that Cr^{3+} dopant has a detrimental effect on the photocatalytic activity of the catalyst regardless of the dopant content. The change of

coloration observed after drying of the materials indicate the presence of Cr(VI) species such as $[\text{Cr}_2\text{O}_7]^{2-}$ corresponding to an oxidation state equal to VI while the oxidation state was equal to III before treatment at 100°C. In this case, the redox potential of the photogenerated e^- is too low to reduce the Cr(VI) species to Cr(III) and then $[\text{Cr}_2\text{O}_7]^{2-}$ ions act as irreversible $e^- - h^+$ traps, hence poisoning the catalyst. In the literature, enhancement of the photocatalytic activity of Cr-doped catalyst has been reported exclusively in the case of Cr^{3+} substitutional doping [13, 48].

In the case of $\text{TiO}_2\text{-Eu}^{3+}$ catalysts, no significant effect of the dopant content has been observed suggesting that the small metal oxide “clusters” dispersed at the surface of the TiO_2 particles do not participate in the photocatalytic process. These results are in agreement with an earlier reported study [25].

The difference observed for $\text{TiO}_2\text{-La}^{3+}$ catalysts compared to the $\text{TiO}_2\text{-Eu}^{3+}$ catalysts could be explained by the different ionic radius of La^{3+} and Eu^{3+} , leading to the possibility of forming fewer Ti-O-La bonds due to substitution of Ti^{4+} and La^{3+} atoms at the interface between the TiO_2 particle and the metal oxide nanoclusters [14]. In this case, La^{3+} can act as an electron trap, thus promoting a reduction of the $e^- - h^+$ recombination rate.

The effect of high temperature thermal treatment on the morphology and photocatalytic activity has been studied for different catalysts ($\text{TiO}_2\text{-La-C'}$, $\text{TiO}_2\text{-La-Fe-C'}$, $\text{TiO}_2\text{-Eu-B}$ and $\text{TiO}_2\text{-Eu-Fe-B}$). As expected, the results obtained in the case of calcined catalysts show that the thermal treatment causes a decrease in the photocatalytic activity due to sintering and crystal growth. However, it can be observed that the detrimental effect of the high temperature thermal treatment is much more significant in the case of $\text{TiO}_2\text{-La}^{3+}\text{-Fe}^{3+}$ and $\text{TiO}_2\text{-Eu}^{3+}\text{-Fe}^{3+}$ catalysts compared to the $\text{TiO}_2\text{-La}^{3+}$ and $\text{TiO}_2\text{-Eu}^{3+}$ catalysts. This can be explained by the intrinsic effect of the dopant on the sintering and crystal growth. Indeed, Fe^{3+} doping has been previously found to favour the crystallization, while La^{3+} and Eu^{3+} hindered the sintering and crystal growth [25].

To summarize, the results of the photocatalytic activity measurements of the different single-doped and co-doped catalysts developed in the present study demonstrated that Fe^{3+} and La^{3+} dopants can induce a significant enhancement in the activity of the catalyst for the degradation of the 4-NP after 7 h under illumination, with an optimum dopant content being observed. Many suggestions can be proposed to explain the role of the dopant but the detailed mechanism for the photocatalytic activity of metal ion-doped semiconductor remains a controversial issue.

5. Conclusions

This paper highlights the environmentally-friendly aqueous sol-gel process for producing Fe^{3+} , Cr^{3+} , La^{3+} or Eu^{3+} single-doped TiO_2 photocatalysts as well as $\text{La}^{3+}\text{-Fe}^{3+}$ and $\text{Eu}^{3+}\text{-Fe}^{3+}$ co-doped TiO_2 catalysts without any calcination step.

The physicochemical properties of the catalysts were characterized by using the same suite of complementary techniques described earlier, including ICP-AES, XRD, UV-Vis spectroscopy, nitrogen adsorption-desorption and Mössbauer spectroscopy for iron bearing species. It has been found that the morphology of the catalysts can be tailored by adjusting the value of the $\text{NO}_3\text{:Ti(IV)}$ mole ratio. On the one hand, in the case of $\text{NO}_3\text{:Ti(IV)}$ mole ratio equal to 0.2, the catalysts are purely microporous and composed of nanocrystallites of anatase with a size of 6-7 nm and a specific surface area varying from 181 to 298 $\text{m}^2 \text{g}^{-1}$. On the other hand, in the case of a $\text{NO}_3\text{:Ti(IV)}$ mole ratio equal to 0.1, mesopores appear when La^{3+} dopant corresponding to a La(III):Ti(IV) mole ratio of 0.5% is introduced. This particular modification is suggested to be due to a reduction of the repulsive barrier between the particles due to the addition of large amount of La^{3+} into the reaction system, thus facilitating the agglomeration of the nanocrystallites and leading to a more open structure. Furthermore, Mössbauer spectroscopy provides evidence that iron is still in the Fe^{3+} oxidation state even after the calcination step.

A screening of the photocatalytic activity has been performed in order to assess the performances of the single-doped and co-doped catalysts. Several features depending on the dopant nature were observed. Fe^{3+} and La^{3+} dopants can induce a significant enhancement of the activity of the catalyst with optimum dopant content being respectively observed for Fe(III):Ti(IV) mole ratio equal to 0.76% and La(III):Ti(IV) mole ratio equal to 0.5%. Moreover, Eu^{3+} doping seems to slightly reduce the photocatalytic activity while Cr^{3+} doping poisoned the catalyst. It was also highlighted that a calcination step at 500°C decreases the catalytic activity. So the perspective of a large-scale production of an active photocatalyst without any solvent and without any high temperature treatment can be envisaged, which is a great breakthrough from an industrial point of view.

A range of potential mechanisms are identified to explain the role of the metal ions in the photocatalytic degradation process.

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GRAPHICAL ABSTRACT

The activity of different TiO_2 single-doped and co-doped catalysts has been estimated by the mean normalized 4-NP conversion with standard deviation reached after 7 h under illumination and compared to the TiO_2 -undoped catalyst.