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Reverse micelle strategy for effective substitutional Fe-doping in small-sized CeO₂ nanocrystals: Assessment of adsorption and photodegradation efficiency of ibuprofen under visible light / Tamaro, Olimpia; Paparo, Rosanna; Chianese, Marica; Ritacco, Ida; Caporaso, Lucia; Camellone, Matteo Farnesi; Masenelli, Bruno; Lamirand, Anne D.; Bluet, Jean-Marie; Fontana, Marco; Pinto, Gabriella; Illiano, Anna; Amoresano, Angela; Serio, Martino Di; Russo, Vincenzo; Esposito, Serena. - In: CHEMICAL ENGINEERING JOURNAL. - ISSN 1385-8947. - 479:(2024).

[10.1016/j.cej.2023.147909]

Availability:

This version is available at: 11583/2984584 since: 2023-12-18T10:18:43Z

Publisher:

Elsevier

Published

DOI:10.1016/j.cej.2023.147909

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Journal Pre-proofs

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PII: S1385-8947(23)06641-X
DOI: <https://doi.org/10.1016/j.cej.2023.147909>
Reference: CEJ 147909

To appear in: *Chemical Engineering Journal*

Received Date: 18 August 2023
Revised Date: 22 November 2023
Accepted Date: 4 December 2023

Please cite this article as: O. Tamaro, R. Paparo, M. Chianese, I. Ritacco, L. Caporaso, M.F. Camellone, B. Masenelli, A.D. Lamirand, J-M. Bluet, M. Fontana, G. Pinto, A. Illiano, A. Amoresano, M.D. Serio, V. Russo, S. Esposito, Reverse micelle strategy for effective substitutional Fe-doping in small-sized CeO₂ nanocrystals: Assessment of adsorption and photodegradation efficiency of ibuprofen under visible light, *Chemical Engineering Journal* (2023), doi: <https://doi.org/10.1016/j.cej.2023.147909>

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1 **Reverse micelle strategy for effective substitutional Fe-doping in small-**
2 **sized CeO₂ nanocrystals: assessment of adsorption and**
3 **photodegradation efficiency of ibuprofen under visible light**

4
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27 **Abstract**

28 Reverse micelle nanoreactors were successfully designed to synthesize small-sized ceria nanocrystals
29 (3.5-4.2 nm) with a sizeable amount of substitutional iron. Undoped and doped CeO₂ catalysts with
30 an iron content (0.50-10 mol %) compliant with the nominal value were prepared and tested for the
31 first time for the removal of ibuprofen both in the dark and under UV or visible light irradiation.

32 The effective inclusion and distribution of iron in the ceria lattice were ascertained through in-depth
33 physicochemical characterization. In particular, X-ray diffraction suggested the formation of an F-
34 type crystal structure, ruling out the formation of separate iron-containing crystalline phases. On the
35 other hand, substitutional doping of CeO₂ with Fe atoms favoured the formation of Ce³⁺ defects and
36 vacancy sites (VOs) with a maximum for the sample with 2.5 mol % iron (Fe2.5), as evidenced by
37 X-ray photoelectron spectroscopy (XPS) measurements and Raman spectroscopy. UV-Vis
38 spectroscopy showed that the optical properties were successfully modified by the presence of iron,
39 which causes a gradual decrease in band gap as iron content increases. The experimental evidence
40 was further verified and supported by density functional theory calculations. DFT calculations also
41 revealed that the surface iron and oxygen vacancies are the preferential sites for ibuprofen adsorption.
42 Nevertheless, it was found under dark conditions that adsorption capacity does not monotonically
43 increase with iron content, revealing contrasting roles of surface characteristics. Indeed, catalytic
44 experiments have identified a trade-off between adsorption and photodegradation, identifying Fe2.5
45 as the best-performing catalyst for ibuprofen removal under visible light irradiation. These results
46 were discussed by considering the key properties of the catalysts as well as their different surface
47 charge determined by ζ potential measurements. The best catalyst was tested through reuse
48 experiments that proved its stability over 4 cycles. Finally, an attempt was made to identify the
49 photodegradation by-products, allowing the detection of 1-ethenyl-4-(2-methylpropyl)benzene as the
50 main by-product.

51

52 **Keywords:** Substitutional Fe doped CeO₂, Reverse micelle, Ibuprofen, Photodegradation, DFT.

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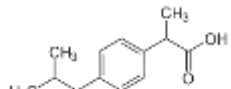
55

56 **1. Introduction**

57 Pharmaceuticals are considered emerging environmental pollutants due to the increase in their
 58 consumption and consequent accumulation in water [1]. Ibuprofen (IBU) (Table 1), is among the
 59 most widespread non-steroidal anti-inflammatory drugs (NSAIDs) in the world, whose presence in
 60 wastewater is a serious concern because it is not biodegradable [2]. The detected concentrations for
 61 ibuprofen in wastewater treatment plants are in the ranges of 55–69 $\mu\text{g}\cdot\text{L}^{-1}$ [3]. Over the last few
 62 years, to address this environmental concern, several chemical, physical and biological methods have
 63 been proposed [4]. Chemical methods include advanced oxidation processes (AOPs), coagulation-
 64 flocculation, electrocoagulation, chemical oxidation, and ion exchange [4]. Among those, AOPs can
 65 degrade recalcitrant pollutants with a rapid reaction rate and high removal efficiency due to the
 66 generation of reactive free radicals [5].

67

68 **Table 1** - Structure and properties of ibuprofen

Compound	IUPAC name	Molecular formula	Molecular weight	Solubility in water	Structure
IBU	2-[4-(2-methyl propyl) phenyl]propanoic acid	$\text{C}_{13}\text{H}_{18}\text{O}_2$	206.28 g/mol	21 mg/L (at 25 °C)	

69

70 The use of semiconductors has broadened AOPs to heterogeneous photocatalysis, a process operating
 71 at room temperature and atmospheric pressure [5–8]. Moreover, the combination, through the design
 72 of an appropriate catalyst, with solar reactors makes this method stand out from others in terms of
 73 environmental friendliness and cost-effectiveness through the use of renewable energy [9–11].
 74 Indeed, nowadays, new photocatalysts active in the visible range are attracting increasing interest
 75 among the scientific community [9].

76 Although some formulations for the catalytic photodegradation of ibuprofen under visible light were
 77 explored, the proposed solutions suffer from the complicated design of the photocatalyst [12–17], and
 78 typically the experiments are conducted in harsh reaction conditions (e.g., powerful lamps, highly
 79 concentrated systems [14,15]). The challenge is therefore to design simple, inexpensive, high-
 80 performance catalysts for optimal degradation of ibuprofen under visible light irradiation.

81 Cerium oxide was selected for its many trade-offs between reactivity, photochemical stability, cost-
 82 effectiveness, and the environmentally friendly nature of CeO_2 nanoparticles (CeO_2 -NPs) [18–21].

83 The photocatalytic activity of cerium oxide can be enhanced, increasing the photo-absorption
 84 capability, by replacing a small fraction of Ce^{4+} with a different cation [22,23]. Among heteroatom
 85 dopants, transition metals are particularly appealing as they can create defect states in the band gap
 86 or introduce energy levels into it. In this regard, iron is considered one of the most attractive
 87 candidates on account of its environmental compatibility, abundance, and low cost [24]. One of the
 88 most intriguing features of using Fe^{3+} as a dopant is the possibility of further promoting the generation
 89 of oxygen vacancies (VOs) and the reversible conversion between the $\text{Ce}^{4+}/\text{Ce}^{3+}$ valence state.
 90 [25,26]. Oxygen vacancies not only extend the absorption edge but are reported to delay the electron–

91 hole recombination rates, thus increasing the separation efficiency of carriers for enhanced
92 photocatalytic performances [27,28].

93 In conclusion, the introduction of Fe trivalent ions can be considered a powerful tool for rational
94 defect engineering. Indeed, the beneficial effect of iron doping is reported by a certain number of
95 papers for the photodegradation of model dye molecules under visible irradiation, recently reviewed
96 [22]. Nevertheless, it must be considered that the influence of metal dopant and VOs on the ceria
97 properties is interrelated to the concentration, distribution or position of Fe and defects in the ceria
98 lattice [29]. In particular, the extent to which these features occur can be strongly impacted by the
99 preparation method [30].

100 In this scenario, it should be noted that many methods reported in the literature suffer from poor
101 reproducibility and control of process parameters, often failing to achieve real doping or, on the other
102 hand, requiring harsh operating conditions [31–36]. The hydrothermal method was exploited by Cai
103 et al. [32] for preparing Fe-doped ceria materials with different doping amounts. They obtained a
104 catalyst with a crystallite size of approximately 100 Å and observed that the low Fe³⁺ doping could
105 effectively improve the concentration of Ce³⁺, enhancing the degradation ability of the model dye
106 Acid Orange 7 (AO7). However, despite the versatility of the hydrothermal approach, it still
107 represents a “black box” method as is impossible to have strict control over the process. Channei et
108 al. [36] used flame pyrolysis to produce photocatalysts based on Fe-doped CeO₂ nanoparticles for the
109 conversion of both formic acid and oxalic acid. This method, such as the aforementioned
110 hydrothermal method, does not easily allow the control and variation of synthesis parameters
111 invalidating the simplicity of the experimental setup [37].

112 In this perspective, it is important to have a method that goes beyond the trial-and-error approach and
113 allows rigorous control of the composition of the catalyst, preserving its homogeneity and promoting
114 improved optical, structural, and morphological properties.

115 Based on the previous considerations, in our work, we bring the reader's attention to a Fe-doped ceria
116 system, so far never adopted for the photodegradation of ibuprofen. A further outcome of this research
117 was the development of a versatile and reliable synthesis protocol, capable of exploiting the
118 recognised advantages and potential of the one-pot reverse micelle approach. From a practical point
119 of view, a significant advantage of the method is its scalability, including synthesis in microfluidic
120 systems, for the production of larger quantities of catalysts [38–44].

121 The homogeneity of the final material is due to atomic-scale mixing, which in turn is ensured by the
122 presence of a small aqueous core, where the reaction takes place. This mixing allows to easily promote
123 the presence of the dopant in the oxide lattice. The size and shape of these small water domains can
124 be controlled by varying the ratio between the liquid phases (water and oil) and selecting the right
125 surfactant in terms of both type (non-ionic, anionic, cationic and amphoteric) and amount. As a result,
126 not only the intimate contact of the metal precursor is well confined, but also the relative nucleation
127 on growth steps can be easily monitored [45].

128 A pure ceria and iron-doped ceria with metal contents of 0.5, 2.5, 5 and 10 mol % Fe were prepared
129 channelling the reactions that usually take place in aqueous media into the small domains of the
130 reverse micelles.

131 To assess the physicochemical properties and to understand the structure/composition-activity
132 relationship of Fe-doped CeO₂ in the photodegradation of ibuprofen, an in-depth characterisation was
133 conducted. In detail, the prepared catalysts were characterised using various analytical techniques
134 such as inductively coupled plasma mass spectrometry (ICP-MS), Thermogravimetric analysis
135 (TGA), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Field

136 emission scanning electron microscopy (FESEM), Diffuse reflectance spectroscopy (DR/UV-Vis),
137 Raman spectroscopy, N₂ adsorption/desorption at -196 °C, X-ray photoelectron spectroscopy (XPS)
138 and ζ-potential measurements.

139 Density Functional Theory (DFT) calculations were performed in order to investigate the stability
140 and the effects on the electronic and structural properties of the CeO₂(111) in the presence of
141 substitutional and interstitial Fe atoms. The calculations suggest that, in a wide range of temperatures
142 and pressure, the thermodynamically most stable structures are the ones where Fe atoms substitute
143 Ce sites in the presence or absence of oxygen vacancies in agreement with the experimental
144 observations. Additional calculations were performed to investigate the interaction between undoped
145 and Fe-doped ceria surfaces with ibuprofen in order to identify preferential sites for adsorption.

146 The catalysts were tested both in the dark and under either UV or visible irradiation, to compare the
147 performance of each synthesized material. A preliminary kinetic model was implemented to measure
148 the activity of each catalyst in terms of both ibuprofen adsorption and related photodegradation. Reuse
149 experiments were conducted to test the stability of the most active material, further assessed by post-
150 reaction characterizations. Finally, an attempt was made to determine the photodegradation products
151 via specific analytical methods (i.e., GC and LC-MS).

152

153 2. Materials and methods

154 Cyclohexane (ACS reagent ≥ 99.5%), cerium nitrate hexahydrate, iron chloride (reagent grade 97%),
155 ammonia (ACS reagent 28-30%), 1-butanol (ACS reagent ≥ 99.4%), polyoxyethylene (10) cetyl ether
156 (Brij C10) and ethanol (puriss ≥ 99.8%) were purchased by Sigma-Aldrich and used without further
157 modification. Bi-distilled water has been used for the preparation of salt solution. Ibuprofen solutions
158 were prepared using 4-isobutyl- α -methylphenylacetic acid, 99% (manufactured by Alfa Aesar).

159

160 2.1 Precipitation by reverse micelles

161 In a typical synthesis, adapted from the literature [46,47], the oil/surfactant phase is prepared by
162 dissolving 8.2 g of surfactant (Brij C10) in 100 mL of cyclohexane under stirring at room temperature.
163 An aqueous solution is prepared by dissolving the proper amount of cerium and iron precursors in
164 distillate water to achieve a final concentration of 0.5M. The volume of the aqueous precursor solution
165 has been selected to obtain a w_0 value of 25 (w_0 is defined as the water-surfactant molar ratio). The
166 aqueous solution is slowly added dropwise to the oil phase to obtain appropriate water-in-oil (w/o)
167 micelles. To preserve the optical transparency of the emulsion, avoiding the formation of flocculates,
168 4 mL of co-surfactant (1-butanol) are also added. The optimised protocol involves alternating the
169 additions of water and the co-surfactant. Finally, 5.4 mL of precipitating agent, ammonia solution,
170 are slowly dripped. The mixture is stirred for 1.5h at room temperature. The solid phase is then
171 collected by centrifugation, washed twice with ethanol and dried under a hood for 2 days. The dried
172 powder has been manually ground before being calcinated at 120 °C for 6 h. The amounts of cerium
173 and iron were calculated to obtain a nominal composition expressed as a molar % of iron equal to 0
174 mol % (CeO₂), 0.5 mol % (Fe0.5), 2.5 mol % (Fe2.5), 5 mol% (Fe5) and 10 mol % (Fe10). Samples
175 Fe2.5 after its use as a catalyst for the ibuprofen degradation under visible light was labelled
176 Fe2.5_post reaction.

177

178 2.2 Structural, morphological and surface characterization

179 Thermogravimetric analysis was performed on Mettler-Toledo TGA/SDTA 851e instrument. The
180 curves were recorded in air increasing the temperature from 25 to 800 °C at the rate of 10 °C/min.

181 Inductively coupled plasma mass spectrometry (ICP-MS) analysis (ICAPQ Thermo Scientific) was
182 applied to determine the effective composition of the prepared catalysts, expressed as Fe/Ce molar
183 ratio. Before analysis, samples are subjected to an extraction process with a hot nitric acid solution to
184 ensure complete dissolution of the interest elements. The subsequent dilutions method is used to
185 achieve the concentration range used for calibration curve preparation.

186 X-ray powder diffraction (XRPD) was performed on a Philips X'Pert diffractometer equipped with a
187 Cu K α radiation (2θ range = 5° - 90°; step = 0.02° 2θ ; time per step = 1 s). Lattice parameters and
188 cell volumes were determined by UnitCell Software, while the crystallite size (L) has been calculated
189 by Scherrer formula: $L = \frac{k\lambda}{\beta\cos\theta}$, k is a constant equal to 0.90, λ is the X-ray wavelength equal to
190 0.154 nm, β is the full width at half maximum, and θ is the half diffraction angle.

191 The optical properties of the powders were recorded on a UV-Vis Varian Cary 5000
192 spectrophotometer equipped with a DR integration sphere in the 200–600 nm range. The indirect
193 band gap values are obtained by applying the Tauc plot method referring to the formula
194 $(F(R)h\nu)^{1/2} = f(h\nu)$.

195 The vibrational properties of the samples have been analysed with Raman spectroscopy. Spectra were
196 collected and recorded at room temperature with a LabRAM HR spectrometer (Jobin Yvon-Horiba),
197 using a X50 confocal microscope and an excitation wavelength of 532 nm. The excitation power was
198 kept low to ensure no photodegradation of the samples. The spectra were dispersed with 1800 gr/mm
199 grating, leading to a 1 cm⁻¹ accuracy.

200 Transmission Electron Microscopy characterization was carried out with a Thalos F200X instrument
201 (ThermoFisher) and Energy Dispersive X-ray spectroscopy (EDX) spectra were acquired with four
202 Silicon drift detectors (SDD). The catalysts as dry powders were dispersed in isopropyl alcohol and
203 subsequently drop-casted onto Cu holey carbon grids. Before insertion in the TEM column, the
204 samples were plasma-cleaned in Ar atmosphere. Thermo Scientific Velox software was used for the
205 analysis of TEM and EDX data. The crystallographic model for cubic CeO₂ (Fm-3m space group) is
206 provided in the Crystallography Open Database (COD ID: 4343161). To complete the morphological
207 characterization a field emission scanning electron microscopy (FE-SEM) was used (ZEISS
208 MERLIN instrument (Oberkochen, Germany)).

209 Textural properties have been evaluated through N₂ physisorption and desorption at 77K
210 (Quantachrome Autosorb1 Instruments.). Before the measurement, the sample was outgassed under
211 a high vacuum at 120°C for 3 hours to remove pollutants previously adsorbed. From the isotherm
212 obtained by nitrogen adsorption, the specific surface area (SSA) of the samples was calculated
213 according to the BET (Brunauer–Emmet–Teller), total pore volume, V_p, was determined from the
214 amount of adsorbed N₂ at p/p°=0.98. BJH pore size distribution was determined by the desorption
215 branch of isotherms [48,49].

216 X-ray photoelectron spectroscopy (XPS) measurements were carried out in a Prevac spectrometer
217 using a focused monochromatic Al K α X-ray source (1486.6 eV) with a pass energy of 40 meV for
218 survey scans and 20 meV for detailed scans. Despite our efforts, sample charging occurred and was
219 only partially compensated by an electron flood source. Binding energies were then shifted from one
220 core level to another. To analyse the spectra, the O1s signal was shifted to reach O α at 529 eV, while

221 the Ce3d signal referred to as v''' was set at 898.4 eV. Some peak broadening may have resulted
 222 from the residual charge. All the peaks were fitted with a Voigt shape function.

223 ζ -potential curves were obtained by measuring the electrophoretic mobility as a function of pH at
 224 30°C with a Litesizer (Anton Paar Instruments, Worcestershire, UK). The samples were prepared
 225 with a starting concentration of 1 mg/50mL, and subsequently, 0.1 M NaOH or 0.1 M HCl were added
 226 to varying the pH. The ζ -potential measurements were carried out in an Omega cuvette (Anton Paar)
 227 accessory. The measurements were performed in triplicate.

228 FT-IR 4700LE (JASCO, Tokyo, Japan) using the ATR (attenuated total reflectance) was used to
 229 obtain Fourier transform infrared (FTIR) spectra, the spectrum was obtained at a resolution of 2 cm⁻¹
 230 over the range of 400-4000 cm⁻¹. Firstly, the sample of pristine photocatalyst Fe2.5 was mixed with
 231 potassium anhydrous bromide (KBr) (m/m, 1:2000), and the mixture was pressed to obtain a pellet.
 232 KBr was used also as reference material. To identify the interaction between IBU and Fe2.5 catalyst,
 233 the pellet of Fe2.5 was covered with a drop of saturated IBU solution and dried in an oven at 60°C
 234 for one hour before the analysis.

235

236 2.3 Computational Details

237 Density Functional Theory (DFT) calculations were performed within Periodic Boundary Conditions
 238 (PBC) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional based on the
 239 generalized gradient approximation (GGA) [50] and ultrasoft pseudopotentials [51]. The spin
 240 polarized Kohn-Sham equations were solved in the planewave pseudopotential framework, with the
 241 wavefunction basis set and the Fourier representation of the charge density being limited by kinetic
 242 cutoffs of 60 and 500 Ry, respectively. The Quantum Espresso code [52] was employed for all
 243 calculations. It is well established that a reliable description of both stoichiometric and reduced ceria-
 244 based materials can be achieved by adding a Hubbard U term to the GGA energy functional acting
 245 on the f states of the Ce ions. Therefore, all the calculations reported in this work were performed at
 246 the DFT+U level, as implemented by Cococcioni and de Gironcoli [53], employing a U value of 4.5
 247 eV. This is consistent with previous literature reporting values between 4.5 and 5 eV [54–65]. In all
 248 calculations the Brillouin zone integration was performed on the Γ point only.

249 All the calculations were performed on the (111) termination of CeO₂ (Fig. SI.1), being the most
 250 stable one and the most present in the experiment (see Fig. 1a). We are aware that this represent a
 251 simplification of the system prepared from experiments but from a computational point of view is not
 252 possible to capture the complexity of the real system. The Ibuprofen (IBU) molecule is anionic in
 253 experimental pH-neutral conditions [66], therefore it was simulated in its deprotonated form when
 254 adsorbed on the CeO₂(111) surface. The proton released by the molecule is transferred to O3c (tri-
 255 coordinated O) atoms of the surface similarly to previous theoretical studies [67–70].

256 The CeO₂ (111) surface was modelled using a (5x4) slab supercell with three O-Ce-O trilayers (180
 257 atoms) and separated by more than 20 Å of vacuum in the direction perpendicular to the surface.
 258 During the optimizations, the bottom tri-layer of the slab was fixed to simulate the equilibrium bulk-
 259 like position, while the upper two tri-layers and the organic ligand were fully relaxed. The O-defective
 260 systems were modeled by removing O3c and O4c atoms from the surface and subsurface layers of
 261 the CeO₂ (111) slab (VO_x). The formation energies of the oxygen vacancies were computed as
 262 $E_{FORM(VO_x)} = E_{VO_x} - E_{CeO_2} + \frac{1}{2}E_{O_2}$, where E_{CeO_2} is the energy of the stoichiometric surface, while
 263 E_{VO_x} and E_{O_2} are the energies of the surface with oxygen vacancies and of the gas phase O₂ molecule,
 264 respectively.

265 The adsorption energy of IBU was computed using the formula $E_{ads} = E_{CeO_2/IBU} - (E_{CeO_2} +$
 266 $E_{H-IBU})$, where $E_{CeO_2/IBU}$ is the energy of the combined system (namely the surface plus the anionic
 267 IBU), E_{CeO_2} is the energy of the stoichiometric and/or O-defective surface (E_{VOx}) alone, and E_{H-IBU}
 268 is the energy of the neutral IBU in gas phase.

269 The substitutional and interstitial Fe-doping effects were evaluated by replacing and adding Ce atoms
 270 in all considered systems.

271 In order to analyze the thermodynamic stability of different structures in the absence and in the
 272 presence of i) Fe dopant and ii) oxygen vacancies as a function of temperature and pressure, the
 273 formalism of approximate *ab initio* thermodynamics was employed [71–74]. According to this
 274 formalism, the Gibbs energies of the formation of the different ceria systems depend on the
 275 temperature and pressure through the following expression (Eq.1):

$$276 \Delta G_{ads}(T, p) = \frac{1}{A} \{ E_{tot} - E_{CeO_2} + N_0^V \mu_0(T, p) + N_{Ce}^V [E_{CeO_2}^{bulk} - 2\mu_0(T, p)] - \mu_{Fe} \} \quad (1)$$

277 where A is the surface area, E_{tot} and E_{CeO_2} are the total energies of the considered ceria system and
 278 stoichiometric ceria surface, respectively. The quantities N_O and N_{Ce} represent the number of O and
 279 Ce vacancies present in the structure under consideration, whereas $E_{CeO_2}^{bulk}$ is the energy of a formula
 280 unit of the CeO_2 bulk phase. Finally, μ_{Fe} and μ_O are the oxygen and iron chemical potentials. The
 281 chemical potential of Fe, μ_{Fe} , is set to be the total energy per atom of the bulk Fe crystal, whereas the
 282 upper bound of the chemical potential of O_2 , $\mu_O(T, p)$, is given by the total energy of molecular
 283 oxygen, $\frac{1}{2} E_{O_2}$. This upper bound is taken as the zero of our energy scale by using $\Delta\mu_O(T, p) = \mu_O - \frac{1}{2}$
 284 E_{O_2} . In addition, assuming that volume and entropy contributions are negligible in $\Delta G_{ads}(T, p)$ [73],
 285 the Gibbs energies are approximated by the total energies of our DFT calculations.

286 Electronic properties were investigated only for the most stable systems. In addition, to determine the
 287 approximate oxidation states of anions and cations the charge analysis was performed following the
 288 Bader's theory since the charge enclosed within the Bader volume can be considered a good
 289 approximation of the total electronic charge of an atom [75–77].

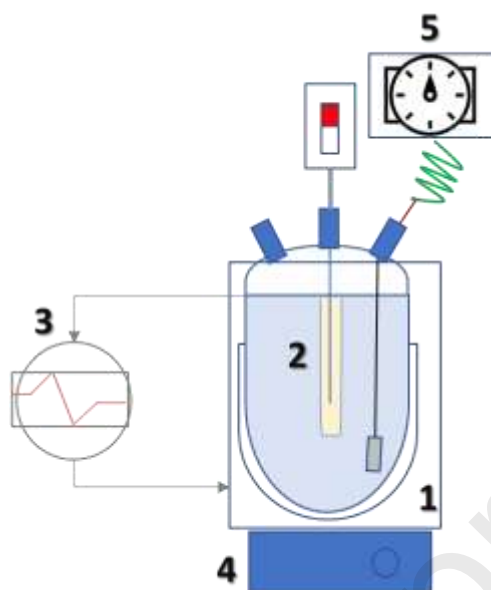
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291 2.4 Catalytic and kinetic tests

292 The photodegradation experiments were conducted in a 1.5 L jacketed glass vessel, closed with a
 293 three-neck lid, as reported in Scheme 1. The reactions were carried out using a co-axial lamp,
 294 connected to the reactor through the central neck of the lid. In particular, two different lamps were
 295 used: a lamp irradiating in the visible region (Sylvania T5, with a power of 4W and a colour
 296 temperature of 6500 K, solar emission spectrum, potential difference 220V, and geometry 14 cm x
 297 1.5 cm), or a lamp irradiating in the UV region (Toshiba FL4BLB, with a power of 4W and emission
 298 at a wavelength of 365 nm, potential difference 220 V, and geometry 15 cm x 1.5 cm). The irradiance

299 of the lamp in the experimental apparatus was estimated to be 510 W/m². One neck of the lid was left
 300 free for collecting samples during the reaction, while the last neck is used for measuring the solution
 301 temperature through a dedicated thermocouple. The reaction temperature was controlled using an
 302 ultra-thermostat while the dispersion agitation was ensured by magnetic stirring. The airflow rate was
 303 set through an electronic gas flowmeter regulator (supplied by Bronkhorst). Air dispersion was
 304 enhanced by connecting the outlet of the gas flowmeter regulator to a sintered filter of 50 mesh,

305 immersed in the liquid-solid dispersion. This technical solution allowed it to reach a high gas-liquid
 306 surface area, minimizing eventual gas-liquid mass transfer limitations.



307
 308

309 **Scheme 1:** Reaction system sketch. 1 Batch reactor, 2 lamps, 3 ultra-thermostat, 4 stirring plates, 5
 310 digital flowmeter regulator.

311

312 As ibuprofen is characterized by relatively low solubility in water (21 mg/L, 25 °C) [78], the solutions
 313 (with an initial concentration, $C_{IBU,0}$, of 12.4 mg/L) have been prepared and kept in stirring overnight
 314 at room temperature and covered with aluminum foil to protect the solution from the light. After the
 315 total dissolution of ibuprofen, the solution is transferred into the reactor, stirred at 750 rpm and
 316 warmed up at 30°C. At this point, the catalyst ($\rho_B=0.07\text{g/L}$) was loaded into the reactor. It is important
 317 to underline that the operation conditions were chosen from preliminary tests to measure the catalytic
 318 activity of the catalysts synthesized in this work.

319 Three different types of kinetic experiments were conducted: (i) adsorption; (ii) under UV irradiation;
 320 (iii) under visible irradiation. In the first case, the system was covered with aluminum foils to prevent
 321 any contact with the solution with the solar light. In the other two cases, a specific lamp was adopted
 322 as previously stated. Also in the latter cases, the system was covered with aluminum foil. Airflow
 323 was adjusted using the digital flow meter and was set at a fixed flow (50mL/min), allowing it to reach
 324 full saturation of oxygen in the water. Of course, no air was fed during the adsorption experiments.
 325 The reaction was then started by switching on the lamp and prosecuting until a maximum time of 5h.

326 Before any subsequent operation, a first sample was collected to check the initial ibuprofen
 327 concentration ($C_{IBU,0}$); subsequently, samples were collected every 30 minutes for the first 2 hours of
 328 reaction, and every hour for the remaining three hours (0, 30, 60, 90, 120, 180, 240 and 300 minutes).
 329 Each sample was then centrifuged at 3300 rpm for 30 minutes, and the resulting liquid sample was
 330 analyzed by UV-VIS spectroscopy (UV-Vis Jasco V-550), see Supplementary Information for details
 331 (Fig. SI.2 and Equation SI-1, i.e., the calibration curve).

332

333 2.4.1 Regeneration experiments

334 The stability of the most active catalyst was tested via reuse experiments, adopting the following
335 reaction conditions: $T=30^{\circ}\text{C}$, $C_{\text{IBU},0}=12.4\text{mg/L}$, $\rho_{\text{B}}=0.07\text{ g/L}$, visible light, Fe_{2.5} catalyst. In
336 particular, the catalyst was recovered after each photodegradation test, by filtering it on a Buchner
337 funnel. Before reusing it, the catalyst was washed several times on the funnel itself using water, and
338 then was recovered by filtration and oven-dried for 12 h at 60°C . The procedure was repeated for
339 four cycles [79].

341 2.4.2 Photodegradation products identification

342 A dedicated kinetic experiment was performed to identify the reaction products. The experiment was
343 performed using the Fe_{2.5} catalyst under visible irradiation, adopting an initial concentration of
344 ibuprofen of 12.4 mg/L , a catalyst loading of 0.07 g/L , a stirring rate of 750 rpm , and a temperature
345 of 30°C .

346 LC-MS analysis was performed by an Agilent HPLC system (1260 Series) coupled to an Agilent
347 6230 TOF mass spectrometer apparatus. The HPLC separation was carried out on a reverse-phase
348 C18 column (Poroshell 120 EC-C18 3x50 mm 2.7 μm from Agilent Life Sciences) by using water
349 and acetonitrile as mobile phases A and B, respectively, both acidified with 0.1% formic acid. A
350 linear gradient was employed by increasing mobile phase B from 50% to 95% over 9 min at a flow
351 rate of 0.3 mL min^{-1} . The injection volume of each sample was $20\text{ }\mu\text{L}$ and the MS source was an
352 electrospray ionization (ESI) interface in the positive ion mode with a capillary voltage of 3000 V ,
353 gas temperature at 325°C , dry gas (N_2) flow at 5 L min^{-1} and the nebulizer pressure at 35 psi , the
354 fragment at 50 V . The MS spectra were acquired in a mass range of $50\text{--}1000\text{ m/z}$ with a rate of
355 1 spectrum/s, abundance threshold 200 (0.015 relative thresholds).

356 GC-MS analyses were performed on a 5390 MSD quadrupole mass spectrometer (Agilent
357 Technologies) equipped with a gas chromatograph by using a Polysiloxane DB-5 column ((5%-
358 Phenyl)-methylpolysiloxane, Agilent Technologies) ($30\text{m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) from Phenomenex.
359 The injection temperature was 250°C , the oven temperature was increased and held at 50°C for three
360 minutes and then increased to 150°C at 10°C/min , increasing to 230°C at 14°C/min and finally to
361 280°C at 15°C/min held for 7 min. Electron Ionization mass spectra were recorded by continuous
362 quadrupole scanning at 70 eV ionization energy, in the mass range of $\text{m/z } 40\text{--}550$ analysis. Each
363 sample was measured in triplicate.

364

365

366 3. Results and discussion

367

368 3.1 About the adopted reverse micelle approach

369 Although the co-precipitation-based synthesis method is extensively used, with a very simple set-up,
370 it suffers from poor control over particle size and homogeneity in mixed oxide systems [80].

371 In this work, the aforementioned drawbacks were overcome by channelling the reactions that
372 normally take place in aqueous media into the small domains of reverse micelles. Specifically, an
373 aqueous solution containing the iron and cerium precursor was added to a solution of the non-ionic

374 surfactant, Brij C10, in cyclohexane, generating a water-oil microemulsion. The cage-like
375 environment provided by the microemulsion with the simultaneous presence of the cerium and iron
376 precursors, enabled excellent control of the final stoichiometry, resulting in homogeneity and mixing
377 on an atomic scale, ultimately favouring the effective inclusion of iron heteroatoms in large amounts,
378 as discussed hereafter [80–84].

379 The synthesis parameters, in particular the type and nature of the surfactant and the water/surfactant
380 ratio, were optimized after careful variation. The value w , defined as the water-surfactant molar ratio
381 ($[\text{H}_2\text{O}/\text{BrijC10}]$), is considered a key parameter for tuning the size of the spherical droplet, affecting
382 the dynamics of water and defining the spatial confinement of the reaction [85,86]. The occurrence
383 of chemical reactions was clearly visible through the colour change of the macrosystem, which moved
384 from a colourless/pale yellow to purple-dense, turning yellow after the fixed reaction time (estimated
385 at one and a half hours). The formation of the purple slurry was attributed to the generation of
386 insoluble Ce^{3+} species that after the complete oxidation turned to yellow Ce^{4+} species [46,87]. The
387 obtained material was recovered by centrifugation, washed to purify from the oil/surfactant, and left
388 catalysts to dry under the hood. Then, the dried powders were heat treated at 120 °C for 6h. The
389 absence of significant quantities of organic residues, confirming the effectiveness of the protocol
390 without the need to use high calcination temperatures, was revealed by the thermogravimetric analysis
391 (Fig. SI.3). The thermal behaviour of the material was explained by identifying three regions in the
392 thermogravimetric curve: (i) from room temperature to 120 °C where the weight loss is due to
393 physisorbed water, (ii) 200-350 °C related to the removal of chemisorbed water occurs, (iii) 400-800
394 °C characteristic of combustion of organic compounds [88–90]. The synthesis procedure was
395 designed to ensure the highest reproducibility. The effective presence of iron species into the ceria
396 phase was highlighted by the different colour of the powders, changing from light yellow for pure
397 ceria to a reddish-yellow with increasing in the Fe contents (Fig. SI.4).

398 The results of the quantitative analysis performed by ICP-MS are shown in Table 2. The Fe/Ce ratio
399 is in excellent agreement with the nominal value, showing that the adopted synthesis protocol
400 effectively preserves stoichiometry and avoids material losses during the production steps.

401

402 3.2 Structural, textural and surface properties

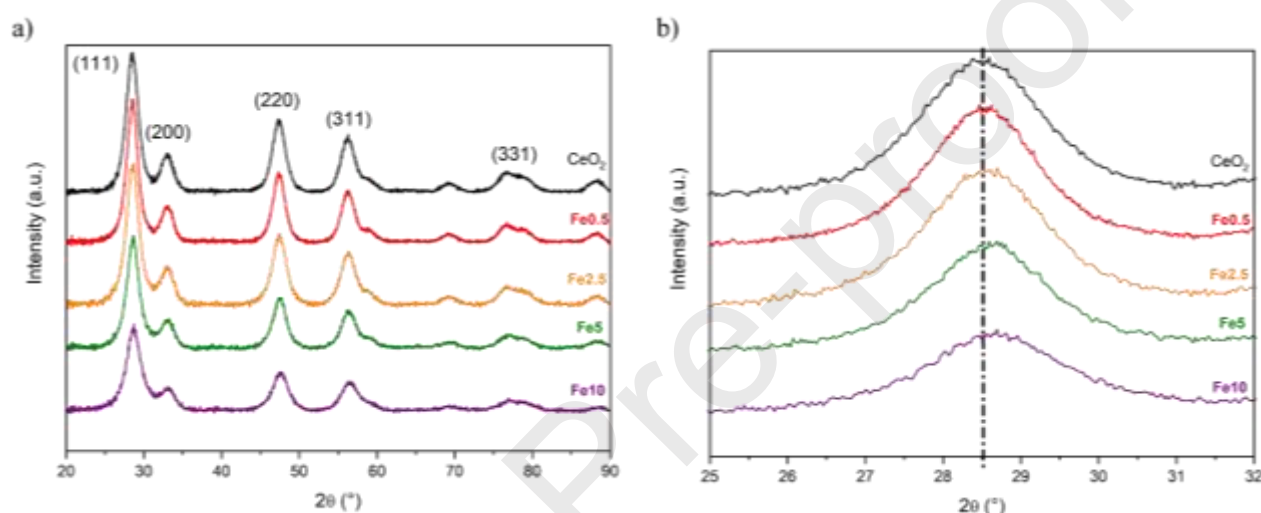
403 Cerium oxide occurs in the fluorite phase where the cerium atoms are organised in a face-
404 centered cubic lattice structure with 8-fold coordination, while the oxygens are present as OCe_4 units
405 [91]. Defect chemistry and the numerous studies conducted on doped and undoped nanometric CeO_2
406 crystal structure have unequivocally stated that its reactivity and performance of heterogeneous
407 catalysis are surprisingly modulable by engineering the defects and surface structure using a flexible
408 and reliable synthesis procedure [92,93].

409 XRD diffraction patterns of ceria and Fe-containing ceria samples are reported in Fig. 1a. The
410 pristine ceria shows an XRD profile corresponding to a cubic fluorite structure (JCPDS files 34-
411 0394), where the peak at 28.5°, 33.3°, 47.1° and 56.1° can be associated with the planes 111, 200,
412 220, and 311, respectively [46]. Although the diffraction patterns of Fe-containing samples reveal
413 that the F-type crystalline structure is retained, the diffraction lines show a progressive shift towards
414 higher 2-teta values, Fig. 1b [46]. As reported by many authors, an isomorphic substitution of Ce^{4+}
415 ions (ionic radius 0.97 Å, coordination number CN=8) by smaller Fe^{3+} ions (ionic radius 0.78Å,
416 CN=8) can account for the lattice shrinkage, appearing as a displacement of the diffraction patterns
417 towards higher angles [25,93]. The observed lattice constraint follows Vegard's law [94] as suggested
418 by the lattice parameters reported in Table 2 and further evidenced by Fig. SI.5. Substitutional doping
419 with the formation of oxygen vacancies, one oxygen vacancy paired with two M^{3+} for charge

420 neutrality, is a dominant mechanism for ceria doped with aliovalent cations [93,95]. Nevertheless,
 421 the small size of Fe^{3+} also allows for a dopant interstitial compensation mechanism where three Fe^{3+}
 422 in substitution sites are coupled to one in interstitial sites. This last mechanism leads to a decrease in
 423 oxygen vacancy concentration. The further increase in iron content may subsequently promote
 424 epitaxial growth on the CeO_2 surface [25,96]. In this scenario, the adopted synthesis method was
 425 decisive in promoting substitutional doping, limiting the formation of crystalline phases attributable
 426 to iron oxides. The type of doping was also supported by DFT calculation (*vide infra*).

427 Moreover, the control exerted by the aqueous core during synthesis is successfully reflected in the
 428 formation of small-sized crystallites (Table 2), compared to the more conventional methods [96–98]

429



430

431

432 **Fig. 1:** a) XRD patterns of the synthesized samples in 2theta range 20°-90° and b) enlarged view of
 433 (111) diffraction peak.

434

435 **Table 2:** Summary of analytical data: chemical composition calculated from ICP-MS elemental
 436 analysis and structural parameters obtained from the cell refinement of the XRD patterns.

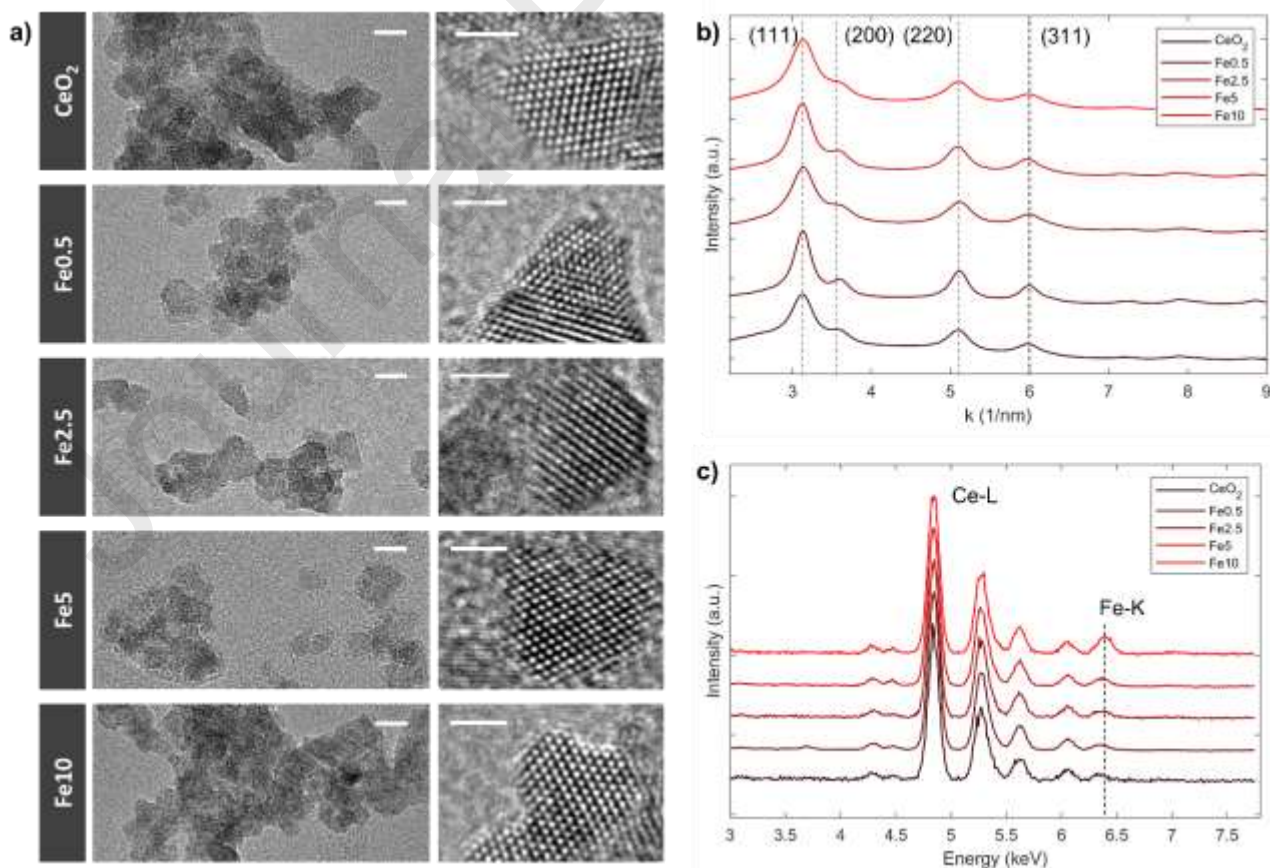
Sample	Nominal ratio Fe/Ce (molar %)	Actual ratio		Lattice Parameter (Å) ^a	Cell Volume (Å ³)	Crystallite size, L (Å) ^b
		Fe/Ce ICP-MS (molar %)				
CeO_2	-	-		$5.4269 \pm 3 \cdot 10^{-4}$	$159.83 \pm 2 \cdot 10^{-2}$	42

Fe0.5	0.5	0.66	$5.4259 \pm 3 * 10^{-4}$	$159.74 \pm 2 * 10^{-2}$	44
Fe2.5	2.58	2.87	$5.4234 \pm 3 * 10^{-4}$	$159.52 \pm 2 * 10^{-2}$	40
Fe5	5.31	4.3	$5.4162 \pm 3 * 10^{-4}$	$158.89 \pm 2 * 10^{-2}$	40
Fe10	11.2	11.1	$5.4030 \pm 3 * 10^{-4}$	$157.72 \pm 2 * 10^{-2}$	34

437 ^a for fluorite phase; ^b Calculated using Scherrer equation due to (1 1 1) plane

438

439 Further insight into the morphology and structure of the iron-doped ceria catalysts is provided by
 440 Transmission and Scanning Electron Microscopy (Fig. 2 and Fig.SI.6, respectively). Based on TEM
 441 images (Fig. 2a), the catalyst powders are constituted of aggregates of approximately spherical
 442 nanoparticles. Inspection of high-resolution images reveals that the nanoparticles are single
 443 crystalline, with a crystalline structure corresponding to cubic CeO₂ (Fm-3m space group). It is worth
 444 pointing out that the characteristic size of the nanoparticles is in the order of 5 nm or lower, in
 445 accordance with the crystallite size estimation based on the application of the Scherrer formula on
 446 XRD data.



447

448 **Fig. 2:** a) TEM high-resolution images of the different Fe-doped CeO₂ catalysts (scalebar: left
 449 column 5 nm, right column 2 nm). Rotationally-averaged selected-area electron diffraction patterns
 450 are provided in b). Representative EDX spectra are shown in c).

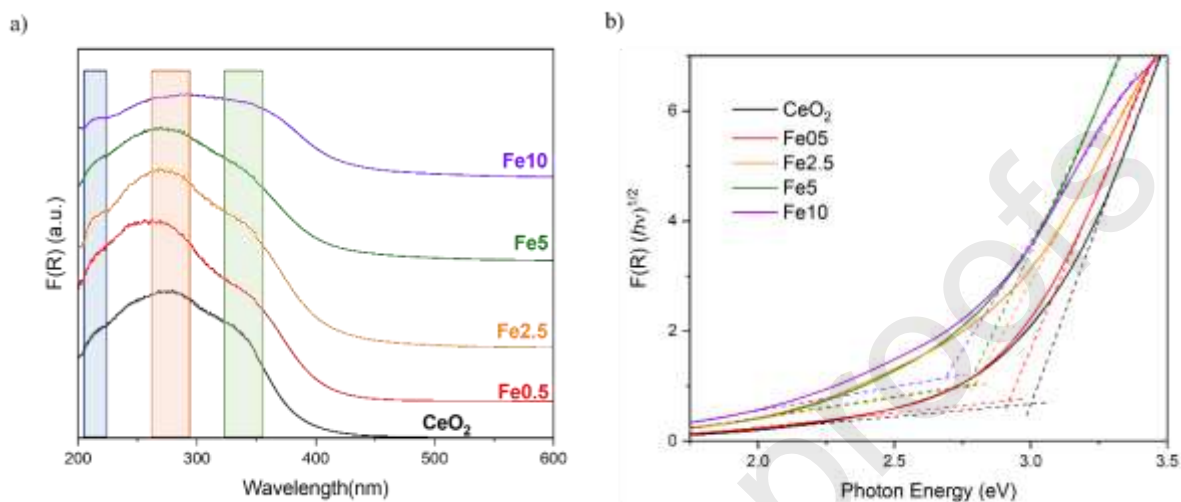
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452 Moreover, from high-resolution images, there is no evidence of secondary iron-containing crystalline
 453 phases. This is confirmed by rotationally-averaged selected area electron diffraction (SAED) patterns,
 454 such as the ones provided in Fig. 2b. For each Fe-containing catalyst sample, the diffraction patterns
 455 only show peaks corresponding to the (111), (200), (220), and (311) family of crystallographic planes
 456 of cubic CeO₂, in agreement with the previously discussed XRD results. Finally, EDX spectra of the
 457 catalysts (Fig. 2c) indicate the presence of Fe in all the samples besides pristine CeO₂. It is interesting
 458 to notice that the contribution from the Fe K α line (\sim 6.4 keV) in EDX spectra correlates with the
 459 nominal increase of Fe in the catalysts, confirming that the crystalline nanoparticles host an increasing
 460 amount of Fe ions, without significant changes in the F-type crystalline structure of CeO₂. The SEM
 461 micrographs (Fig.SI.6) show a quasi-spherical shape of nanoparticles with a uniform distribution, in
 462 agreement with the morphologies obtained from TEM data. To further confirm the presence of Fe in
 463 all samples a compositional analysis has been done also by EDS. The atomic ratio Fe/Ce obtained
 464 (average in 5 spots) is in good accordance with the theoretical molar ratio and experimental ICP data
 465 (see Table SI.1 for details). The optical properties of the prepared materials were evaluated by UV-
 466 Vis diffuse reflectance spectroscopy. The D(R) spectra are shown in Fig. 3a. The UV-Vis spectrum
 467 of pure CeO₂, black line, consisted of a strong absorption band located in the 200-400 nm range where
 468 different transitions can be observed. The absorption at low wavelength, one centered at 215 nm and
 469 the other at around 275 nm (blue rectangle and green rectangle in Fig. 3a, respectively), are generally
 470 attributed to charge-transfer transitions between O 2p and Ce 4f orbital. In particular, the absorption
 471 due to Ce³⁺ \leftarrow O²⁻ charge transfer is observed at 215 nm while the peak at a higher wavelength is
 472 ascribed to Ce⁴⁺ \leftarrow O²⁻ transition [97,99]. The shoulder at 340 nm is assigned to interband transitions
 473 [46]. The reported behaviour is also observed in the spectra of iron-containing samples; however, a
 474 careful examination reveals some modifications.

475 The shift to the lower wave number of the main peak recorded for the Fe0.5 sample could be caused
 476 by the isolated Fe³⁺ species[100,101]. Indeed, Fe Oh and Td species show the typical transitions in
 477 the UV range, allowing a not easy assignment due to overlapping absorption range with ceria. The
 478 absorption at 215 nm appears more prominent when increasing the iron doping percentage up to
 479 Fe2.5, thus suggesting a more pronounced presence of defective sites [102]. The spectrum recorded
 480 for the Fe10 sample (purple curve) shows a feature at about 380 nm that is generally assigned to the
 481 presence of oligomeric hematite-like clusters, as reported by Schwidder et al [42]. However, the
 482 typical d-d transitions of α -Fe₂O₃, located at 533 nm, are not observed. The lack of stoichiometric iron
 483 phase is in accordance with the XRD results, whereas the oligomeric clusters are in accordance with
 484 the Raman results, which evidence a contribution at (\sim 670 cm⁻¹) only into the sample at higher iron
 485 loading (*vide infra*). The spectra of all the iron-doped catalysts show a red shift in the absorption
 486 edge, indicative of the Ce-Fe interaction.

487 The effect of iron doping on the optical band gap was assessed by Tauc plot relation. In Fig. 3b
 488 $(F(R)(h\nu)^{1/2})$ is plotted versus the photon energy, $h\nu$, and the indirect band gap energy (E_g) was
 489 obtained by applying the double tan approximation [103]. The band gap value of pristine CeO₂ was
 490 found to be 3.0 eV. The effective inclusion of the Fe species in the ceria lattice results in a decrease
 491 in E_g , ascribable to the introduction of vacant 3d orbitals between the valence and conduction bands
 492 of CeO₂ [104].

493 Table 3 shows that E_g values decrease monotonically with iron content [36,60]. This trend is also
 494 observed in the theoretical E_g values calculated for the undoped and Fe-doped CeO_2 discussed in the
 495 following DFT study section. The band gap values obtained in the iron-doped samples reported here
 496 are somewhat lower than those reported in the literature for the same compositions [36,60,105–107].
 497 Once again, all the previous features can be attributed to the adopted reverse micelle strategies.



498

499

500 **Fig. 3:** a) DR UV-Vis spectra of synthesized samples plotted as Kubelka-Munk function $F(R)$. b)
 501 The indirect band gap calculation of pristine and Fe-doped porous CeO_2 based on the Kubelka-
 502 Munk function by Tauc plot relation using the double tan approximation. CeO_2 (black curve); Fe0.5
 503 (red curve), Fe2.5 (orange curve), Fe5 (green curve) and Fe10 (purple curve).

504

505 Significant information on the fate of iron in ceria nanocrystals can be obtained from Raman. The
 506 spectra corresponding to the iron-doped samples are shown in Fig. 4a along with that of pure CeO_2
 507 nanocrystals. Three main contributions are observed. The prominent peak corresponds to the F_{2g} peak
 508 and it results from the vibration of the O sublattice. It stands at 458.5 cm^{-1} for the pure CeO_2
 509 nanocrystals, some 6.5 cm^{-1} lower than the position of pristine bulk CeO_2 . This shift is consistent with
 510 the reported decrease of peak position with particle size reduction [91] and a Gruneisen parameter
 511 value of 1.57. For instance, Spanier et al. [108] reported a 4 cm^{-1} redshift for 6 nm nanocrystals. The
 512 peak shows an asymmetry towards low wavenumbers. Such an asymmetry is often seen in nanocrystal
 513 samples and related to size dispersion [91,109,110].

514 As iron is incorporated into the nanocrystals, the F_{2g} peak mode is further softened and broadened.
 515 Such behaviour was previously observed by Popovic et al. [111] for Fe-doped CeO_2 nanocrystals.
 516 The trend is not strictly monotonous with the nominal Fe concentration. Fig. 4b shows the correlation
 517 between the F_{2g} peak shift ($\Delta\omega$) and the corresponding variation of the peak FWHM (full-width-at-
 518 half-maximum). The variation is linear as previously observed by Popovic et al. However, the slope
 519 of our curve is -6.9, slightly higher than that reported in [111], with a value of -5.3. This behaviour
 520 originates from two causes: grain size and strain effect (causing homogeneous line broadening) and
 521 charges delocalization in oxygen-deficient ceria. Since all the samples have about the same
 522 nanocrystal mean size, neither the mode softening nor the line broadening can be attributed to any
 523 size effect. The observed linear variation thus results from changes in strain within the nanocrystals
 524 and charge delocalization. The two phenomena are hard to disentangle without further modelling.

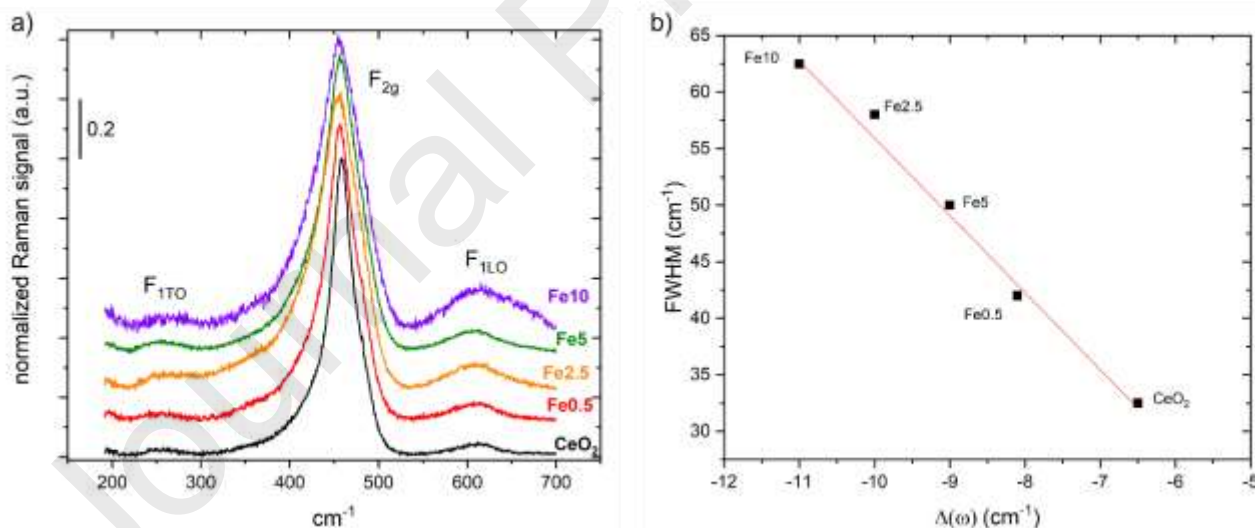
525 However, the actual occurrence of such a variation is the signature that the samples are oxygen
 526 deficient and that charge delocalization happens for 4f electrons located at Ce(Fe)-VO-Ce(Fe)
 527 orbitals. This charge delocalization is generally favourable to the photocatalytic activity. This is
 528 confirmed in our case where the sample Fe2.5 shows both the highest delocalization and the highest
 529 photocatalytic activity (see Fig. 11). We exclude from our analysis the Fe10 sample that cannot be
 530 considered as simply doped ceria since it probably contains oligomeric species at its surface,
 531 detrimental to its catalytic activity.

532 Two supplementary peaks are noticed at 270 cm^{-1} and 606 cm^{-1} respectively. They are assigned to
 533 the F_{1TO} and F_{1LO} phonon modes. These vibrations are forbidden in pristine CeO_2 but are often seen
 534 in nanocrystal samples as a result of the long-range symmetry breaking of the crystals. The magnitude
 535 of the F_{1LO} peak increases with Fe content as evidenced in Fig. SI.7 where the change in the ratio
 536 between the F_{1LO} contribution and the F_{2g} contribution is plotted versus the sample composition.
 537 The F_{1LO} feature can be assigned to defects involving dopant cation complexes close to VO [112]. It
 538 can be clearly observed that moving from sample Fe0.5 to sample Fe2.5 the ratio is almost doubled,
 539 indicating the increased presence of the aforementioned VO-related complexes.

540 For the Fe10 sample, on top of the F_{1LO} feature, a second contribution at approximately 670 cm^{-1}
 541 appears. This contribution cannot be assigned to the presence of VO but rather to the presence of Fe
 542 at high content [112]. As already mentioned, this sample cannot be considered in the strict sense as
 543 doped ceria.

544

545



546

547 **Fig. 4:** a) Raman spectra of pristine and Fe-doped CeO_2 nanocrystals for different doping
 548 concentrations. All spectra are normalized to the maximum intensity of the F_{2g} peak. b) Variation of
 549 the F_{2g} peak FWHM concerning its position variation as a function of the Fe concentration in CeO_2
 550 nanocrystals. $\Delta\omega$ is referred to the value of pristine CeO_2 .

551

552 The textural properties were evaluated by N_2 adsorption at low temperatures ($-196\text{ }^\circ\text{C}$). The
 553 adsorption/desorption isotherms, Fig. SI.8a, resemble type IV, typical of mesoporous material with a
 554 hysteresis loop indicating block-neck pores shape (hysteresis type H2). All the studied samples have

555 a BET-specific surface area higher than or equal to $180 \text{ m}^2 \text{ g}^{-1}$ Table 3, with the exception of the
 556 sample Fe10 that shows a surface area of $274 \text{ m}^2 \text{ g}^{-1}$. Considering that the surface area is interparticle,
 557 the discordant value of Fe10 can be explained by the smaller particle size, Table 2. The limited
 558 particle growth observed at high iron contents may be correlated with the presence of iron-containing
 559 species on the surface [46,93]. The pore size distribution (PSD) evaluated by the BJH method on
 560 desorption branches, Fig.SI.8b, suggests that the synthetic route is effective for the preparation of
 561 mesoporous (doped) ceria.

562 The designed reverse micelles synthesis route allows for obtaining a very high surface area compared,
 563 not only with different methods [33,107,113] but also with similar procedures reported in the
 564 literature [46,47].

565

566 **Table 3:** Energy of band gap (E_g) and textural properties of pristine and Fe-doped CeO_2 sample

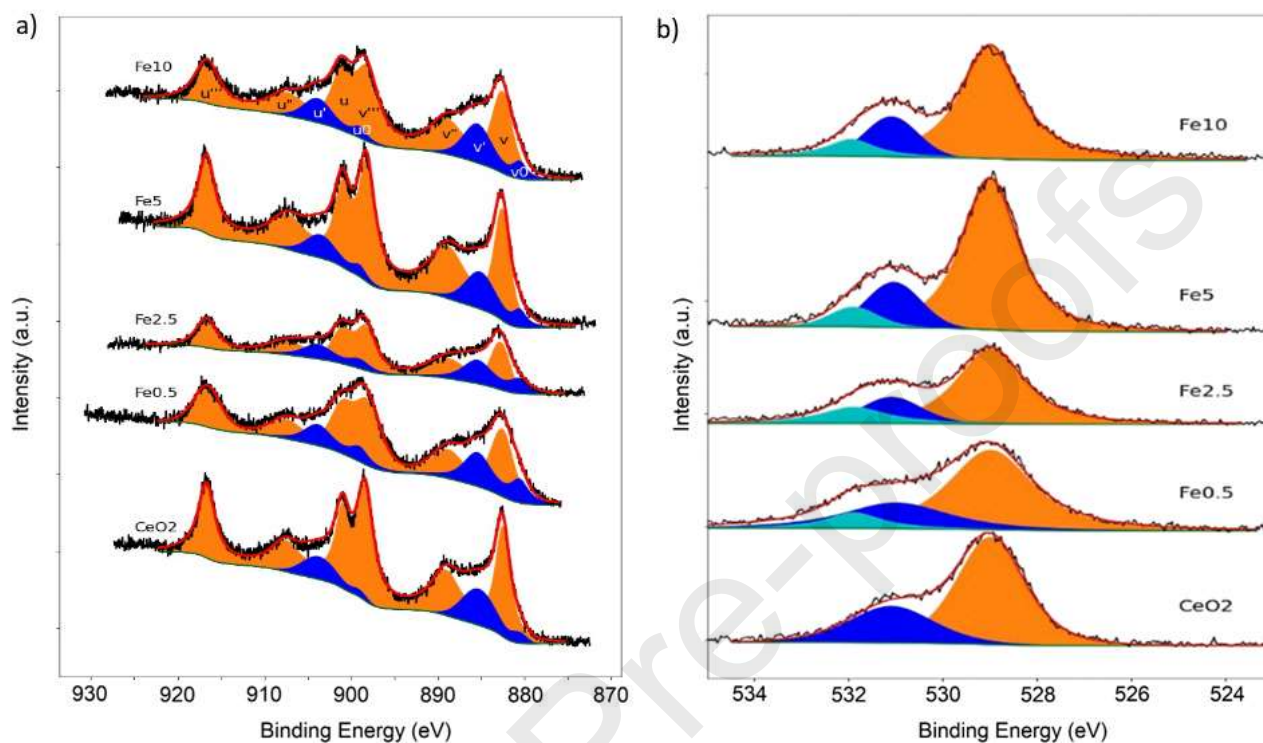
567	Sample	E_g (eV)	BET SSA ($\text{m}^2 \text{ g}^{-1}$)	V_p ($\text{cm}^3 \text{ g}^{-1}$)
568				
569	CeO_2	3.00	182	0.196
570				
571	Fe0.5	2.91	180	0.184
572				
573	Fe2.5	2.79	191	0.188
574				
575	Fe5	2.77	189	0.192
576				
577	Fe10	2.68	274	0.280

575 In order to have a better
 576 surface a XPS analysis was
 577 spectrum, although highly
 578 deconvolved with some precautions [114,115]. Here Ce3d XPS spectra, shown in Fig. 5a, were
 579 solved with five $3d_{5/2}$ components denoted as v_0 (880.6 eV), v (882.6 eV), v' (885.45 eV), v'' (888.85
 580 eV) and v''' (898.4 eV) with ± 0.3 eV resolution and their $3d_{3/2}$ counterparts (called u_x) separated by
 581 18.45 eV (± 0.15 eV) with a ratio u_x/v_x of $1.5(\pm 0.1)$. The amount of surface Ce^{3+} ion was
 582 determined using the area of v_0 , u_0 , v' and u' peaks, while v , u , v'' , u'' , v''' and u''' were assigned
 583 to surface Ce^{4+} ion.

584 The two ions appear for different environments of Ce atoms, resulting in different charge transfers.
 585 Ce^{3+} is indeed present in Ce_2O_3 , while CeO_2 is made of Ce^{4+} ions. Since the O1s core level is sensitive
 586 to changes in the coordination of the oxygen atoms, its deconvolution should also allow the evaluation
 587 of the charge transfer between oxygen and cerium atoms. Three components are usually considered
 588 to resolve XPS spectra of the O1s core level in CeO_2 . The first one, labeled $\text{O}\alpha$ at 529 eV, is usually
 589 associated with lattice oxygen, i.e. Ce^{4+} in CeO_2 . Following [116], $\text{O}\beta$ feature at 531 eV and $\text{O}\gamma$
 590 feature at 532 eV are attributed to surface hydroxyl groups, resulting from the dissociation of
 591 adsorbed water and irreversibly adsorbed molecular water, respectively. These energies (± 0.1 eV)
 592 were fixed to fit our XPS data, as shown in Fig. 5b. Finally, relative atomic concentration was

593 calculated as the ratio of the normalized intensity of one element with a given valence over the
 594 normalized intensity of that element (whatever the valence), with a sensitivity factor calculated as the
 595 product of theoretical inelastic mean free path and cross section.

596



597

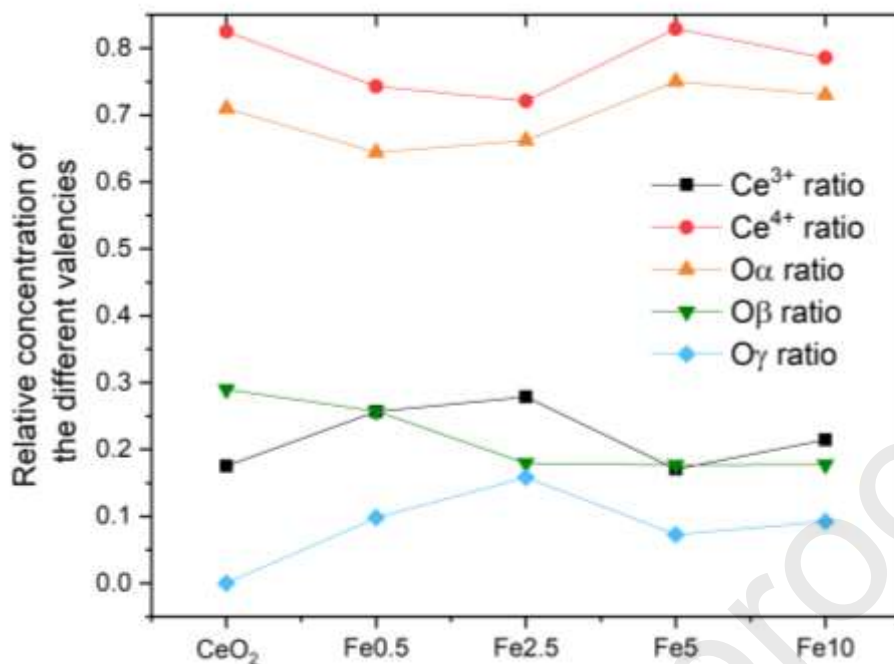
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600 **Fig. 5:** Experimental and fitted XPS spectra. Ce3d (a) and O1s (b) core level spectra as a function
 601 of the Fe concentration in CeO₂ nanocrystals. Experimental data are in black, Shirley background in
 602 green. The sum of 5 components of doublets (2 of Ce³⁺, blue area, 3 of Ce⁴⁺, orange area) are used
 603 to fit the Ce3d signal (a) or of 3 components (O α , O β and O γ , areas in orange, blue and cyan,
 604 respectively) to fit O1s signal in red.

605

606



607

608 **Fig. 6:** Relative atomic composition of the synthesized pristine and doped CeO₂ nanocrystals as a
 609 function of Fe content.

610

611 As shown in Fig. 6, the Ce⁴⁺ relative atomic concentration follows nicely that of O_α. Both signals
 612 decrease as the Fe content increases from CeO₂ to Fe_{2.5} and next decrease and reach an almost
 613 constant value. This is consistent since both signals come from the CeO₂ units in the nanocrystal bulk.
 614 Remarkably, the variation of the Ce³⁺ relative atomic concentration is opposite to that of Ce⁴⁺. This
 615 reveals that the increase in Fe content from CeO₂ to Fe_{2.5} promotes the enrichment of Ce³⁺ within
 616 the Ce. Adding more Fe does not lead to more Ce³⁺ ions. On the contrary, it appears that the further
 617 addition of Fe atoms, beyond Fe_{2.5}, is less effective in generating Ce³⁺ ions.

618 As demonstrated by DFT calculations (see below), the generation of Ce³⁺ ions is related to the
 619 generation of VOs. The evolution of the oxygen concentration cannot be directly seen in the XPS
 620 spectra since, as stated above, there is no XPS feature directly related to VOs. Consequently, even
 621 though the analysis of the Ce³⁺ feature remains delicate since the X rays may induce the reduction of
 622 ceria during the observation [117], its evolution remains a relevant indication of the VOs
 623 concentration. Interestingly, one can note that the minimum Ce⁴⁺ concentration (thus the maximum
 624 of Ce³⁺ and VOs concentrations) is concomitant with the maximum catalytic activity.

625 To conclude the discussion, the analysis of the Fe2p core level signal would have been highly
 626 relevant. However, Fe2p signal is very weak, although increasing with doping, and at the same
 627 energies as the signal of Ce M45N45V Auger electrons (see supplementary Fig. SI.9). From its
 628 analysis only 3% atomic concentration was found when 10% was expected. As XPS is sensitive to
 629 the extreme surface (first few nms), it indicates that Fe might be inhomogeneously distributed in the
 630 nanocrystals.

631

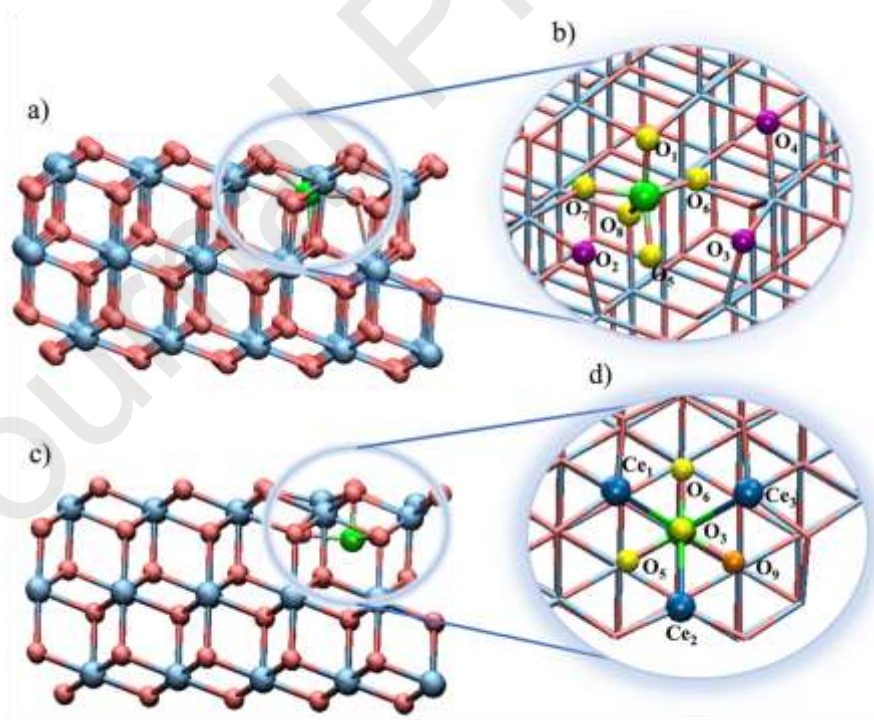
632 3.3 DFT study

633

634 *3.3.1. Fe-doped CeO₂ surfaces characterization*

635 Density functional theory (DFT) calculations were performed to investigate the effects of Fe-doping
 636 on the structural and electronic properties of CeO₂ (111) surfaces. We have considered the scenario
 637 in which iron atoms substitute surface and subsurface Ce sites (Fe@Ce) as well as interstitial doping,
 638 where Fe atoms occupy interstitial sites in the crystal structure (Fe_{Int}).

639 The optimized geometry of the system with surface substitutional Fe doping (Fe@Ce₁), reported in
 640 Fig. 7a, results in more stable than the subsurface one (Fe@Ce₂) by 1.1 eV. The presence of such a
 641 Fe substitutional point defect induces a rearrangement of the neighboring O atoms. As a result, on the
 642 doped CeO₂ (111) surface, two non-equivalent O atoms (O₁ and O₄) and two equivalent (O₂=O₃) O
 643 sites are present, whereas in the subsurface layer all the O atoms (O₅, O₆ and O₇) results to be
 644 equivalent (see Fig. 7b). In this configuration, the Fe atom relaxes inward and binds to an O atom of the
 645 surface O₁, to three O atoms of the second layer O₅, O₆ and O₇, and to an O atom of the third layer
 646 O₈ (yellow O in Fig. 7b). The Fe-O bond lengths are found to be in the range of 1.84-2.14 Å, and
 647 therefore, corresponding to the distances in α - and γ -Fe₂O₃ (1.89-2.10 Å) [118]. In addition, the Bader
 648 charge of the substitutional Fe dopant is 14.28 e⁻ similar to those computed for the metal in α - and γ -
 649 Fe₂O₃ (14.34 and 14.49 e⁻). The Fe-O bond lengths of the five-coordinate moiety and the Bader charge
 650 calculations suggest that in our system the iron atom has an oxidation state of +3. In the doped surface,
 651 the Bader charges of the Ce atoms (9.6 e⁻) are consistent with the presence of Ce⁴⁺, indicating that no
 652 Ce⁴⁺ is reduced to Ce³⁺ in presence of the Fe dopant (see PDOS Fig. SI.10a). In the presence of a
 653 substitutional Fe atom in the CeO₂ system the computed value of the bandgap is 1.7 eV, thus 0.2 eV
 654 lower with respect to the undoped case, that is 1.9 eV (compare Fig. SI.10a and SI.10b).



655

656 **Fig. 7.** Panel a) optimized structure of Fe@Ce₁ (111). Panel b) First and second coordination spheres
 657 of the Fe dopant. Ce, O, O_{1,5-8}, O₂₋₄ and Fe surface atoms are represented in balls and sticks and
 658 depicted in blue, red, yellow, purple and green, respectively. Panel c) optimized structure of Fe_{Int}.

659 Panel d) coordination sphere of the interstitial Fe dopant. Ce, O, O_{3,5,6}, O₉ and Fe surface atoms are
 660 represented in balls and sticks and depicted in blue, red, yellow, orange, and green, respectively.

661

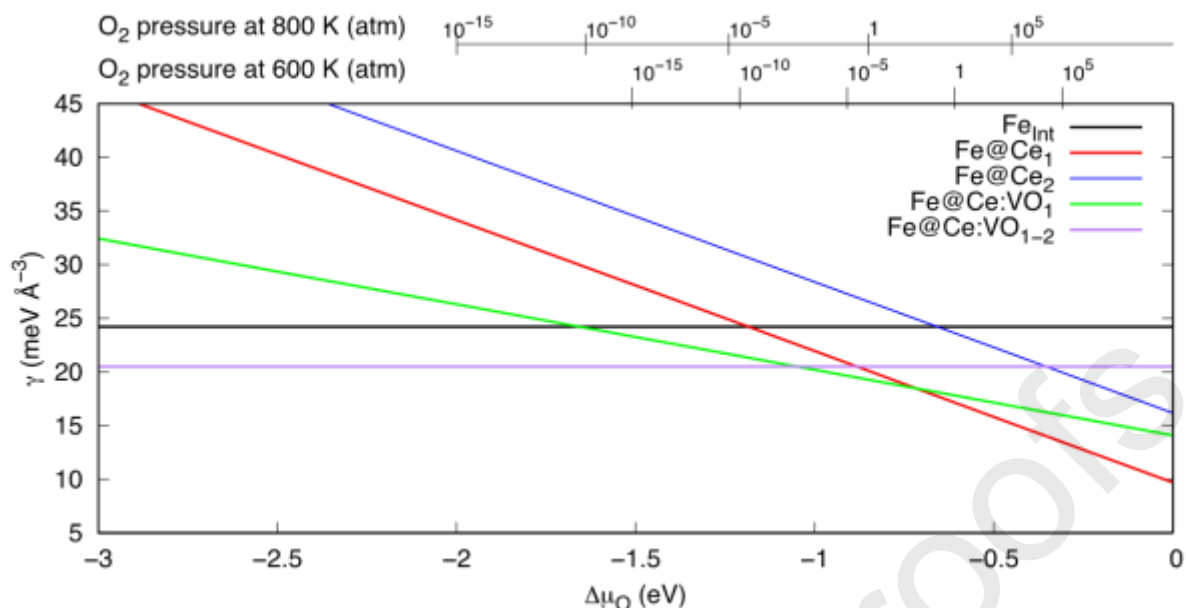
662 Fig. 7.c shows the optimized structure of the Fe_{Int} system. Also in this case, the presence of the
 663 interstitial Fe dopant induces structural distortions on the surface. In fact, the Fe atom relaxes outward
 664 binding to the surface O₃ atoms and to the three O atoms of the second layer O₅, O₆ and O₉, (yellow
 665 and orange O in Fig. 7d). The formation of these new Fe-O bonds and the breaking of the pre-existing
 666 Ce-O bonds generates three reduced Ce³⁺. The Bader charges of these Ce atoms (9.9 e⁻) are consistent
 667 with the presence of Ce³⁺, also confirmed by the formation of two bandgap states below the Fermi
 668 level (black peaks in Fig. SI.11a of the SI) and by the spin density analysis, where the electron excess
 669 on the Ce³⁺ are indicated with black densities analogously to the colors of the respective bandgap
 670 peaks (Fig. SI.11c). In Fe_{Int} system the computed value of the bandgap is 1.7 eV similar to the
 671 substitutional Fe doping (compare Fig. SI.10a and SI.11a). For both doping types, the theoretical $\Delta\Delta E$
 672 (eV) related to the band gap energy variation of the undoped and doped surfaces is in line with the
 673 experimentally calculated one and reported in Table 3.

674 Next, we have considered the formation of O vacancies on the most stable Fe@Ce₁ system. The
 675 presence of a Fe substitutional point defect generates four non-equivalent O atoms, namely O₁,
 676 O₂=O₃, O₄ in the outermost layer and O₅=O₆=O₇ in the subsurface layer, as discussed above (Fig. 7b).
 677 It is, therefore, possible to create four non-equivalent oxygen vacancies: VO₁, VO₂₌₃ and VO₄ in the
 678 external layer and VO₅₌₆₌₇ in the subsurface layer. The computed values of the formation energies
 679 (E_F) of VO₁, VO₂₌₃, VO₄ and VO₅₌₆₌₇ are found to be 0.7, 0.8, 2.13 and 1.1 eV, respectively. Our
 680 results show low formation energies for those oxygen vacancies arising from oxygen atoms directly
 681 coordinating or close enough to the Fe dopant (see VO₁, VO₂₌₃ and VO₅₌₆₌₇) and high E_F for those
 682 far from the iron atom. This occurs because the oxygen atoms very close to Fe are more affected by
 683 the structural distortions generated by the Fe dopant. The formation of a second oxygen vacancy VO₂
 684 on the most stable reduced surface VO₁ (Fe@Ce₁:VO₁₋₂) is also favored, with an E_F of 0.9 eV,
 685 suggesting that the Fe dopant is likely the center of the oxygen vacancy cluster. A close inspection of
 686 the Bader charges, PDOS and spin density plots of the most stable Fe@Ce₁:VO₁ (111) system shows
 687 that the formation of an O vacancy leads to the reduction of two Ce⁴⁺ atoms that are formally Ce³⁺
 688 (see Fig. SI.12).

689 To define the relative stability of the Fe-doped systems containing different types and or number of
 690 atoms depending on pressure and temperature, we have employed the formalism of ab initio
 691 thermodynamics as detailed described in the Experimental Section.

692 Fig. 8 shows a plot of the Gibbs energies $\Delta G_{\text{ads}}(T, p)$ of the system discussed above as a function of
 693 the O chemical potential including a conversion to oxygen partial pressures at several relevant
 694 temperatures. It is possible to identify three thermodynamically stable phases. The first phase, which
 695 holds for values of $\mu_o > -0.7$ eV, corresponds to the system where a Fe atom substitutes a surface Ce
 696 ion, Fe@Ce₁ (red line). Under O-rich conditions this structure becomes the thermodynamically most
 697 stable one. The second most stable structure is the one obtained by removing a surface O atom from
 698 the Fe@Ce₁ system (green line). This structure becomes thermodynamically stable in the range -1.05
 699 $< \mu_o < -0.7$ eV (purple line). Finally, for $\mu_o < -1.05$ the Fe@Ce₁ system in the presence of two surface
 700 O vacancies becomes thermodynamically stable. These findings are in line with the experimental data
 701 suggesting that in the presence of Fe atoms substituting Ce ions the formation of O vacancies is
 702 favored. In addition, we predict that subsurface substitutional and interstitial Fe doping are never
 703 thermodynamically stable (blue and black lines, respectively).

704



705

706 **Fig. 8.** Gibbs energies $\Delta G_{\text{ads}}(T, p)$ for substitutional, interstitial Fe atom in CeO_2 (111) and for
 707 reduced $\text{Fe@Ce}_1\text{:VO}_1$ and $\text{Fe@Ce}_1\text{:VO}_{1-2}$ (111) as a function of the oxygen chemical potential $\Delta\mu_{\text{O}}$
 708 in eV.

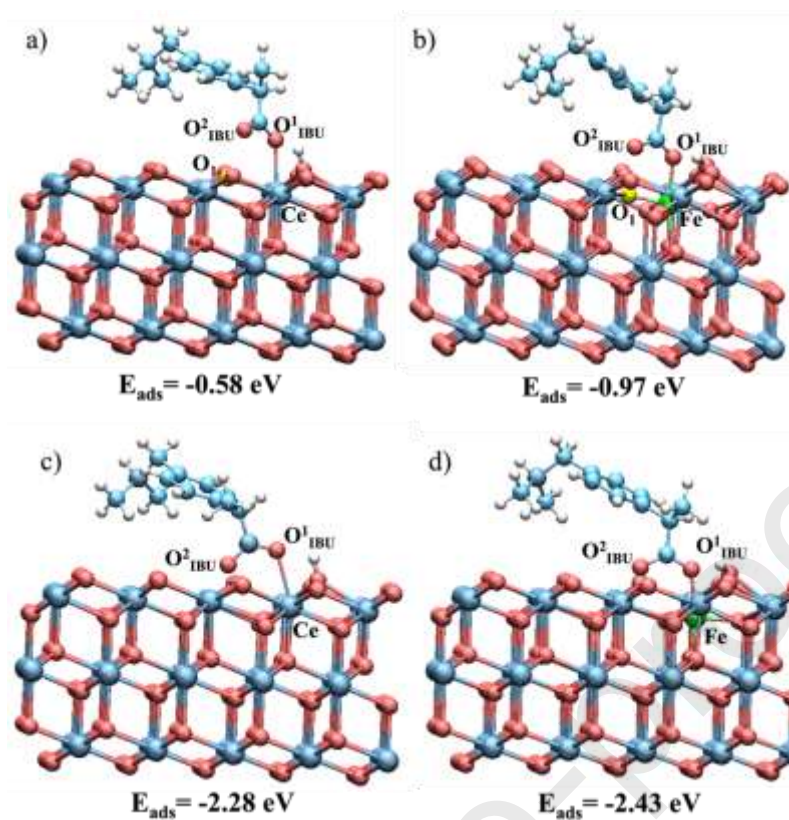
709 3.3.2. Ibuprofen absorption on the surfaces

710 The interaction of IBU with stoichiometric (reduced) undoped CeO_2 (111) and the most stable
 711 Fe@Ce_1 surfaces was investigated, simulating IBU in its deprotonated form according to the
 712 experimental conditions.

713 Fig. 9 shows the optimized geometries of the most stable configurations of the IBU adsorbed on
 714 $\text{CeO}_2(111)$, Fe@Ce_1 (111), $\text{CeO}_2\text{:VO}_1(111)$, and $\text{Fe@Ce}_1\text{:VO}_1(111)$ (panel a-d, respectively).

715 IBU interacts with $\text{CeO}_2(111)$ through an ionic-like bond between an oxygen atom of its carboxylate
 716 group (O^1_{IBU}) and a surface Ce atom of 2.38 Å and an E_{ads} of -0.58 eV (Fig. 9a). In Fe@Ce_1 (111),
 717 the ligand binds the surface by a covalent-like bond between O^1_{IBU} and the Fe dopant of 2.12 Å and
 718 an E_{ads} of -0.98 (Fig. 9b). In the stoichiometric system, the Fe dopant presence improves the
 719 adsorption energy of IBU by 0.4 eV due to i) the greater orbital availability of Fe^{3+} with respect to
 720 Ce^{4+} to host electrons and, thus, form new bonds and to ii) the structural distortions generated by the
 721 substitutional dopant. In fact, in the presence of Fe, the surface oxygen atom O_1 goes down towards
 722 the subsurface oxygen layer allowing a better interaction of the ligand with the Fe@Ce_1 (111) surface.

723 These energy stabilizations are also reflected in the reduced undoped and Fe-doped systems (Fig. 9c
 724 and 9d, respectively). The experiments are performed in aqueous solution and, therefore, water
 725 molecules will fill surface O vacancies of the ceria surface leading to a hydroxylated surface.
 726 However, if we assume that O vacancies are present on the catalysts, IBU molecules will adsorb on
 727 $\text{CeO}_2\text{:VO}_1$ (111) and $\text{Fe@Ce}_1\text{:VO}_1$ (111) through an ionic and covalent bond of 2.56 and 2.10 Å,
 728 respectively, and with E_{ads} of -2.28 and -2.43 eV for the undoped (panel c in Fig.9) and Fe-doped
 729 (panel d in Fig.9) reduced systems. Therefore, the hypothetical presence of the surface oxygen
 730 vacancy VO_1 improves the ligand E_{ads} of about 1.5 eV with respect to the stoichiometric surfaces as
 731 O^2_{IBU} tends to occupy the vacant site stabilizing the IBU adsorption.



732

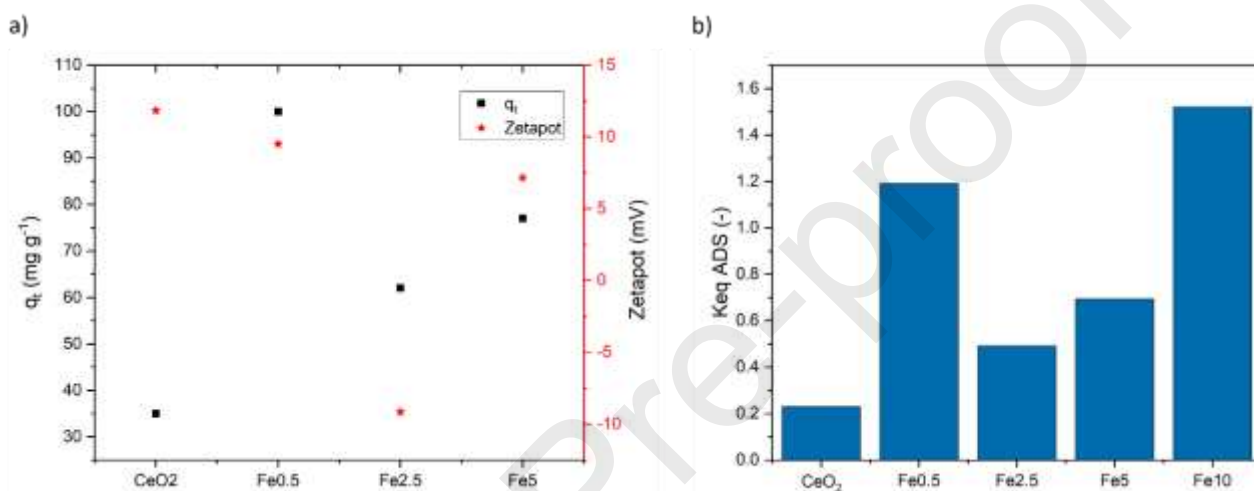
733 **Fig. 9.** Optimized structure of a) CeO_2 (111), b) Fe@Ce_1 (111), c) $\text{CeO}_2@\text{VO}_1$ (111) and d)
734 $\text{Fe@Ce}_1:\text{VO}_1$ (111) with the corresponding E_{ads} (eV). Ce, O and $\text{O}^{1-2}_{\text{IBU}}$, O_1 , C, H and Fe surface
735 atoms are represented in balls and sticks and depicted in blue, red, yellow, cyan, white and green,
736 respectively.

737

738

739 3.4 Ibuprofen adsorption and photodegradation activity

740 Adsorption and photodegradation tests were conducted to investigate the performance of each
 741 synthesized catalyst. An attempt was made to justify the adsorption efficiency with the main
 742 properties of the catalysts. Except for the Fe10 sample, we do not observe any significant difference
 743 in terms of SSA and pore size. These findings lead us to speculate that the adsorption behaviour of
 744 IBU, except for Fe10, should not be determined by textural properties but could reflect differences in
 745 surface charge [93]. For this reason, the ζ -potential values at the pH of ibuprofen solution (pH=4.6),
 746 extrapolated from the ζ -potential curves (Fig. SI.13), were plotted vs the maximum adsorption
 747 capacity ($q_t=(C_{IBU,0}-C_{IBU})/\rho_B$), measured in dedicated experiments adopting the following
 748 experimental conditions: $T=30\text{ }^\circ\text{C}$, $C_{IBU,0}=12.4\text{ mg L}^{-1}$, $\rho_B=0.07\text{ g L}^{-1}$, reaction time of 300 min (Fig.
 749 10a).



750

751 **Fig. 10** – a) Potential (ζ) of the pristine and Fe-doped CeO₂ vs the adsorption capacity. b) Trend of
 752 the adsorption equilibrium constant. The present experimental conditions were adopted for each
 753 experiment: $T=30\text{ }^\circ\text{C}$, $C_{IBU,0}=12.4\text{ mg L}^{-1}$, $\rho_B=0.07\text{ g L}^{-1}$, reaction time of 300 min.

754

755 From the results shown in Fig. 10a, it is interesting to observe that Fe0.5 and Fe5 samples are
 756 positively charged at pH=4.6, namely the pH of the ibuprofen solution, while Fe2.5 is negatively
 757 charged. It is worth mentioning that the surface of both ceria and doped ceria is not “naked” but
 758 hydroxylated. Thus, being ibuprofen a weak acid (pKa 4.41), in water it is partially dissociated in its
 759 anionic form. Therefore, the strongest interactions are expected to be with positively charged
 760 materials. Accordingly, the adsorption efficiency passes through a minimum for the Fe2.5 catalyst
 761 where the surface is negatively charged, inhibiting the ibuprofen adsorption. The different surface
 762 charge may be related to the type of hydroxyls exposed by Fe-CeO₂ surfaces, their distribution and
 763 their location with respect to oxygen vacancies [119,120].

764 The CeO₂ sample shows an opposite trend showing a very low adsorption efficiency even if the
 765 surface is positively charged, a finding not explainable by the above-mentioned hypothesis. But it is
 766 important to remind that from DFT computations (see Fig. 9), the adsorption energy of ibuprofen
 767 improves when it interacts with Fe rather than Ce, clearly leading to a lower adsorption efficiency
 768 compared with the samples containing Fe. As previously stated, the Fe10 sample is not included in
 769 the trend of doped samples discussion, because of its different properties such as very high surface
 770 area and the presence of surface oligomers (*vide supra*) that may promote higher adsorption
 771 efficiency. Furthermore, the type of adsorption was further evaluated by FT-IR spectroscopy. The

772 spectra obtained from the Fe2.5 sample and from the same sample after contact with a saturated
 773 ibuprofen solution are shown in Fig. SI.14. The spectra show a broad band between 3750 and 3000
 774 cm^{-1} due to O-H stretching vibration of surface hydroxyl groups and undissociated water
 775 characterized by its bending mode at 1630 cm^{-1} [121,122]. Bands at around 1364 and 1529 cm^{-1} can
 776 be attributed to carbonate species, whose presence results from interactions of CeO_2 with atmospheric
 777 carbon dioxide [123]. Metal-oxygen vibrations are generally observed at low wavenumbers, below
 778 800 cm^{-1} . The absence of new chemical bonds in the post-saturation sample, inferred from the
 779 absence of new peaks in the saturated Fe2.5 catalyst, suggests a physisorption mechanism.

780 To measure the relative influence of adsorption and photodegradation contribution, the results were
 781 interpreted with a simplified kinetic model. The model was written taking into consideration a
 782 constant volume ideal batch reactor, where at the beginning of the reaction the ibuprofen solution is
 783 loaded to the vessel and the reaction is considered to occur in isothermal conditions. The rate
 784 expressions were developed, considering that ibuprofen (IBU) is adsorbed on the surface of the
 785 photocatalysts (*) leading to an adsorbed specie (IBU*), as in Eq. 2.



787 The reversible rate expression reported in Eq. 3 was adopted to describe the adsorption rate.

$$788 \quad r_{\text{ADS}} = k_{\text{ADS}} \left(c_{\text{IBU}} - \frac{1}{K_{\text{eqADS}}} c_{\text{IBU}^*} \right) \quad (3)$$

789 The mentioned rate expression was included in the mass balance equation valid for a batch system,
 790 see Eq. 4.

$$791 \quad \frac{dc_{\text{IBU}}}{dt} = -r_{\text{ADS}} \cdot \rho_B \quad (4)$$

792 The ordinary differential equation was solved in MATLAB R2023a environment, using *ode45*
 793 function, and the related adsorption kinetic and equilibrium constants were obtained by parameter
 794 estimation activity on the adsorption kinetic experiments. In detail, the objective function, defined as
 795 the square root of the squares of the residuals, was minimized using *lsqnonlin* algorithm. The results
 796 of the parameter estimation activities are reported in Figs 10b and Table 4.

797 As shown in Fig. 10b, the adsorption equilibrium constants follow the same trend as the adsorption
 798 capacity (q_t), being both quantities related to each other whose trend was previously explained via ζ
 799 -potential curves.

800 As adsorption is a physical phenomenon, its velocity depends on the effective diffusivity of ibuprofen
 801 molecules in the catalyst pores, thus the lumped kinetic constants reported in Table 4 are dependent
 802 on both the porosity and tortuosity of the catalysts. Being the pore volumes of each material very
 803 similar (see Table 3), the expected kinetic constants shall fall in the same range, as obtained by
 804 parameter estimation and reported in Table 4.

805

806 **Table 4** – Adsorption rate, adsorption equilibrium and degradation rate constants values. The
 807 experimental conditions were adopted for each experiment: $T=30^\circ\text{C}$, $C_{\text{IBU},0}=12.4 \text{ mg L}^{-1}$, $\rho_B = 0.07 \text{ g}$
 808 L^{-1} , reaction time of 300 min.

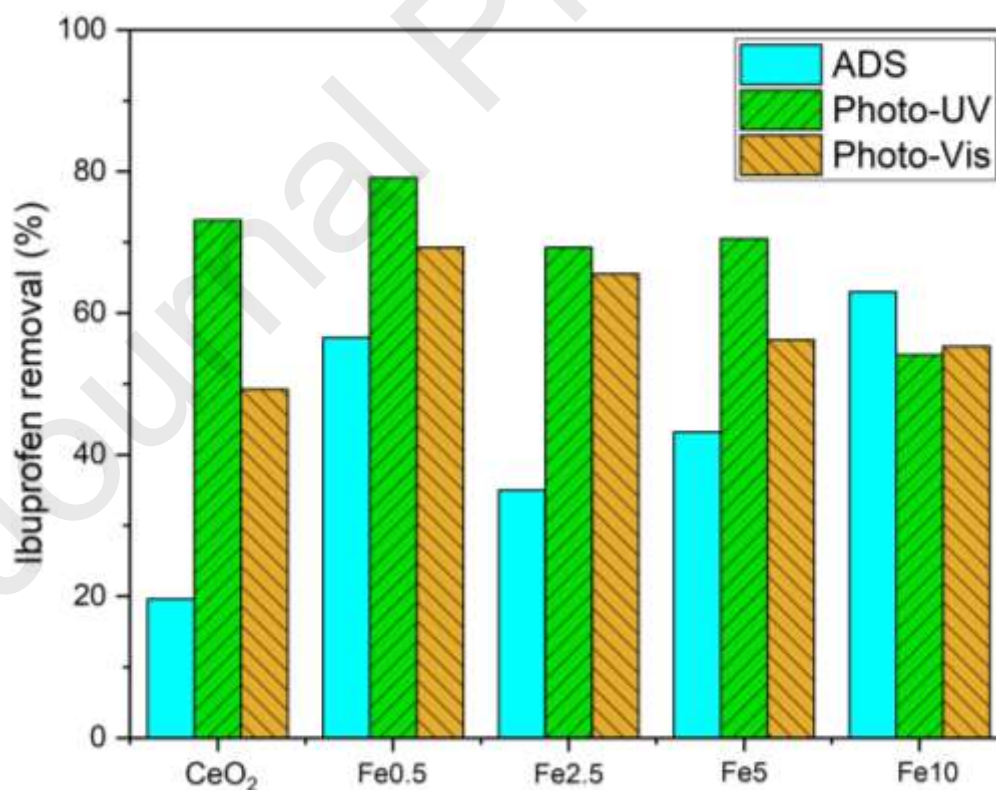
809

810 The experiments were conducted in the presence of UV irradiation. The results are reported in Fig. 11, that UV irradiation is more efficient than for all the catalysts. (see Table 3), which to mainly exploit UV light. The onset of absorption in the ceria lattice samples. For this samples can be visible irradiation.

Sample	k_{ADS} ($L g^{-1} min^{-1}$)	K_{eqADS} (-)	k_{DEG} ($L g^{-1} min^{-1}$)
CeO₂	0.09 ±0.02	0.23 ±0.01	0.03 ±0.01
Fe0.5	0.25 ± 0.01	1.19 ±0.02	0.03 ±0.01
Fe2.5	0.16 ±0.02	0.49 ±0.02	0.11 ±0.01
Fe5	0.23 ±0.02	0.69 ±0.02	0.04 ±0.01
Fe10	0.37 ±0.02	1.52 ±0.03	0.0010± 0.0003

photodegradation conducted either in or visible main results are where it is evident is slightly more visible irradiation. The band gap value at the value of 3 eV allows the material the absorption of presence of iron in induces a shift in the in the studied reason, the doped more active under. However,

827 performance between UV and
828 visible irradiation is a delicate balance of several factors, including band gap, surface defects and
829 intra-band gap defect states (that can also act as recombination centres). The performance of the
830 catalysts under visible irradiation is indeed promising for a scale-up process, considering the low
831 lamp power and the used dosage of the catalysts.



832

833 **Fig. 11** –Trend of the ibuprofen removal percentage per each catalyst, under either dark or UV or VIS
834 irradiation. The present experimental conditions were adopted for each experiment: $T=30^{\circ}C$, $C_{IBU,0}=12.4 mg$
835 L^{-1} , $\rho_B=0.07 g L^{-1}$, reaction time of 300 min.

836

837 Qualitatively, the best catalyst in terms of the overall removal of ibuprofen under visible irradiation
 838 is Fe0.5. Nevertheless, it is worth to be mentioned that during the photodegradation experiment, both
 839 adsorption and chemical reactions occur. For this reason, we have modified the aforementioned
 840 simplified mode, including a degradation step, described by the following rate expression.

$$841 \quad r_{DEG} = k_{DEG} \cdot c_{IBU^*} \quad (5)$$

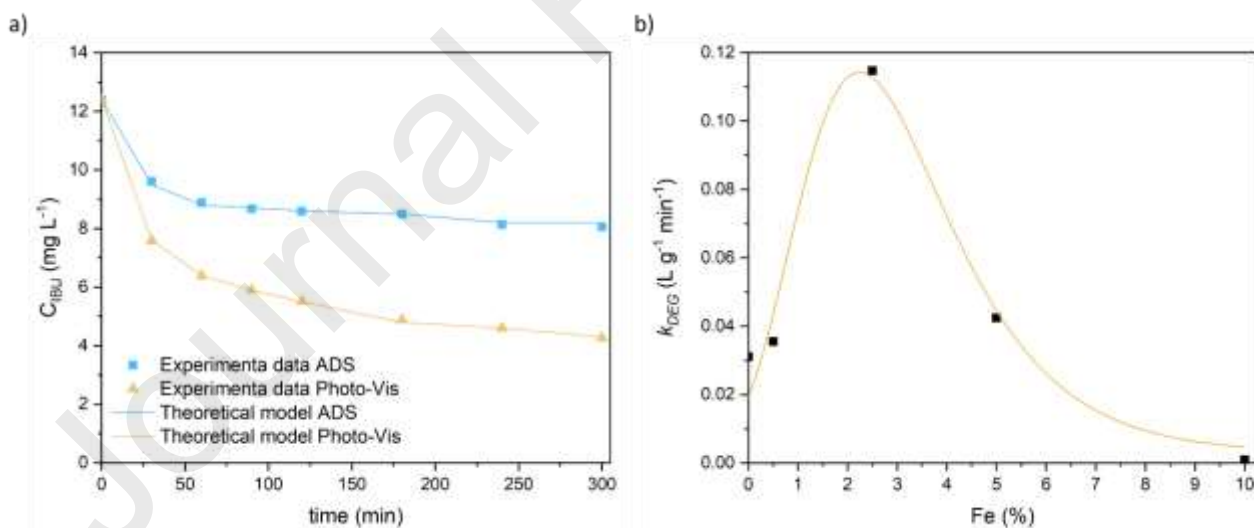
842 It must be pointed out, that we are implicitly assuming that photodegradation occurs in series to the
 843 adsorption process, while it could occur also in parallel. This simplification can be considered
 844 reasonable as we are interested in retrieving the order of magnitude of the kinetic constants to compare
 845 the activity of each catalyst. Further, the ibuprofen photolysis in the absence of the catalyst was
 846 neglected as proved experimentally [113].

847 Thus, the mass balance equation needs to be further modified, supposing that IBU* undergoes
 848 photodegradation, Eq. 6.

$$849 \quad \frac{dc_{IBU^*}}{dt} = (+r_{ADS} - r_{DEG}) \rho_B \quad (6)$$

850 In detail, Fig. 12a shows an example of data fit for the Fe2.5 catalyst: as revealed, a good fit was
 851 obtained both for adsorption and photodegradation experiments under visible irradiation. The results
 852 of the parameter estimation activities for all catalysts are reported in Table 4 and Fig. 12b.

853



854

855 **Fig. 12.** a) Example of data fit on the kinetic data measured using the Fe2.5 catalyst for both dark and
 856 photodegradation experiments under visible irradiation ($T=30^{\circ}C$, $C_{IBU,0}= 12.4 mg L^{-1}$, $\rho_B= 0.07 g L^{-1}$). Symbols represent the experimental data and lines the calculated profiles. b) Plot of the degradation
 857 constant as a function of Fe loading.
 858

859

860 Fig. 12b clearly illustrates that Fe2.5 is the best performing photocatalyst as it shows the highest
 861 degradation constant.

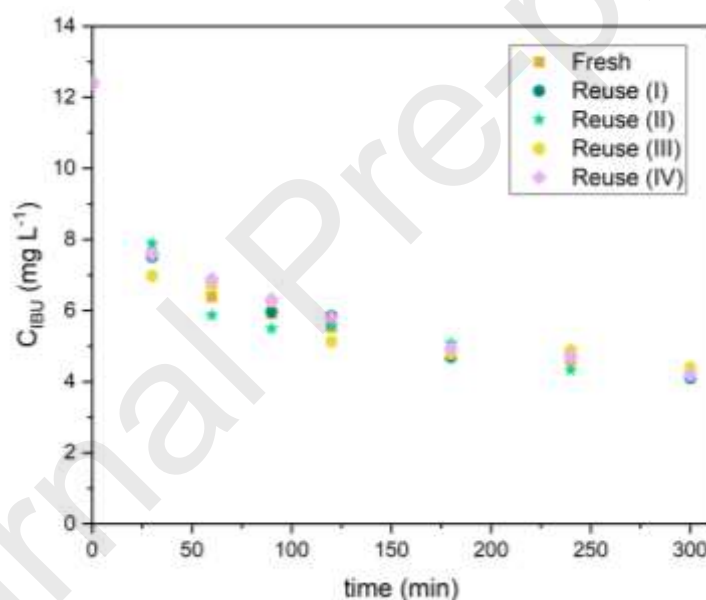
862 Raman and XPS findings revealed (*vide supra*) that Fe2.5 has the highest content of Ce³⁺ and defects-
 863 related oxygen vacancies. Raman results also suggested the highest charge delocalization for Fe2.5
 864 (Fig. 4).

865 As extensively presented in the literature, the presence of oxygen vacancies can lead to increased
 866 photo-oxidation performance as they constitute trapping centres for photogenerated electrons,
 867 effectively limiting the rate of electron-hole recombination [124,125].

868 Finally, by comparing the band gap values with the degradation kinetic constant, it is possible to see
 869 that the activity passes through a maximum, as classically reported in the literature [126], thus it is
 870 possible to define an optimal band gap value of 2.79 eV (see Table 3).

871 For the mentioned reasons, it is interesting to further investigate the performance of Fe2.5 in terms
 872 of stability. Thus, reuse experiments were conducted under visible light irradiation. As reported in
 873 Fig. 13, the activity of Fe2.5 did not change after four cycles of photodegradation tests, demonstrating
 874 good stability, thus a potential use in continuous apparatus, allowing the scale-up of the process from
 875 batch to continuous operation.

876



877

878 **Fig. 13** – Reuse of the photocatalyst Fe2.5 in four photodegradation tests. The present experimental
 879 conditions were adopted for each experiment: $T = 30^{\circ}\text{C}$, $C_{\text{IBU},0} = 12.4 \text{ mg L}^{-1}$, $\rho_{\text{B}} = 0.07 \text{ g L}^{-1}$, reaction
 880 time of 300 min.

881

882 To further ascertain the stability of the catalyst, some relevant characterizations were conducted on
 883 the Fe2.5 sample after the reaction. The obtained results clearly showed no substantial changes in the
 884 nanocatalyst properties after the catalytic test. Indeed, the XRD diffraction pattern of the Fe2.5_post
 885 reaction (Fig SI.15a) shows the occurrence of the fluorite phase without any significant distortion of
 886 the structure.

887 Thermogravimetric analysis (Fig. SI.15b) analysis reports only a small variation on the region of
 888 chemisorbed water compared with the pristine catalyst, indicating that no organic by-products were
 889 adsorbed on the catalyst surface.

890 In accordance with XRD analysis, electron diffraction (see figure Fig. SI.15c) confirms that the cubic
891 fluorite structure of the catalyst is retained after the catalytic tests and that no secondary crystalline
892 phases are formed. The presence of Fe in the nanostructures is recognized by EDX analysis, with
893 comparable EDX spectra (Fig. SI.15d) before and after the catalytic reaction. Moreover, based on
894 HR-TEM images (Fig.SI.15e), it is interesting to notice that the catalytic reaction does not induce
895 morphological or structural changes on the nanoparticles, which also preserve their characteristic size
896 of approximately 5 nm.

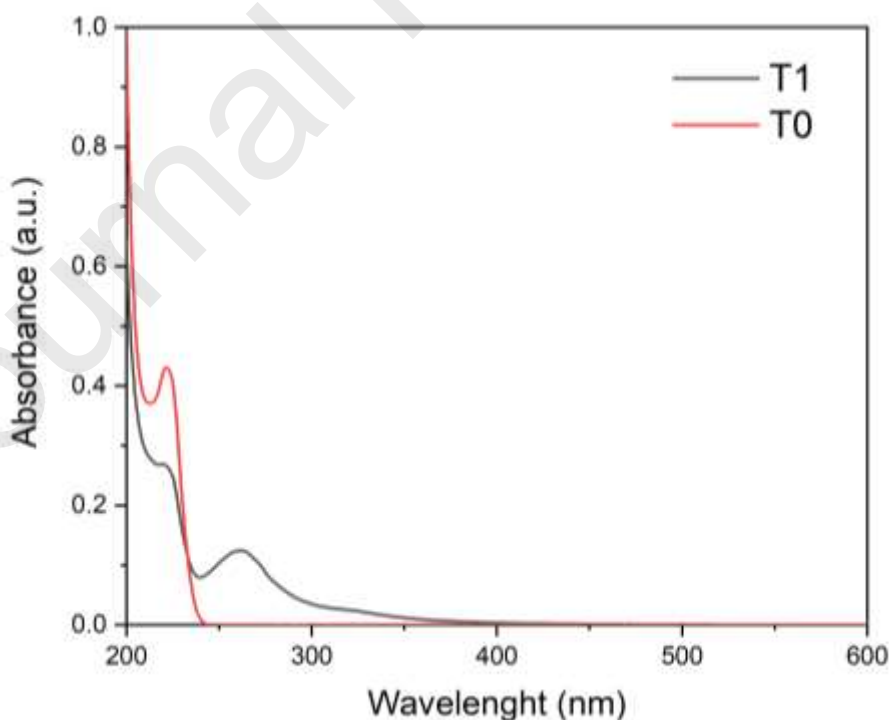
897 Finally, XPS analysis performed on the sample post-catalysis shows first no contamination. Ce3d
898 spectra obtained before and after photocatalysis are quite similar (Fig. SI.16a). A minor change of the
899 v component (at 882.6 eV) can be seen, meaning that the Ce^{4+} contribution may have increased
900 slightly. However, that variation is so small that it hardly affects its 3d3/2 counterpart. Consequently,
901 in accordance with the other analyses, the XPS study confirms that the photocatalytic tests did not
902 induce significant changes in the photocatalyst.

903

904 3.4 Identification of degradation by-products

905 A further objective of this work was the identification of possible degradation products.

906 The samples collected during the kinetic experiments were analysed via UV-Vis spectrophotometry
907 and allowed the identification of an absorbance peak characteristic of an unknown chemical
908 compound, at the wavelength $\lambda=260$ nm. Fig. 14 shows an example of the absorbance spectrum
909 obtained at two different times, collected during a kinetic run conducted imposing the following
910 reaction conditions: catalyst Fe_{2.5}, $T=30^{\circ}C$, $C_{IBU,0}=12.4mg/L$, $\rho_B=0.07 g/L$. In particular, the T0 sample
911 was collected at time=0, while T1 at time = 30 min of reaction time.



912

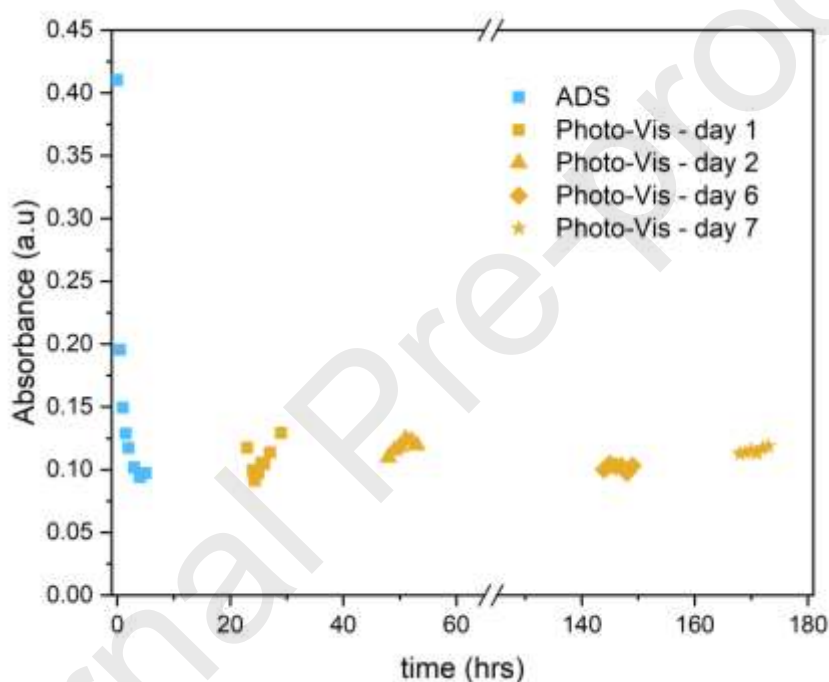
913 **Fig. 14:** Comparison between absorbance spectra of samples T0 (sample collected at time = 0) and T1
914 (sample collected at time = 30 min), collected during a kinetic run conducted imposing the following
915 reaction conditions: catalyst Fe_{2.5}, $T=30^{\circ}C$, $C_{IBU,0}=12.4mg L^{-1}$, $\rho_B=0.07 g L^{-1}$.

916

917 As Fig. 14 reveals, the peak at $\lambda=260$ nm is not present when analysing ibuprofen in water solution
 918 (T0). The additional peak was detected in every photodegradation test but with an absorbance variable
 919 with the experimental time. In particular, the absorbance increases as the reaction proceeds,
 920 simultaneously with the decrease of the absorbance measured at $\lambda=220$ nm.

921 Thus, it is important to carry out a more sophisticated analysis to understand the nature of the chemical
 922 compounds present during the photodegradation tests. The identification of the by-product generated
 923 by the reaction was conducted by performing an adsorption test and subsequent photodegradation.
 924 The samples were analysed using a UV-Vis spectrophotometer to monitor the absorbance peaks for
 925 ibuprofen and the by-products identified, further identified by LC-MS analysis.

926 The results obtained from the spectrophotometer analysis are shown in Fig. 15.



927

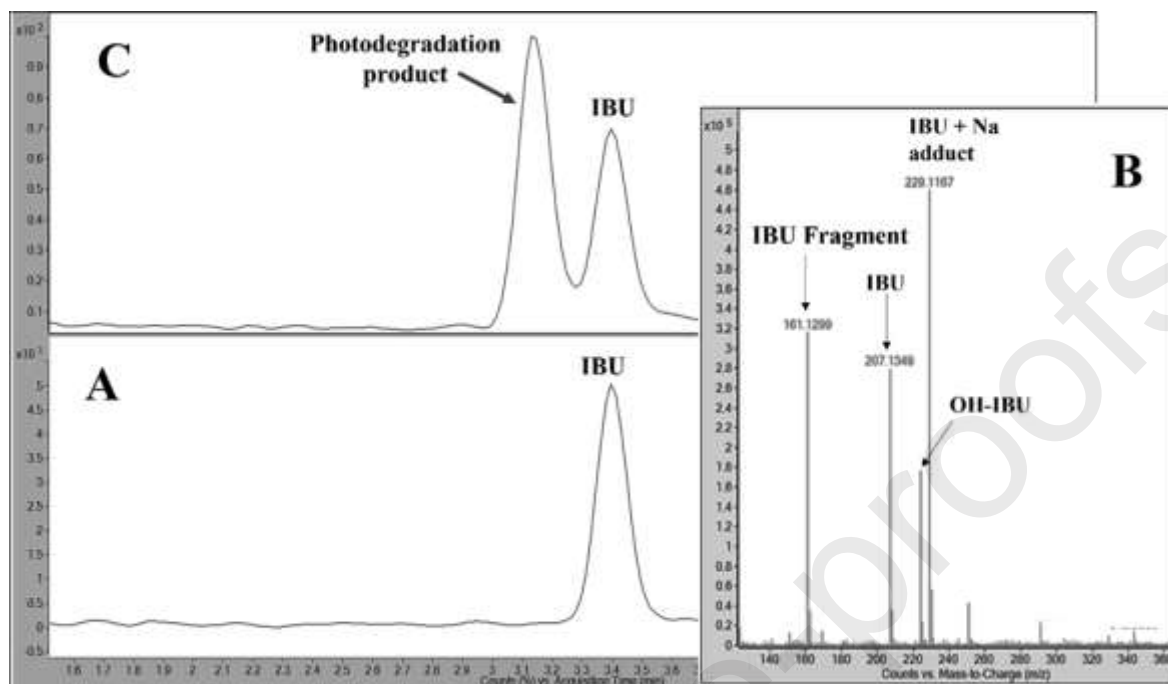
928 **Fig. 15:** Results obtained from spectrophotometer analyses. Experimental conditions: catalyst
 929 $\text{Fe}_{2.5}$, $T = 30^{\circ}\text{C}$, $C_{\text{IBU},0} = 12.4 \text{ mg L}^{-1}$, $\rho_{\text{B}} = 0.07 \text{ g L}^{-1}$.

930

931 From the results reported in Fig. 15, it is possible to note that in dark, the absorbance recorded at the
 932 wavelength of $\lambda=220$ nm decreases, due to a decrease of ibuprofen concentration in the liquid solution
 933 due to the related adsorption on the catalyst. Starting from the first day of photodegradation, the
 934 absorbance measured at $\lambda=220$ nm remains constant for 7 days of reaction. The observed trend could
 935 be explained by the formation of by-products, showing an absorption at the same wavelength as
 936 ibuprofen.

937 The identification of neo-formed by-products obtained from the ibuprofen photodegradation was also
 938 performed by LC-MS analysis. The MS analysis was preliminarily performed on the standard solution
 939 (T0) of ibuprofen to set up the chromatographic conditions and MS parameters. The ion current of
 940 the chromatographic peak (3.4 min, Fig. 16 panel A) detected in the mixture at T0 was assigned to
 941 the molecular ion ($\text{M}+\text{H}^+$) of ibuprofen (IBU) at 207.1 m/z in addition to the hydroxylated form

942 (223.1 m/z) and the sodium adduct species (229.1 m/z) (Fig. 16, exploded panel B). Interestingly, an
 943 MS signal at 161.1 m/z was detected in the standard mixture (T0) due to the residue fragmentation
 944 occurring within the ESI source causing the loss of formic acid from the starting molecule.

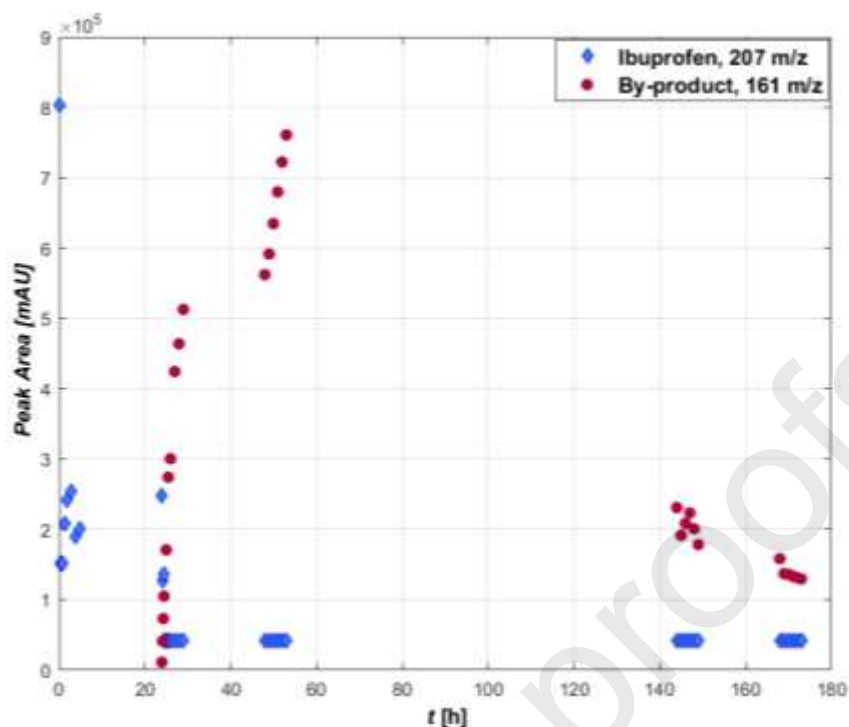


945

946 **Fig. 16:** Total ion current (TIC) chromatogram of the standard mixture (T0) (panel A) and the relative
 947 MS spectrum of peak at 3.4 min (panel B). TIC chromatogram of the mixture at the reaction time of
 948 24 h (T10) (panel C).

949

950 Then, each aliquot analysed via UV-VIS spectrophotometry was further analysed via LC-TOF, to
 951 monitor the formation of the main by-products along the whole photodegradation experiment. The
 952 results reported in Fig. 17 demonstrated a marked decrease in ibuprofen after the first 30 min of
 953 reaction time (adsorption phase) followed by small variations of the peak area up to T10, Fig. 16
 954 panel C, (roughly 24 h of reaction) till reaching a constant value of roughly the 5% of the initial value
 955 (T0 sample) (Fig. 17).



956

957 **Fig. 17:** Monitoring of kinetics of ibuprofen degradation and formation of by-products by mass
 958 spectrometry analysis.

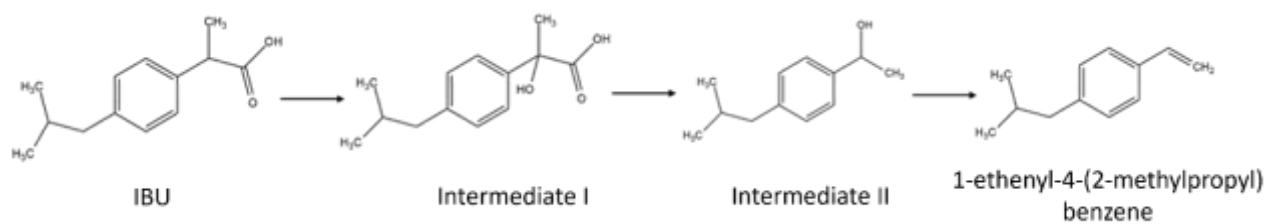
959

960 The occurrence of neo-formed by-product started to appear at T8, corresponding to the start of the
 961 photodegradation step, displaying a chromatographic peak at a retention time shift of 0.3 min (3.1
 962 min) from the intact ibuprofen. The identification of by-product at 161 m/z assigned to the 1-ethenyl-
 963 4-(2-methylpropyl)benzene (C₁₂H₁₆) was confirmed by GC-MS analysis where the fragments
 964 originated from the electron impact (IE) source were compared to the NIST database (Fig. SI.17).

965 Furthermore, a significant increase of by-product was observed up T23 (roughly after 2 days) where
 966 it reached the highest concentration. Then, after the second day, a drastic reduction of the product
 967 was recorded.

968 The presence of the mentioned by-product was already reported in the literature as possible
 969 intermediate in a more complex mechanism involving several degradation species. In particular, Rao
 970 et al., [127], reported that 1-ethenyl-4-(2-methylpropyl)benzene is produced by the dehydration and
 971 decomposition of two intermediates as described in Scheme 2. In the present work, the mentioned
 972 two intermediates were not detected, probably because the related reactions of formation and
 973 disappearance are relatively fast in the presence of Fe_{2.5} catalyst.

974



975

976 **Scheme 2:** Possible degradation pathway of IBU with formation of by-product detected in the present
977 study.

978

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981 **Conclusions**

982 Meticulous synthesis strategies for the preparation of robust and efficient photocatalysts are at the
983 forefront of rapidly evolving fields, such as the removal of emerging contaminants in visible light-
984 activated photocatalytic processes.

985 To avoid a trial and error approach we have selected a reliable and valuable bottom-up approach, the
986 reverse micelle method, that allows to closely control the crystallographic and electronic properties
987 of the ceria nanostructured photocatalysts. With controlled precipitation within the micelle nano-
988 reactors, undoped and iron-substituted (0.50-10 mol %) ceria nanoparticles consisting of single
989 crystals were successfully prepared. The sample with the highest iron content is the only one that
990 shows the presence of oligomeric species on the surface while the other samples show an effective
991 inclusion of substitutional iron in the ceria lattice.

992 The effect of the different iron content in the various samples revealed the role of iron heteroatoms
993 in the delicate balance between adsorption and relative photodegradation of ibuprofen. Light was
994 shed on the relationship between composition-structure and activity through numerous catalytic
995 experiments, conducted both in the dark and under UV or visible irradiation. The results were
996 supported by a combination of advanced characterisation techniques and DFT calculations, showing
997 that the doping of the CeO₂(111) surface with a substitutional Fe atom i) causes a decrease in the
998 band gap of the system, improving the catalytic performance of the catalyst, ii) favours the formation
999 of vacant sites (VO_x) when the oxygen atoms are directly coordinated with the dopant or very close
1000 to it, iii) favours the IBU adsorption both in the stoichiometric and reduced model. Despite the
1001 presence of iron and vacancies being beneficial for ibuprofen adsorption, experimentally we find a
1002 non-linear trend of the adsorption capacity with the iron content. The latter was explained by
1003 measuring the z-potential of each sample, finding that adsorption is more efficient when the catalyst
1004 surface is positively charged. The combination of this effect and the non-linear trend of ibuprofen
1005 adsorption with Fe content leads to the identification of an optimal composition of the photocatalyst,
1006 namely 2.5 mol% Fe doped CeO₂. The mentioned material showed good stability along 4 cycles of
1007 re-use experiments, demonstrating to be a promising material for a future application in flow.

1008 Finally, GC-MS and HPLC-MS analyses were conducted on the samples collected in a dedicated
1009 experiment conducted with Fe2.5 catalyst under visible irradiation, allowing the identification of 1-
1010 ethenyl-4-(2-methylpropyl)benzene as the main by-product.

1011

1012

1013 **List of abbreviations**

IBU *Ibuprofen* 1014

(*) *Free site* 1015 **List of symbols**

(*IBU*) *Ibuprofen*

(*IBU**) *Ibuprofen adsorbed into the solid*

AOPs *Advanced oxidation processes*

NSAIDs *Non-steroidal anti-inflammatory drugs*

$C_{IBU,0}$ *ibuprofen initial concentration* ($mg L^{-1}$)

C_{IBU} *concentration of ibuprofen at t time* ($mg L^{-1}$)

C_{IBU^*} *concentration of adsorbed ibuprofen* ($mg L^{-1}$)

k_{ADS} *adsorption kinetic constant* ($L (g min)^{-1}$)

k_{DEG} *desorption kinetic constant* ($L (g min)^{-1}$)

K_{eqADS} *adsorption constant* (-)

qt *adsorbed amount* ($mg g^{-1}$)

r_{ADS} *adsorption rate* ($mg g^{-1} min^{-1}$)

r_{DEG} *desorption rate* ($mg g^{-1} min^{-1}$)

t *time* (min)

T *temperature* ($^{\circ}C$)

1016

1017 ***Greek symbol***

ρ_B *sorbent bulk density* (g L^{-1})

1018

1019 **Acknowledgments**

1020 Miss Sonia Romano is cordially acknowledged for the experimental and numerical support given for
1021 the realization of the present study.

1022

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1402 Highlights

- 1403 • Reverse micelle synthesis fosters Fe doping of nanocrystalline CeO₂
1404 • 2.5 mol % iron-doped ceria leads to high charge delocalization
1405 • Efficient visible-light photodegradation of ibuprofen with 2.5 mol % Fe-CeO₂
1406 • Substitutional Fe favours the oxygen vacancies formation and ibuprofen adsorption.
1407 • The by-product of the ibuprofen degradation is 1-ethenyl-4-(2-methylpropyl)benzene.

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