Photocatalytic properties of TiO₂ and Fe-doped TiO₂ prepared by metal organic framework-mediated synthesis

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ABSTRACT

The Ti-containing metal organic framework (MOF) MIL-125 has been used as sacrificial precursor to obtain TiO₂ materials through the MOF-mediated synthesis route. In this study, Fe³⁺ was deposited on the surface of MIL-125 after its hydrothermal synthesis. Targeted Fe-doped titania photocatalysts were prepared through the direct calcination in air of Fe/MIL-125 crystals and/or by using a two-step method, including carbonization in inert atmosphere followed by calcination in air. The relationship between the synthesis conditions and the properties of the Fe-doped titania nanopowders, such as Fe content, porosity, phase composition and particle size was investigated. From elemental mapping, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, UV–Vis absorption spectroscopy and photoluminescence emission spectra, the presence of highly dispersed Fe³⁺ ions incorporated into the TiO₂ crystal lattice was confirmed, which led to a significant red shift of photoresponse towards visible light and reduced the recombination rate of electron-hole pairs at low iron content. By varying the pre-carbonization temperature, both crystal size and phase composition in the final materials were modulated. The performance of Fe-doped titania materials in photocatalytic water-splitting was tested for hydrogen evolution. Optimal photocatalytic performance was found at 0.15 and 0.5 *wt. %* iron concentration and exceeded those of non-doped titania and commercial anatase both under visible and UV light irradiation, respectively, and among the highest reported in literature for these systems.

Keywords: Metal Organic Frameworks, MOF-mediated synthesis, Fe-doped titania, H₂ production, water splitting

1. Introduction

The future of energy supply depends on the development of new utilization strategies for sustainable sources (i.e. the efficient valorization of solar light). The production of hydrogen is considered one of the most promising solutions, having no carbon footprint and delivering a CO₂-free energy cycle.[1] This strategy can be pursued by artificial photosynthesis (APS), where light-harvesting, charge generation and separation and catalytic reactions processes take place. Owing to its excellent photostability, high resistance to corrosion, nontoxicity and low production cost, TiO₂ (titania) remains the most promising material for photocatalytic H₂ production among the various oxide photocatalyst.[2, 3] However, its applicability under solar irradiation is limited by the wide band gap energy (anatase TiO₂, $E_g = 3.2$ eV) and the high recombination rate of the photoexcited electron-hole pairs.[4, 5] Different approaches have been followed to overcome these issues, such as TiO₂ surface modification introducing defects, adding oxygen vacancies and/or Ti³⁺ by different treatment methods [6], phase structure modulation of TiO₂ (ratio of anatase and rutile) [7, 8] and doping TiO₂ with different transition metallic/non-metallic elements [9-12]. Regarding the latest approach, Fe has been widely reported to be the most promising for this purpose [3, 12-19] and has shown an outstanding behaviour, under both UV and visible light irradiation, for degradation of environmental pollutants [13, 15-17], CO₂ reduction [20], NO_x removal [21] and, more recently, in water splitting for hydrogen production [3, 12, 18, 19]. Fe³⁺ ions enhance the generation of shallow charge-trapping centers in the TiO₂ lattices, reducing the electron-hole recombination rate. Therefore, incorporating iron ions into the TiO₂ crystal lattice provides a photocatalyst not only with excitability by visible light, but also with lower recombination rate of electrons and holes. However, the nature and structure of Fe-doped titania photocatalysts are very complex, and the photocatalytic performance of these materials strongly depends on the synthesis method, concentration of iron in the photocatalysts and on the iron precursor itself. The optimal iron

concentration in Fe-doped titania photocatalysts reported for water splitting is mostly found between 0.1 and 1 wt. % [4, 13, 21, 22], although Sun *et al.* [12] reported active photocatalysts with an iron concentration of 4 wt. %. This might be explained by the fact that different synthesis methods may accommodate the iron ions in distinctive positions in the TiO₂ crystal structure. The most widely used synthesis methods for the preparation of Fe-doped TiO₂ materials with high photocatalytic activities include sol-gel and solvothermal techniques [12, 13, 18], co-deposition [17, 23] and, more recently, microwave hydrothermal methods [19]. Nevertheless, these synthesis methods usually require multiple steps and a precise control of the preparation conditions. In fact, the solid-state synthesis of TiO₂ still remains a challenge in terms of phase composition, porosity, particle size, morphology and, in general, the nanoscale synthesis of metal oxides (MOs) particles using a simple and controllable method.

In this regard, significant attention is now being directed towards the use of metal-organic frameworks (MOFs) as sacrificial precursors and templates, offering high surface area, dispersion, and long-range ordering, giving exceptional opportunities to synthesize diverse metal oxide morphologies by using different thermal treatment conditions. The preparation of MOs using MOFs as solid precursors involves the use of the MOF-mediated synthesis route (MOFMS), which implies the thermal decomposition of the MOF under controlled atmosphere [24, 25]. Porous anatase TiO₂ prepared by direct calcination of MIL-125(Ti) has been used as an anode material for lithium-ion battery applications [26, 27]. Using a similar strategy, Khaletskaya *et al.* [28] reported the preparation of gold/titania photocatalysts for CO₂ reduction prepared by direct calcination of gold supported on NH₂-MIL-125 nanocrystals. On the other hand, pyrolysis of MIL-125(Ti) under inert atmosphere results in TiO_x/C composites which have been used for the oxidation of dibenzothiophene [29] and for the photodegradation of methylene blue in aqueous solutions [30].

Herein, we report the physicochemical and photocatalytic properties of Fe-doped titania prepared by using the MOFMS technique, either using direct calcination or carbonization under inert conditions followed by calcination in air of Fe supported on MIL-125(Ti). The effect of iron doping concentration and thermal treatment conditions of Fe-doped titania for photocatalytic water splitting were analysed, with special emphasis on their performance under visible light irradiation. The novelty of this work arises from the versatility of using the MOFMS route to tune the physicochemical properties of titania crystallites such as porosity, particle size, surface composition and phase structure (ratio of anatase and rutile phase), which can be extended for the synthesis of other metal-doped TiO₂/MOs using MOFs as solid precursors.

2. Experimental

2.1. Synthesis of MIL-125(Ti)

MIL-125 was synthesized by slightly modifying the method reported by Wang *et al.* [26] In a typical synthesis, 3.0 g terephthalic acid (98%, Sigma-Aldrich), 6 ml anhydrous methanol (99.8 %, Sigma-Aldrich), 54 ml anhydrous N,N-Dimethylformamide (99.8 %, Sigma-Aldrich) and 1.56 ml of Titanium (IV) isopropoxide (97 %, Sigma-Aldrich) were mixed under inert atmosphere. The mixture was then placed in a 125 ml teflon-lined autoclave, and heated at 150 °C for 24 h. Upon cooling down, the white suspension of MIL-125(Ti) was filtered and washed under stirring with 30 ml methanol for 1 h. The resulting solid was filtered and dried at 150 °C under vacuum for 3 h. The final product yield (weight %), related to the initial mass of the organic linker, was 40 wt. % for MIL-125(Ti).

2.2. Synthesis of the photocatalysts

Fe impregnation procedure: 1 g MIL-125(Ti) was dispersed in 20 ml methanol. The iron solution was prepared by adding the desired amount of Fe(NO₃)₃·9H₂O (99.999 %, Sigma-Aldrich) in 10 ml methanol to obtain 0.15 - 2 wt.% Fe dispersed on TiO₂ after calcination of the

impregnated samples. This iron solution was added drop wise to the MOF slurry and stirred for 24 h at 60 °C. The impregnated sample was dried in a rotary evaporator at 40 °C at a reduced pressure of 350 mbar. The resulting materials were dried at 80 °C overnight.

Calcination of MIL-125(Ti) and Fe/MIL-125(Ti): TiO₂ and Fe/TiO₂ powders were prepared following two different routes (see Scheme 1). The first one was the direct calcination of the impregnated Fe/MIL-125 nanocrystals and MIL-125(Ti) at 450 °C for 2 h (heating rate of 5 °C/min) in air flow (150 cm³ STP/min). A second route consisted of a two-step thermal treatment method, including carbonization in inert atmosphere followed by calcination in air. Accordingly, Fe-impregnated MIL-125(Ti) was firstly carbonized under continuous N₂ (purity 99.999%, Air Liquide) flow (150 cm³ STP/min) in a tubular furnace at 500, 700 and 900 °C at a heating rate of 2 °C/min and maintained for 4 h. The carbonized samples were cooled inside the furnace under N₂ flow and then calcined at 450 °C for 2 h under 150 cm³ STP/min of air. Commercially available TiO₂ anatase (99 %, Sigma Aldrich) has been used for comparative studies. Scheme 1 summarizes the preparation procedure and notation of the photocatalysts.

Scheme 1. Preparation procedure and notation of the photocatalysts.

2.3. Characterization

Thermogravimetric Analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA851e system. 10-15 mg of sample was heated from room temperature up to 700 °C at a heating rate of 5 °C/min in an air flow of 100 cm³_{STP} min⁻¹.

N₂ physisorption isotherms at -196 °C were performed in a Tristar II 3020 model equipment of Micromeritics Instruments. Prior to the experiments, the samples were degassed overnight at 150 °C. From the N₂ adsorption isotherm the BET area (S_{BET}) was calculated applying the BET equation and the micropore volume (V_{micro}) was obtained using the Dubinin-Radushkevich method [31]. The mesopore volume (V_{mes}) was calculated as the difference between the adsorbed volume at a relative pressure of 0.95 and the micropore volume (V_{micro}). Finally, the Barrett, Joyner and Halenda (BJH) method, applied to N₂ adsorption data using the adsorption branch, was used for assessment of the mesopore size distribution [32].

The X-Ray Diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using monochromatic Co- $K\alpha$ radiation ($\lambda = 0.179026$ nm). The average particle size of TiO₂ in the catalysts was estimated from the Debye-Scherrer equation applied to the most intense (101) and (110) diffractions ($2\theta = 29.5^\circ$ and 32.0°) for anatase and rutile, respectively, using a shape factor $K = 0.9$. The phase compositions of the photocatalysts were semi-quantitatively estimated using the reference intensity ratio (RIR) method and the Bruker Eva S-Q software. A single reflection was used per phase, with the highest intensities ((101) at 29° for anatase (PDF01-0562) and (101) at 32° for rutile (PDF0-1292); absorption correction was omitted, and the results were adjusted so that the sum of $X_{\text{phase}} = 1$.

For elemental analysis, the Fe-doped TiO₂ samples were analysed by Mikroanalytisches Laboratorium KOLBE (Mülheim an der Ruhr, Germany).

X-ray photoelectron spectroscopy (XPS) was carried out on a $K\text{-}\alpha$ Thermo Fisher Scientific Spectrometer using monochromatic Al- K radiation at room temperature and chamber pressure of

about 10^{-8} mbar. For the analysis of the XPS data, the binding energy of carbon (*1s*) was set at 284.5 eV and used as reference while the deconvolution of the peaks was done using Gaussian-Lorentzian curves and a Shirley type background line. The squared difference between experimental and calculated curves was minimized by least-squares.

UV-Vis diffuse reflectance spectra were obtained using a Perkin-Elmer Lambda 40 spectrophotometer. Dry powder samples were loaded in quartz cell and the spectra were collected in the 200-700 nm wavelength range. BaSO₄ was used as a blank. Photoluminescence (PL) emission spectra were measured on an Edinburgh Instruments FLS920 at room temperature under the excitation light at 250 nm. X-Ray absorption spectroscopy (XAS) spectroscopy was measured at the Fe K-edge on beamline BM23 at ESRF, Grenoble, France. Measurements were recorded in the fluorescence mode.

Transmission electron microscopy (TEM) images were obtained using a FEI Talos F200X transmission electron microscope at an accelerating voltage of 200 kV. To determine the dispersion of elements present in the synthesized materials, energy dispersive X-ray (EDX) elemental mapping was also analyzed. The particle size distributions were obtained by counting between 100 and 200 particles on each sample.

2.4. Photocatalytic hydrogen evolution reaction test

The set up used for photocatalytic reaction tests has been described in detail in our previous work [33, 34]. It consisted of a custom-made stirred Pyrex-glass reactor with a 42.1 cm³ capacity, an analysis system comprising a light illuminating source (500 W Xe/Hg lamp (66983, Newport)), a gas chromatography (CP 9001 gas chromatograph (Chrompack)) and a KSLA gas pump. The pump was used to ensure an adequate mixing of gases in the stainless steel tubes and the headspace of the reactor (5 mL/min continuous operation). A water circulation facility is applied to keep the reactor temperature constant.. The hydrogen produced in 24 h was monitored

every hour by the GC equipped with a thermal conductivity detector and a molecular sieve 5A column. Argon was used as carrier gas at a flow rate of 30 cm³/min.

In a typical experiment, 50 mg of fresh photocatalyst was suspended in 17.5 mL distilled water and 7.5 mL methanol, used as a hole scavenger [19, 22, 35, 36]. The suspension was then placed in the reactor and an argon flow of 30 mL/min was applied until the system was free of oxygen, monitored by the GC analysis. Subsequently, the UV/Vis lamp was switched on, and the hydrogen evolution was followed by GC analysis. All photocatalytic experiments were carried out at 30 °C monitored by a thermocouple. Blank experiments revealed that no hydrogen was produced without catalyst and light irradiation under detection limits.

3. Results and discussion

3.1. Characterization of the photocatalysts

MIL-125 is an ideal candidate as support and sacrificial precursor to prepare porous TiO₂ after a simple calcination step [26, 27]. The calcination conditions such as temperature, heating rate and holding time are key parameters to control the porosity and chemical phase of the resulting metal oxides. Therefore, before conversion of Fe/MIL-125 samples into Fe/TiO₂ bulk oxides, it was of primary importance to study their thermal decomposition behaviour under air. The TGA profiles in air for MIL-125 and selected Fe/MIL-125 samples with 0.2, 0.3 and 0.8 wt. % Fe are shown in Figure 1. MIL-125 is stable in air up to 400 °C and is fully converted to TiO₂ at temperatures above 480 °C. The residual weight after treatment at 700 °C is 41 %, which results in a high yield to TiO₂. After adding iron to MIL-125, the oxidation resistance of the impregnated samples is reduced due to the iron oxide centers, which are able to catalyze the gasification of the MOF. The calcination of these samples resulted in Fe doped titania photocatalysts with ca. 0.5, 0.75 and 1.2 wt. % Fe (Table 2). The Fe/MIL-125 impregnated sample was carbonized at different temperatures, namely 500, 700 and 900 °C, for 4 h under continuous N₂ flow. In general, during

the carbonization process of MOFs at relatively high temperatures, the organic linker decomposes, causing collapse of the MOF structure, and partially pyrolyzes releasing products like CO, CO₂ and H₂O, thus resulting in M@C (M= metal) composites [24, 29]. The yield of this treatment, defined as the weight of the carbonized MIL-125 MOF relative to the raw material, on a dry basis, was 53, 51 and 48 % for Ti@C-500, -700 and -900, respectively, indicating a deeper devolatilization of the carbonaceous precursor with the carbonization temperature. Furthermore, an increase of carbonization temperature may produce a certain ordering of the carbon structure, thus increasing the oxidation onset temperature. The TGA profiles of the Ti@C-based samples are depicted in Figure 1b. Indeed, the most oxidation resistant Ti@C-based sample is the one carbonized at 900 °C, which oxidizes significantly above 400 °C (Figure 1b). According to these results, and as pointed out in Section 2, the impregnated MOF and the Ti@C-based samples were all calcined in air at 450 °C for 2 h in order to get rid of the major part of the residual organic linker and carbon, and to reach an optimum between porosity, crystallinity and anatase phase content of the resulting TiO₂. The elemental analysis performed on these samples confirmed that after calcination the bulk oxide samples did not present any carbon.

Figure 1. TGA patterns of MIL-125 and $x\text{Fe}/\text{MIL-125}(\text{Ti})$ ($x = 0.2, 0.3$ and $1 \text{ wt. \% Fe}$) samples (a) and Ti@C (solid line) and Fe-Ti@C (dashed line) samples (b).

Figure 2 shows N₂ adsorption–desorption isotherms for MIL-125 (Fig. 2a), for the bare TiO₂ and Fe-doped titania samples prepared by the one-step calcination process (Fig. 2a) and for the Fe-Ti@C-T composites (Fig. 2b) and 0.5Fe/TiO₂-T photocatalysts prepared by the two-step process (Fig. 2b). Table 1 summarizes the textural parameters, derived from N₂ adsorption–desorption isotherms. The isotherm for MIL-125 matches well with type I classified by IUPAC, characteristic of microporous materials with some contribution of mesoporosity. After calcination, the shape of the isotherms reveals that the increase in iron content from 0 to 2 wt. % Fe causes a widening of the porous structure of the bulk oxide, with a larger hysteresis loop at relative pressures between 0.5-0.9. The bare photocatalyst, 0Fe/TiO₂, presents a H2 hysteresis loop, often associated to pores with narrow necks and wide bodies, however H4 type hysteresis loops can be observed at medium/high relative pressures for Fe-doped TiO₂ samples, related to narrow slit-like pores [37]. The commercial TiO₂ anatase presents the lowest adsorption of N₂.

Figure 2. Nitrogen adsorption-desorption isotherms at -196 °C of MIL-125(Ti), bare TiO₂ and Fe-doped titania by the direct calcination process (0.5, 0.75 and 2 wt. % Fe) (a) and Fe-Ti@C composites (solid line) and 0.5Fe/TiO₂-T samples by the two-steps process (dash line) (b).

Likewise, the N₂ physisorption isotherms for the Fe-Ti@C composites and the corresponding Fe-doped titania samples (0.5 wt.% Fe) obtained after carbonization followed by calcination of

0.2Fe/MIL-125 is attributed to slit-shaped pores, and the type I adsorption behaviour typical for microporous materials. Interestingly, higher carbonization temperatures result in Ti@C composites with a higher amount of N₂ adsorbed at low relative pressures, probably due to a greater extent of volatile matter released at higher temperatures. However, 0.5Fe/TiO₂-900 obtained after calcination of Fe-Ti@C-900 results in the sample with the lowest N₂ adsorbed at low relative pressure. In general, the BET areas values (S_{BET}) and the mesopore volume values (V_{mes}) vary from 72-157 m²/g and 0.108-0.263 cm³/g (Table 1), respectively, which are larger than reported Fe-doped titania materials prepared by co-precipitation, hydrothermal and sol-gel processes[11, 17, 21, 22]. From the BJH pore size distributions (Figure S1), which is especially suited for assessment of mesopore size distribution, it is observed that the incorporation of iron to the titania (≤ 2 wt.%) by the MOFMS route produces a widening of its mesoporosity. As expected, increasing the iron content the BET (S_{BET}) surface area values decrease because of the pores partial blockage.

Table 1. Textural properties (from N₂ physisorption), and phase composition and particle size (from XRD) of the photocatalysts.

	N ₂ isotherm			XRD		
	S_{Total}^a (m ² /g)	V_{micro}^b (cm ³ /g)	V_{mes}^c (cm ³ /g)	Phase	Composition ^d / wt. %	Particle size / nm
TiO ₂ -Aldrich	3	0.001	0.003	Anatase	100	51.0
MIL-125(Ti)	1265	0.540	0.070	n.a. ^d	n.a.	n.a.
0Fe/TiO ₂	90	0.032	0.124	Anatase	100	8.8
0.5Fe/TiO ₂	125	0.044	0.220	Anatase	100	8.6
0.75Fe/TiO ₂	117	0.041	0.231	Anatase	100	8.8
1.2Fe/TiO ₂	102	0.037	0.215	Anatase	100	8.8
2Fe/TiO ₂	99	0.035	0.193	Anatase	100	9.7
0.5Fe/TiO ₂ -500	157	0.061	0.262	Anatase/Rutile	85.5/14.5	9.3/11.3
0.5Fe/TiO ₂ -700	134	0.045	0.263	Anatase/Rutile	51.1/48.9	13.5/17.4

0.5Fe/TiO ₂ -900	72	0.026	0.184	Anatase/Rutile	23.4/76.6	10.8/21.0
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^a BET area; ^b Micropore volume obtained by application of the Dubinin–Radushkevich equation applied to the N₂ isotherm; ^c Mesopore volume calculated as $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$; ^d n.a.: not applicable, ^e Semi-quantitative (S-Q) weight percentage of the phases obtained from XRD. PDF01-0562 for anatase and PDF01-1292 for rutile.

XRD patterns of the TiO₂-based samples are shown in Figure 3. Bare TiO₂ (Fig. 3a) exhibits the most intense diffraction at 29.5 ° resulting from the presence of the anatase (101) crystal plane, as reported for TiO₂ crystallites obtained by direct calcination of MIL-125 [26-28]. Similar diffraction XRD patterns are shown for the Fe-doped titania (0.4, 0.75 and 2 wt.% Fe) samples prepared by direct calcination. 0.5Fe/TiO₂-500 also exhibits anatase reflections as the predominant phase (Figure 3b), although rutile was also detected in lower concentration. The main diffraction at 37.0° is assigned to the (110) plane of rutile. The sample pre-carbonized at 700 °C, 0.5Fe/TiO₂-700, is characterized by a mixture of anatase and rutile of *ca.* 52 and 49 wt.%, respectively, whereas 0.5Fe/TiO₂-900 contained rutile as the predominant phase (about 77 wt.%) due to the high pre-carbonization temperature. The respective crystal phases are denoted by ‘A’ and ‘R’ for anatase and rutile, respectively. Interestingly, the XRD of all the Fe-doped titania samples do not show any reflection shifting or reflections characteristic of Fe₂O₃ oxide formation, as reported before for Fe supported on TiO₂ [38]. This fact points out the dominant effect of the mesoporous character of the bulk oxides and thus, the high dispersion of Fe species without significant change in TiO₂ structure [22].

In summary, direct calcination or combining carbonization followed by calcination allows to tune the chemical and structural nature of TiO₂. Thus, either anatase, rutile or a mixture of both phases can be obtained while a high porosity prevails. This can be attributed to a “templating” effect of the carbon matrix during the carbonization step at high temperatures, which avoids the collapse of the porous structure during the thermal treatment while tuning the chemical phase composition and crystal size of the metal oxide obtained after calcination. In addition to this, the MOF itself also offers an unique alternative as sacrificial template/precursor for the synthesis of

TiO₂ nanoclusters with high porosity and small particle size because its ordered crystalline structure, large internal surface area and small size of the Ti-oxo/hydroxo building units.

Figure 3. X-ray diffraction patterns of bare TiO₂ and Fe-doped titania (0.5, 0.75 and 2 wt.% Fe) samples prepared by direct calcination a), and Fe-doped titania (0.5 wt.% Fe) samples prepared by the two-step process. XRD pattern of Fe₂O₃ is also shown (uppermost pattern) b).

The average crystallite sizes of TiO₂ were determined by applying the Debye–Scherrer equation to the anatase (101) and rutile (110) diffraction peaks and the results are shown in Table 1. The average crystallite sizes of bare TiO₂ and Fe-doped TiO₂ were estimated to be ~8 nm and differences of crystallite size, caused by metal dopant concentration were insignificant. Similar crystallite sizes have been reported for microwave hydrothermal synthesis of Fe-doped titania [19]. However, the average TiO₂ crystallite size in the samples prepared by the two-step process shows a clear dependence on the pre-carbonization temperature, with larger particles being formed in the samples treated at higher temperatures. The effect on the size of the TiO₂ nanoparticles is more comprehensible from TEM analysis.

Figure 4a, b and c shows TEM images of synthesized Fe-Ti@C composites after pyrolysis at 500, 700 and 900 °C, respectively, of impregnated MIL-125 with 0.20 wt. % Fe. TEM images clearly show a successive increase in the average particle size of Ti nanoparticles as the temperature of pyrolysis increases, as revealed by the corresponding particle size distribution (PSD) histograms. The sample pyrolyzed at 500 °C shows very narrow particle size distribution with average particle size between 9 to 10 nm, in agreement with the XRD results and slightly higher to the resultant TiO₂ nanoparticles obtained after direct calcination conditions. Similarly, Fe-Ti@C-700 sample reveals crystallite sizes around 15-17 nm. However, the width of the PSD increases considerably at 900 °C and a population of irregular crystallites showing size around 28 nm and around 50 nm is visible. The pyrolysis of the samples before its calcination, allows to tune not only the chemical phase composition of the resultant metal oxide, but also the particle size distribution. EDX elemental mapping of 0.5Fe/TiO₂-500, -700 and -900, after pyrolysis and calcination (Figure S2) shows a high dispersion of Fe on the TiO₂, indicating that a high iron dispersion prevails after the two steps approach.

Figure 4. TEM images and PSD of Fe-Ti@C-500 (a, d), Fe-Ti@C-700 (b, e) and Fe-Ti@C-900 (c, f) composites.

TEM micrographs and EDX elemental maps of 0.5Fe/TiO₂ are also illustrated in Figure 5. Figure 5a-c reveals that crystallite sizes were homogeneous in all the samples. The EDX elemental maps and EDX pattern (Figure 5e-h and 5i, respectively) evidence that Ti, O and Fe were uniformly distributed within the catalyst samples.

Figure 5. TEM images (a, b, c), STEM-HAADF image (d) and EDX elemental maps showing the spatial distribution of Ti (e), Fe (f) and O (g) of 0.5Fe/TiO₂ sample.

After elucidating the chemical nature of bulk Ti present in the Fe/TiO₂-based materials from XRD, XPS was also used to characterize the surface chemistry of the photocatalysts. The main elements found on the surface of the Fe-doped titania samples were titanium and oxygen, with lower amount of iron as shown the representative survey spectrum for 0.5Fe/TiO₂ in Figure S3. In this spectrum, C_{1s} is an instrumental impurity. The spectra corresponding to Ti_{2p}, O_{1s} and Fe_{2p}, were collected. Figure 6 and 7 show some representative XPS spectra for the Ti_{2p}, O_{1s} and Fe_{2p} regions, respectively, whereas Table 2 summarizes the values of the binding energies and the mass surface and bulk concentrations obtained from XPS and ICP-OES analysis, respectively. As expected, the amount of surface iron increases as the iron content increases. In all cases, the mass surface concentrations from XPS are similar to the bulk Fe concentration (measured by ICP-OES) indicating a high dispersion of Fe in the TiO₂.

Figure 6a shows the XPS Ti_{2p} spectra of the different photocatalysts obtained by direct calcination of Fe/ML-125(Ti), and Figure 6b shows the deconvolution of the Ti_{2p} spectrum for 0Fe/TiO₂. The Ti_{2p} spectra of titanium display the characteristic doublet corresponding to the spin-orbit coupling ($2p_{3/2}$, $2p_{1/2}$), with the most intense peak of the Ti $2p_{3/2}$ component at a binding energy of about 458.6 eV assigned to Ti⁴⁺ in TiO₂ lattice, and a low intensity peak at *ca.* 460.2 eV, which is assigned to the presence of Ti³⁺ ions in Ti₂O₃ [7]. This points out that both TiO₂ and Ti₂O₃ are formed in the titania nanocrystals from the MOF-mediated synthesis route using MIL-125 as solid precursor. The presence of Ti³⁺ in the photocatalysts can be envisioned as an advantage for photocatalytic applications under visible light since the ionic radius of Ti³⁺ (0.81 Å) is closer to that of Fe³⁺ (0.79 Å) than Ti⁴⁺ (0.75 Å)[39]. Therefore, the presence of Ti³⁺ may enhance the isomorphic substitution of Ti³⁺ by Fe³⁺ during the catalyst synthesis¹³. The Ti³⁺/Ti⁴⁺ ratio in the surface of the photocatalysts has been calculated from the deconvolution of Ti_{2p} region for each component and the values are reported in Table 2.

A very interesting feature observed in the surface of the Fe-doped photocatalysts is that low iron content produces a slight decrease in the binding energy of the maxima of the Ti_{2p} peak with respect to the bare photocatalyst (Figure 6a and Table 2). This result can be explained either by the incorporation of Fe^{3+} ions in the anatase crystal structure substituting Ti^{4+} ions, or by the formation of mixed oxide structures with Fe (oxidation state Ti^{3+}) after doping with low Fe concentrations. However, increasing dopant concentration ($> 0.5wt. \%$) produces a slight shift of the peak to higher binding energies, decreasing the Ti^{3+}/Ti^{4+} ratio.

A gradual increase of the Ti^{3+}/Ti^{4+} ratio for the photocatalysts prepared by the two-step process from 0.33 for 0.5Fe/ TiO_2 -500 to 0.54 for 0.5Fe/ TiO_2 -900 was also observed (Table 2). The carbonization step performed on these samples, before calcination, may enhance the reducibility of Ti^{4+} to Ti^{3+} by electron donors such as H_2 , carbon or lattice oxygen in TiO_2 , which is favoured at higher carbonization temperatures.

The O_{1s} XPS region of the different photocatalysts obtained by direct calcination and by the two-step method are presented in Figure 6c and 6d, respectively. The O_{1s} spectrum is decomposed in two peaks; the peak at about 530 eV is associated with the binding energy of O^{2-} in TiO_2 lattices, whereas the shoulder at higher binding energy (532 eV) suggests the presence of a high amount of hydroxyl groups and chemisorbed water on the surface of TiO_2 [7, 13]. Figure 6c shows that the surface concentration of hydroxyl groups and chemisorbed water increases as the amount of surface iron increases, whereas 0.5Fe/ TiO_2 -T ($T = 500, 700$ and $900\text{ }^{\circ}C$) samples prepared by the two-step approach contain mostly surface hydroxyl groups and chemisorbed water probably from the pyrolysis of the MOF (Figure 6d), which partially may remain on the TiO_2 surface crystallites after the calcination step.

Figure 6. (a) XPS spectra of Ti_{2p} region for different Fe-doped titania photocatalysts, (b) representative XPS spectra of Ti_{2p} region for $0Fe/TiO_2$ showing the deconvolution and (c,d) XPS spectra of O_{1s} region for the photocatalysts prepared by direct calcination or the two-step method, respectively.

The chemical state of iron on the surface of the photocatalysts is presented in Figure 7. Figure 7a shows the XPS Fe_{2p} spectra of the photocatalyst with different iron contents and Figure 7b shows

the deconvolution of the Fe_{2p} spectrum for $0.75\text{Fe}/\text{TiO}_2$. The Fe_{2p} spectrum (Fig. 7b) displays the characteristic spin-coupled doublet ($2p_{3/2}$, $2p_{1/2}$) with an area ratio of 0.5 and a distance between peaks of 13.1 eV and two satellite peaks with binding energies approximately 8 eV higher than the corresponding Fe_{2p} peaks[40]. The component at a binding energy of about 710.8 eV is assigned to Fe^{3+} species whereas the component at lower binding energies, about 709.6 eV, is associated to the presence of Fe^{2+} species [18, 40]. Deconvolution of the Fe_{2p} spectra for all the photocatalysts showed that both Fe^{2+} and Fe^{3+} species were present on the surface of the photocatalyst. Table 2 summarizes the surface $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio calculated from the deconvolution of the curves. At low iron content a mixture of Fe^{3+} and Fe^{2+} is present, while the fraction of Fe^{3+} increases with increasing iron content from 62 and 65 wt. % for 0.5 and $0.75\text{Fe}/\text{TiO}_2$ to 70 % for $2\text{Fe}/\text{TiO}_2$.

Figure 7. XPS spectra (Fe_{2p} region) for Fe-doped titania (0.5, 0.75, 1.2 and 2 wt.% Fe) samples prepared by direct calcination and (b) representative XPS spectra of $0.75\text{Fe}/\text{TiO}_2$ showing the deconvolution.

Table 2 Ti and Fe mass surface and bulk concentrations (wt. %) obtained by XPS and ICP-OES analysis for the photocatalysts and values of binding energies (*BE*) for Fe_{2p3/2} and Ti_{2p3/2}.

XPS						ICP-OES			UV-vis DRS	H ₂ production rate ^a
Sample	Fe _{2p} / wt.	<i>BE</i> Fe _{2p3/2} / eV	Fe ³⁺ /Fe ²⁺	<i>BE</i> Ti _{2p3/2} / eV	Ti ³⁺ /Ti ⁴⁺	Ti / wt. %	Fe / wt. %	Fe/Ti %	TiO ₂ optical band gap (eV)	μmol g _{cat} ⁻¹ h ⁻¹
MIL-125(Ti)	n.d.	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	n.a.	3.6	32
TiO ₂ -Aldrich	n.d.	n.d.	n.a.	458.68	0.10	n.d.	n.d.	n.a.	3.39	19 / 0.25 ^b
0Fe/TiO ₂	0	n.a.	n.a.	458.28	0.18	n.a.	n.a.	n.a.	3.33	76 / 1.9 ^b
0.15Fe/TiO ₂	0.04	n.d.	n.d.	458.12	0.23	58.44	0.17	0.3	3.31	203
0.5Fe/TiO ₂	0.5	708.68	1.6	458.08	0.36	54.84	0.42	0.8	3.30	230 / 12 ^b
0.75Fe/TiO ₂	1.0	709.78	1.9	458.49	0.12	54.44	0.76	1.4	3.20	182
1.2Fe/TiO ₂	1.7	710.38	2.2	458.61	0.10	55.19	1.18	2.1	3.17	119 / 2.7 ^b
2Fe/TiO ₂	2.7	710.78	2.3	458.78	0.10	52.63	2.14	4.1	2.99	36
0.5Fe/TiO ₂ -500	0.4	710.28	n.d.	457.99	0.32	54.84	0.42	0.8	3.29	185
0.5Fe/TiO ₂ -700	0.3	709.78	n.d.	457.93	0.41	54.84	0.42	0.8	3.25	132/ 9 ^b
0.1Fe/TiO ₂ -700	0.04	n.d.	n.d.	458.12	0.47	58.44	0.17	0.3	3.27	215 / 23 ^b
0.5Fe/TiO ₂ -900	0.3	710.78	n.d.	457.66	0.54	54.84	0.42	0.8	3.25	44

^a H₂ production rate under UV light, ^b H₂ production rate under Vis light

XAS characterization of some representative samples was also performed to determine the local atomic structure of iron in the TiO₂ matrix. Figure 8a shows the fluorescent X-ray absorption near edge (XANES) spectra of α-Fe₂O₃ and Fe-doped titania samples with 0.5 and 2 wt.% iron content prepared by direct calcination method. At high dopant concentration (2 wt.% iron) the XANES spectrum is similar to that obtained for α-Fe₂O₃ (hematite), with the Fe K-edge position at about 7127 eV. However, for 0.5Fe/TiO₂ the edge position remains the same, confirming that iron remains in +3 oxidation state, but the shape of XANES spectrum changes. To gain more insight into the nature of the Fe species in TiO₂, the local structure around the Fe atoms was studied by extended X-ray absorption spectroscopy (EXAFS). The Fourier transform (FT) curves

of the Fe K^2 -weighted spectra for α -Fe₂O₃, 0.5Fe/TiO₂ and 2Fe/TiO₂ samples and of the Ti K^2 -weighted for TiO₂ are shown in Figure 8b. The FT curve of TiO₂ is characterized by two main peaks; the first peak at $R = 1.53$ Å is ascribed to Ti—O bond, which is more intense than the second peak at $R = 1.53$ Å associated to Ti—Ti bond. On the other hand, α -Fe₂O₃ is also characterized by two peaks; $R = 1.47$ Å attributed to Fe—O bond, which is less intense than the second peak at $R = 2.57$ Å due to Fe—Fe bond [41]. The FT curve of 0.5Fe/TiO₂ catalyst clearly differ from that of 2Fe/TiO₂, indicating variations in the local structure of iron in the samples studied. The FT curve of 0.5Fe/TiO₂ is similar to that of TiO₂ anatase phase, which suggests that Fe atoms are incorporated into the lattice of anatase and located at the substitutional sites of Ti atoms, in line with previous XAS studies on Fe-doped TiO₂ samples [17, 41, 42]. However, for 2Fe/TiO₂ the intensity of the Fe—O peak decreases and the intensity of the Fe—Fe peak increases severely, indicating that part of Fe atoms begin to aggregate and form α -Fe₂O₃ clusters. In view of the XANES and EXAFS results, iron seems to be present at the substitutional sites of Ti atoms for low Fe content (0.5 wt.%), whereas at high dopant concentration (2 wt.%) most of Fe atoms are present as α -Fe₂O₃ aggregates.

Figure 8. Fe K-edge XAS spectra (a) and the FT curves of Fe K-edge EXAFS spectra of α -Fe₂O₃, 0.5Fe/TiO₂ and 2Fe/TiO₂ (b). The FT curve of Ti K-edge EXAFS of anatase is also added in b).

The optical absorption properties and energy band gap of the bare and iron-doped TiO₂ samples were studied by UV-Vis absorption spectroscopy, as shown in Figure 9 and Table 2. Bare TiO₂ catalysts absorb mainly UV light while there is a red shift in the absorption band edge when increasing the iron doping of the TiO₂ matrix (Fig. 9a). This seems to be associated to the new energy levels introduced into the band gap of TiO₂ by Fe³⁺/Fe²⁺ species [21].

The E_g of 0Fe/TiO₂ sample is 3.33 eV (3.2 eV typically reported for anatase), which gradually decreases with increasing iron doping concentration to 2.9 eV for the highest iron concentration (2 wt. %). The absorbance spectra of the pre-carbonized sample at the highest temperature, 0.5Fe/TiO₂-900 (Fig. 9b), shows a higher narrowing of the band gap, which might be due to the formation of the rutile phase, as detected by XRD, and to the higher contribution of Ti³⁺ on these samples, as revealed by XPS [4]. Reduced TiO₂, which contains Ti³⁺, has been demonstrated to induce oxygen vacancy states between the valence and the conduction bands, which would contribute positively to the visible light absorption [43].

Figure 9. Diffuse reflectance spectra of TiO₂-Aldrich, and the bare and Fe-doped TiO₂ samples prepared by the one-step (a) and two-step (b) calcination process.

PL emission spectra are often used to investigate the separation efficiency of photogenerated electron-hole pairs on semiconductor materials [18, 44, 45]. Low PL intensity indicates a low density of electron-hole recombination, consequently more photogenerated charge carriers can participate in the photochemical reaction, improving the photocatalytic activity of the samples. In this study, the PL spectra of the bare TiO₂ and some representative Fe-doped titania samples with different iron contents (0.15, 0.5 and 1.2 wt.% Fe) were examined in the wavelength range of 300-480 nm, under the excitation of 250 nm, as shown in Figure 10. PL spectrum of commercial TiO₂-Aldrich (Anatase) is also presented for comparison. These samples display several emission peaks at around 400, 425, 440 and 468 nm under the excitation of 250 nm. The broad peak at 400 nm is due to the free-excitation emission of band gap [46], the sites emitting at 420-450 nm are attributed to tetrahedral Ti(IV) ones[47] and the latter (468 nm) is the emission signal originated from the charge-transfer transition from Ti³⁺ to oxygen anion in a TiO₆ octahedral complex [46, 48]. Although the PL intensity decreased in both the bare TiO₂ (0Fe/TiO₂) and Fe-doped TiO₂ samples compared to TiO₂-Aldrich, the reduction is significantly greater in those samples with moderate iron dopant concentration (0.5Fe/TiO₂ and 0.15Fe/TiO₂-700), demonstrating electron-hole recombination is efficiently suppressed in these two samples. This suppression is a consequence of Fe³⁺ incorporated into TiO₂, which may favour the migration of photo-produced electron to iron, thus improving the electron-hole separation at low doping concentration. However, the PL intensity of 1.2Fe/TiO₂ increases, indicating that the recombination of electron and hole is promoted at high doping concentration. This may be due to the excess of Fe³⁺, which can act as recombination center for the photogenerated charge carriers [22].

Figure 10. Photoluminescence spectra of TiO_2 -Aldrich, Fe-doped titania by the direct calcination process (0, 0.5 and 1.2 wt. % Fe) and 0.15Fe/ TiO_2 -700 sample by the two-steps process.

3.2. Photocatalytic performance of the samples

The photocatalytic performance of the different samples was tested for UV and Vis light-driven H_2 evolution using a sacrificial electron donor. Figure 11a shows the hydrogen evolution rate of the photocatalysts prepared by direct calcination and different iron contents and in Figure 11b the hydrogen evolution rate of the samples prepared by the two-step approach, both under UV light. A good linear relationship between time and amount of hydrogen produced per gram of catalyst is obtained after 4 h of reaction, which is used to calculate the hydrogen production rates ($\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$), which are included in the last column of Table 2.

Pure MIL-125 is only active under UV irradiation due to its large optical band gap (3.6 eV). The reaction rate was found to be initially $32 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ (Figure 10b), but the activity decreases with time due to the low stability in aqueous solution of this MOF [49].

The maximum hydrogen production was obtained for the sample with 0.5 wt.% of iron, which showed by XPS (Table 2) and XAS characterization (Figure 8) that about 62 wt.% of the total surface Fe content was Fe^{3+} and located at the substitutional sites of Ti atoms. The rate increased

from 76.0 to 230 $\mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ for 0.5Fe/TiO₂ with respect to 0Fe/TiO₂, indicating a 3–fold enhancement in hydrogen production under UV light by the incorporation of iron in the TiO₂ matrix. With increasing Fe³⁺/Fe²⁺ ratio and total iron content on the TiO₂ crystallites the hydrogen evolution rate gradually decreased, which may be associated to the role of excess Fe³⁺ as a (photo-generated electron) recombination site [22].

A second aspect to be considered is related to the presence of rutile in the TiO₂ structure. A similar hydrogen evolution rate was observed for 0.5Fe/TiO₂-500 as for 0.5Fe/TiO₂, but it decreased significantly for the samples pre-carbonized at 700 and 900 °C. This behaviour could be attributed not only to the high contribution of rutile phase in those samples thermal treated at higher temperatures (Table 1), but also to the increase of the TiO₂ crystallite sizes (or lower surface areas). Unlike our case, Wang *et al.* [7] reported the beneficial effect of dual-phase TiO₂ (anatase/rutile) structure and Fe-doping in the photodegradation of methyl orange. In this context, Scanlon *et al.* [8] reported that the presence of anatase in combination with rutile phase may lower the effective band gap of TiO₂ composite materials and thus facilitate an efficient electron-hole separation, increasing the photoactivity of anatase-rutile composite materials over their individual counterpart. Nevertheless, when the amount of rutile is below a proper fraction or is dominant, like in our case, the photocatalytic activity of dual-phase TiO₂ crystallites may become worse owing to the intrinsic lower photocatalytic activity of the rutile phase [7].

Furthermore, Figure 11b also shows that the photocatalysis of Fe-doped dual-phase titania samples depended on the Fe-concentration. Sample 0.15Fe/TiO₂-700 (51 wt. % anatase and 49 wt% rutile) improved the H₂ production from 132 to 215 $\mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ compared to that of 0.5Fe/TiO₂-700 with the same titania phase composition. The main origin of the photocatalytic activity comes likely from the iron dopant concentration, and interestingly, there is a correlation between the size of the photocatalysts particles and the optimum iron content, in agreement with Zhang *et al.* [50].

Figure 11. Hydrogen evolution in 30 % methanol aqueous solution under the irradiation of UV light of TiO₂-Aldrich and the Fe-doped titania photocatalysts obtained by direct calcination of Fe/MIL-125(Ti) (a) and by the two-step process (b).

Similar behaviour was observed for the photocatalysts tested under visible light illumination, Figure 12, where an increased H₂ evolution rate was observed at moderate iron doping. The Vis-light H₂ production rate was enhanced by a factor of about 6 and 11 for 0.5Fe/TiO₂ and 0.15Fe/TiO₂-700, respectively, relative to that of 0Fe/TiO₂, demonstrating the positive effect of Fe. Therefore, our results evidence that incorporating Fe in TiO₂ by the MOFMS route enhances

water splitting to produce H₂ under UV and Vis light illumination. Compared with other Fe-doped TiO₂ synthesis methods, Khan *et al.*[22] reported an improvement in hydrogen production rate of 25 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ in aqueous methanol under visible light for 0.5 wt.% Fe-doped TiO₂ prepared by hydrothermal method. Most recently, Zhao and collaborators[19] have reported hydrogen production rate values between 8.3-109.5 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ under visible light irradiation for 0.02-1 wt.% Fe-doped TiO₂ synthesized by direct microwave-hydrothermal synthesis. These Fe-doped TiO₂ photocatalysts presented similar BET areas and crystallites sizes as those reported in the current work and were also tested under similar reaction conditions (reactor temperature and methanol and catalyst concentration). Higher hydrogen production rates of 220.59 and 248.2 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ in aqueous ethanol under UV and visible light irradiation, respectively, were found for 4 wt.% Fe/TiO₂ prepared by one-step solvothermal method[44].

It is also noted that the hydrogen evolution rate of the undoped TiO₂ photocatalyst (0Fe/TiO₂) is higher than of the commercial TiO₂, one of the best commercially available photocatalysts. Therefore, the improvements observed for the TiO₂ and Fe-doped titania samples prepared by the present method may be attributed, on the one hand, to their smaller crystal size and appropriate higher surface area and mesopore volume, which can promote the diffusion of reactants and gaseous products, as well as provide more adsorption and photocatalytic reaction active sites. On the other hand, other parameters, like the presence of surface defect sites, such as Ti³⁺ and oxygen vacancies, and surface hydrophilicity, may also play a crucial role for the enhanced photocatalytic activity [17].

On this question, the XPS (Figure 6, Table 2), revealed that Ti⁴⁺ and Ti³⁺ are present on the surface of TiO₂ and Fe-doped TiO₂ crystallites prepared by MOFMS, and that the carbon formed during the pyrolysis process may reduce part of Ti⁴⁺ in the surface of TiO₂ into Ti³⁺. Several reports have proven that the presence of Ti³⁺ species induced oxygen vacancy states between the valence and the conduction bands, contributing to the visible light absorbance and enhancement

of the photocatalytic activity [43]. This would explain the slightly higher hydrogen evolution rate for 0Fe/TiO₂ than for TiO₂-Aldrich under visible irradiation (Figure 11). In fact, the (Fe-doped) titania powders prepared in the present work turned blue after the irradiation under UV and visible light, characteristic of Ti³⁺ formation [6, 51], whereas TiO₂-Aldrich powder remained colourless (Figures S4, S5). The Ti_{2p} spectra of 0.5Fe/TiO₂ after photocatalytic water splitting under UV light for 24 h is shown in Figure S6. It must be said that the XPS of 0.5Fe/TiO₂-used sample was measured immediately after reaction, with a minimum time of exposure to air atmosphere. The Ti_{2p} spectrum corresponding to the used photocatalysts shifted to lower binding energies [18], confirming the generation of Ti³⁺ by UV light illumination and thus, the formation of oxygen vacancies in the surface of the photocatalyst during photocatalytic water splitting.

Figure 12. Hydrogen evolution in 30 % methanol aqueous solution under the visible light irradiation of TiO₂-Aldrich, 0Fe/TiO₂ and selected Fe-doped titania photocatalysts.

Regarding the use of iron as dopant, the beneficial effect of Fe²⁺/Fe³⁺ was described as a electron and hole-trapping agent (Eqs. (2-5)), where the excited electrons are retained for a short time before transferring again [4, 12, 17]. The charge transfer steps can be described as follows:

According to this process, the recombination rate of the electron-hole pairs of titania is reduced in the presence of Fe^{2+}/Fe^{3+} , therefore the photocatalytic activity of Fe-doped titania photocatalysts is improved. As mentioned before, the best photocatalytic activity for H_2 evolution was observed for 0.5Fe/TiO₂ and 0.15Fe/TiO₂-700 in agreement with the PL results showed in Figure 10. From these results, it is clear that a moderate Fe concentration on titania can greatly improve the separation efficiency of electron-holes pairs. However, an excess of Fe^{3+} may behave as a recombination center as well, equations (6) and (7). Furthermore, the excessive number of Ti^{3+} ions on the photocatalyst surface could also act as a recombination center for holes and electrons. Therefore, an optimal content of Ti^{3+} and Fe^{3+} in the Fe-doped titania crystallites is desirable.

In addition, doping with iron introduces oxygen vacancies in the crystal lattice and titania surface, favouring the adsorption of water and formation of surface hydroxyl groups, as evidenced from the O_{1s} region in XPS (Figure 6c and 6d). These hydroxyl groups may react with photogenerated holes producing hydroxyl radicals, equation (8), beneficial for an efficient separation of photo-induced electron-hole pairs [52, 53].

Regarding the role of methanol, it is used in the present study as sacrificial agent and hole scavenger [19, 35, 36]. During the photocatalytic process, the excited electrons partially migrate to the active surface sites, producing adsorbed hydrogen atoms ($H_{ads}^{\bullet}$). Such radicals can cause the reduction of water on the catalyst surface and produce hydrogen, whereas the photogenerated holes and $OH^{\bullet}$ (eq. (8)) can react with methanol to water, carbon dioxide and other oxidized intermediates promoting water spitting to produce hydrogen.

Therefore, from these results it is clear that there is a great catalyst synthesis challenge related to the state of the Fe-doped titania crystallites since phase composition, crystal size, porosity, iron content, presence of surface defects (Ti^{3+} and oxygen vacancies), etc. may directly affect the modulation of the band gap and the efficiency of separating photo-induced electron and holes, which contribute to the photocatalyst performance.

4. Conclusions

Fe-doped titania materials with high porosity and tuneable particle size and chemical phase were successfully prepared by the MOF-mediated synthesis route (MOFMS), either by direct calcination in air of Fe/MIL-125(Ti) crystals or by a two-step method, including carbonization in inert atmosphere followed by calcination in air. The photocatalytic activity of the prepared Fe-doped titania nanopowders has been tested in photocatalytic water-splitting by measuring hydrogen evolution.

According to XPS and XAFS characterization, at low dopant concentration Fe^{3+} ions have substituted Ti^{4+} and/or Ti^{3+} sites of the TiO_2 crystal structure. This MOFMS, also favours a well and uniform dispersion of $Fe^{3+/2+}$ species in the bulk of TiO_2 which can capture photoinduced electrons and holes, reducing the recombination rate, and enhancing the photocatalytic activity.

However, an excess of Fe^{3+} content ($> 0.5 \text{ wt.}\%$ Fe) in the titania structure causes lower hydrogen production rates due to increased recombination chances over these centers.

The crystallite size does not change as a function of the Fe content, and only the anatase phase is observed in the direct-calcined samples at 450°C . There is a considerable effect of the temperature on the phase and size of the TiO_2 nanoparticles prepared by the two-step process.

A high rutile concentration and crystal size results in a decreased hydrogen evolution rate. The samples with $0.5 \text{ wt.}\%$ Fe dopant prepared by direct calcination and $0.15 \text{ wt.}\%$ Fe pre-carbonized at 700°C presented the best photocatalytic activity, under both UV and visible light irradiation and are among the highest reported systems.

Thus, a versatile and simple method for the preparation of Fe-doped titania photocatalysts with tuneable chemical phase composition, crystal size and high surface area has been described. This MOFMS technology could be potentially applicable to other oxide bulk materials.

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