ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 98 (1996) 171-181

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photocatalytic properties of iron-doped titania semiconductors

M.I. Litter [a,*], J.A. Navío [b]

[a] Unidad de Actividad Química, Comisión Nacional de Energía Atómica, Av. del Libertador 8250, 1429 Buenos Aires, Argentina
[b] Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, and Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, 41012 Sevilla, Spain

Received 13 December 1995; accepted 29 February 1996

Abstract

An exhaustive review on the photochemical properties of iron-doped TiO_2 semiconductors is presented. Photocatalytic reactions (reductions and oxidations) using Fe-containing TiO_2 on different organic and inorganic substrates are reported. Different aspects relating to structural, surface and photophysical properties of these photocatalysts are extensively discussed. The origin of the photoactivity of this kind of mixed oxides is considered with regards to previously proposed physical and chemical processes and on the role of the iron content.

Keywords: Photocatalysis; Iron-doped titania; Semiconductors; Metal oxides

1. Introduction

TiO_2 is the most widespreadly used photocatalyst, due to its optical and electronic properties, low cost, chemical stability and non-toxicity. However, the search for new materials in heterogeneous photocatalysis has been a matter of interest in the last years because of the large technological implications of the processes involved. Doping titania with metal transition ions was envisaged as a good tool to improve photocatalytic properties, principally because an enhancement of the response to the visible region was expected. Some brief mentions to this subject have appeared in the literature [1-4], but there does not exist a complete and exhaustive revision. Therefore, it seems relevant to describe and update the work performed so far in this field.

In particular, iron(III)-doped TiO_2 has been the topic of many investigations including preparation, characterization, spectroscopic features, dynamics of charge transfer, trapping and recombination, and photocatalytic behavior. Although we will mention other metals for the sake of comparison, our review will be focused essentially on iron-doped TiO_2.

2. Photocatalytic reactions

2.1. Photoreduction of dinitrogen to ammonia

A great deal of work was put into the possibility of replacing the Haber process (which uses drastic temperature and pressure conditions) for the more economical and milder photocatalytic reduction of nitrogen to ammonia, based on the use of irradiated semiconductor (SC) powders. The values of the conduction band of anatase and rutile [5] are thermodynamically able to reduce N_2 to NH_3. However, TiO_2 was found inactive for this reaction due to kinetic reasons, and iron-doped titania was visualized as a potentially useful material. The reaction:

$$N_2(g) + 3H_2O(l) \xrightarrow[SC]{h\nu} 2NH_3(g) + 1.5O_2(g) \quad (1)$$

has been extensively reviewed [6–9]. We will comment briefly on this topic, it being significantly important in fields such as agriculture and industry. However, it is worthwhile to mention that a great controversy on the feasibility of the photocatalytic nitrogen reduction is today in the literature [9–14].

The first report was that of Schrauzer and Guth [15] who tested various wet iron-free and iron-doped TiO_2 powders prepared by impregnation and fired at 1000 °C. They found that iron ions improved ca. four times the activity for N_2 photoreduction (UV irradiation) in gas-solid regime; the maximum activity corresponded to the 0.2 wt.% iron sample. Ammonia was produced here from N_2 and H_2O together with traces of hydrazine. The more active samples produced about 6 μmol NH_3 and less than 0.5 μmol N_2H_2 in 3 h. Comparing samples doped with different transition metal ions (Co, Mo, Ni), the better activity was found for iron. The enhancement of the activity in doped samples was attributed to the iron-induced transformation of anatase to rutile that, according to

---

* Corresponding author.

1010-6030/96/$15.00
PII S1010-6030(96)04343-2

the authors, was more active. However, Radford and Francis [16] observed that undoped samples were inactive and that metallic iron-doped TiO_2 in the anatase form (prepared by metal vapor synthesis) showed much more activity than rutile samples. In Schrauzer and Guth's work, the activity of pure TiO_2 was probably due to iron contained as an impurity [7]. Later, Schrauzer et al. [17] reported the reduction of nitrogen to ammonia using desert sands composed of TiO_2 and a low amount of iron.

The catalytic nature of this process was questioned by Van Damme and Hall [18] and by Formenti and Teichner [19] on the basis that the reaction was actually the photoassisted stoichiometric decomposition of the hydroxylated TiO_2 surface. In addition, factors such as the decline of the reaction after a few hours, the low turn-over number and the endoergonicity of the involved reaction were also criticized.

Further work was reported in a series of articles [8,20–28] which made successive advances on the subject. Samples of iron-doped titania (0.05–10 at.%) prepared by impregnation or coprecipitation and fired at various temperatures were tested for nitrogen (water-saturated) reduction under near-UV irradiation. Fixed and fluidized bed laboratory reactors at gas-solid regimes in continuous flow were used. The preparation and characterization of these samples were described in most of these papers and especially in references [29–30] (see below). The main results can be summarized as follows.

(a) The ammonia production from photoactive samples was about 3–6 μmol h^{-1} g^{-1}. The yields increased with the temperature in the reactor.

(b) Specimens were divided in two types depending on the iron content. Those with loadings of up to 1 at.%, forming solid solutions, were active irrespective of the TiO_2 phase (anatase or rutile). The other specimens (Fe > 1 at.%), having excess of iron in islands of Fe_2O_3, Fe_2TiO_5 or both, were less active. Also, samples fired at high temperature showed a very low activity.

(c) Samples with a very low iron content were only slightly active. The best yield was found between 0.2–1.0 at.% iron content; from these, 0.5 at.% Fe samples prepared by coprecipitation were the most efficient of all the firing temperatures. When iron exceeded 2 at.%, a net decrease in activity was observed. Coprecipitated specimens were generally more active than samples prepared by impregnation. The difference in activity was more remarkable among samples fired at low temperature (500 °C).

(d) Pure TiO_2 (anatase or rutile), Fe_2O_3 and Fe_2TiO_5 were practically inactive.

(e) No deactivation of the catalysts was found up to 5–7 h of the reaction. At longer times, declining in the activity was observed, but it could be restored by heating the catalyst in air at 550 °C.

(f) Supporting the catalyst over γ-Al_2O_3 afforded higher yields of ammonia (ca. 10 times), depending on the doped titania/γ-Al_2O_3 ratio.

(g) Comparison of Fe(III)-doped with Cr(III)-doped samples showed that the last specimens were less photoactive, Cr_2O_3 being completely inactive.

A recent article [31] describes the photocatalytic (near-UV light) reduction of N_2 in aqueous suspensions over (Fe, Ru or Os)/TiO_2 catalysts prepared by deposition of metals from their salts over prereduced TiO_2. The results were essentially the same as those of references [20–28].

Coprecipitated hydrous oxides of Fe(III) and Ti(IV) in water suspension were reported to be able to photocatalyze dinitrogen reduction using visible irradiation [32]. The activity of the complex catalyst was higher than that of pure hydrous ferric oxide (prepared similarly), which also catalyzed the reaction.

The feasibility for the photocatalytic reduction of N_2 on Fe-doped titania was strongly criticized by Edwards et al. [9,10,13,14] mainly by its ineffectiveness (micromolar yield or lower in most of the cases). They affirm that no unequivocal reports of artificial photocatalytic synthesis of ammonia from nitrogen and water on heterogeneous catalysts can be found in the literature [9]. In their own experiments, the authors did not detect evidences for reductive fixation of N_2 after several attempts using different samples of TiO_2, Fe/TiO_2, Fe_2O_3, NiO, Al_2O_3 and SiO_2. In addition, they observed NH_3 oxidation under UV irradiation over Fe/TiO_2 under O_2, N_2, Ar or H_2. Bourgeois et al. [33] also reported a failure of impregnated samples of Fe-doped titania to photoreduce N_2.

Nevertheless, the criticism was rejected by Augugliaro and Soria [11] and by Palmisano et al. [12] by the following reasons: (a) the photoreduction experiments of Edwards et al. were carried out with non-characterized samples on whose photocatalytic activity the authors doubt; (b) most of the experiments were conducted in aqueous suspensions where N_2 photoreduction was not generally observed; (c) undetected contamination could invalidate the findings; (d) reaction conditions such as mass of catalyst, irradiation time, irradiated surface area or temperature inside the reactor were not accurately described; (e) NH_3 photo-oxidation could have been favored by the shorter-UV light used in these experiments. The discrepancies keep on being found in the present, and it would be advisable to pursue new research in this field in very controlled and precise conditions.

The mechanistic aspects about N_2 photofixation have been considered in some of the above cited articles [6,7,18, 20,27,31,33] but there are some doubts concerning the actual steps of the reactions. In this sense, Bickley and Navío [34,35] have developed some ideas about the natural photofixation of N_2 in terrestrial atmospheres, considering that hydrogen evolution from water vapor over hydroxylated reduced TiO_2 under UV radiation is completely suppressed in the presence of oxygen. The photofixation of N_2 could occur through two alternative steps: (i) via a reductive step to form ammonia which is subsequently photooxidized to NO_x^{z-} species (NO_2^-, NO_3^-) by either oxygen or photogenerated hydrogen peroxide or (ii) by an oxidative step to form NO_x^{z-} and its subsequent photoreduction to NH_3 by hydrogen photogenerated radicals. As Fe/TiO_2 oxides can be compared with reduced TiO_2 due to the electron accepting nature of iron, similar processes can be tentatively proposed for N_2 photofixation on these doped oxides.

2.2. *Other photocatalytic reactions*

2.2.1. *Splitting of water or hydrogen production*

Closely related to N_2 photoreduction is the splitting of water, whose feasibility was largely sought by many groups in the 1980s and constituted an important goal to improve the research and technology in semiconductor photocatalysis. As in the case of N_2, bare TiO_2 was found inactive unless platinized and coated with NaOH, or doped with RuO_2 [6].

In their study, Schrauzer and Guth [15] observed that, in the absence of N_2, water could be photosplitted with higher yields on Fe/Ti doped oxides than on pure titania (we have already mentioned the possibility of iron impurifying the samples).

$$H_2O(l) \xrightarrow[sc]{h\nu} H_2(g) + \frac{1}{2} O_2(g) \qquad (2)$$

The efficiency was however lower than in photoelectrochemical devices (about 1 μmol h^{-1}). In the presence of nitrogen, hydrogen was not detected but oxygen was likewise produced. Acetylene inhibited H_2 production, indicating that the reduction of water had taken place, the formed hydrogen reducing acetylene to methane, ethane, ethylene and C_3 hydrocarbons.

Photoevolution (at 366 nm) of H_2 in low amounts (4–5 μmol $h^{-1}g^{-1}$) from a water-containing EDTA solution on Fe/TiO_2 (anatase) catalysts prepared by impregnation was achieved under Ar [36]. Samples with a low Fe content were more active than the more loaded ones.

The photoreduction of nitrate and nitrite under argon over Fe-doped TiO_2 was essayed [37]; N_2 was produced from nitrite, but no reduction of nitrate was observed.

2.2.2. *Oxidations*

In the same Ref. [37], the photo-oxidation of nitrogen and photo-decomposition of ammonia under argon or oxygen over Fe-doped titania pretreated with hydrogen peroxide was attempted, yielding in all cases a mixture of nitrate and nitrite. This reinforces the proposed pathways for nitrogen photofixation mentioned in Section 2.1.

The photo-oxidation (near-UV light) of neat toluene under O_2 [38] was achieved using 0.5 and 5 wt.% iron-doped TiO_2 prepared by impregnation. Benzaldehyde, benzyl alcohol and benzoic acid as the main products and traces of 2-, 3-, and 4-cresols were detected in all experiments. Pure TiO_2 (calcined previously 24 h at 500 °C) was more active than iron-doped TiO_2 in concentrated suspensions of catalysts (2.5 g dm^{-3}); at a less concentration (1.25 g dm^{-3}), the 0.5 wt.% iron sample was more active, especially for benzaldehyde formation. The 5 wt.% iron sample, in which the pseudobrookite phase was present, was less photoactive.

Phenol and 4-nitrophenol oxidations in water suspensions were also investigated [8,25,28,39]. Pure TiO_2 specimens in the anatase form were photoactive in all experimental conditions, in contrast to N_2 photoreduction. The activity of rutile specimens for this type of photoreactions depended on the preparation technique or the experimental conditions. Calcination at high temperature, for example, caused dehydroxylation of samples and a subsequent lowering of the activity [40,41]. Pure Fe_2O_3 and Fe_2TiO_5 were found inactive for these reactions. All Fe-doped samples displayed similar or lower activity than TiO_2 (anatase), and a net decrease in activity occurred in the more loaded samples.

The photocatalytic oxidation of nitrite to nitrate [42] was carried out over Fe-doped titania samples (0.2–10 wt.% iron content), the 0.5 wt.% sample showing the maximum activity. Above this concentration, the presence of iron was detrimental. Pure Degussa P-25 TiO_2 (calcined at 500 °C, similarly to the doped samples) showed higher initial rates than the doped oxides, whereas the opposite occurred at longer irradiation times.

The photocatalytic activity of iron-doped titania for degradation of oligocarboxylic acids was recently reported by us [43]. 0.5 and 5 wt.% Fe samples prepared by impregnation of TiO_2 (Degussa P-25) with $Fe(NO_3)_3$ were found as effective as the precursor for oxalic acid and EDTA degradation under short-UV light (254 nm). In contrast, doped samples were less efficient than TiO_2 for malonic acid oxidation. Under near-UV light, the doped catalysts were less active than P-25 for degradation of the three substrates. Samples prepared by impregnation with iron(III)-acetylacetonate were tested for oxalic acid and EDTA degradation and compared with those prepared by impregnation with iron nitrate [44]. No difference in the photoactivity (and always lower than pure Degussa P-25) was found for both types of specimens, although the former presented iron more homogeneously distributed into the TiO_2 matrix (see Section 3). Activity increased slightly up to 2 wt.% iron content and then decreased. In contrast to bare TiO_2, some photodegradation of oxalic acid under visible light could be observed, especially with the 5 wt.% iron sample.

2.2.3. *Q-sized particles*

Ultrasmall (Q-sized) semiconductor particles (1–10 nm) possess substantially different photophysics than large powder particles, and show outstanding photocatalytic behavior due to the increased bandgap, which sets the positions of the conduction and the valence band to more negative and more positive values, respectively. For this reason, a special mention to this type of samples will be made.

Bahnemann et al. [45–47] found that Fe-doped TiO_2 colloids (5 nm diameter, 0.1–50 at.% iron content) showed higher yields for dichloroacetic acid photodegradation (near-UV light) than pure Q-sized TiO_2 prepared analogously. The maximum quantum yield was reported for the 2.5 at.% Fe-TiO_2 sample. The 50 at.% iron sample exhibited, in addition, some photoactivity under visible light irradiation (436 nm).

Choi et al. [48–49] showed that doping TiO_2 (Q-sized particles, 2–4 nm) with Fe^{3+} (and other transition metal ions) at 0.1–0.5 at.% significantly increased the photoactivity for CCl_4 reduction and $CHCl_3$ oxidation. Iron proved to be the best dopant compared with Mo^{5+}, Ru^{3+}, Os^{3+}, Re^{5+}, V^{4+} and Rh^{3+}, and the maximum activity (15-fold higher than that of TiO_2) for chloroform degradation at 320 nm was found for the 0.5 at.% sample.

Photoactivity for oxalic acid oxidation [50] under near-UV light using colloidal (13 nm) particles of 10 wt.% iron doped TiO_2 was found similar to that using equally prepared naked TiO_2, but lower than that shown by Degussa P-25. Some activity with the doped sample was observed under visible irradiation (400–650 nm).

3. Structural, surface and photophysical properties of iron-doped titania semiconductors

A detailed knowledge of the structural features and photophysical properties of the materials is essential to understand their photochemical behavior. The preparation procedure, in its minimal details, seems to be very important in determining the properties of each sample. As many of the results reveal, photoactivity is extremely dependent on the type of sample. For example, in Ref. [49], a reduced activity for chloroform degradation was found when, after the preparation, Q-sized iron-doped titania particles were submitted to thermal treating (100–400 °C) and agglomeration took place. In another case, higher quantum efficiencies for photooxidation of 4-chlorophenol were found when using transparent colloid particles of vanadium-doped TiO_2 in comparison with the undoped catalyst. However, when the catalysts were slurry suspensions whose only difference in the preparation was in the final drying stage (freeze-drying instead of rotary evaporation), the photoactivity was lower than that of the precursor [49,51].

The phase composition and perfection, solubility, location and dispersion of iron in the different phases greatly vary in the specimens, depending on the steps of the preparation technique. Factors such as optical transitions, morphology, surface area, presence of defects, etc., largely affect the behavior of the samples as photocatalysts. However, no direct correlation between photophysics and photoactivity could be generally found. As a conclusion, a reinforced emphasis must be given in the future to explain how the different variables really affect the samples and to establish the preparation method that can improve the useful properties of these promising catalysts.

The method (v.g. impregnation, coprecipitation), amount of added dopant and thermal treatment of the sample after the processing affect the morphology of samples. TiO_2 particles can be simply substitutionally doped by iron, can be mixtures with iron oxides, or coexisting mixed oxides such as pseudobrookite can be present. In fact, as the Fe^{3+} radius is similar to that of Ti^{4+} [52], the substitution of iron in the matrix is an easy process. Several structural studies on the iron(III)-TiO_2 system [53–55] have revealed that Fe^{3+} enters the TiO_2 lattice substitutionally, being easier in rutile due to the open channels present in this structure.

Different methods of doping TiO_2 were reported in an early article, together with the effect on the properties of the products [56]. In most of the cases reviewed here, samples for photocatalytic purposes were prepared by impregnation of commercial or laboratory prepared titania with a Fe(III) solution of known concentration, or by coprecipitation from $TiCl_3$ or $TiCl_4$ and Fe(III) salts. At the end, samples were fired at different temperatures (from 500–1000 °C) [29,57]. In Table 1, properties of some of the samples prepared by these methods are reported, taken from Refs. [7,8,29,57]. Samples were thoroughly characterized by different techniques such as X-ray diffractometry, BET surface area, SEM, TEM, XPS, thermogravimetric analysis and magnetic susceptibility measurements, EPR, IR, Mössbauer, diffuse reflectance and absorption spectroscopies; several articles report the results [29,58–61]. Depending on the firing temperature and the amount of iron incorporated, the following conclusions can be extracted:

(a) As mentioned in Section 2.1, two types of specimens are formed. During the calcination, the preadsorbed precursor (iron nitrate, for example) is decomposed, and the iron initially present at the surface diffuses into the bulk producing a solid solution. Specimens containing up to 1 at.% Fe are substitutional solid solutions in which Fe^{3+} is dispersed in the lattice of TiO_2. Specimens with higher iron contents accommodate any excess of iron as minute particles or small aggregates of iron oxides (hematite) and/or mixed oxides (Fe_2TiO_5) at the surface of the solid solution particles. Of course, some intermediate states could be present, depending on the transformation of anatase to rutile and on the solubility limit of iron in both phases.

(b) Samples with low iron content (0.5–1 at.%), fired at low temperature (500–550 °C) consisted essentially of anatase, as SEM results showed. However, IR and EPR results suggested evidence of rutile phases even in coprecipitated samples containing 0.5 at.% Fe, which cannot be detected by SEM [8,27]. More loaded samples or specimens fired at higher temperature presented more rutile, because iron and temperature catalyze the anatase-to-rutile transformation [62,63]. However, the incorporation of iron did not catalyze this transformation at low temperatures (at least up to 550 °C) [39]. Actually, the ease of phase transformation depends on the nature of the TiO_2 precursor. The phase transformation is catalyzed by transition ions only when they are effectively dissolved inside the support phase [64].

(c) Enrichment of the surfaces by Fe species commences at temperatures as low as 500 °C, not detectable by X-ray diffraction but evidenced by DRS and XPS studies [59] and by IR spectroscopy [60] (segregation of iron oxide at 500 °C at contents higher than 1 at.% can be seen from vibrational bands at 450–460 cm^{-1}, ascribed to α-Fe_2O_3). At iron concentrations higher than 1 at.%, the formation of hematite

Table 1
Properties of Fe-doped titania samples prepared by impregnation (IM) or coprecipitation (CP) (taken from Refs. [7,8,29 and 57]

Sample	Fe content (at.%)	Firing temperature (°C)	Phases [a]	Surface area ($m^2 g^{-1}$)
TiO_2[b]	0	–	A, R	44
CP	0.2	500	A	44
CP	0.5	500	A, R (traces)	27
CP	0.5	650	R, A	17
CP	0.5	800	R	2
CP	0.5	1000	R	≅1
CP	1.0	500	A, R (traces)	57
CP	1.0	650	R, A	14
CP	1.0	800	R	2
CP	1.0	1000	R	≅1
CP	2.0	500	A, R (traces)	24
CP	2.0	650	R, A	12
CP	2.0	800	R, PB (traces)	3
CP	2.0	1000	R, PB (traces)	≅1
CP	5.0	500	A, R	34
CP	5.0	650	R, A (traces)	9
CP	5.0	800	R, PB	3
CP	5.0	1000	R, PB	≅1
CP	10.0	500	A, R (traces), H (traces)	54
CP	10.0	650	R, PB, H (traces)	11
CP	10.0	800	R, PB, H (traces)	3
CP	10.0	1000	R, PB, H (traces)	≅1
IM	0.5	500	A, R	30
IM	0.5	650	R, A	17
IM	0.5	800	R, A (traces)	8
IM	0.5	1000	R	< 1
IM	1.0	500	A, R	30
IM	1.0	650	R, A	11
IM	1.0	800	R, PB (traces)	2
IM	1.0	1000	R	< 1
IM	2.0	500	A, R (traces)	33
IM	2.0	650	R, A, PB (traces), H (traces)	8
IM	2.0	800	R, PB	< 1
IM	2.0	1000	R, PB	< 1
IM	5.0	500	A, R	30
IM	5.0	650	R, A (traces)	9
IM	5.0	800	R, PB	< 1
IM	5.0	1000	R, PB	< 1
IM	10.0	1000	R, PB	< 1

[a] In decreasing order of abundance.

[b] Degussa P-25; A = anatase; R = rutile; H = hematite; PB = pseudobrookite.

phases could be observed, as the solubility of iron in rutile is lower than in anatase. Results of ESR, which detects only a fraction of Fe^{3+} in solid solution, indicated first a solubility lower than 0.5% [29], but recent results by magnetic susceptibility measurements [57,58,65] established a higher incorporation (> 1.2 at.%). Pseudobrookite was only observed when firing at high temperatures (800–1000 °C), because there is little tendency for bulk reactions between Fe_2O_3 and TiO_2 at 500 or 550 °C [58].

(d) Samples fired at 500–650 °C showed a dependence on the preparation method. Those prepared by coprecipitation and fired at the lowest temperature showed a simple and uniform behavior, consisting mainly on anatase. Impregnated samples were less reproducible: they were mixtures of anatase and rutile, varying from sample to sample. In samples fired at the highest temperatures, irrespective of the preparation method, TiO_2 was always in the rutile phase [29].

(e) The surface area of the specimens decreased together with an increasing firing temperature; on the contrary, the iron content, although causing variations, did not noticeably influence the surface area [30,39,63]. The nature of the precursor is also important for the surface area. Samples prepared by impregnation of P-25 with iron acetylacetonate showed specific surface areas higher than those prepared from iron nitrate and similar to the precursor [44].

(f) SEM and EDX measurements, confirmed by other complementary techniques such as DRS and TPD indicated a very large distribution of shapes and dimensions of the particles, together with different distributions of iron in the particles. This depended on the preparation method: coprecipitated samples showed a homogeneous distribution of iron within the particles, whereas, impregnated samples, due to the imperfect diffusion of iron to the bulk of the TiO_2 grains, presented a very inhomogeneous distribution of the dopant between particles and even within one particle. A concentration gradient was also found, evidencing some enrichment in iron on the external surface [57,59,60].

(g) IR spectra of samples fired at the highest temperatures showed dehydroxylation of TiO_2 [8,27]. FTIR monitoring of basic and acid adsorbants in impregnated iron-doped samples fired at 550 °C indicated surface acid-base properties similar to a likewise prepared precursor. This suggests that the presence of Fe^{3+} does not sensibly change the content and nature of surface-OH groups [39]. In contrast, iron-doped titania samples prepared from Degussa P-25 presented a less amount of acid and basic hydroxyl sites than the undoped substrate [43,66].

(h) The impregnation method seems to be not properly suitable for a good dispersion of iron. To improve the uniformity in the samples, some modifications were essayed. According to Rives et al. [67], the use of a ferrous salt as $Fe(NH_4)_2(SO_4)_2.6H_2O$ to impregnate anatase yields more uniform samples. Changing the firing temperature from 500 to 550 °C also induced a more facile diffusion of iron in the lattice of anatase preventing, in addition, the anatase-to-rutile transformation [39]. In this case, X-ray diffractometry showed Fe_2O_3 peaks but no rutile in samples with more than 3 at.% iron content. By using Fe(III) acetylacetonate [44] strong evidences of a more homogeneous distribution of iron were observed.

(i) Coprecipitation from different precursors have been performed, leading to the improvement in the properties of the samples. Sol-gel techniques using Ti(IV)-isobutylate or n-butylate and Fe(III)-acetylacetonate as precursors and ulteriously calcined at 500 °C for 6 h yielded iron-doped titania samples containing essentially the anatase structure [68–69]. X-ray patterns showed that the increase of Fe loading did not change the phase composition until ca. 6% Fe content, where the rutile phase appeared with the complete disappearance of the anatase phase. Amorphous and multiphasic products could be observed from EXAFS spectra only in the high-loaded samples. Recent unpublished results from Navío et al. [70] in samples prepared from $TiCl_4$ and $Fe(acac)_3$ by sol-gel techniques showed that even at Fe contents higher than 5%, anatase was the only detected phase.

The absorption and diffuse reflectance spectra of doped particles or single crystals showed an enhancement of the intrinsic absorption edge of TiO_2 from 380 nm to higher wavelengths, the onset of the absorption shifting to the red with the iron content. The absorbance in the range 400–650 nm was higher than that of TiO_2 [24,30,43,44,59,71–73]. In most of the samples with high iron contents, a broad band centered at 500 nm could be seen. Impregnated samples prepared from iron nitrate showed spectra of ill crystallized structures, indicating a large dispersion and disorder of Fe^{3+} species in the lattice and surface [30,43,44,59]. In heavily doped samples, the presence of other iron phases (Fe_2O_3, Fe_2TiO_5) was suggested from the spectra, especially in the UV range [43,44]. The higher absorbances of these samples were attributed to the accumulation of iron-rich layers at the surfaces as indicated by SEM (see f above) [59]. All samples fired at 1000 °C showed similar spectra, irrespective of the iron content, suggesting that the surface layer of the particles had a quite different composition (pseudobrookite). Samples prepared by impregnation with Fe(III)-acetylacetonate yielded more structured spectra, indicating a more homogeneous distribution of iron [44]. In Fig. 1 are depicted the spectra of these samples from Ref. [44]. The assignment of bands will be reported in the next section. In the recently prepared samples by Navío et al. by a sol-gel technique [70], bands in the visible range were less pronounced, indicating the absence of accumulated surface iron-rich layers, as confirmed by XPS results.

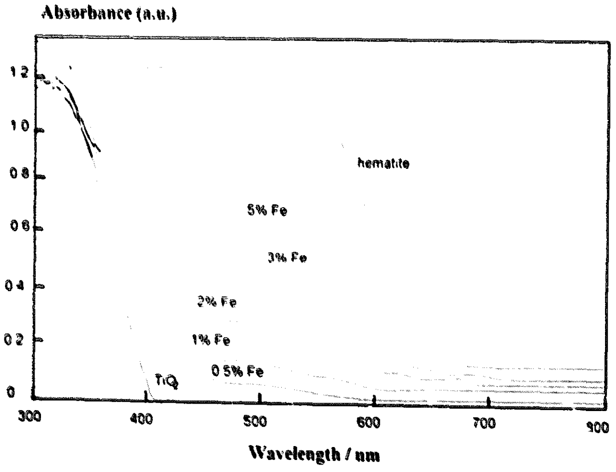

Fig. 1. DRS spectra of iron-doped titania prepared by impregnation of TiO_2 (Degussa P-25) and iron (III)-acetylacetonate (adapted from Ref. [44]).

As it is known, in Q-sized particles, the bandgap is shifted to the blue compared with larger particles (369 nm vs. 388 nm in pure anatase). The spectroscopic features of doped particles, however, correlate to those of larger-sized samples: the bandgap is shifted to longer wavelengths and an absorption band centered at ca. 470 nm appears in samples with high iron content [45,49,50,74].

4. Origin of the photoactivity

4.1. Low-loaded samples

According to the results, it is clear that the iron content is an essential variable to define the activity of the samples. Mono- or multiphasic samples behave in different ways. We will first address the samples with a low iron content where only one phase is present.

The nature of the photocatalytic reaction is also important to evaluate the factors that affect photoactivity. Reductive processes such as nitrogen reduction or water photosplitting are thermodynamically possible with pure TiO_2 [5], but are restricted by kinetic constraints They are, however, attainable with Fe-doped specimens. On the contrary, in oxidative processes, which do take place with bare TiO_2, Fe-doped catalysts do not enhance the reactivity or are detrimental.

It has been proposed that doping TiO_2 with lower valence cations results in decreased rates of water cleavage because of the shift of the flat-band to a more anodic position and the enhancement of the depletion layer thickness [75]. On the contrary, it was affirmed [6,25,39] that the augmented activities found in some reactions with Fe-doped titania are due to the higher diffusion length of the minority carriers in comparison with pure TiO_2 (2 μm vs. 1 μm) [76]. Conversely, and as found [25], doping with Cr(III) resulted in decreased reactivity, attributed to a lower diffusion length (0.2 μm). However, this explanation is not suitable for very small particles whose dimension is much smaller than the diffusion length or where a depletion layer does not exist.

Dopants introduce energy levels into the bandgap, which are responsible for the red shift of the intrinsic absorption edge of TiO_2 and of the enhancement of visible light absorption, as mentioned in the previous section. The red shift of the absorption edge in Fe(III)-doped titania, observed in very early articles [71,72], has been attributed to the excitation of 3d-Fe^{3+} electrons to the TiO_2 conduction band (charge-transfer transition) [71,74,77]. The broad band that appears at ca. 470 nm in increasingly concentrated samples can be ascribed to the d-d transition $^2T_2g \rightarrow {}^2A_2g$, ^2T_1g or to charge-transfer transitions between dopant ions via the conduction band ($Fe^{3+} + Fe^{3+} \rightarrow Fe^{4+} + Fe^{2+}$). The increased absorption in the visible can be due also to transitions implicating surface states or native defects in the lattice [44,49,50,77]. However, there is no direct correlation between the light absorption ability and the photocatalytic rate. Factors related to the electronic structure seem to be more important, associated to the fact that dopant ions influence charge separation, charge-carrier recombination and interfacial charge-transfer rates, acting as mediators and affecting the quantum efficiencies. In fact, no visible light sensitized photoconductivity in 10 wt.% iron-doped TiO_2 could be observed, in spite of the high absorbance of the samples in this region. The lack of photoconductivity was ascribed to a high recombination rate of generated electron-hole pairs [50].

Under irradiation, electrons-hole pairs are produced in the conduction and valence bands of TiO_2, and successive events take place.

Charge-pair generation

$$TiO_2 + h\nu \longrightarrow e_{cb}^- + h_{vb}^+ \tag{3}$$

Charge trapping

$$Ti^{4+} + e_{cb}^- \longrightarrow Ti^{3+} \tag{4}$$

$$>OH^- + h_{vb}^+ \longrightarrow Ti^{4+} + >OH^{\bullet} \tag{5}$$

Recombination

$$e_{cb}^- + h_{vb}^+ \longrightarrow TiO_2 \tag{6}$$

$$Ti^{3+} + >OH^{\bullet} \longrightarrow Ti^{4+} + >OH^- \tag{7}$$

Interface electron transfer

$$e_{cb}^-(Ti^{3+}) + Ox \longrightarrow Ox^- \tag{8}$$

$$h_{vb}^+(>OH^{\bullet}) + Red \longrightarrow Red^+ \tag{9}$$

where Ox is an electron acceptor (oxidant) and Red is an electron donor (reductant).

Mizushima et al., through either semi-empirical calculations from optical absorption data or photocurrent measurements [77,78] proposed the energy levels of transition metal ions in rutile (Fig. 2). These levels have been recently confirmed by an embedded-cluster discrete variational method of calculation, although with differences in some cases, particularly in Fe^{3+} [79]. Depending on the doping metal ion, electron or hole trapping may take place. Irradiation of iron-doped samples can lead to the following additional steps.

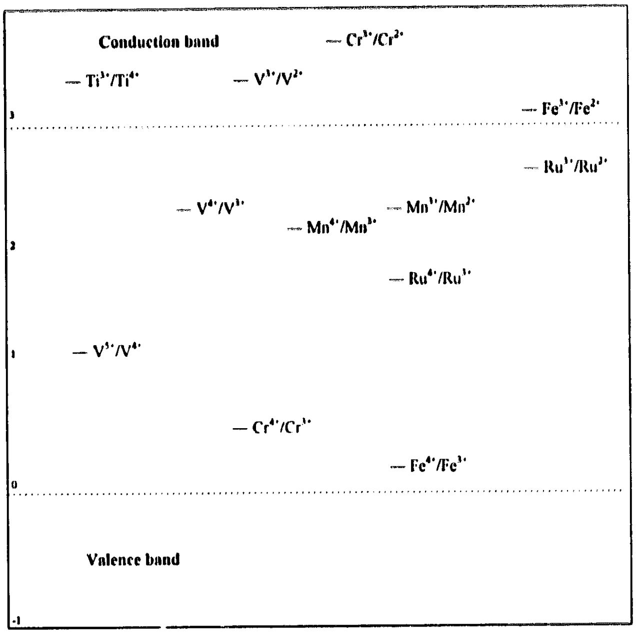

Fig. 2. Energy level diagram of transition metal ions in rutile.

Charge-pair generation

$$Fe^{3+} + h\nu \longrightarrow Fe^{4+} + e_{cb}^- \tag{10}$$

$$Fe^{3+} + h\nu \longrightarrow Fe^{2+} + h_{vb}^+ \tag{11}$$

Charge trapping

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \tag{12}$$

$$Fe^{3+} + h^+ \longrightarrow Fe^{4+} \tag{13}$$

Charge release and migration

$$Fe^{2+} + Ti^{4+} \longrightarrow Fe^{3+} + Ti^{3+} \tag{14}$$

$$Fe^{4+} + >OH^- \longrightarrow Fe^{3+} + OH^{\bullet} \tag{15}$$

Recombination

$$Fe^{2+} + h^+ \longrightarrow Fe^{3+} \tag{16}$$

$$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^- \tag{17}$$

$$Fe^{4+} + e^- \longrightarrow Fe^{3+} \tag{18}$$

$$Fe^{4+} + Ti^{3+} \longrightarrow Fe^{3+} + Ti^{4+} \tag{19}$$

Interfacial charge transfer

$$e^-(Fe^{2+}) + Ox \longrightarrow Ox^- \tag{20}$$

$$h^+(Fe^{4+}) + Red \longrightarrow Red^+ \tag{21}$$

All processes leading to products must be effective for photocatalysis; consequently, charge trapping reactions (Eqs. (4), (5), (12), (13)) must be fast in relation with recombination reactions (Eqs. (6), (7), (16)–(19)) to enhance charge separation.

In the case of iron-doped titania, as the Fe^{4+}/Fe^{3+} level in rutile is proposed to lie within the bandgap [77] and the Fe^{3+}/Fe^{2+} level is very close to the conduction band (see Fig. 2), both electron (Eq. (12)) or hole trapping (Eq. (13)) can occur at Fe(III) centers. Some authors conclude from EPR or spectroscopic evidences after steady-state or flash photolysis irradiation, that bulk Fe(III) ions are better electron traps than Ti(IV) ions [26,27,29,45]. However, EPR and absorption spectroscopic evidences of Fe(IV) formation in Fe-doped titania have been obtained [71,72,80]. In this way, iron centers act as shallow traps for valence band holes randomly trapped in Fe(IV) sites at 0.12 eV over the TiO_2 valence band, whereas electrons are trapped at Ti(IV) surface sites (Eq. (4)) (see Fig. 7 in Ref. [74]). As tunnelling between trapped charge carriers makes a significant contribution to recombination, the rate constant for this process decreases with the distance separating the electron-hole pair [74]. In addition, the recombination rate increases with the dopant concentration because the distance between trapping sites in a particle decreases with the number of dopants. On the contrary, if the iron content is very low, there are fewer trapping sites available, thus reducing the activity [49].

In anatase, irrespective of which process takes place, electron or hole trapping can reduce the rate of recombination increasing their lifetimes [74,81]. Inhibition of electron-hole recombination was indeed found in substitutionally doped colloidal semiconductor crystallites. The mean lifetime of a single electron-hole pair in 120-Å-sized TiO_2 colloidal particles increases from 30 ns [82] to minutes or hours in 0.5 at.% Fe-doped titania [49,74]. Navío et al. [83] demonstrated that reduction of MV^{2+} to MV^+ (monitored by laser flash photolysis) was more efficient in the case of iron-doped (low loading) samples than in TiO_2. This substantiates a lower recombination rate in doped samples in comparison with TiO_2. Recent studies on time-resolved microwave conductivity [81] also corroborate the inhibition of carrier recombination within Fe-doped samples and support the hypothesis that holes are trapped at Fe(IV) sites. In conclusion, the inactivity of the undoped TiO_2 samples in reduction reactions is due mainly to the high recombination rate of the electron-hole pairs, validated by time-resolved experiments.

However, in Cr(III)-doped titania samples, electron trapping is not possible, as the Cr^{3+}/Cr^{2+} level lies within the conduction band (see Fig. 2). As a consequence, the immobilized hole quickly recombines with a mobile electron, accounting for the low reactivity of these doped samples [25].

Detrapping and/or transfer of trapped charges to the interface to initiate the photoreactions must also be efficient processes. In Fe(III)-doped samples, electrons are either directly trapped at Ti(IV) surface sites (Eq. (4)) or in deeper Fe(III) sites (Eq. (12)); in this case, the trapped electron can be easily transferred from Fe^{2+} to a neighboring surface Ti^{4+} because of the proximity of the energy levels [49] (see Fig. 2).

Nevertheless, charge-transfer reactions (Eqs. (8), (9), (20), (21)) are slow processes (up to 1 s); results on time-resolved microwave conductivity [81] indicate that the trapped hole in the Fe(IV) site is transferred to an adsorbed substrate in a submilisecond reaction while the interface electron transfer occurs on the ms scale. In Q-sized particles, due to the lack of band bending, both electrons and holes are readily available at the interface (or very close to it), where the electron transfer occurs, with a consequent high photoreactivity. Correlated quantum yields for oxidation and reduction reactions have been found in these systems [49]. It is necessary to recall, however, that the preparation procedure of samples, as stated in the previous section, can induce the formation of defect sites acting as recombination centers, or can give different surface morphologies (such as hydroxyl density), which can modify the interfacial electron-transfer rates [81].

All the above energetic considerations are not valid in larger particles; dopants are here isolated far from the surface, with a much lower chance of transferring trapped charge carriers. The above mentioned correlation for oxidation and reduction reactions is thus not expected. It has been said [25] that in photoreduction processes in gas-solid regimes, the addition of dopants sets a permanent space charge region whose electric force improves the efficiency of the electron-hole separation and the charge-transfer processes. There exists an optimal value of the number of dopants for which the space charge region can be established, and of the thickness of the space charge layer in relation to the penetration depth of the light into the solid, for which all the photons absorbed generate electron-hole pairs efficiently separated. This explains the changes in activities with different iron contents [25]. Also, as a result of particle agglomeration, dopants are more likely to serve as recombination centers than as trap sites for eventual charge transfer at the interface.

Other factors, such as water or nitrogen adsorption, which might be important, do not influence very much reactivity. Rives et al. [67] demonstrated that combinations of TiO_2 and Fe_2O_3 have surfaces rich in Ti until 80 wt.% Fe_2O_3. Consequently, the adsorption of nitrogen and water on these samples is not essentially different from sample to sample. No substantial differences have been found in samples with different anatase and rutile content, although nitrogen is more easily adsorbed on the former [8]. In conclusion, low yields generally found in photoreduction of nitrogen to ammonia are mainly due to the high activation energy of the reaction, the low nitrogen adsorption (higher in anatase than in rutile) and to ammonia photodecomposition to N_2.

For oxidation reactions in large particles, generally performed in liquid-solid systems, a different explanation was proposed [8,25,28]. In these systems, the energy of the valence band is sufficient to oxidize phenol and most of the organic substrates; the contact between TiO_2 and the electrolyte sets a Schottky barrier at the interface, and the electric field in the depletion layer is sufficient to hasten the electron-hole separation. Here, oxygen molecules behave as traps for electrons, favoring the charge separation and enhancing the lifetimes of holes. Thus, differently to N_2 photoreduction, phenol and other substrates can be easily oxidized on pure TiO_2, the process not being kinetically hampered. The presence of iron induces a displacement of the Fermi level but does not affect the effectiveness of the electron-hole pair separation in comparison with pure anatase. On the contrary, the presence of dopants in a liquid–solid regime can alter the morphology of the surface of the precursor, changing the number of active sites, the type of surface groups and the acid-base properties; surface recombination can be enhanced by these factors, affecting negatively photoreactivity. Also, phases with more rutile can be less active due to the dehydroxylation caused by the transformation from anatase or by thermal treating. Dehydroxylation affects photo-oxidations because it reduces hole trapping by surface hydroxyls (Eqs. (5) and (15)), enhancing recombination and oxygen or organic species adsorption [41,84]. A decrease in the specific surface area is also found in samples prepared by coprecipitation or impregnation and submitted to thermal treatment; this factor can also affect the photoactivity.

4.2. *Heavily loaded samples*

Concentrated samples are a totally different case because phases other than TiO_2 are present in the specimens. Hematite and pseudobrookite are easily detected in samples with more than 2 at.% iron (see Section 3) and photoactivity is seriously reduced, as it was observed in all the reactions considered in Section 2. As mentioned, Navío et al. [83] observed a higher electron injection to MV^{2+} in 0.5 wt.% Fe-doped titania than in pure TiO_2, but the reverse occurred in 5 wt.% Fe samples, in which the pseudobrookite phase was present.

Fe_2O_3 and Fe_2TiO_5 have energy bandgaps lower than TiO_2 (2.2 eV [85] and 2.18 eV [86] compared with 3.2 eV for anatase [5]). Hydrogen or nitrogen photoreductions are not possible on these semiconductors due to the positive flat-band potential position. Photo-oxidations are also limited, depending on the redox potential of the substrates. In hematite, it was proposed that holes are created in a deep Fe(IV) trap of low oxidizing power and direct oxidation by valence band holes or hydroxyl radicals production is less favored with respect to TiO_2. Also, oxygen reduction (which is necessary to prevent oxide photocorrosion, see below) is less thermodynamically possible. In addition, reduced mobility of charge carriers, short hole-diffusion length (20–40 Å) and a fast recombination rate are responsible for the small efficiency of hematite in photocatalytic processes [43,87–91]. For pseudobrookite, a similar behavior is expected. The fact that the impregnated specimens are less active than the coprecipitated ones must be due to the enrichment of iron on the surfaces that provokes the appearance of small amounts of these iron oxide phases. The formation of heterojunctions or coupled semiconductors has been suggested in mixed oxides [32,43,44 59,92]. In the case of multiphasic samples of TiO_2, α-Fe_2O_3 and Fe_2TiO_5, electrons and holes can be derived to the iron or mixed oxide phase, setting the energy levels of the conduction or valence band to inadequate values for charge transfer to adsorbed substrates and promoting electron-hole recombination (Fig. 3).

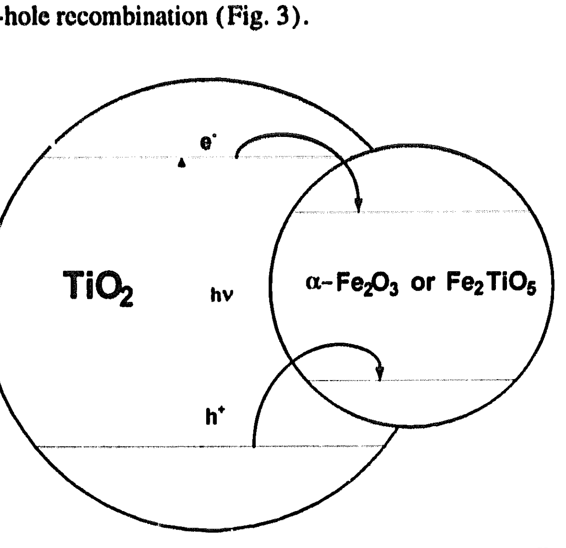

Fig. 3. Qualitative diagram of coupled semiconductors for TiO_2 and α-Fe_2O_3 or Fe_2TiO_5.

4.3. *Photoactivity originated in surface complexes or in homogeneous photolysis*

Surface complexes formed between strong (highly adsorbed) reductant ligands and surface active centers may lead to an enhancement of the overall rates through:

$$>\mathrm{Ti^{IV}(Fe^{III})}-\mathrm{L}+h\nu \longrightarrow\ >\mathrm{Ti^{III}(Fe^{II})}+\mathrm{L_{ox}} \qquad (22)$$

The formation of surface complexes was proposed in photochemical reactions [43–45,88–91,93–97]. These surface complexes may exhibit charge-transfer absorption bands at energies in the UV and visible ranges similar to those of the corresponding homogeneous complexes, and analogous photolytic behavior, leading to charge-transfer reactions. Also, if Fe^{3+} is put in solution as the result of photocorrosion (see next section), homogeneous photolysis through LMCT reaction can take place. These processes (the second one being probably more efficient) were proposed to explain the small but detectable degradation of oxalic acid under visible irradiation over Fe-doped titania catalysts [44]. Although iron as a dopant enhances the absorption in the visible with respect to TiO_2, the low photoconductivity observed at those wavelengths [50] precludes photochemical reactions in this range, due to an enhanced recombination of the photogenerated pairs. Thus, photocatalytic processes under visible irradiation seem to be possible only when visible-absorbing homogeneous or surface complexes between the substrate and the oxide can be formed. Oxalic acid can be photodegraded because Fe(III)-oxalate complexes still absorb at wavelengths in the visible (until 470 nm) [43,44]. Sclafani et al. [8] also emphasize the importance of photoFenton-type processes due to Fe^{3+} in solution.

5. Photocorrosion of iron-doped catalysts

Some iron dissolution was observed to take place in Fe-doped materials, deriving from an electron attack to Fe(III) centers [43–45]:

$$\begin{tikzcd} e^- + >\mathrm{Fe^{III}} \arrow[r] & >\mathrm{Fe^{II}} \arrow[r] \arrow[d, "O_2"] & \mathrm{Fe^{II}_{diss}} \\ & >\mathrm{Fe^{III}} & \end{tikzcd} \qquad (23)$$

The mechanism of photocorrosion is similar to that proposed for photodissolution of iron oxides [88–90,93–97]. In the presence of oxygen, reoxidation of $>Fe^{2+}$ occurs at a high rate before detaching from the surface. For this reason, the photocorrosion of iron-doped titania in photocatalytic reactions under oxygen is generally low (less than 15%). However, photodissolution of the sample is undesirable because it can cause inactivation of the catalyst by enhancing its particle size, reducing the surface area or decreasing the amount of active hydroxyl groups. The more loaded samples seem to be more stable, probably because of the presence of hematite or pseudobrookite, which are probably less easily photocorroded [43,44].

6. Conclusions

In our opinion, a great effort has been put in the search of new materials to replace TiO_2 by doping with iron and other transition metal ions. In spite of the lack of photoactivity under visible irradiation (which was expected due to the absorption of samples in this range), these materials present good and, in some cases, better photocatalytic activity in relation with the precursor. A big controversy exists nowadays about the potentiality of iron-doped titania for the photoreduction of nitrogen to ammonia, which is denied by some groups and asserted by others.

According to the experimental evidences reported in this review, it is possible to say that iron-doped TiO_2 photocatalysts could be more efficient than TiO_2 mainly if the following considerations can be accomplished.

(a) The recombination rate is decreased by the presence of ions acting as electron or hole traps. To achieve a decrease on the recombination process, the preparation method should be carefully chosen to prevent the creation of recombination centers such as defects or multiphases in which the mobility of charge carriers can be reduced.

(b) For the sake of comparison, iron-doped samples should be prepared analogously to the precursor to yield specimens of similar properties: specific surface area, anatase-to-rutile ratio, particle size, amount of surface hydroxyl groups, no defects or sites acting as recombination centers, etc.

(c) No separated phases of iron oxide or mixed oxides such as hematite or pseudobrookite, less active than TiO_2, should be formed. In this sense, the iron content plays an essential role and should be less than 2 at.%. Also, a homogeneous distribution of iron on the surface and into the TiO_2 particle should be warranted.

(d) The photocorrosion of samples should be hindered by competition with oxygen.

In spite of the controversial results in the photocatalytic efficiency of iron-doped titania, the goals of research in this field are still interesting and it seems valuable to persevere in the exploration of new methods of preparation and in the study of the remarkable photophysical and photochemical behavior of these materials.

Acknowledgements

J.A.N. wish to thank Dirección General de Investigaciones Científicas y Técnicas (DGICYT-Spain), PB93-0917 for supporting part of this work. We also thank to Consejo Nacional de Investigaciones Científicas (Spain) and Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) for an interchange grant. M.I.L. is a member from CONICET.

References

[1] N. Serpone and E. Pelizzetti (eds.), *Photocatalysis, Fundamentals and Applications*, Wiley, New York, 1989, pp. 169, 369.

[2] M.A. Fox and M.T. Dulay, *Chem. Rev.*, *93* (1993) 341.

[3] A.L. Linsebigler, G. Lu and J.T. Yates Jr., *Chem. Rev.*, *95* (1995) 735.

[4] M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.*, *95* (1995) 69.

[5] M.V. Rao, K. Rajeshwar, V.R. Pal Verneker and J. DuBow, *J. Phys. Chem.*, *84* (1980) 1987.

[6] M. Schiavello and A. Sclafani, in M. Schiavello (ed.), *Photoelectrochemistry, Photocatalysis and Photoreactors*, NATO-ASI Ser., Ser. C, No. 146, Reidel, Dordrecht, 1985, p. 503.

[7] V. Augugliaro and L. Palmisano, in M. Schiavello (ed.), *Photocatalysis and Environment. Trends and Applications*, Kluwer, 1988, p. 425.

[8] A. Sclafani, L. Palmisano, in M. Schiavello (ed.), *Res. Chem. Interm.*, *18* (1992) 211.

[9] J.A. Davies, D.L. Boucher and J.G. Edwards, in. D.C. Neckers, D.H. Volman and G. von Bünau (eds.), *Advances in Photochemistry*, Vol. 19, Wiley, New York, 1995, p. 235.

[10] J.G. Edwards, J.A. Davies, D.L. Boucher and A. Mennad, *Angew. Chem. Int. Ed. Engl.*, *31* (1992) 480.

[11] V. Augugliaro and J. Soria, *Angew. Chem. Int. Ed. Engl.*, *32* (1993) 550.

[12] L. Palmisano, M. Schiavello and A. Sclafani, *Angew. Chem. Int. Ed. Engl.*, *32* (1993) 551.

[13] J.A. Davies and J.G. Edwards, *Angew. Chem. Int. Ed. Engl.*, *32* (1993) 552.

[14] D.L. Boucher, J.A. Davies, J.G. Edwards and A. Mennad, *J. Photochem. Photobiol. A: Chem.*, *88* (1995) 53.

[15] G.N. Schrauzer and T.D. Guth, *J. Am. Chem. Soc.*, *99* (1977) 7189.

[16] P.P. Radford and C.G. Francis, *J. Chem. Soc., Chem. Comm.*, (1983) 1520.

[17] G.N. Schrauzer, N. Strampach, L.N. Hui, M.R. Palmer and J. Salehi, *Proc. Natl. Acad. Sci. USA*, *80* (1983) 3873.

[18] H. Van Damme and W.K. Hall, *J. Am. Chem. Soc.*, *101* (1979) 4373.

[19] M. Formenti and S.J. Teichner, in D.A. Dowden and C. Kemball (eds.), *Catalysis*, Vol. 2, The Chemical Society, London, 1978, p. 87.

[20] V. Augugliaro, A. Lauricella, L. Rizzuti, M. Schiavello and A. Sclafani, *Int. J. Hydrogen Energy*, *7* (1982) 845.

[21] V. Augugliaro, F. D'Alba, L. Rizzuti, M. Schiavello and A. Sclafani, *Int. J. Hydrogen Energy*, *7* (1982) 851.

[22] M. Schiavello, L. Rizzuti, A. Sclafani, I. Majo, V. Augugliaro and P.L. Yue, in T.N. Verizoglu, K. Fueki and T. Ohta (eds.), *Hydrogen Energy Progress*, Vol. IV, Pergamon, Oxford, p. 821.

[23] P.L. Yue, F. Khan and L. Rizzuti, *Chem. Eng. Sci.*, *38* (1983) 1893.

[24] M. Schiavello, L. Rizzuti, R.I. Bickley, J.A. Navío and P.L. Yue, *Proc. VIIIth. Intern. Congress on Catalysis*, Berlin, Germany, July 1984, Vol. III, Verlag Chemie, Basel, 1984, p. 383.

[25] L. Palmisano, V. Augugliaro, A. Sclafani and M. Schiavello, *J. Phys. Chem.*, *92* (1988) 6710.

[26] J.C. Conesa, J. Soria, V. Augugliaro and L. Palmisano, in C. Morterra, A. Zecchina and G. Costa (eds.), *Structure and Reactivity of Surfaces*, Elsevier, Amsterdam, 1989, p. 307.

[27] J. Soria, J.C. Conesa, V. Augugliaro, L. Palmisano, M. Schiavello and A. Sclafani, *J. Phys. Chem.*, *95* (1991) 274.

[28] R.I. Bickley, L. Palmisano, M. Schiavello and A. Sclafani, in L. Guczi et al. (eds.), *New Frontiers in Catalysis Proceed. 10th. Intern. Congress on Catalysis*, 19–24 July, 1992, Budapest, Hungary, Elsevier, Amsterdam, 1993.

[29] D. Cordishi, N. Burriesci, F. D'Alba, M. Petrera, G. Polizzotti and M. Schiavello, *J. Solid State Chem.*, *56* (1985) 182.

[30] R.I. Bickley, T. González-Carreño and L. Palmisano, *Preparation of Catalysts IV*, Elsevier, Amsterdam, 1987, p. 297.

[31] N.N. Rao, S.D. Manjubala and P. Natarajan, *Applied Catal. B: Environ.*, *5* (1994) 33.

[32] K. Tennakone, C.A.N. Fernando, S. Wickramanayake, M.W.P. Damayanthi, L.H.K. Silva, W. Wijeratne, O.A. Illeperuma and S. Punchihewa, *Solar Energy Mater.*, *17* (1988) 47.

[33] S. Bourgeois, D. Diakite and M. Perdereau, *React. Solids*, *6* (1988) 95.

[34] R.I. Bickley, J.A. Navío and V. Vishwanathan, Paper presented at the *6th. Intern. Conf. on Photochem. Conversion and Storage of Solar Energy*, Paris, July 1986.

[35] R.I. Bickley and J.A. Navío-Santos, in G. Grassi and D.O. Hall (eds.), *Photocatalytic Production of Energy-Rich Compounds*, Elsevier, London, 1985, p. 105.

[36] S. Zielinski and A. Sobczynski, *Acta Chim. Hung.*, *120* (1985) 229.

[37] G.N. Schrauzer, T.D. Guth, J. Salehi, N. Strampach, L.N. Hui and M.R. Palmer, in E. Pelizzetti and N. Serpone (eds.), *Homogeneous and Heterogeneous Photocatalysis*, NATO-ASI Ser., Ser. C. No. 174, D. Reidel, Hingham, MA, 1986, p. 509.

[38] J.A. Navío, M. García Gómez, M.A. Pradera Adrián and J. Fuentes Mota, in Guisnet et al. (eds.) *Heterogeneous Catalysis and Fine Chemicals II*, Elsevier, Amsterdam, 1991, p. 445.

[39] L. Palmisano, M. Schiavello, A. Sclafani, C. Martin, I. Martin and V. Rives, *Catal. Lett.*, *24* (1994) 303.

[40] A. Sclafani, L. Palmisano and E. Davi, *New J. Chem.*, *14* (1990) 265.

[41] A. Sclafani, L. Palmisano and M. Schiavello, *J. Phys. Chem.*, *94* (1990) 829.

[42] A. Milis, J. Peral and X. Domènech, *J. Mol. Catal.*, *87* (1994) 67.

[43] M.I. Litter and J.A. Navío, *J. Photochem. Photobiol. A: Chem.*, *84* (1994) 183.

[44] J.A. Navío, G. Colón, M.I. Litter and G.N. Bianco, *J. Mol. Catal. A. Chem.*, *106* (1996) 267.

[45] D.W. Bahnemann, *Isr. J. Chem.*, *33* (1993) 115.

[46] D.W. Bahnemann, D. Bockelmann, R. Goslich, M. Hilgendorff and D. Weichgrebe, in D.F. Ollis and H. Al-Ekabi (eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, p. 301.

[47] D. Bockelmann, R. Goslich and D.W. Bahnemann, *Sol. Ther. Energy Util.*, *6* (1992) 397.

[48] W. Choi, A. Termin and M.R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 1091.

[49] W. Choi, A. Termin and M.R. Hoffmann, *J. Phys. Chem.*, *98* (1994) 13669.

[50] N. Serpone, D. Lawless, J. Disdier and J.M. Herrmann, *Langmuir*, *10* (1994) 643.

[51] S.T. Martin, C.L. Morrison and M.R. Hoffmann, *J. Phys. Chem.*, *98* (1994) 13695.

[52] J.E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, 2nd. edn., Harper & Row, New York, 1978, Spanish Trans., p. 77.

[53] J.S. Thorp and H.S. Eggleston, *J. Mater. Sci. Lett.*, *4* (1985) 1140.

[54] A. Amorelli, J.C. Evans, C.C. Rowlands and T.A. Egerton, *J. Chem. Soc. Faraday Trans. 1*, *83* (1987) 3541.

[55] A. Amorelli, J.C. Evans and C.C. Rowlands, *J. Chem. Soc. Faraday Trans. 1*, *85* (1989) 4031.

[56] M.A. Malati and W.K. Wong, *Surf. Technol.*, *22* (1984) 305.

[57] R.I. Bickley, J.S. Lees, R.J.D. Tilley, L. Palmisano and M. Schiavello, *J. Chem. Soc. Faraday Trans.*, *88* (1992) 377.

[58] R.I. Bickley, T. González-Carreño and L. Palmisano, *Mater. Chem. and Phys.*, *29* (1991) 475.

[59] R.I. Bickley, T. González-Carreño, A.R. González-Elipé, G. Munuera and L. Palmisano, *J. Chem. Soc. Faraday Trans.*, *90* (1994) 2257.

[60] J.A. Navío, M. Macías, M. González-Catalán and A. Justo, *J. Mater. Sci.*, *27* (1992) 3036.

[61] N.G. Maksimov, I.I. Mikhailova and V.F. Anufrienko, *Kinet. Catal. (Engl. Transl.)*, *13* (1973) 1162.

[62] Y. Iida and S. Ozaki, *J. Am. Ceram. Soc.*, *44* (1961) 120.

[63] A. Nobile, Jr. and M.W. Davis, Jr., *J. Catal.*, *116* (1989) 383.

[64] P.M. Rao, B. Viswanathan and R.P. Viswanathan, *J. Mater. Sci. 30* (1995) 4980.

[65] D. Gazzoli, G. Minelli and M. Valigi, *Mater. Chem. and Phys.*, *21* (1989) 93.

[66] J.A. Navío, M. Macías, M. González-Catalán, J.M. Marinas and J.M. Campelo, *XIII Iberoamerican Symposium on Catalysis*, El Escorial, Madrid, July 6–10, 1992.

[67] A.B. Rives, T.S. Kulkarni and A.L. Schwaner, *Langmuir*, *9* (1993) 192.

[68] M.V. Tsodikov, O.V. Bukhtenko, O.G. Ellert, W.M. Shcherbakov and D.I. Kochubey, *J. Mater. Sci.*, *30* (1995) 1087.

[69] J.A. Navío, M.V. Tsodikov, V. Ya. Kugel, E.V. Slivinskiy, Yu. V. Maksimov, I.P. Suzdalev and D.I. Kochubey, *8th. Intern. Workshop on Glasses and Ceramics from Gels*, Faro, Portugal, September 18–22, 1995.

[70] J.A. Navío, M.I. Litter et al., unpublished results.

[71] O.W. Johnson, W.D. Ohlsen and P.I. Kingsbury, Jr., *Phys. Rev.*, *175* (1968) 1102.

[72] B.W. Faughnan and Z.J. Kiss, *Phys. Rev. Lett.*, *21* (1968) 1331.

[73] M. Radecka, M. Rekas and K. Zakrzewska, *Solid State Phenomena*, *39–40* (1994), 113.

[74] J. Moser, M. Grätzel and R. Gallay, *Helv. Chim. Acta*, *70* (1987) 1596.

[75] K.E. Karakitsou and X.E. Verykios, *J. Phys. Chem.*, *97* (1993) 1184.

[76] H.P. Maruska and A.K. Ghosh, *Solar Energy Mater.*, *1* (1979) 237.

[77] K. Mizushima, M. Tanaka, A. Asai and S. Iida, *J. Phys. Chem. Solids*, *40* (1979) 1129.

[78] K. Mizushima, M. Tanaka and S. Iida, *J. Phys. Soc. Jpn.*, *32* (1972) 1519.

[79] S.D. Mo, L.B. Lin and D.L. Lin, *J. Phys. Chem. Solids 55*, (1994) 1309.

[80] M. Grätzel and R.F. Howe, *J. Phys. Chem.*, *94* (1990) 2566.

[81] S.T. Martin, H. Herrmann, W. Choi and M.R. Hoffmann, *J. Chem. Soc. Faraday Trans.*, *90* (1994) 3315.

[82] G. Rothenberger, J. Moser, M. Gratzel, N. Serpone and D.K. Sharma, *J. Am. Chem. Soc.*, *107* (1985) 8054.

[83] J.A. Navío, F.J. Marchena, M. Roncel and M.A. De la Rosa, *J. Photochem. Photobiol. A: Chem.*, *55* (1991) 319.

[84] V. Augugliaro, L. Palmisano, A. Sclafani, C. Minero and E. Pelizzetti, *Toxicol. Environ. Chem.*, *16* (1988) 89.

[85] M.P. Dare-Edwards, J.B. Goodenough, A. Hamnett and P.R. Trevellick, *J. Chem. Soc. Faraday Trans. 1*, *79* (1983) 2027.

[86] D.S. Ginley and M.A. Butler, *J. Appl. Phys.*, *48* (1977) 2019.

[87] J. Moser and M. Grätzel, *Helv. Chim. Acta*, *65* (1982) 1436.

[88] M.I. Litter, E.C. Baumgartner, G.A. Urrutia and M.A. Blesa, *Environ. Sci. Technol.*, *25* (1991) 1907.

[89] M.I. Litter and M.A. Blesa, *Can. J. Chem.*, *70* (1992) 2502.

[90] M.I. Litter, M. Villegas and M.A. Blesa, *Can. J. Chem.*, *72* (1994) 2037.

[91] C. Kormann, D.W. Bahnemann and M.R. Hoffmann, *J. Photochem. Photobiol. A: Chem.*, *48* (1989) 161.

[92] K. Tennakone, W.D.W. Jayatilake, U.S. Ketipearahchi, W.C.B. Kiridena, M.A.K.L. Dissanayake and O.A. Illeperuma, *J. Photochem. Photobiol. A:Chem.*, *58* (1991) 323.

[93] C. Siffert and B. Sulzberger, *Langmuir*, *7* (1991) 1627.

[94] M.I. Litter and M.A. Blesa, *J. Colloid Interface Sci.*, *125* (1988) 679.

[95] M.I. Litter and M.A. Blesa, *Can. J. Chem.*, *68* (1990) 728.

[96] B.C. Faust, M.R. Hoffmann and D.W. Bahnemann, *J. Phys. Chem.*, *93* (1989) 6371.

[97] B.C. Faust and M.R. Hoffmann, *Environ. Sci. Technol.*, *20* (1986) 943.