

Role of $\text{Fe}^{3+}/\text{Fe}^{2+}$ as TiO_2 dopant ions in photocatalytic degradation of carboxylic acids

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Abstract

The photocatalytic degradation of organic carboxylic acids by Fe-doped TiO_2 has been studied. Results indicate that Fe is extracted by means of the formation of a $[\text{Fe-carboxylic acid}]^{n+}$ complex by which the organic molecule is degraded. Fe^{2+} ions that remain in solution after the degradation go back to the catalyst surface due to their reaction with the photogenerated holes in the TiO_2 . This way the catalyst is reactivated becoming ready for a new degradation process. XPS studies have confirmed these results. Also, it has been observed that the catalyst preparation method affects the photoactivity of the formed complexes. The catalyst with lower Fe content and prepared from $\text{Fe}(\text{NO}_3)_3$ by the incipient wetness impregnation method degrades the formic acid more readily than the undoped catalyst and the catalysts prepared by other methods. Complexes formed by means of the iron interaction with formic and maleic acids are more photoactive than those formed with acetic or acrylic acids. The slower degradation of these last acids could be related with the photo-Kolbe reaction or other reduction processes. FTIR studies have been conducted with the goal of identifying the intermediates generated from the interaction of the different acids with the catalysts surface.

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1. Introduction

One of the most interesting research fields in photocatalysis is the effect of the catalyst doping with the goal of improving its activity. It has been indicated that the doping of semiconductors such as TiO_2 with Fe, Pt, Cr, etc. can modify its structure or morphology, speeding up or slowing down the h^+/e^- couple recom-

bination speed, and consequently enhance or reduce its catalytic behaviour. In this way some authors have shown that the partial substitution of Ti by Sn atoms in the TiO_2 lattice leads to the electron-hole recombination speed reduction [1]. Also, other authors have indicated that Cr and Mo oxides increase the photocatalytic phenol oxidation rate by TiO_2 [2,3] or that the TiO_2 platinisation improves the photocatalytic ethanol oxidation [4].

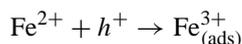
However, the use of Fe as a TiO_2 dopant has not yielded good results [5]. Dissolved Fe^{3+} ions have evidenced a good photocatalytic activity by means of

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the photo-Fenton reaction [6–8], but when the metal is deposited on TiO₂, it does not enhance the semiconductor photocatalytic ability. Until now, Fe has been used as a TiO₂ dopant because of its complexing capacity. This fact could in a certain extension favour the approach and adsorption of reagents to the semiconductor. Nonetheless, in recent studies developed by our research group a previously unreported property of the Fe-doped catalysts was discovered [9,10]. Iron present on the TiO₂ surface as Fe₂O₃ is able to interact with formic acid or maleic acid which extracts the metal from the catalyst surface as a complex. Then, the Fe³⁺-organic acid complex is photochemically degraded, the Fe³⁺ ions are reduced to Fe²⁺ and finally the metal ions go back to the TiO₂ surface by means of the following reaction:



With the goal of improving our knowledge about the mechanism by which this process occurs the formic acid degradation has been tested by using Fe-doped catalysts prepared by different methods and from different precursors. Additionally, the ability of some of these catalysts (those showing faster formic acid degradations) at degrading other carboxylic acids such as acetic and acrylic was studied.

2. Experimental

2.1. Catalysts synthesis

2.1.1. *x*Fe-TiO₂(n) and *x*Fe-TiO₂(a) (*x* = wt.% of iron)

TiO₂ was Degussa P-25 (80% anatase). Doping was performed by impregnation of TiO₂ with aqueous solutions of Fe(NO₃)₃ (in *x*Fe-TiO₂(n), method (n)) or aqueous solutions of iron acetylacetonate (in *x*Fe-TiO₂(a), method (a)) by an incipient wetness impregnation method [11] at 298 K as follows. The mixture (TiO₂ and Fe precursor) was stirred during 48 h. Later, water was evaporated by heating at 393 K during 24 h. Finally, the catalysts were calcined at 773 K.

2.1.2. *x*Fe-TiO₂(sg)

Sol-gel iron-doped samples were synthesised from iron acetylacetonate and TiCl₄ according to the procedure that has been already described [12].

2.1.3. Experimental conditions

The following experimental conditions were employed for all experiments: 250 ml glass vessels reactors, carboxylic acid (50 ppm) and catalysts (2 g l⁻¹) concentrations, carboxylic acid-catalysts suspensions were continuously stirred and air-bubbled (100 ml min⁻¹). Also, before switching the UV-lamp on, the suspension was air-bubbled and stirred for 15 min (in the dark) in order to favour the organic chemisorption onto the catalyst surface.

2.1.4. Equipments

A 800 W Xenon UV-lamp (Solarium Facial UV-A HPA 8068, ENCO, emission maxima around 385 nm) was employed as a UV light source. Remaining organic acid concentrations at different reaction times were HPLC-measured by using a reverse phase column (C18) Zorbax ODS 5 μm (Jones Chromatography) and a 0.2 M phosphoric acid mobile phase, using a UV detector (λ = 210 nm). Organic carbon (TOC), total carbon (TC) and inorganic carbon (IC) were made by using a TOC Shimadzu 5000-A. Dissolved iron was quantified by atomic absorption spectrophotometry with a Varian equipment model Zeeman provided with an automatic dispersor and a graphite furnace.

BET surface area of the catalysts has been measured by using a Gemini III 2375 surface area analyser (Micromeritics). Samples of the catalysts (0.2 g) were placed in glass tubes (15 cm long × 0.8 cm wide) and treated with N₂ at 373 K for 24 h before measuring. Then, a vacuum pump was used to extract N₂ and the catalyst free space was determined by using He gas. Adsorption-desorption curves containing 25 points each with N₂ at 78 K were employed for surface area measurements.

Table 1
Surface area of the different catalysts

Catalyst	Surface area (m ² g ⁻¹)
Bare-TiO ₂	50.0
0.5Fe-TiO ₂ (n)	47.3
5Fe-TiO ₂ (n)	46.8
0.5Fe-TiO ₂ (sg)	57.2
3Fe-TiO ₂ (sg)	44.0
0.5Fe-TiO ₂ (a)	44.0
5Fe-TiO ₂ (a)	41.8

Catalysts were impregnated with the corresponding carboxylic acid–water saturated solutions for FTIR experiments. After 15 min catalysts were placed between two CaF_2 windows for the spectral analysis. An FTIR spectrophotometer model RS/1 (UNICAM) was used. Intervals of $2000\text{--}1000\text{ cm}^{-1}$, a resolution of 2 cm^{-1} and a forward and reverse moving mirrors speed of 10

and 6.2 kHz , respectively, were used. Water reference spectrum has been subtracted to all spectra.

X-ray diffraction (XRD) patterns were obtained by using a Siemens D-500 diffractometer ($\text{Cu K}\alpha$, $\lambda = 1.5432\text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was carried out on a Leybold Heraeus LHS-10 spectrometer, working with constant energy pass of 50 eV ,

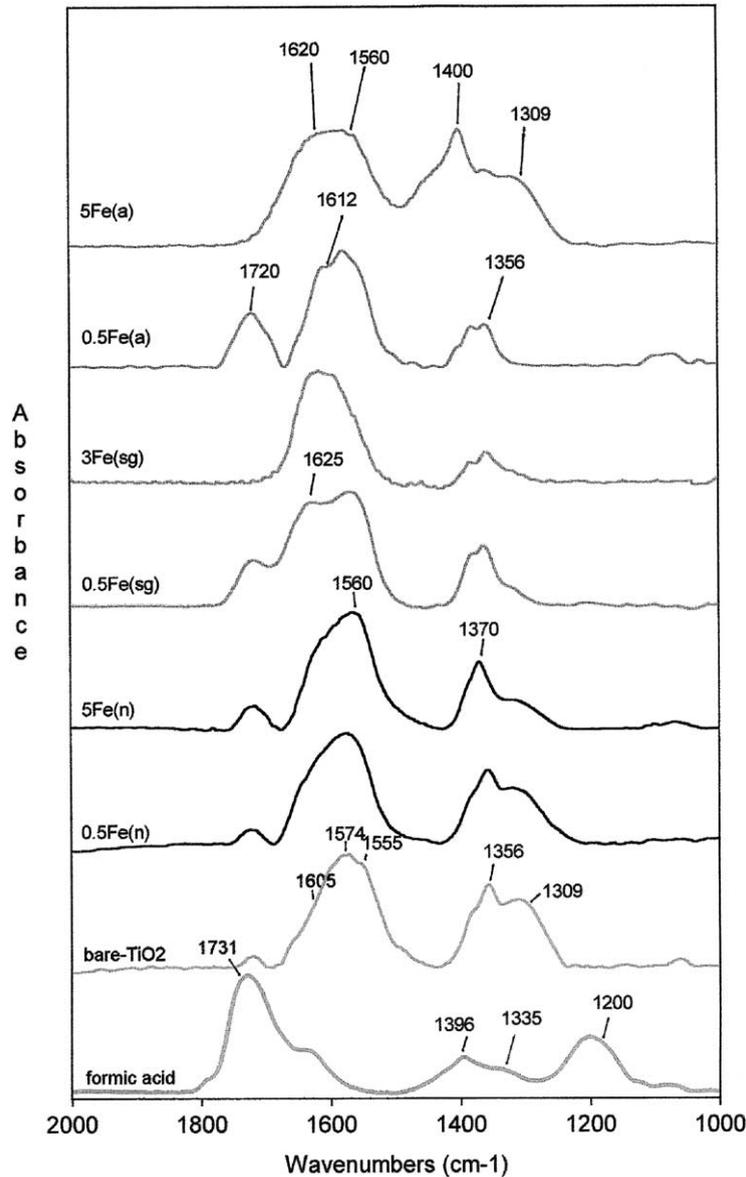


Fig. 1. IR spectra from the interaction of a 1:1 (w/w) formic acid–water solution with the catalysts: bare- TiO_2 , $0.5\text{Fe-TiO}_2(\text{n})$ ($0.5\text{Fe}(\text{n})$); $5\text{Fe-TiO}_2(\text{n})$ ($5\text{Fe}(\text{n})$); $0.5\text{Fe-TiO}_2(\text{sg})$ ($0.5\text{Fe}(\text{sg})$); $3\text{Fe-TiO}_2(\text{sg})$ ($3\text{Fe}(\text{sg})$); $0.5\text{Fe-TiO}_2(\text{a})$ ($0.5\text{Fe}(\text{a})$); and $5\text{Fe-TiO}_2(\text{a})$ ($5\text{Fe}(\text{a})$).

and using Al K α radiation as excitation source. Before XPS recording a final pressure of 10^{-9} Torr was attained. C (1s) was used as internal reference.

3. Results and discussion

3.1. XRD and surface area measurements

Catalysts used in this study have already been characterised by XRD analyses and surface area measurements in previous works [9,12]. According to those results it was observed that iron is present in the catalysts prepared by the methods (n) and (a), mainly as α -Fe $_2$ O $_3$. In these catalysts the characteristic TiO $_2$ anatase and rutile phases were identified, in the expected amounts for TiO $_2$ Degussa P-25. On the contrary, in the catalysts prepared by the method (sg) iron oxides or TiO $_2$ rutile phases were not observed, indicating the iron atoms incorporation to the TiO $_2$ anatase structure. In addition to this, the surface area measurements indicated that the presence of Fe on the catalysts surface did not significantly modify their surface area. Only for the higher Fe containing catalysts and those prepared by methods (a) and (sg) a 10–16% surface area change was determined with regard to Degussa P-25 TiO $_2$ (Table 1).

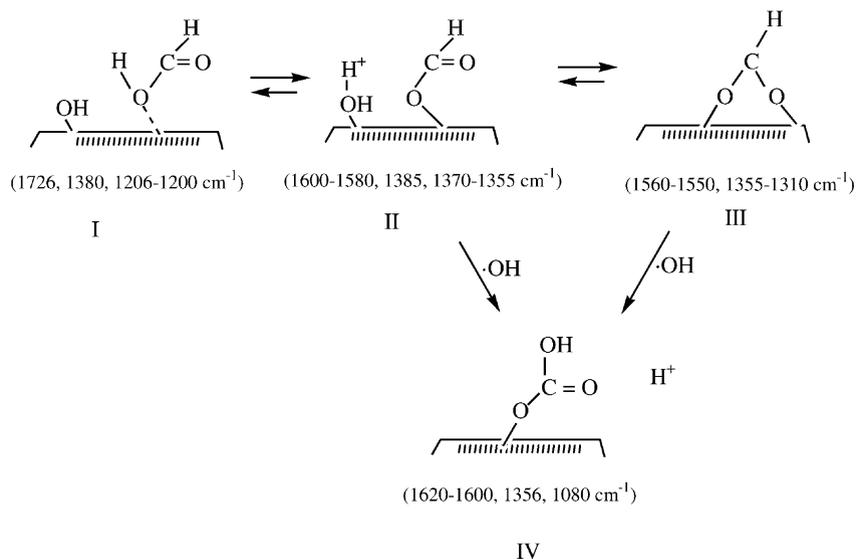
4. Degradation studies of the different carboxylic acids

4.1. Formic acid

4.1.1. FTIR analysis

Fig. 1 shows the spectra obtained from the interaction of a 1:1 (w/w) formic acid–water solution with the different catalysts. In previous works the formic acid interactions with the catalysts bare-TiO $_2$, 0.5Fe-TiO $_2$ (n) and 5Fe-TiO $_2$ (n) were described [9]. This way, the acid interaction with the catalysts yields formates as illustrated in Scheme 1.

The band that in the bare-TiO $_2$ appears at 1356 cm $^{-1}$ beside the shoulder at 1605 cm $^{-1}$ is attributed to the presence of hydrogen carbonates. The band at 1309 cm $^{-1}$ in addition to the band at 1555 cm $^{-1}$, from the deconvolution of the band centred at 1574 cm $^{-1}$, can be attributed to type III species shown in Scheme 1. The spectrum from the 0.5Fe-TiO $_2$ (n) interaction with the formic acid is quite similar to that of the catalysts 5Fe-TiO $_2$ (n), but with a subtle change in the relative intensity of the bands. However, in the catalyst 5Fe-TiO $_2$ (n) the larger presence of the type II species (Scheme 1) is clearly observed according to the bands at 1560 and 1370 cm $^{-1}$. In the catalysts 0.5Fe-TiO $_2$ (a), 3Fe-TiO $_2$ (sg) and 0.5Fe-TiO $_2$ (sg) no type III species (absence of bands in the region



Scheme 1. Correlation between formic acid coordination to the catalyst surface and the corresponding wavenumbers.

between 1355 and 1310 cm^{-1}) are visible. Nevertheless, the presence of hydrogen carbonates is more clearly observed, due to the characteristic bands at 1356 and $1620\text{--}1610\text{ cm}^{-1}$. On the other hand, in the catalyst prepared by the method (a) with the highest iron content ($5\text{Fe-TiO}_2(\text{a})$) the band due to the $\nu(\text{COO}^-)$ s at 1400 cm^{-1} is considerably shifted towards higher wavenumbers and presents an intensity increase with respect to those obtained with the other catalysts.

This way it has been determined that the spectra from the formic acid interaction with the catalysts prepared by the method (n) are quite similar to those obtained with the catalyst bare- TiO_2 . However, the spectra obtained from these catalysts are significantly distinct from those of catalysts prepared by methods (a) and (sg).

4.1.2. Degradation study

Fig. 2 shows the TOC concentration diminution (in %) during an aqueous 50 ppm formic acid solution photocatalytic degradation using the different catalysts. The catalyst $0.5\text{Fe-TiO}_2(\text{n})$ degrades the acid slightly faster than the catalyst bare- TiO_2 . The

rest of catalysts with the same concentration of iron ($0.5\text{Fe-TiO}_2(\text{a})$ and $0.5\text{Fe-TiO}_2(\text{sg})$) are significantly worse, achieving total degradation after 5 h of reaction. In fact, it has been indicated that catalysts prepared by acetylacetonate impregnation may contain carbon impurities after the precursor thermal decomposition by the burning process that could negatively affect its photocatalytic activity [13]. In addition to this, in catalysts prepared by the sol-gel method the absence of a perfect matrix lattice like that of Degussa P-25 could negatively affect their photocatalytic activity [14]. With regard to catalysts containing larger iron contents, the one prepared by means of the method (n) (the $5\text{Fe-TiO}_2(\text{n})$) shows again the better catalytic behaviour. In fact, the catalyst $3\text{Fe-TiO}_2(\text{sg})$ did not give any TOC reduction.

HPLC analyses of the samples at different reaction times show the presence of intermediates with retention times that correspond to those of Fe^{2+} and Fe^{3+} complexes. With the goal of confirming the presence and determining the concentration of Fe ions in the solution the samples were analysed by atomic absorption spectroscopy. Results from the different catalysts are shown in Fig. 3. In the catalysts $0.5\text{Fe-TiO}_2(\text{n})$ and

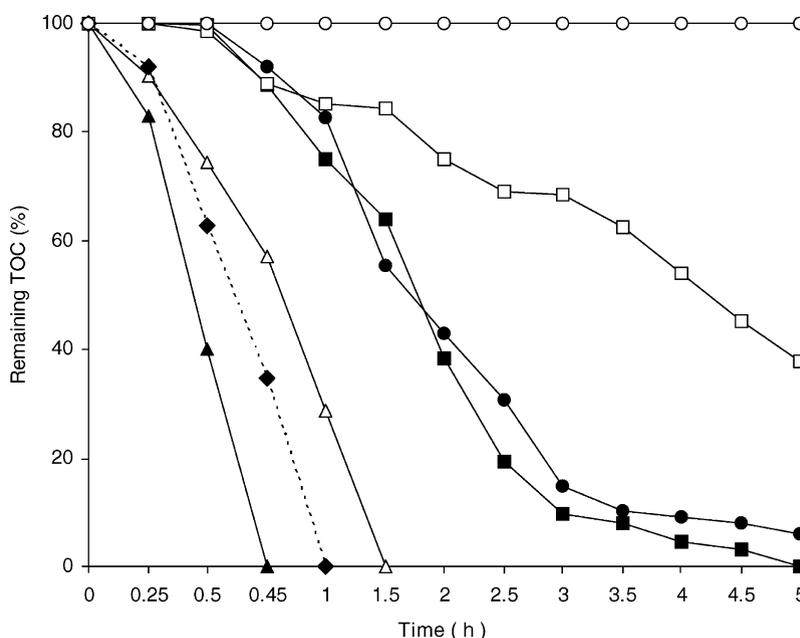


Fig. 2. TOC reduction during the degradation of formic acid solution (50 ppm): (◆) bare- TiO_2 ; (▲) $0.5\text{Fe-TiO}_2(\text{n})$; (△) $5\text{Fe-TiO}_2(\text{n})$; (●) $0.5\text{Fe-TiO}_2(\text{sg})$; (○) $3\text{Fe-TiO}_2(\text{sg})$; (■) $0.5\text{Fe-TiO}_2(\text{a})$; and (□) $5\text{Fe-TiO}_2(\text{a})$.

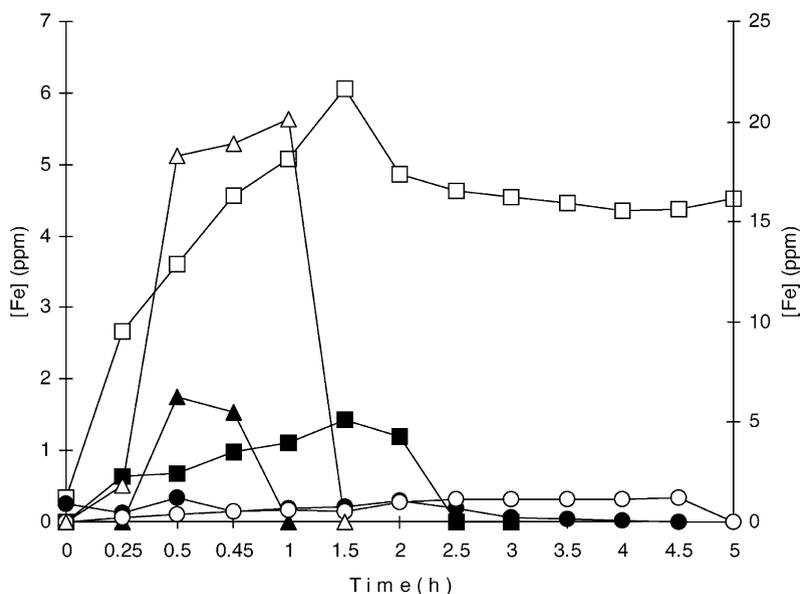


Fig. 3. Dissolved Fe concentration during the degradation of a 50 ppm formic acid solution: (▲) 0.5Fe-TiO₂(n); (△) 5Fe-TiO₂(n); (●) 0.5Fe-TiO₂(sg); (○) 3Fe-TiO₂(sg); (■) 0.5Fe-TiO₂(a); and (□) 5Fe-TiO₂(a).

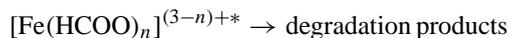
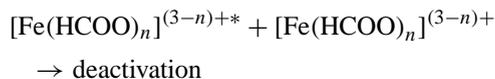
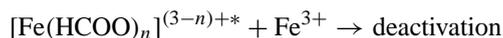
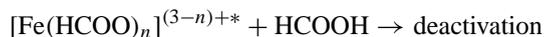
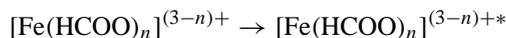
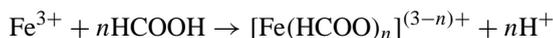
5Fe-TiO₂(n) Fe ions appear and disappear from the solution. This process occurs at the time of the formic acid degradation. The following facts

- no photocorrosion processes, as previously reported are observed [9,10] in this catalysts;
- the precipitation of iron is not observed after the experiments;
- the same catalytic behaviour was observed when the catalysts were reused;

suggest that in the case of catalysts prepared by the method (n), the iron is extracted from the catalyst surface as a photoactive complex that yields the acid degradation. According to the obtained results (catalyst reutilisation and dissolved iron disappearance), once the formic acid has been degraded the iron goes back to the catalyst surface.

Also, dissolved iron is detected in catalysts prepared by method (a), but in these cases the degradation process is much slower. Also the iron extraction and return to the catalyst surface is slower. In the catalysts prepared by the method (sg) Fe ions were hardly detected in the solution. In these catalysts the degradation is slower, even the catalyst 3Fe-TiO₂(sg) is not able to degrade the formic acid.

Different authors [15] have suggested that the Fe interaction with formic acid gives photochemically active [Fe-(HCOO)_n]⁽³⁻ⁿ⁾⁺ complexes. They also have indicated that these complexes can be deactivated by means of the combination with other molecules of formic acid or other Fe³⁺ ions, or the combination with other complexes:



The obtained results suggest that the catalysts prepared by the method (n) mainly lead to the formation of photoactive complexes, without interferences from the other molecules that can deactivate them. The best example of this is the catalyst with the lower iron content (0.5Fe-TiO₂(n)) since it degrades the formic acid

Table 2
5Fe-TiO₂(n) catalyst nomenclature after different treatments

Catalyst	Treatment
5Fe-TiO ₂ (n)	Unused catalyst
5Fe-TiO ₂ (n)-a	Catalyst 5FeTiO ₂ (n) after reaction for 45 min with formic acid (25 ppm) + <i>hν</i> + air
5Fe-TiO ₂ (n)-b	5Fe-TiO ₂ (n) catalyst after contact with Fe ²⁺ (20 ppm) for 20 min
5Fe-TiO ₂ (n)-c	5Fe-TiO ₂ (n)-b catalyst after reaction with formic acid (25 ppm) for 15 min + <i>hν</i> + air
5Fe-TiO ₂ (n)-d	5Fe-TiO ₂ (n)-a catalyst after reaction with Fe ³⁺ (20 ppm) for 20 min
5Fe-TiO ₂ (n)-e	5Fe-TiO ₂ (n)-d catalyst after reaction with formic acid (25 ppm) for 15 min + <i>hν</i> + air
5Fe-TiO ₂ (n)-f	5Fe-TiO ₂ (n) catalyst after reaction with formic acid (25 ppm) for 1.5 h + <i>hν</i> + air

more readily than bare-TiO₂. On the contrary, catalysts with a higher Fe content or prepared by methods (a) and (sg) seem to get deactivated by the reactions commented above. Other possibility is that the formed complexes in these last catalysts were less photoactive. In fact, FTIR studies have shown differences in the interaction of the acid molecule with the different catalysts surfaces and this could favour the interaction of the formed complex with the molecules.

The experiments about the formic acid degradation have shown that the catalyst preparation method determines the photoactive Fe-formic acid formation. Also, the present study has revealed that catalysts prepared by means of method (n) give more photoactive complexes. With the goal of studying the catalysts surfaces, during the iron extraction and turning back process, the catalyst 5Fe-TiO₂(n) has been studied by XPS under different conditions.

4.2. XPS studies

The extraction of Fe³⁺ ions from the catalyst surface surely generates the surfacial charge destabilisation and possible restructuring. With the goal of studying the catalysts surface and how the metal return occurs the catalyst surface was analysed by means of XPS. As already mentioned the catalyst 5Fe-TiO₂(n) was selected for these experiments. The catalyst was treated with formic acid, Fe²⁺ and Fe³⁺ salts and its surface was later analysed. Tables 2 and 3 show the proposed nomenclature after every treatment and the XPS results, respectively.

Some authors have indicated that the binding energy (BE) of Fe³⁺ ions is 711.2 and that of Fe²⁺ is 709.3. BE modifications in this range are given by mixtures of both oxidation states [16]. Hence, the Fe²⁺ and Fe³⁺ ions amounts have been calculated from the

Table 3
XPS results after different treatments

Catalyst	Fe (2p) % (BE)	Ti (2p) % (BE)	O (1s) % (BE)
Bare-TiO ₂	–	31.48 (458.5)	61.01 (529.7)
5Fe-TiO ₂ (n)	6.51 (711.2) ^a	28.33 (458.5)	55.77 (529.8)
5Fe-TiO ₂ (n)-a	4.09 (710.7) ^b	32.91 (458.5)	59.19 (529.9)
5Fe-TiO ₂ (n)-b	5.68 (711.2) ^c	26.78 (458.5)	6.92 (529.7)
5Fe-TiO ₂ (n)-c	3.26 (710.8) ^d	31.12 (458.5)	58.57 (529.9)
5Fe-TiO ₂ (n)-d	4.47 (710.5) ^e	30.52 (458.5)	60.03 (529.6)
5Fe-TiO ₂ (n)-e	2.20 (710.5) ^f	30.69 (458.5)	61.13 (529.6)
5Fe-TiO ₂ (n)-f	6.41 (710.7) ^g	28.90 (458.5)	58.68 (529.8)

^a Fe³⁺ = 6.51.

^b Fe³⁺ = 3.01; Fe²⁺ = 1.08.

^c Fe³⁺ = 5.68.

^d Fe³⁺ = 2.57; Fe²⁺ = 0.69.

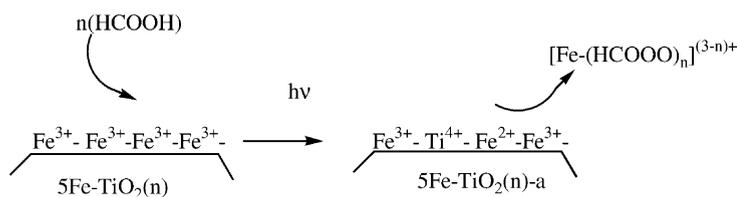
^e Fe³⁺ = 2.82; Fe²⁺ = 1.65.

^f Fe³⁺ = 1.42; Fe²⁺ = 0.78.

^g Fe³⁺ = 4.72; Fe²⁺ = 1.68.

obtained BE and the total iron atoms concentration on the surface using an equations system.

After the catalyst 5Fe-TiO₂(n) reaction with formic acid for 45 min (catalyst 5Fe-TiO₂(n)-a) a surficial Fe concentration defect with respect to the parent catalyst (5Fe-TiO₂(n)) as a consequence of the metal extraction during the degradation is observed. Also, it has been observed that the Fe that remains on the surface is partially found as Fe²⁺ ions. On the other hand, a surficial Ti concentration increase has also been observed with respect to the parent catalyst. This means that the Fe³⁺ extraction involves the partial surficial concentration and redox state reduction of the remaining Fe atoms. Also, the increment of the number of exposed Ti⁴⁺ atoms in the crystal lattice surface, as a consequence of the Fe³⁺ ions extraction, contribute to equilibrate the charge defect. In fact, several authors indicate that Ti⁴⁺ ions can easily occupy holes formed by the leaving of Fe³⁺ ions in hematites [17]. According to this, the catalyst 5Fe-TiO₂(n) transformation to 5Fe-TiO₂(n)-a can be illustrated as follows:

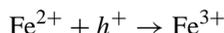


When the catalyst 5Fe-TiO₂(n)-a is treated with a Fe²⁺ solution (5Fe-TiO₂(n)-b) the system partially recovers the initial state, because though all the iron present on the surface is found as Fe³⁺ ions, there is a Ti and Fe defect on the surface with respect to the initial catalyst. Nonetheless, when the catalyst 5Fe-TiO₂(n)-b is reused in the formic acid photodegradation (catalyst 5Fe-TiO₂(n)-c) the observed behaviour is almost the same as that obtained when the catalyst 5Fe-TiO₂(n) was initially used.

However, when the catalyst 5Fe-TiO₂(n)-a is treated with a Fe³⁺ solution (catalyst 5Fe-TiO₂(n)-d) the system does not recover. In this case only a slight surficial Fe²⁺ ions and O atoms concentrations increment, and a small oxygen BE diminution are observed.

These results seem to indicate that iron returns to the catalyst surface as Fe²⁺ ions, probably by means of

their oxidation by the holes generated by the incident light on the TiO₂ particle:



The subtle iron concentration increment in the catalyst 5Fe-TiO₂(n)-d could be attributed to the transformation of Fe³⁺ into Fe²⁺, by means of an incipient photo-Fenton reaction. When the catalyst 5Fe-TiO₂(n)-d is reused in the formic acid photocatalytic degradation the iron extraction from the surface is again observed (5Fe-TiO₂(n)-e).

Lastly, when the catalyst 5Fe-TiO₂(f), obtained after the formic acid photocatalytic degradation for 1.5 h, almost all the Fe was recovered on the catalyst. Also, the Ti concentration on the surface is only slightly higher than the initial one. However, in this case and differently to the observed in the experiment with Fe²⁺ (catalyst 5Fe-TiO₂(b)) some Fe still exists as Fe²⁺. In fact, in this catalyst during the degradation it was observed that the Fe did not return quickly to the catalyst surface but it remained in solution

forming a non-photoactive complex with formic acid that could decompose and release free Fe³⁺ ions to the solution.

Maleic acid degradation studies have already been carried out with the catalysts 0.5Fe(n) and 5Fe(n) and have shown a similar behaviour to that observed with formic acid [10]. This shows the iron extraction and return to the catalyst surface as a photoactive complex. With the goal of testing if these catalysts behave similarly with other acids, also the results obtained with acetic and acrylic acids are shown.

4.3. Acetic acid

Fig. 4 shows the spectra from a 1:1 (w/w) acetic acid-water solution interaction with the catalysts bare-TiO₂, 0.5Fe-TiO₂(n) and 5Fe-TiO₂(n). As a general rule, when the acid interacts with the surface of

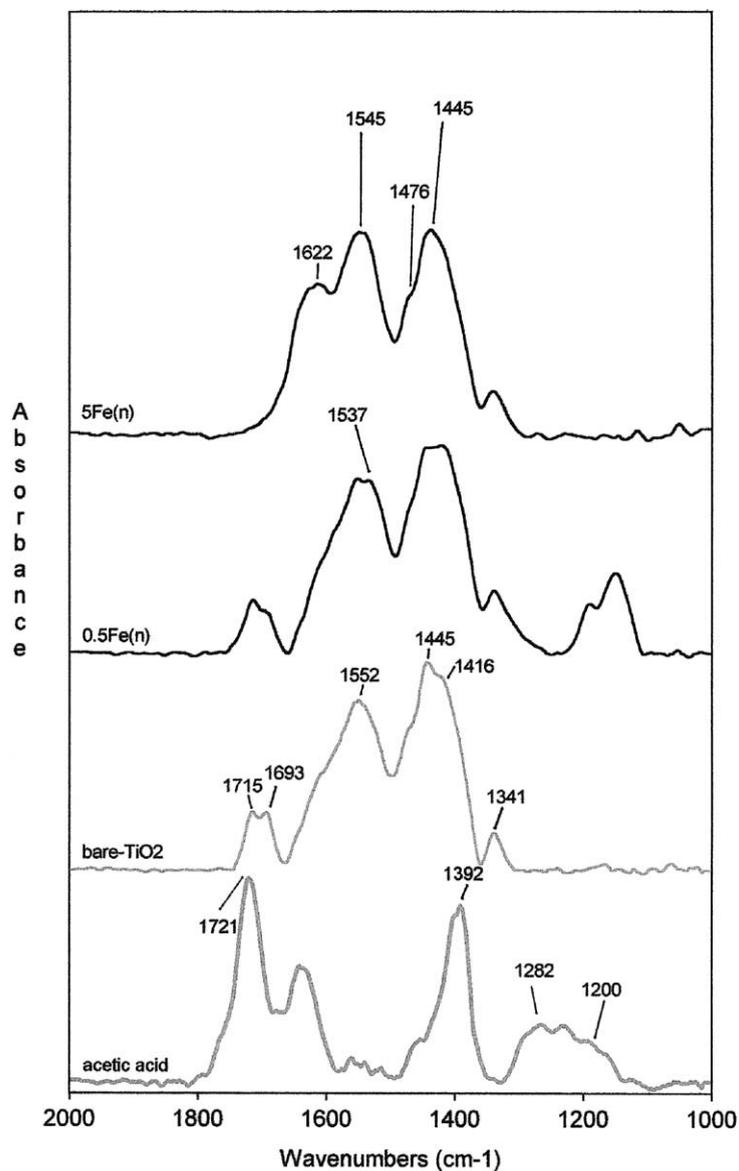


Fig. 4. IR spectra from the interaction of a 1:1 (w/w) acetic acid–water solution with the catalysts: bare-TiO₂; 0.5Fe-TiO₂(n) (0.5Fe(n)); and 5Fe-TiO₂(n) (5Fe(n)).

any of the catalysts the intensity of the bands due to the $\nu\text{C}=\text{O}$, δOH and $\delta\text{OC}-\text{OH}-\nu\text{OC}-\text{OH}$ (vibrations at 1721, 1392, 1282–1200 cm^{-1} , respectively) are considerably reduced compared to those corresponding to the aqueous acetic acid solution. Only in some cases the $\nu\text{C}=\text{O}$ vibration appears but in two bands at 1715 and 1693 cm^{-1} with much lower intensities than

those from the free acetic acid. Oppositely, new bands showing considerable intensities appear at 1552 cm^{-1} , 1537 and 1545 cm^{-1} in the spectra from the catalysts bare-TiO₂, 0.5Fe-TiO₂(n) and 5Fe-TiO₂(n), respectively. Also, a band at 1445 cm^{-1} is present in the spectra from all the catalysts. These bands are attributed to symmetric and asymmetric vibrations of the formed

Table 4

Relation between the different acetates vibrations ($\nu(\text{COO}^-)_{\text{as}}$, $\nu(\text{COO}^-)_{\text{s}}$ and $\delta(\text{CH}_3^-)$) and their respective electronegativity

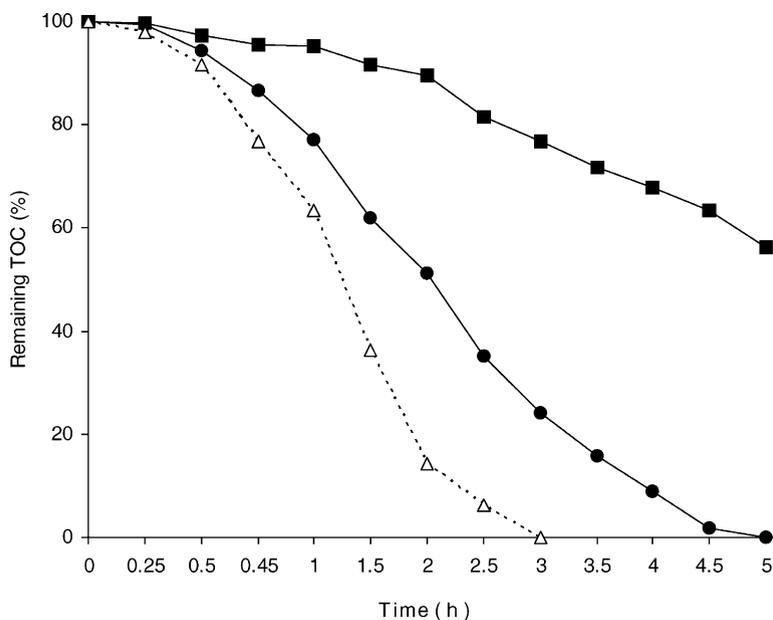
Acetate	$\nu(\text{COO}^-)_{\text{as}}$	$\nu(\text{COO}^-)_{\text{s}}$	$\delta(\text{CH}_3^-)$	Metal electronegativity
$\text{CH}_3\text{-COOLi}$	1574	1428	1351	1.0
$\text{CH}_3\text{-COONa}$	1574	1449	1379	0.9
$\text{CH}_3\text{-COOK}$	1574	1459	1369	0.8
$\text{CH}_3\text{-COOZn}$	1562	1451	1371	1.6
$\text{CH}_3\text{-COOMn}$	1562	1428	1351	1.5
$\text{CH}_3\text{-COOTi}^*$	1552	1442	1341	1.5
$\text{CH}_3\text{-COOC}_{\text{Co}}$	1538	1455	1333	1.9
$\text{CH}_3\text{-COOPb}$	1531	1402	1333	1.9

Fe electronegativity = 1.8.

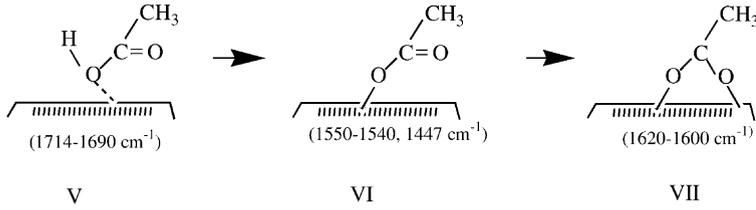
acetates ($\nu(\text{COO})_{\text{as}}$, $\nu(\text{COO})_{\text{s}}$) as a consequence of the loss of the O–H group. The band present in the spectra from all the catalysts at 1341 cm^{-1} is attributed to the $\delta(\text{CH}_3)_{\text{s}}$ deformation vibration. This band is considerably shifted towards lower wavenumbers with respect to the free acetic acid. In fact, it has been indicated that the methyl group vibration is very sensitive to the electronegativity of close atoms, being the symmetric deformation particularly sensitive [18–20]. As Table 4 shows, the wavenumber of the $\nu(\text{COO})_{\text{as}}$ and $\delta(\text{CH}_3)_{\text{s}}$ vibrations are directly affected by the

electronegativity of the metal that forms the salt [21]. Fe has a higher electronegativity than that of Ti. Consequently, any variation of the wavenumber of these vibrations should be observed if acetic acid is interacting with Fe. In fact, the band due to the $\nu(\text{COO})_{\text{as}}$ vibration appears slightly shifted towards lower wavenumbers (1540 cm^{-1}) revealing a Fe-acetic acid interaction.

Also, shoulder-looking bands at $1620\text{--}1613$ and 1424 cm^{-1} are observed and attributed to the formation of acetate species. This way, the FTIR results

Fig. 5. TOC reduction during the degradation of a 50 ppm acetic acid solution: (Δ) bare-TiO₂; (●) 0.5Fe-TiO₂(n); and (■) 5Fe-TiO₂(n).

seem to indicate the existence of an equilibrium among the following species:

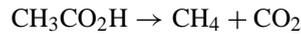


When the Fe concentrations increases the $\nu\text{C}=\text{O}$ band intensity tends to get lower, though the $\nu(\text{COO}^-)$ as band intensity between 1620 and 1613 cm^{-1} is augmented. In the catalyst 5Fe-TiO₂(n) the $\nu\text{C}=\text{O}$ vibration band is not observed, while the intensity of the band at 1622 cm^{-1} is considerably incremented. According to this, it seems that a high Fe concentration in the catalyst favours the formation of Ti acetates of the VII type.

Fig. 5 shows the results from a 50 ppm acetic acid aqueous solution degradation by the different

catalysts. Differently from that observed with the previous acids (formic and maleic acid), the catalyst

0.5Fe-TiO₂(n) shows a lower acetic acid degradation ability than that of bare-TiO₂. Again, similarly to the obtained by the other studies, the catalyst 5Fe-TiO₂(n) shows the worst catalytic behaviour. This difference could be explained by the possible photo-Kolbe process due to the interaction of the acid with the catalyst surface, as suggested by some authors [22]:



The formation of types VI and VII salts (following scheme) could favour photo-Kolbe process:

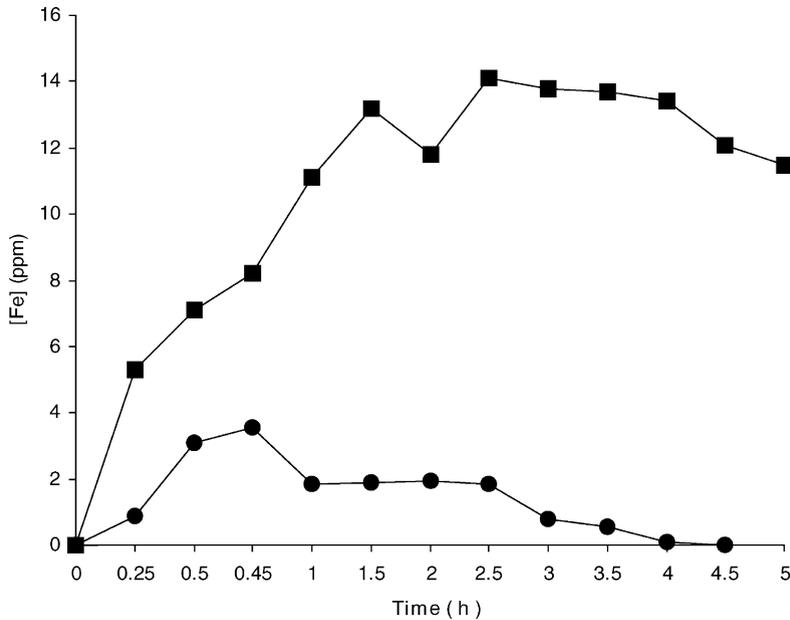
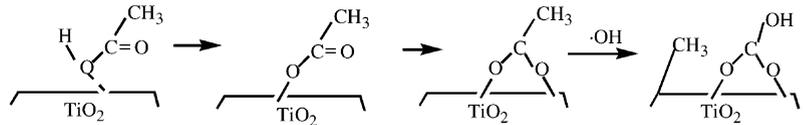


Fig. 6. Dissolved Fe concentration during the degradation of a 50 ppm acetic acid solution: (●) 0.5Fe-TiO₂(n); and (■) 5Fe-TiO₂(n).

Additionally, atomic absorption analyses at different reaction times during the acid degradation have been carried out (Fig. 6). As it can be observed, the Fe extraction-return process also occurs, and coincides with the acid degradation evolution, but the complex formed does not seem to be more efficient at the acid degradation than TiO_2 .

4.4. Acrylic acid

The spectra from the acrylic acid interaction with the catalysts bare- TiO_2 , 0.5Fe- TiO_2 (n) and 5Fe- TiO_2 (n) are shown in Fig. 7. This interaction generates significant changes in the acid spectrum. Though the $\nu\text{C}=\text{O}$ vibration keeps its wavenumber (1729 cm^{-1})

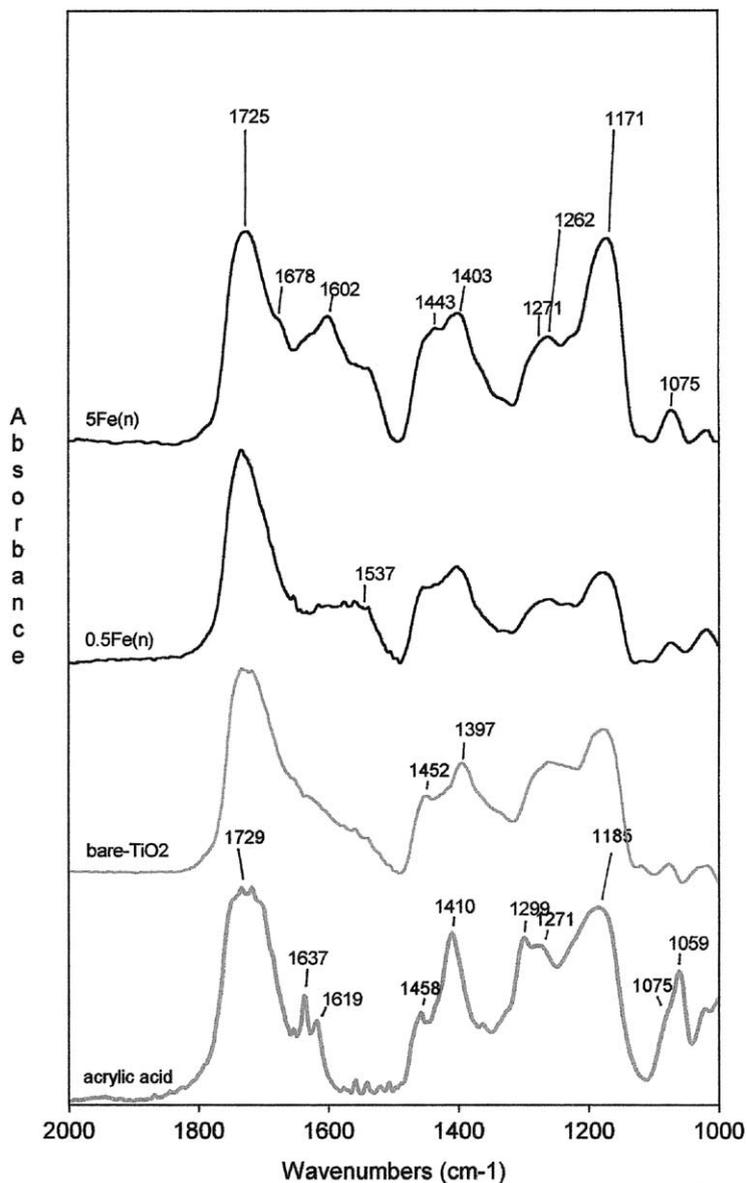


Fig. 7. IR spectra from the interaction of a 1:1 (w/w) acrylic acid–water solution with the catalysts: bare- TiO_2 ; 0.5Fe- TiO_2 (n) (0.5Fe(n)); and 5Fe- TiO_2 (n) (5Fe(n)).

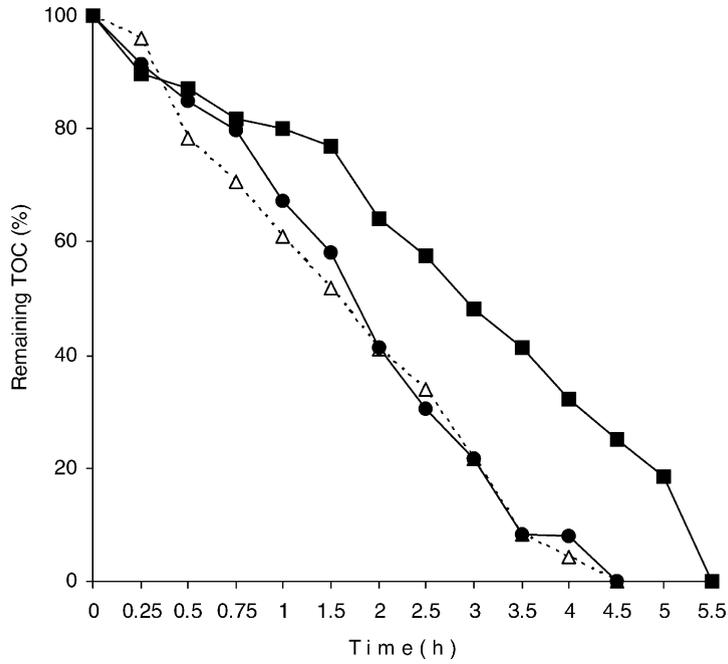


Fig. 8. TOC reduction during the degradation of a 50 ppm acrylic acid solution: (Δ) bare-TiO₂; (●) 0.5Fe-TiO₂(n); and (■) 5Fe-TiO₂(n).

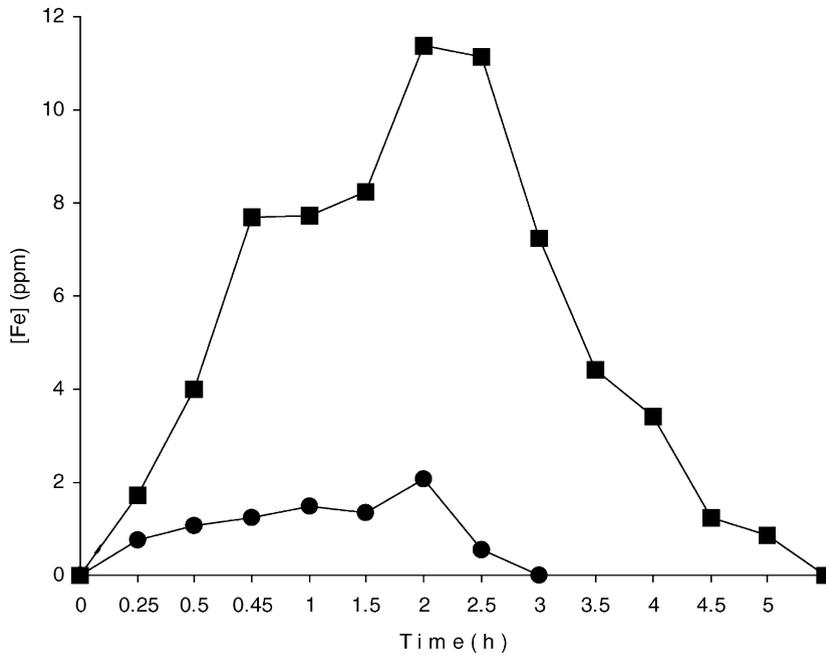
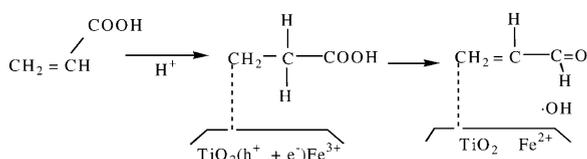


Fig. 9. Dissolved Fe concentration during the degradation of a 50 ppm acetic acid solution: (●) 0.5Fe(n); and (■) 5Fe(n).

the $\nu\text{C}=\text{C}$ vibration at $1637\text{--}1619\text{ cm}^{-1}$ almost disappears. Additionally, the δCH and $\nu\text{C}-\text{C}$ vibrations at 1410 and 1299 cm^{-1} , respectively, are shifted towards lower wavenumbers ($1400\text{--}1397$ and $1270\text{--}1262\text{ cm}^{-1}$) with respect to the free acrylic acid spectrum. Only for the doped catalysts a clear band at 1537 cm^{-1} is visible and it could be attributed to the formed carboxylate $\nu(\text{COO}^-)$ s vibration. Similarly to the obtained with the acetic acid, in the catalyst $5\text{Fe-TiO}_2(\text{n})$ spectrum a sharp band appears at $1620\text{--}1602\text{ cm}^{-1}$ that can be attributed to carboxylate species.

Also in this catalyst, a shoulder at 1678 cm^{-1} , characteristic of the carbonyl group, and the $\nu\text{C}-\text{O}$ vibrations shift towards lower wavenumbers, 1262 and 1171 cm^{-1} are clear. This bands (1678 , 1262 and 1170 cm^{-1}) correlate quite well with those of the acrolein. This suggests the acrylic acid reduction on the catalyst surface, probably enhanced by the presence of iron:



Similar reduction processes by TiO_2 doped with Mo, Cu or Au have been described in the literature [23–27].

The acrylic acid degradation studies (Fig. 8) show, similarly to the experiments with acetic acid, that the doped catalysts do not improve the bare- TiO_2 catalytic behaviour. In this study the iron extraction is also observed (Fig. 9) during the acrylic acid degradation. However, it seems that the complex formed as a consequence of the iron interaction with acrolein does not favour the acid degradation. In fact, in these studies it can be observed that the iron returns to the catalyst surface occurs before the acid degradation is completed.

FTIR studies suggested the possible presence of acrolein as a consequence of the acrylic acid reduction by the catalyst containing higher Fe load. This could be hindering the degradation process.

5. Conclusions

The results obtained in this work has evidenced the following.

- Aliphatic carboxylic acids such as formic, maleic, acetic and acrylic can interact with the iron present on the catalysts surface and extract it.
- Complexes formed by means of the interaction of formic and maleic acids with the surface of the catalysts doped with iron are more photoactive than those formed by means of the interaction of acetic or acrylic acid.
- Complexes formed by the interaction of formic and maleic acid with Fe^{3+} could generate the degradation of the corresponding acid much more quickly than the undoped TiO_2 .
- The catalyst $0.5\text{Fe-TiO}_2(\text{n})$ shows a higher ability to give photoactive Fe-formic acid and Fe-maleic acid complexes than that of the catalyst $5\text{Fe-TiO}_2(\text{n})$.
- Catalysts with the same Fe load than that of $0.5\text{Fe-TiO}_2(\text{n})$, but obtained by means of different precursors or preparation methods, such as $0.5\text{Fe-TiO}_2(\text{a})$ and $0.5\text{Fe-TiO}_2(\text{sg})$ present a lower catalytic activity at the formic acid degradation due the lower photoactivity of the formed complexes. Generally speaking, catalysts with higher Fe content give less photoactive formic acid-Fe complexes.
- XPS studies have revealed that once the Fe^{3+} ions are extracted the catalyst surface undergoes a restructuring process in which Ti^{4+} ions seem to play an important role. Only if Fe^{2+} ions are present (in the adequate concentration) the surface may achieve its previous structure.

Acknowledgements

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