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The effect of aliphatic carboxylic acids on the photocatalytic degradation of *p*-nitrophenol

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Abstract

The effect of the presence of formic, oxalic and acetic acids on photocatalytic degradation of *p*-nitrophenol has been studied. Adsorption and FTIR studies indicated that the presence of such acids modifies *p*-nitrophenol interaction with TiO_2 surface, which is more rapidly degraded. The higher degradation rate constants have been correlated with interaction changes and radicals generated in the degradation of carboxylic acids.

The presence of H_2O_2 did not affect the mechanism responsible for the faster *p*-nitrophenol degradation in the presence of acetic or oxalic acids. However, formic acid seems to hamper the production of $OH^{\bullet}$radicals from H_2O_2 degradation.

Keywords: *p*-Nitrophenol; TiO_2; Carboxylic acid; FTIR; Photocatalysis

1. Introduction

In recent years considerable research effort has been devoted to the application of photocatalytic processes to the abatement of organic pollutants in water. Many of these studies have been focused on individual organic compounds such as phenols, pesticides, etc. [1–5]. However, aqueous wastes from industries, agriculture and dwellings are usually complex mixtures of different pollutants. Thus, it is important to determine the applicability of photocatalysis to known mixtures of organics.

As in other heterogeneous catalytic processes, the behaviour of photocatalysts can be modified depending on the affinity of the studied molecules for the adsorption centres [6,7].

The effect of the presence of a second molecule on the photocatalytic process has been investigated in studies regarding the degradation of organic compounds with inorganic salts. Catalytic changes were observed as a result of the formation of double layers on TiO_2 surface, which inhibit the adsorption of the organic molecules to be degraded [8]. It has also been indicated that the inorganic ions present on the catalyst surface can react with photogenerated holes and/or $^{\bullet}OH$ radicals resulting in the modification of catalyst activity [9,10]. Furthermore, other studies showed that some ions, such as sulphates, can stabilise the semiconductor's crystalline structure, thus favouring the catalytic process [11].

Additionally, experiments with mixtures of organic compounds have proved that the presence of acetates can significantly modify the photocatalytic behaviour of phenol, catechol or resorcinol [12,13]. Therefore, these results suggest that the presence of another adsorbate in the reaction mixture can affect the process, mainly by competing for adsorption centres or modifying TiO_2 surface distribution.

One of the most important features of TiO_2 surface is the existence of hydroxyl groups with different acid–base characters, in addition to adsorbed water molecules [14,15]. The surface distribution of these groups is modified by pH according to the following equilibria [8]:

$$\mathrm{pH} < \mathrm{pzc}: \quad \mathrm{Ti{-}OH} + \mathrm{H}^+ \rightarrow \mathrm{TiOH_2}^+$$

$$\mathrm{pH} > \mathrm{pzc}: \quad \mathrm{Ti{-}OH} + \mathrm{OH}^- \rightarrow \mathrm{TiO}^- + \mathrm{H_2O}$$

These surface hydroxyl groups participate directly in the formation of $^{\bullet}OH$ radicals and constitute reagent and

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intermediate adsorption centres as well. However, the adsorption of organic compounds can also neutralize these surface groups, thus modifying their distribution.

As mentioned above, the majority of aqueous wastes are mixtures of different compounds. Accordingly, to optimize the process it is necessary to study the effect of mixtures on their individual degradation. In addition to this, carboxylic acids are intermediates in the majority of photocatalytic degradation processes and exert an important effect on the degradation of some phenolic compounds. Therefore, to obtain a better picture of the effect of the presence of carboxylic acids on photodegradability, we studied the degradation of *p*-nitrophenol at different concentrations of formic, oxalic and acetic acids.

2. Experimental

2.1. Experimental conditions

Aqueous suspensions containing 40 ppm of *p*-nitrophenol and 2 g/l catalysts (Degussa P-25 TiO_2 powder, 80% anatase and 20% rutile) in 250 ml glass vessels were continuously stirred and air-bubbled (100 ml/min). All the experiments were performed at pH 5 and at a constant temperature of 25 °C. The organics chemisorption on the catalyst surface was favoured by air-bubbling and stirring for 45 min before switching on the UV-lamp. The *p*-nitrophenol degradations by TiO_2 and without carboxylic acid have been considered as reference reactions.

The adsorption studies were performed in the dark and with constant stirring. These experiments lasted 2 h and samples were taken every 15 min. No adsorption changes were observed after the first 15–30 min.

2.1.1. Equipment

A 60 W Solarium Philips HB175 equipped with four 15 W Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum around 365 nm) was used as UV source. Remaining *p*-nitrophenol (Aldrich) concentrations at different reaction times were HPLC-measured using a Macherey-Nagel CC 250/4 NUCLEOSIL 100-5 PROTECT 1 and a acetonitrile–water–acetic acid (40:59.5:0.5) mobile phase, using a UV detector ($\lambda = 270$ nm). TOC (total organic carbon), TC (total carbon) and IC (inorganic carbon) were measured with a TOC Shimadzu 5000-A to determine carboxylic acid adsorption.

A FTIR spectrophotometer model RS/1 (UNICAM) was used for spectral analysis.

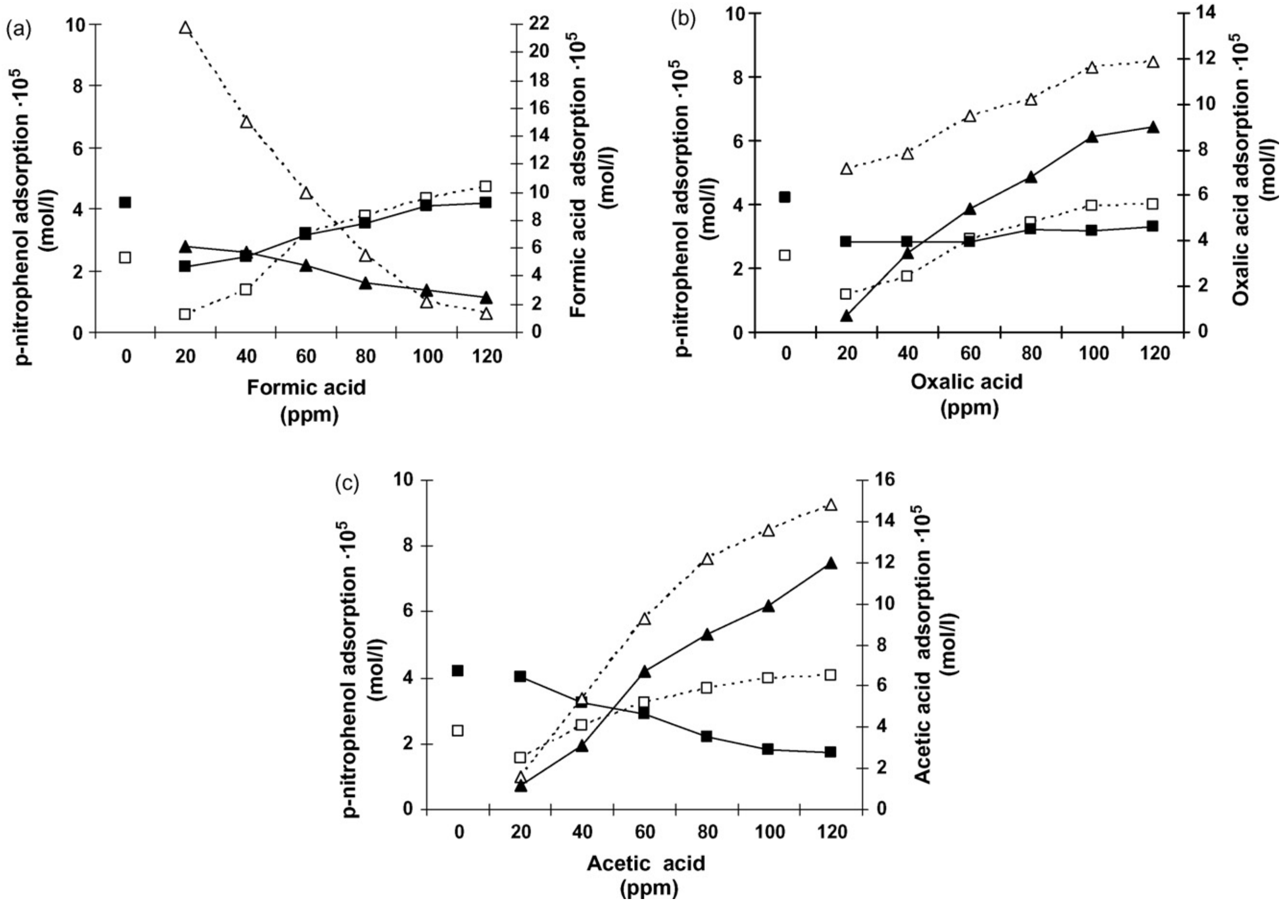


Fig. 1. (a) *p*-Nitrophenol (■, □) and formic acid (△,▲) adsorption in the presence of different concentration of the acid. Solid symbols essays without H_2O_2, empty symbols essays with H_2O_2 (20 mM). (b) *p*-Nitrophenol (■, □) and oxalic acid (△,▲) adsorption in the presence of different concentration of the acid. Solid symbols essays without H_2O_2, empty symbols essays with H_2O_2 (20 mM). (c) *p*-Nitrophenol (■, □) and acetic acid (△,▲) adsorption in the presence of different concentration of the acid. Solid symbols essays without H_2O_2, empty symbols essays with H_2O_2 (20 mM).

Spectra were obtained in the 2000–1000 cm^{-1} region, employing a resolution of 2 cm^{-1} and a forward and reverse moving mirror speed of 10 and 6.2 kHz. Catalysts were impregnated with (1:5, w/w) *p*-nitrophenol–water or (1:2:5, w:w:w) *p*-nitrophenol–carboxylic acid–water mixtures at pH 5 and placed between two CaF_2 windows for FTIR measurements. The spectrum from water molecule adsorbed to TiO_2 is subtracted from all the spectra shown.

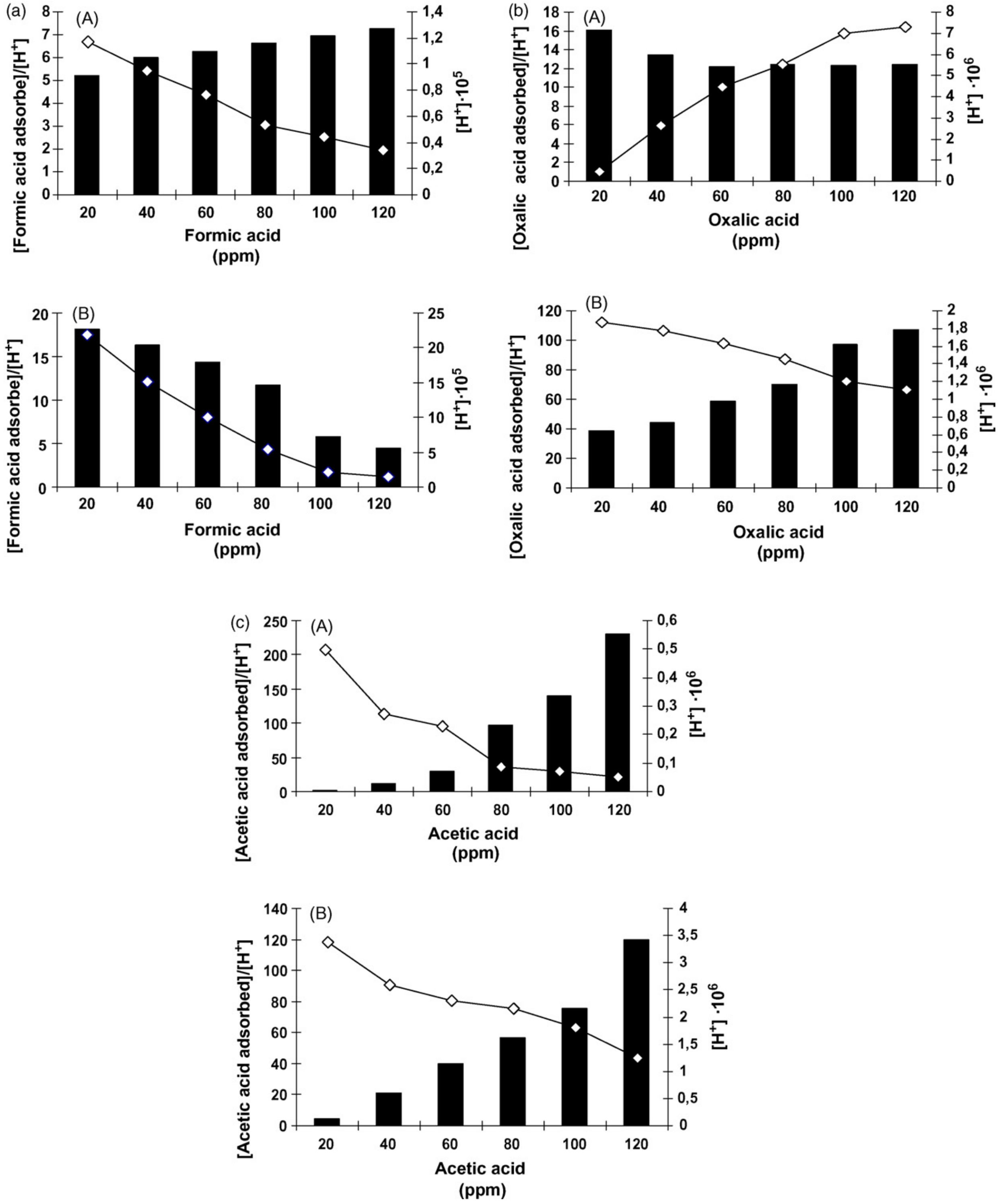


Fig. 2. (a) Ratio of adsorbed formic acid to free proton generated concentrations ([Formic acid]/[H^+]) (■) and free proton generated concentration [H^+] (◇) in adsorption studies of *p*-nitrophenol mixtures with different concentration of this acid. (A) Without H_2O_2, (B) with H_2O_2. (b) Ratio of adsorbed oxalic acid to free proton generated concentrations ([Oxalic acid]/[H^+]) (■) and free proton generated concentration [H^+] (◇) in adsorption studies of *p*-nitrophenol mixtures with different concentrations of this acid. (A) Without H_2O_2, (B) with H_2O_2. (c) Ratio of adsorbed acetic acid to free proton generated concentrations ([Acetic acid]/[H^+]) (■) and free proton generated concentration [H^+] (◇) in adsorption studies of *p*-nitrophenol mixtures with different concentrations of this acid. (A) Without H_2O_2, (B) with H_2O_2.

3. Results

3.1. Adsorption studies

Compound photocatalytic behaviour can be directly or partially controlled by the type and concentration of the adsorbed molecules. This parameter is even more important when a mixture of different compounds is studied. Consequently, previous to degradation experiments, a complete adsorption study was carried out. These adsorption studies were carried out with a constant concentration of *p*-nitrophenol (40 ppm) and different concentrations of carboxylic acid (0–120 ppm).

As indicated in Section 2, adsorption and degradation experiments lasted the same time (2 h) for comparison purposes. However, after the first 15–30 min no adsorption changes were observed. Results from 40 ppm *p*-nitrophenol at different concentrations of the acids, after 2 h of interaction time, are shown in Fig. 1(a–c).

p-Nitrophenol adsorption is considerably diminished at 20 ppm formic acid or oxalic acid concentration with respect to the reference study (only *p*-nitrophenol) (Fig. 1a and b). However, at higher formic concentrations, *p*-nitrophenol adsorption is increased. This is not the case for oxalic acid, since almost no effect on the adsorption of aromatic is observed (Fig. 1b). Nevertheless, acetic acid exerts a different effect on *p*-nitrophenol adsorption, which is slightly lower at 20 ppm than that of reference study and progressively reduced at higher concentrations (Fig. 1c). Also, the adsorption of the acids in presence of *p*-nitrophenol (40 ppm) was analysed (Fig. 1a–c). Contrary to that of *p*-nitrophenol, adsorption of formic acid decreased when the acid concentration was augmented. Nonetheless, adsorptions of acetic and oxalic acids progressively increased when their concentrations were higher. In addition to this, pH evolution was also monitored during adsorption studies. In the reference study, we noticed a proton concentration increment ($\cong 2.52 \times 10^{-5}$) after *p*-nitrophenol interaction with TiO_2 surface. However, this acidity increment is considerably reduced in presence of the carboxylic acids. Fig. 2(a–c) show the ratio of adsorbed acid to free proton generated concentrations ($[Acid]/[H^+]$) and proton concentration increment for each reaction mixture.

As can be observed, this ratio increases at higher formic acid concentrations. Yet, for oxalic acid, the $[A]/[H^+]$ ratio is much higher than that of formic acid, becoming reduced when oxalic concentration is incremented. In the case of acetic, the ratio is also higher than that of formic acid; however it is progressively increased at higher concentrations of the acid.

3.2. *p*-Nitrophenol degradation studies

Degradation experiments lasted 2 h, but the mixture was kept in darkness for 45 min to favour adsorption. Degradation rate constants were calculated according to the Langmuir–Hinshelwood model [16] which provided high regression coefficients (0.989–0.999). In Fig. 3, these constants are compared for the different conditions tested.

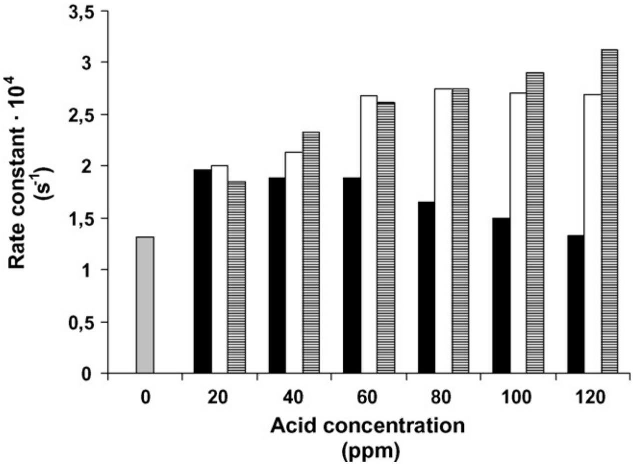


Fig. 3. Rate constant of photocatalytic degradation of *p*-nitrophenol in the presence of different concentrations of formic acid ■, oxalic acid □, acetic acid ▤ and without these acids ▒.

The obtained constant in the presence of 20 ppm of the acid studied is significantly higher than the one from the reference study (without acids). However, at higher concentrations of the formic acid the constant becomes progressively lower while at higher concentrations of oxalic or acetic acid it is increased.

These adsorption and degradation experiments were repeated in presence of H_2O_2 (20 mM). Results are shown in Figs. 1, 2 and 4.

As can be observed, *p*-nitrophenol adsorption in the presence of the oxidant and without the acids is considerably lower (Fig. 1a–c). When any of the acids is added, adsorption is even lower, being progressively incremented at higher concentrations of the acid. Additionally, it must be underlined that formic acid adsorption is much higher than that observed without H_2O_2, being diminished at higher concentrations of the acid (Fig. 1a). Oxalic adsorption is also much higher than that observed in presence of H_2O_2, but increases slightly at higher concentrations. On the contrary, acetic adsorption is lower than

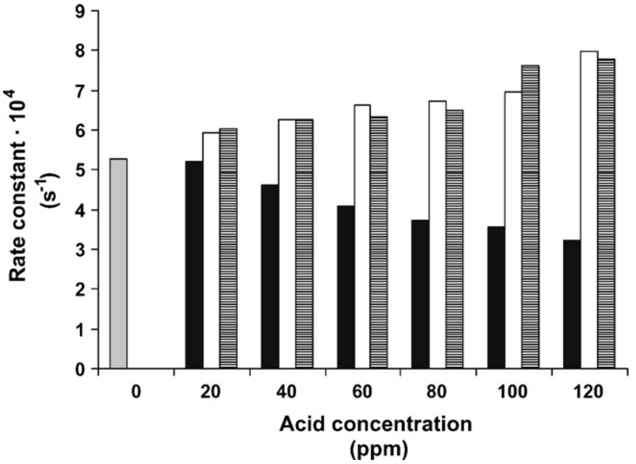


Fig. 4. Rate constant of photocatalytic degradation of *p*-nitrophenol + H_2O_2 in the presence of different concentrations of formic acid ■, oxalic acid □, acetic acid ▤ and without these acids ▒.

that obtained without the oxidant and increases with the concentration of the acid.

The *p*-nitrophenol rate constants in presence of H_2O_2 and in absence of the acids are four times faster. In the experiments with oxalic and acetic acids, in the presence of H_2O_2, the obtained rate constant increment is similar to that obtained without this oxidant Thus, if the reference studies rate constant is subtracted from that obtained from the experiments in presence of oxalic or acetic, and added to the constant from those with *p*-nitrophenol and H_2O_2, a similar value to the constant from experiments with the carboxylic acids and the oxidant is obtained.

Nevertheless, rate constants from experiments with formic acid + H_2O_2, at higher concentrations of the acid, become progressively smaller.

The photocatalytic degradation of *p*-nitrophenol with H_2O_2 and without the catalyst was also studied to determine the effect of the oxidiser alone. The obtained degradation rate constant (0.45×10^{-4}) is much lower than those obtained in the presence of the catalyst. In fact, reaction (1a) occurs at wavelengths lower than 300 nm, where H_2O_2 absorbs more strongly. Therefore, under the experimental conditions employed, the effect of this oxidiser alone must be negligible [17].

$$H_2O_2 \rightarrow 2^{\bullet}OH \tag{1a}$$

3.3. FTIR studies

The interaction of *p*-nitrophenol with TiO_2 surface was studied in presence and absence of the acids, under the experimental conditions indicated above. Fig. 5 shows the obtained spectra in the region between 1800 and 1000 cm^{-1} and the *p*-nitrophenol reference spectrum. In the *p*-nitrophenol–TiO_2 interaction spectrum, the band at 1326 cm^{-1}, attributed to δOH vibration disappears and the band at 1285 cm^{-1} (νCO vibration) is shifted towards higher wavenumbers (1298 cm^{-1}).

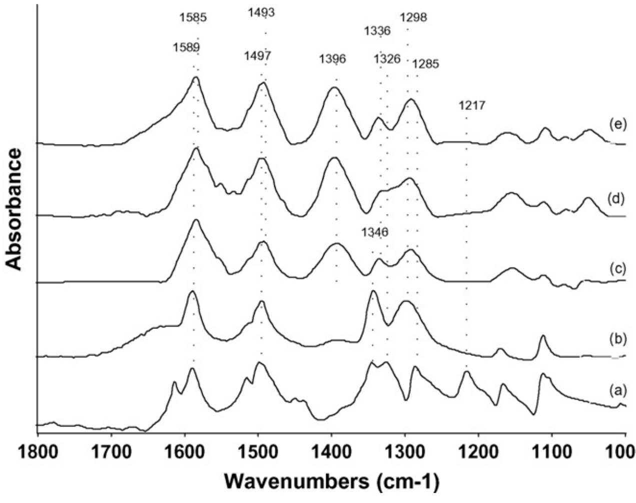
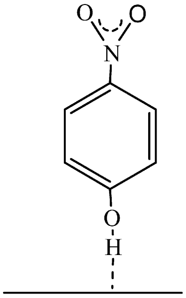


Fig. 5. FTIR spectra from *p*-nitrophenol interactions with TiO_2 (b), TiO_2 + formic acid (c), TiO_2 + oxalic acid (d) and TiO_2 + acetic acid (e). Also, the *p*-nitrophenol reference spectrum is shown (a).

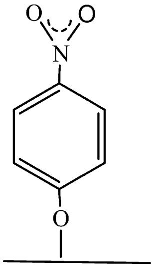
Also, the absence of the band at 1217 cm^{-1}, attributed to ‘‘out-of-plane O–H wag’’ [18] must be underlined.

The disappearance of the bands attributed to δOH and ‘‘out-of-plane O–H wag’’ vibrations, clearly indicates the formation of a phenoxide, as observed in other studies [13,19,20]. Additionally, the shift of the aromatic ring νC=C vibration band in the region between 1500 and 1400 cm^{-1}, is a sign of electrodonation changes of the phenolic substituent [21]. In this case, the band at 1510 cm^{-1} was notably shifted towards lower wavenumbers and its intensity reduced.

These changes suggest the formation of *p*-nitrophenoxides [22] such as:



(I)

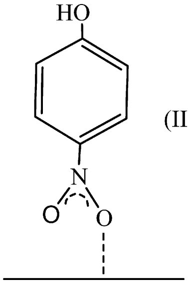


(II)

Similarly to the observations in the absence of the acids, in the spectra from *p*-nitrofenol–TiO_2 interaction in their presence, νCO and ‘‘out-of-plane O–H wag vibrations bands become shifted. In addition to this, the presence of the acids resulted in:

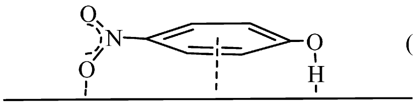
- The appearance of a new band at 1396 cm^{-1}.
- Transformation of the bands attributed to $\nu_s(NO_2)$ and δOH vibrations (1346 and 1326 cm^{-1}, respectively) into one smaller band at 1336 cm^{-1}. Nevertheless, as stated above, in the absence of the acids only the disappearance of the band attributed to δOH vibration was noticed.
- Shift of aromatic ring bands (1589 and 1497 cm^{-1}) towards lower wavenumbers (1585 and 1493 cm^{-1}),
- Modification of the bands attributed to νCH vibration in the 1200–1000 cm^{-1} region.

Changes of $\nu_s(NO_2)$ vibration band relative intensity and wavenumber suggest an interaction by means of the nitro group, as in the following:



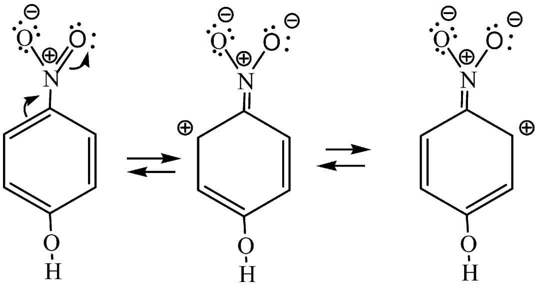
(III)

Moreover, the fact that νCO and ‘‘out-of-plane O–H wag’’ vibration bands show the same shift could indicate the existence of *p*-nitrophenol molecules adsorbed by means of structures I and II. The simultaneous modifications of $\nu_s(NO_2)$ and δOH vibrations bands suggest, as claimed by other authors [23], the horizontal adsorption of *p*-nitrophenol (structure IV). This interaction would also explain the observed νCH and νC=C vibration changes in the 1200–1000 cm^{-1} region.


(IV)

This sort of interaction usually occurs in Bronsted acid centres and could be favoured by the presence of the studied acids.

In addition to this, the band observed in these spectra at 1396 cm^{-1} is characteristic of phenolic compounds with meta substitutions, such as resorcinol. In the aromatic ring, the nitro group is electrophilic and yields electronic deficiency in ortho positions:



These structures can be stabilised the through hydroxyl groups present on TiO_2 surface generating the observed band at 1396 cm^{-1}.

Moreover, FTIR studies on the interaction of the acids with TiO_2 surface have been carried out (Fig. 6).

In the formic acid-TiO_2 interaction spectrum, bands at 1585 and 1362 cm^{-1} attributed to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations respectively, were observed revealing the presence of bidentate formate [24].

The interaction of the acetic acid with TiO_2 surface produces bands at 1552 and 1439 cm^{-1}, attributed to acetate ν_{as} and ν_s vibrations respectively. Different authors have indicated that [25,26] a separation between ν_{as} and ν_s vibration bands, ($\Delta\nu = 107$ cm^{-1}), as the observed in the experiments with TiO_2-acetic acid, is due to the presence of a mixtures of bidentate acetates.

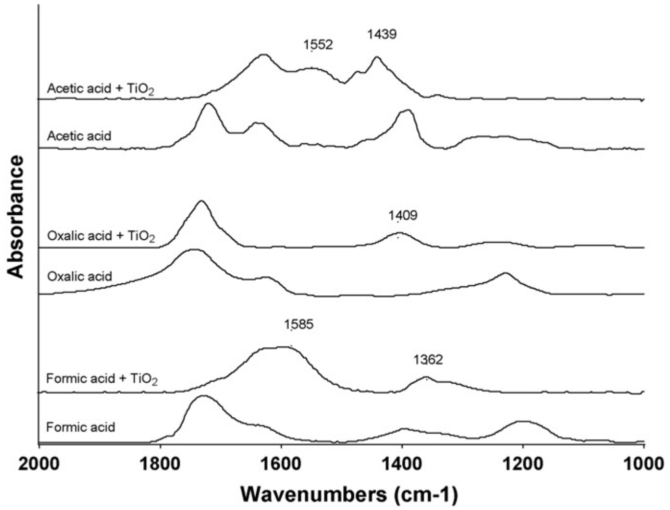
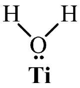


Fig. 6. FTIR spectra of formic, acetic and oxalic acid interaction with TiO_2 surface.

Finally, the interaction of oxalic acid generated a band at 1409 cm^{-1}, which it was attributed to ν(C–O) + ν(C–C) vibrations corresponding to oxalate [27].

4. Discussion

As has been indicated by different studies [28,29], water molecule splitting on TiO_2 surface requires the presence of a pair of centres, one with acidic character (low Ti cations coordination) to initially bond water molecule:



and another, with basic character (exposed bridging oxygen atoms) to accept the proton. These centres should be located at an adequate distance to favour water adsorption and a sufficient interaction among the generated hydroxyl groups. During water interaction with TiO_2, proton concentration is increased, revealing water molecule splitting, adsorption of hydroxyl groups and proton repulsion, probably due to the proximity of centres.

In the study of *p*-nitrophenol-TiO_2 interaction, the observed proton concentration is higher than that of water-TiO_2. Additionally, FTIR analyses indicated the formation of a *p*-nitrophenoxo. *p*-Nitrophenol's hydroxyl group can interact with an adsorbed water molecule in centres located far from basic enough centres to extract the proton and give the reaction:

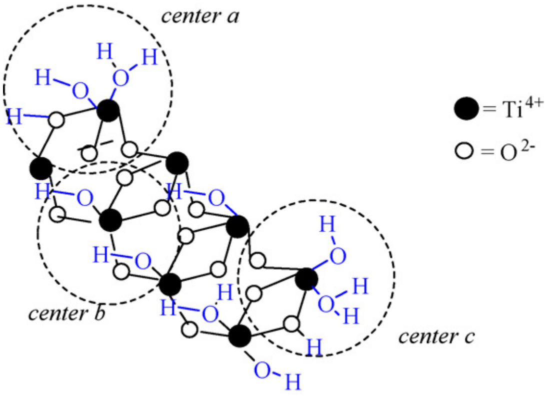
In fact, the ratio of adsorbed *p*-nitrophenol to free protons generated concentrations is 1.7. This means that more than half of the organic molecules could be adsorbed by means of structure II and the rest by structure I.

In addition to this, we have observed that during *p*-nitrophenol interaction in the presence of the carboxylic acids, the concentration of generated protons is considerably reduced. This can be explained by the dissociation inhibition of adsorbed water molecules or by the retention of generated protons on the surface. Also, FTIR analyses have shown that in the presence of these acids, the interaction of phenolic organic is different (structures III and IV). This last structure would be favoured by the presence of Bronsted acid centres. These centres could be generated by protons produced by water splitting which were not desorbed or from the adsorption of the acids. TiO_2 surface interaction with these acids can occur, among others, through the following reactions:

These reactions can generate free protons (1), proton TiO_2 surface (2) or neutralise a surface hydroxyl group to give water (3).

Results from different studies [13–15,30–32] suggest a possible distribution of hydroxyl groups and water coordinated to the surface that can be illustrated by Scheme 1. In this surface distribution, the following centres can be found, among others:

- "Centres a", where Ti^{4+} ions are coordinated with a hydroxyl group, a water molecule, a hydroxyl group with acidic

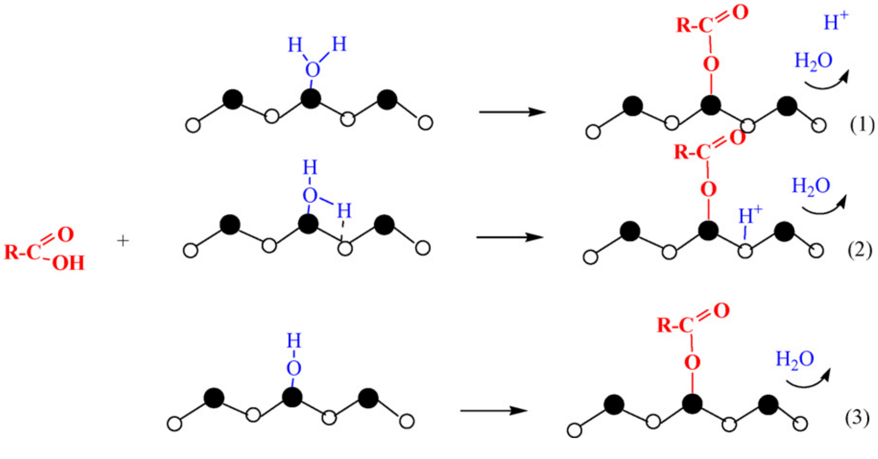


Scheme 1.

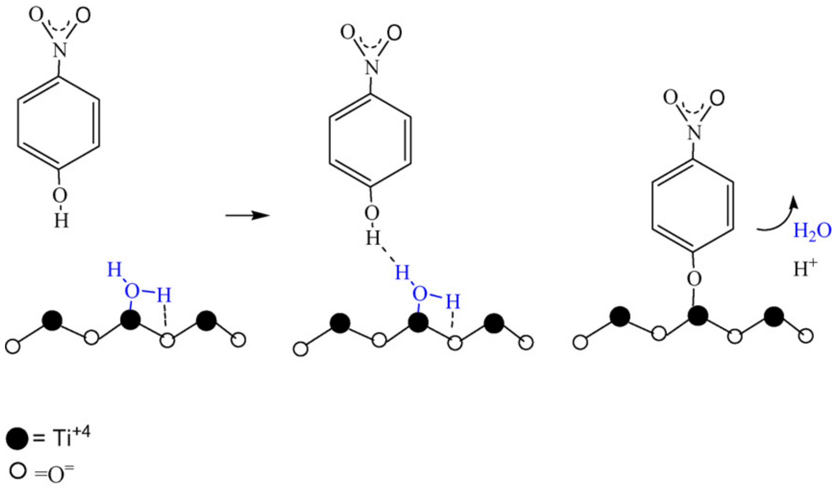
character $(OH)_a$ and different O^{2-} lattice atoms to complete the coordination number.
- ‘‘Centres b’’ in which Ti^{4+} ions are coordinated to hydroxyl groups and different O^{2-} lattice atoms to complete the coordination number.
- ‘‘Centres c’’ similar to centres a, but surrounded by several centres b.

Reactions illustrated in Scheme 2 could imply modifications of this distribution of hydroxyl group and adsorbed water molecules, which can affect photocatalytic degradation, similarly to the neutralization processes when pH is modified, as indicated by other authors [8].

In the experiments with *p*-nitrophenol in the presence of formic acid, the ratio of formic acid to generated free proton concentration increases from 5.2 to 7.2, when the acid concentration is incremented. This means that at low concentrations, a proton is generated for every 5.2 formic molecules adsorbed. That is, for every 5.2 molecules adsorbed, one may occur through reaction (1) and the others by reactions (2) and (3). Yet, at higher concentrations of the acid, fewer molecules interact by means of reaction (1). Additionally, we have observed that at low formic concentrations (20 ppm), *p*-nitrophenol adsorption is considerably reduced with respect to the reference study (Fig. 1a), while if the acid concentration is incremented, *p*-nitrophenol adsorption is progressively increased. It has been indicated [33] that formic acid can displace Ti^{4+}-adsorbed water molecules which can be located on *p*-nitrophenol adsorption centres (Scheme 3). This effect will be more pronounced when more molecules of the acid are



Scheme 2.



Scheme 3.

adsorbed, hence at low formic concentrations. Moreover, at higher formic concentrations, more centres with Bronsted acid features can be generated on the TiO_2 surface, since under these conditions reaction (1a) (Fig. 4) ratio is increased. This would favour *p*-nitrophenol adsorption by structure IV. Also at higher formic concentrations, the acid adsorption is lower, and that of adsorbed water is increased and consequently, *p*-nitrophenol adsorption probably occurs by structures I and/or II.

In addition to this, at higher acetic acid concentrations, the adsorption of *p*-nitrophenol is progressively reduced and that of the acid is increased. In this case, acid concentration to proton ratio is increased (Fig. 5), and the predominance of reactions (2) and (3) is higher than that of formic acid studies. Under these conditions, new Bronsted acid-like centres can be generated by reaction (2) which favour *p*-nitrophenol adsorption by structures III and/or IV and inhibit interaction by structures I and/or II.

In experiments with oxalic acid, the generated free proton ratio was always lower than that of the adsorbed acid. This would imply a large concentration of Bronsted acid-like centres by reaction (2) which would be responsible for *p*-nitrophenol adsorption reduction.

In the presence of H_2O_2 and without the carboxylic acids, *p*-nitrophenol adsorption is significantly reduced when compared to experiments without the oxidiser. It has been suggested that H_2O_2 and water molecules adsorb at the same centres, resulting in displacement of the latter. As *p*-nitrophenol interacts at these same centres (Scheme 3), its lower adsorption can be explained by competition for adsorption centres. Experiments including H_2O_2 and the acids showed that the reduction of *p*-nitrophenol adsorbed was even more pronounced at the lowest concentrations. Nevertheless, at increasing concentrations, *p*-nitrophenol adsorption increases, probably due to the higher presence of Bronsted acid-like centres. In addition to this, in the presence of H_2O_2, the ratio of generated free proton ratio is highly dependant on the acid studied, indicating competition for adsorption centres. The observed difference in acid adsorption in the absence of the oxidising agent can thus be attributed to competition for the same adsorption centres.

In addition to this, results from experiments with H_2O_2 showed that carboxylic acid adsorption and degradation rate of *p*-nitrophenol are positively correlated. The degradation rate of *p*-nitrophenol in the presence of H_2O_2 and absence of the acids is considerably higher than that obtained in the absence of the peroxide. In presence of acetic and oxalic acids, a similar increment to experiment without the oxidant in addition to the increment observed in experiments without H_2O_2.

These results suggest that the mechanism and centres responsible for improved *p*-nitrophenol degradation rate are not affected by H_2O_2.

Adsorption experiments have shown that the presence of the acids significantly reduces *p*-nitrophenol adsorption on TiO_2 surface resulting in a different interaction. Many molecules adsorbed by structures I and/or II may not be photocatalytically degradable, thus even at lower adsorption degradation is not altered.

Nonetheless, new molecules adsorbed by structures III or IV can be responsible for the higher degradation rate observed in the presence of the acids.

In addition to this, *p*-nitrophenol photocatalytic degradation rate without H_2O_2 was never impeded by the presence of the studied acids. The majority of the degradation mechanisms proposed for this class of phenolic compound consider carboxylic acids as intermediates. Consequently, a similar effect to the one observed in this study could be expected, i.e., the alteration of the photocatalytic behaviour of the parental compound. However, previous studies carried out by our research group have revealed that the adsorption centres of these acids are not the same when they act as reagents or intermediates [33].

The photocatalytic degradation of carboxylic acids has been described to happen by means of their reaction with ${}^{\bullet}OH$ radicals or holes (photo-Kolbe reaction) [34,35]:

$$(R\text{-}CH_2\text{-}COOH)_{ads} + {}^{\bullet}OH \rightarrow R\text{-}\dot{C}H\text{-}COOH + H_2O \qquad (2)$$

$$(R\text{-}CH_2\text{-}COOH)_{ads} + h^+ \rightarrow R{-}CH_2{}^{\bullet} + CO_2 \qquad (3)$$

The photogenerated electrons can react with adsorbed oxygen to yield H_2O_2:

$$e^- + O_2 \rightarrow O_2{}^{\bullet -} \qquad (4)$$

$$O_2{}^{\bullet -} + H_2O \rightarrow HO_2{}^{\bullet} + OH^- \qquad (5)$$

$$2HO_2{}^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (6)$$

Other study has indicated [30] that Ti^{4+} ions present on catalyst surface must be completely coordinated by hydroxyl groups and water molecules in an approximate ratio of 50%, without voids or vacancies for oxygen adsorption. Hence, reaction between photogenerated electrons and oxygen has been considered to occur only after water desorption (Scheme 4):

Our results suggest that the acids tend to displace adsorbed water molecules from TiO_2 surface, favouring this reaction.

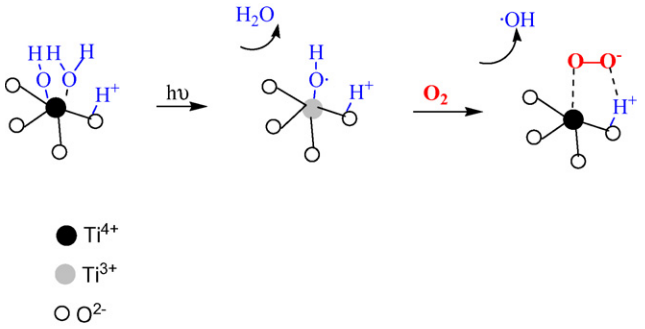
Moreover, $O_2{}^{\bullet -}$ and $HO_2{}^{\bullet}$ radicals can also be generated from oxalic acid degradation [36]:

$$HC_2O_4{}^- + h^+ \rightarrow HCOO\text{-}COO^{\bullet} \qquad (7)$$

$$HCOO\text{-}COO^{\bullet} \rightarrow {}^{\bullet}CO_2{}^- + CO_2 + H^+ \qquad (8)$$

$${}^{\bullet}CO_2{}^- + O_2 \rightarrow CO_2 + O_2{}^{\bullet -} \qquad (9)$$

$$HCOO\text{-}COO^{\bullet} + O_2 \rightarrow HO_2{}^{\bullet} + 2CO_2 \qquad (10)$$



Scheme 4.

These radicals can increment H_2O_2 yield (reaction (5) and (6)) and the consequent degradation of *p*-nitrophenol. In this way, the high concentration of this radical may explain why degradation rate constants were not modified at oxalic concentrations about 80 ppm.

It must also be stressed that in the presence of H_2O_2 and increasing formic acid concentrations, *p*-nitrophenol degradation rate constant becomes progressively lower. The photocatalytic degradation of formic acid by Photo-Kolbe would be:

$$HCOO^- + h^+ \rightarrow CO_2 + H^\bullet \qquad (11)$$

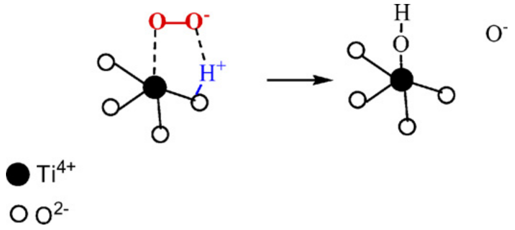
$H^\bullet$ radicals could react with H_2O_2 by:

$$H^\bullet + H_2O_2 \rightarrow H_2O + HO^\bullet \qquad (12)$$

$$HO^\bullet + H_2O_2 \rightarrow H_2O \quad HO_2{}^\bullet \qquad (13)$$

In this way, *p*-nitrophenol degradation rate reduction in presence of H_2O_2 and formic acid can be explained.

Moreover, it has also been indicated that $O_2{}^{\bullet -}$ participates in the regeneration of hydroxyl groups responsible for photogenerated radicals, thus increasing degradation rate [31]:



5. Conclusions

The photocatalytic degradation of *p*-Nitrophenol is significantly increased in presence of formic, acetic and oxalic acids. FTIR studies indicate that *p*-nitrophenol interacts with water molecules adsorbed on TiO_2 surface to give a *p*-nitrophenoxide. However, the acids generate a higher concentration of Bronsted acid-like centres which modify *p*-nitrophenol interaction. The presence of these new species in conjunction with $O_2{}^{\bullet -}$ radicals generated by the degradation of acids or catalyst surface restructuration would be responsible for the faster *p*-nitrophenol degradation.

Experiments with H_2O_2 indicate that the mechanism responsible for the degradation of *p*-nitrophenol improvement in presence of acetic and oxalic acids is not affected by the peroxide. In addition to this, formic acid hampers H_2O_2 degradation.

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References

[1] G. Colón, J.M. Sánchez-España, M.C. Hidalgo, J.A. Navío, J. Photochem. Photobiol. A: Chem. 179 (2006) 20.
[2] D. Vione, C. Minero, V. Maurino, M. Eugenia Carlotti, Tatiana Picatonotto and Ezio Pelizzetti, Appl. Catal. B: Environ. I 58 (2005) 79.
[3] J. Grzechulska, A.W. Morawski, Appl. Catal. B: Environ. 46 (2003) 415.
[4] M. Muneer, M. Qamar, D. Bahnemann, J. Mol. Catal. A: Chem. 234 (2005) 151.
[5] P. Pichat, S. Vannier, J. Dussaud, J.-P. Rubis, Solar Energy 77 (2004) 533.
[6] G. Martra, F. Arena, S. Coluccia, F. Frusteri, A. Parmalia, Catal. Today 63 (2000) 197.
[7] C. Hu, Y. Tang, J.C. Yu, P.K. Wong, Appl. Catal. B: Environ. 40 (2003) 131.
[8] C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J.-M. Herrman, J. Photochem. Photobiol. A: Chem. 158 (2003) 27.
[9] M. Sökmen, A. Özkan, J. Photochem. Photobiol. A: Chem. 147 (2002) 77; M. Abdullan, G.K.-C. Low, R.W. Mattews, J. Phy. Chem. 94 (1990) 6820.
[10] M. Bekbölet, Z. Boyaciolu, B. Özkaraoun, Water Sci. Technol. 38 (1998) 155.
[11] G. Colón, M.C. Hidalgo, G. Munuera, I. Ferino, M.G. Cutrufello, J.A. Navío, Appl. Catal. B: Environ. 63 (2006) 45.
[12] C. Renzi, C. Guillard, J.-M. Herrman, P. Pichat, G. Balde, Chemosphere 35 (1997) 819.
[13] J. Araña, J.M. Doña Rodríguez, O. González Díaz, J.A. Herrera Melián, C. Fernández Rodríguez, J. Pérez Peña, Appl. Catal. A 299 (2006) 274.
[14] C. Arrouvel, M. Digne, M. Breysse, H. Toulhoat, P. Raybaud, J. Catal. 222 (2004) 152.
[15] U. Diebold, Surface Science Reports 48 (2003) 53.
[16] V.A. Sakkas, I.M. Arabatzis, I.K. Konstantinou, A.D. Dimou, T.A. Albanis, P. Falaras, Appl. Catal. B: Environ. 49 (2004) 195.
[17] D.D. Dionysiou, M.T. Suidan, I. Baudin, J.-M. Laîné, Appl. Catal. B: Environ. 50 (2004) 259.
[18] S.T. Martin, Jm.M. Kesselman, D.S. Park, N.S. Lewis, M.R. Hoffman, Environ. Sci. Technol. 30 (1996) 2535.
[19] R. Rodríguez, M.A. Blesa, A.E. Regazzoni, J. Colloid Interface Sci. 177 (1996) 122.
[20] J. Araña, C. Fernández Rodríguez, O. González Díaz, J.A. Herrera Melián, J. Pérez Peña, Catal. Today 101 (2005) 261.
[21] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, Inc., 1973.
[22] C.J. Pouchert, The Aldrich Library of Infrared Spectra, III edition.
[23] A.R. Gandhe, J.B. Fernándes, Catal. Comm. 5 (2004) 89.
[24] S.E. Collins, M.A. Baltanás, Al.L. Bonivardi, J. Catal. 226 (2004) 410.
[25] S. Docuff, M. Henry, C. Sánchez, J. Livage, J. Non Cryst. Solids 89 (1987) 206.
[26] N. Sharma, M. Deepa, P. Varshney, S.A. Agnihotry, Thin Solid Films 401 (2004) 45.
[27] C.B. Mendive, D.W. Bahnemann, M.a. Blesa, Catal. Today 101 (2005) 237.
[28] A.J. Maira, J.M. Coronado, V. Augugliaro, K.L. Yeung, J.C. Conesa, J. Soria, J. Catal 202 (2001) 413.
[29] M.A. Henderson, Langmuir 12 (1996) 5093.
[30] G. Munuera, V. Rives-Arnau, A. Saucedo, J. Chem. Soc. Faraday Trans. I 75 (1979) 736.
[31] A.R. González-Elipe, G. Munuera, J. Soria, J. Chem. Soc. Faraday Trans. I 75 (1979) 748.
[32] G. Munuera, A.R. González-Elipe, J. Soria, J. Sanz, J. Chem. Soc. Faraday Trans. I 76 (1980) 1535.
[33] J. Araña, J.M. Doña Rodríguez, O. González Díaz, J.A. Herrera Melián, J. Pérez Peña, Appl. Surf. Sci. 252 (2006) 8193.
[34] B. Kraeutler, A.J. Bard, J. Am. Chem. Soc. 99 (1977) 7729.
[35] J. Araña, O. González Díaz, J.M. Doña Rodríguez, J.A. Herrera Melián, C. Garriga i Cabo, J. Pérez Peña, J Mol. Catal. 197 (2003) 157.
[36] N. Quici, M.E. Morgada, G. Piperat, P. Babay, R.T. Gettar, M.I. Litter, Catal. Today 101 (2005) 253.