

# Partial or complete heterogeneous photocatalytic oxidation of neat toluene and 4-picoline in liquid organic oxygenated dispersions containing pure or iron-doped titania photocatalysts

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## Abstract

The heterogeneous photocatalytic oxidation of neat toluene and 4-picoline in liquid organic oxygenated dispersions containing pure or iron-doped titania photocatalysts has been studied in a photochemical reactor radiating predominantly at 365–366 nm. The investigation correlates experimental conditions such as structural aspects, surface properties, concentration and chemical nature of the photocatalysts, and illumination times, with chemical yields and selectivity of products. For toluene, the main photocatalytic products found were benzaldehyde, benzyl alcohol and benzoic acid.

In particular, our results show that traces of water present in the reaction system play an important role in the distribution of products. Likewise, the important role of the adsorption effects in photocatalysis based on semiconductors is emphasized. Thus, differences in the affinity and mode of the adsorption of different molecules (i.e., toluene, picolines) should give rise to differences in the distribution of the reaction products.

**Keywords:** Photocatalysis; Toluene; Picolines; Oxidation; Titania

## 1. Introduction

Heterogeneous photocatalysis by semiconductors is a fast growing field of basic and applied research [1,2]. It has been demonstrated that heterogeneous photocatalysis is a means of oxidising organic compounds in the liquid phase, either to yield preparatively useful products [2–5] or to destroy organic pollutants from waste waters [5–8]. Heterogeneous photocatalysis is a process in which the illumination of a semiconductor produces photoexcited electrons ( $e^-$ ) and holes

( $h^+$ ). These photogenerated carriers can migrate to the semiconductor surface and participate in redox reactions that are part of a closed, catalytic cycle. The principle of the method is well established and has been treated extensively in several books [1,9–11].

Titanium dioxide,  $TiO_2$ , has been employed extensively in studies of heterogeneous photocatalysis and it is accepted as one of the best photocatalysts [1–3]. On the other hand, transition metal doping can expand the wavelength range to which suspended metal oxide particles respond to the visible [1–3]. In particular, iron(III)-doped

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TiO<sub>2</sub> samples, Fe/TiO<sub>2</sub>, have been the object of several papers, including preparation and characterization, spectroscopic features, dynamics of charge-transfer trapping and recombination and photocatalytic behavior [1–3]. Enhancement in the rate of photoreaction upon Fe<sup>3+</sup> loading can produce a photocatalyst with an improved trapping-to-recombination rate ratio. This effect seems to be sensitive to dopant level [2].

The heterogeneous oxidation of methylbenzene (toluene), in the liquid phase, using illuminated semiconductor materials, has been studied by Fujihira et al. [12–14] using various experimental conditions. For example, in aqueous media, the total proportion of products, stemming from the photooxidation of the side-chain (benzaldehyde and benzyl alcohol), versus those obtained from hydroxylation of the aromatic ring (cresols), decreases with increasing pH and also in the presence of oxidants [12]; the influence of the type of catalyst used on product distribution has been studied by the same authors [13].

Studying the heterogeneous photocatalytic oxidation of neat toluene, by air [14], benzaldehyde was the only product arising from side-chain photooxidation; depending upon the conditions, 1,2-diphenylethane was also detected. A higher rate of transformation was observed for neat liquid 4-*tert*-butyltoluene converted to 4-*tert*-butylbenzaldehyde [15]. It has been shown that in UV-illuminated TiO<sub>2</sub> acetonitrile suspensions [16], the oxidation rate of the alkyl chain of alkylbenzenes decreased with the number of carbon atoms, with the exception of toluene.

The TiO<sub>2</sub> photocatalytic oxidation of methylpyridines (picolines) in acetonitrile has been studied previously by Fox et al. [17]; in these conditions the picolines are practically converted to inorganic products (mineralization), perhaps because of the presence of water traces in the solvent or adsorbed at the surface of the photocatalyst. Small amounts of side-chain oxidation products (CH<sub>3</sub> → CH<sub>2</sub>OH → CHO → COOH) were found only at short illumination periods and were not even detected for 4-picoline [17].

The aim of this work was to make a detailed study of the photooxidation of toluene and 4-picoline.

## 2. Experimental

Two types of photocatalyst were used in this study: pure TiO<sub>2</sub> (Degussa, P-25) previously calcined in air at 500°C for 24 h, and iron-doped TiO<sub>2</sub>. Iron-doped titania powders, Fe/TiO<sub>2</sub>, containing two selected amounts of Fe<sup>3+</sup> (0.5 and 5 wt.-%) were prepared by the incipient wetness impregnation method of powdered TiO<sub>2</sub> (Degussa, P-25), using aqueous solutions of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merk) containing the required nominal quantity of Fe<sup>3+</sup> ions; after standing for 48 h the liquid phase was evaporated at 110°C for 24 h and the dried solids fired in air at 500°C for 24 h. The iron content of the Fe/TiO<sub>2</sub> samples was checked by atomic absorption using a Perkin-Elmer model 2380 spectrophotometer. Bulk and surface characterization of these samples can be found elsewhere [18]. The hematite sample (α-Fe<sub>2</sub>O<sub>3</sub>) was obtained by calcination of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in air at 500°C for 24 h. The specific surface area of this iron oxide sample was 19.5 m<sup>2</sup> g<sup>-1</sup> and its particle size 0.06 μm.

The surface acidity (sum of Brønsted and Lewis sites) was measured by means of a spectrophotometric titration method [19] using pyridine (pK<sub>a</sub> = 5.3) or benzoic acid (pK<sub>a</sub> = 4.2) as absorbates. BET surface areas of the reported catalysts were determined with a Micromeritics Flowsorb 2200 instrument, using N<sub>2</sub> at 77 K. All chemicals were of at least reagent grade. Before use, toluene was distilled.

The photooxidation experiments were carried out in an Applied Photophysics Ltd. photochemical reactor equipped with a 400 W medium pressure mercury-arc lamp, radiating predominantly at 365–366 nm. This lamp produces more than 5 × 10<sup>19</sup> photons s<sup>-1</sup> within the reaction flask. It was contained in a double-glass immersion well, through which water was passed for cooling. A borosilicate glass sleeve was used to remove short

Table 1  
Some properties of the oxide samples

Type of oxide	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Particle size ( $\mu\text{m}$ )	Acidity ( $\mu\text{m g}^{-1}$ )	Basicity ( $\mu\text{m g}^{-1}$ )	Anatase/rutile (A/R) ratio
TiO <sub>2</sub> (P-25)	46.5	0.03	5.8	13.8	0.57
Fe/TiO <sub>2</sub> (0.5 wt.-% Fe)	29.2	5 <sup>a</sup> + 50 <sup>b</sup>	3.4	4.3	0.45
Fe/TiO <sub>2</sub> (5 wt.-% Fe)	29.6	5 <sup>a</sup> + 180 <sup>b</sup>	3.3	6.5	0.44

<sup>a</sup> Pure TiO<sub>2</sub>.

<sup>b</sup> Aggregates containing Fe.

wavelength radiations (less than 300 nm). A gas inlet reaction flask (400 ml) was used; a double surface condenser was fitted to the reaction flask to prevent 'creep' and loss of vapor.

The powdered photocatalysts were independently suspended in either neat liquid toluene (375 ml) or in a solution of 4-picoline (16.3 g,  $1.75 \times 10^{-1}$  mol) in acetonitrile (350 ml). Oxygen was bubbled through the suspension and a positive pressure of the gas was maintained during the period of illumination. Three milliliter aliquots were taken from the photoreactor at certain time intervals during the illumination. The photocatalyst was separated by centrifugation, to analyse the liquid phase. Products were identified by GC-MS technique using a Kratos-MS 80 RFA instrument fitted to a GC Carlo Erba. Separations were achieved on a CP-SIL 5 CBWCOT (25 m  $\times$  0.32 mm) column whose temperature was programmed from 30°C (10 min) up to (a) 150°C (5 min) for toluene, or (b) 220°C (5 min) for the 4-picoline, at 5°C min<sup>-1</sup> and 10°C min<sup>-1</sup>, respectively. The method of external standards was used for semiquantitative determinations. Qualitative evidence of evolved CO<sub>2</sub> was obtained by bubbling through an aqueous solution of Ba(OH)<sub>2</sub>.

### 3. Results and discussion

#### 3.1. Surface acid–base properties

The distribution of acid and basic sites in the undoped and iron-doped titania photocatalysts, as well as other properties, is given in Table 1 as the respective amount of pyridine or benzoic acid

adsorbed at saturation. BET surface area and anatase/rutile ratio, for each of the catalysts studied, are also reported in the same Table. For the original TiO<sub>2</sub> sample, the anatase/rutile ratio (0.57), as determined by X-ray diffractometry, differs from the ratio reported by the manufacturers (0.80); this value depends on the history of the sample. When the original pure TiO<sub>2</sub> is calcined at 500°C 24 h, a slight decrease in the anatase/rutile ratio is observed. As previously reported [18], Fe/TiO<sub>2</sub> systems present lower anatase/rutile ratios, and the sample with 5 wt.-% Fe shows X-ray peaks assigned to pseudo-brookite (Fe<sub>2</sub>TiO<sub>5</sub>); in addition, the sample with 5 wt.-% Fe contains Fe<sub>2</sub>O<sub>3</sub> as separate phase at the surface [18]. It is remarkable that the mixed oxides have a lower amount of acid and basic hydroxyl groups than does the TiO<sub>2</sub> sample, as determined spectrophotometrically. These data are shown in Table 1 and will be used in the discussion of the photocatalytic activity.

#### 3.2. Heterogeneous photocatalytic oxidation of toluene

The evolution, of products during illumination, is summarized in Table 2 and results from experiments 1 to 6 are plotted in Figs. 1–3. On the whole, it seems that benzaldehyde, benzyl alcohol and benzoic acid were detected as the main products. In experiments 1 and 5, benzyl alcohol was detected only as traces, even for prolonged illumination times; in experiment 3; benzoic acid was detected as negligible traces, and that only after prolonged illumination. It is interesting that under all of the experimental conditions reported here,

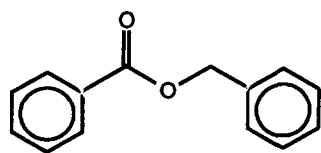
Table 2

Selectivity for benzaldehyde, benzyl alcohol and benzoic acid, in the photocatalytic oxidation of toluene with several photocatalysts. Selectivity expressed in percentage, is referred to the total number of mol of the formed and detected products (CO<sub>2</sub> has not been considered)

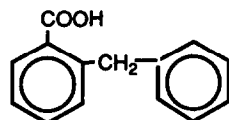
Exp.	Main photogenerated products	Illumination time (h)													
		1		3		5		7		9		11 <sup>g</sup>		12	
		mmol	S (%)	mmol	S (%)	mmol	S (%)	mmol	S (%)	mmol	S (%)	mmol	S (%)	mmol	S (%)
1 <sup>a,c</sup>	Benzaldehyde	3.9	100	9.5	100	11.1	100	15.4	100	8.4	85	9.1	71	8.4	81
	Benzoic acid									1.5	15	3.7	29	2.0	19
2 <sup>a,f</sup>	Benzaldehyde	2.1	100	2.9	100	3.6	68	3.6	38	3.3	34	4.4	34	4.4	33
	Benzyl alcohol					1.7	32	2.1	22	1.9	20	2.8	22	2.3	17
	Benzoic acid							3.8	40	4.4	46	5.8	44	6.5	50
3 <sup>b,c</sup>	Benzaldehyde	1.0	100	3.9	100	4.4	100	6.8	83	5.6	63	6.6	77	4.9	72
	Benzyl alcohol							1.4	17	3.3	37	2.0	23	1.9	28
4 <sup>b,f</sup>	Benzaldehyde	2.2	100	11.2	88	14.2	81	23.2	69	30.9	64	32.2	60	23.2	59
	Benzyl alcohol			1.5	12	1.9	11	5.6	17	9.7	20	13.5	25	9.7	24
	Benzoic acid					1.5	8	5.0	14	7.5	16	8.4	15	6.7	17
5 <sup>c,e</sup>	Benzaldehyde			0.6	100	0.9	100	1.0	100	1.2	100	1.3	100	1.3	100
6 <sup>c,f</sup>	Benzaldehyde	0.5	100	1.9	100	2.9	100	3.3	67	3.0	52	4.0	43	3.7	46
	Benzyl alcohol							1.6	33	1.7	29	2.9	31	2.9	36
	Benzoic acid									1.1	19	2.4	26	1.5	18
7 <sup>d,e</sup>	Benzaldehyde								0.5	100	0.6	100	0.8	100	
8 <sup>d,f</sup>	Benzaldehyde										0.5	100	0.5	100	

<sup>a</sup> TiO<sub>2</sub>. <sup>b</sup> Fe/TiO<sub>2</sub> (0.5 wt.-% of Fe<sup>3+</sup>). <sup>c</sup> Fe/TiO<sub>2</sub> (5 wt.-% of Fe<sup>3+</sup>). <sup>d</sup> Fe<sub>2</sub>O<sub>3</sub>. <sup>e</sup> 2.5 g of catalyst per liter of toluene. <sup>f</sup> 1.25 g of catalyst per liter of toluene. <sup>g</sup> Data shown for experiment 3 are corresponding to 10 h of illumination.

traces of 2-, 3- and 4-cresols were also detected. In addition, in experiment 2, traces of benzyl benzoate (**1**) and *o*-benzyl benzoic acid (**2**) were also found.



1



2

#### Chemical and quantum yields

In principle, two observations may be made about results reported in Table 2. First, for the highest concentration of catalyst used (exps. 1, 3

and 5) comparing the chemical yields in benzaldehyde, for undoped and iron-doped titania samples, the highest activity was exhibited by undoped TiO<sub>2</sub>. However, the Fe/TiO<sub>2</sub> sample with (0.5 wt.-% in Fe<sup>3+</sup>) showed a higher photoactivity than pure TiO<sub>2</sub> or Fe/TiO<sub>2</sub> with (5 wt.-% in Fe<sup>3+</sup>) when a lower concentration of catalyst was used (exps. 2, 4 and 6); in particular, a relatively high chemical yield in benzaldehyde (ca. 0.9) was obtained after 11 h of illumination using the Fe/TiO<sub>2</sub> (0.5 wt.-% in Fe<sup>3+</sup>) sample at a concentration of 1.25 g per liter of toluene (exp. 4).

The second observation is that as expected for a photocatalytic reaction [20], the formation of benzaldehyde increased with increasing amounts of TiO<sub>2</sub> catalyst (exp. 1 and 2, Fig. 1); this depends on the mass of catalyst required for complete absorption of useful photons. However, this was not the situation when Fe/TiO<sub>2</sub> samples were used (exps. 3, 4, 5 and 6; Fig. 2 and Fig. 3), in which the amount of benzaldehyde increased with decreasing amounts of Fe/TiO<sub>2</sub> catalysts.

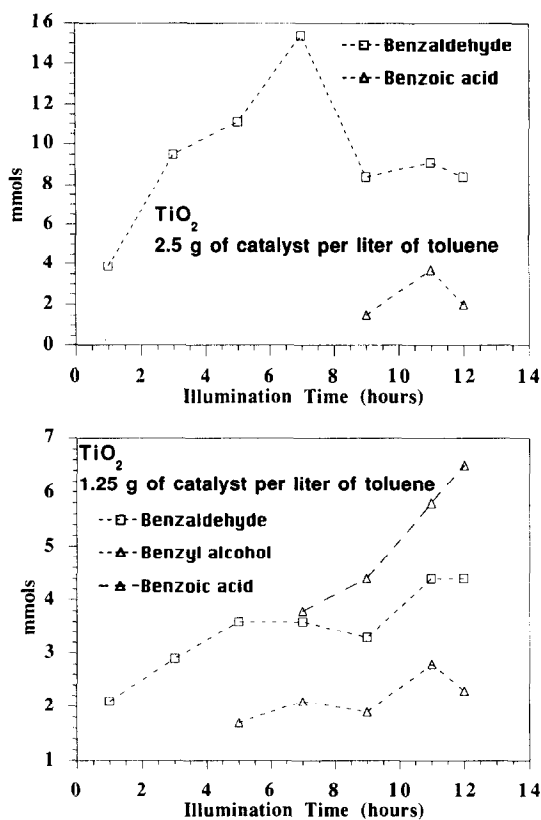


Fig. 1. Evolution of product quantities from heterogeneous photocatalytic oxidation of toluene with pure  $\text{TiO}_2$  photocatalyst at the indicated concentrations of catalyst. (Data from experiments 1 and 2 reported in Table 1).

From results reported in Table 2/Figs. 1–3, it can be inferred that the  $\text{Fe}/\text{TiO}_2$  with 5 wt.-% in  $\text{Fe}^{3+}$  which contains the pseudobrookite phase,  $\text{Fe}_2\text{TiO}_5$ , is the least photoactive at any concentration of catalyst during the heterogeneous photocatalytic oxidation of neat liquid toluene, compared with the other samples studied here. The energy band-gap of  $\text{Fe}_2\text{TiO}_5$  is 2.18 eV — comparable with that of  $\text{Fe}_2\text{O}_3$  (2.2 eV) but smaller than that of  $\text{TiO}_2$  (ca. 3.0 eV); moreover and due to the poor mobility of the electrons photogenerated in  $\text{Fe}_2\text{TiO}_5$  phase, it is very likely that the rate of recombination of the electron–hole pair is greater than that of trapping by substrates. By applying laser techniques, in colloidal semiconductors, Rothemberg et al. [21] have shown that the charge carrier's recombination time is drastically reduced in iron-doped titania. However, this effect seems to be sensitive to dopant level for

although  $\text{Fe}^{3+}$  doping increases carrier lifetimes in  $\text{TiO}_2$  [22], and  $\text{Fe}^{3+}$  doping at below 0.5 wt.-% improves methylviologen,  $\text{MV}^{2+}$ , reduction, it sharply reduces the efficiency at higher levels [23].

Table 3 summarizes the average values of the apparent quantum yields (q.y.) [24] for the different experimental conditions used in this study. These q.y. have been estimated by assuming that all the photons supplied by the lamp are absorbed by the catalyst grains. Thus, for pure  $\text{TiO}_2$ , the q.y. is higher for the more concentrated suspensions; however, in the case of the two  $\text{Fe}/\text{TiO}_2$  samples used here, the higher q.y. is obtained with the lower concentration of catalyst. These differences can be explained in terms of differences in morphology and/or particle size between the catalysts. In fact, it has been shown [25,26] that variations in the particle morphology and size often result in drastic differences in the photocatalytic reactivity, mechanistic implications of par-

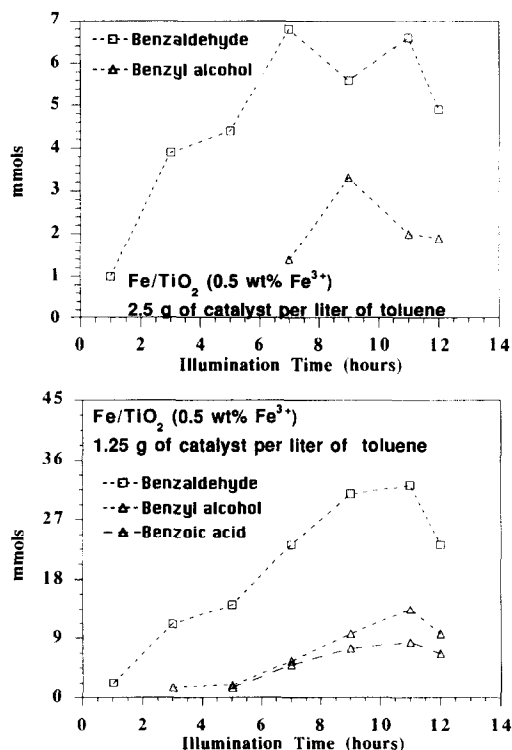


Fig. 2. Evolution of product quantities from heterogeneous photocatalytic oxidation of toluene with  $\text{Fe}/\text{TiO}_2$  (0.5 wt.-%  $\text{Fe}^{3+}$ ) photocatalyst at the indicated concentrations of catalyst. (Data from experiments 3 and 4 reported in Table 1).

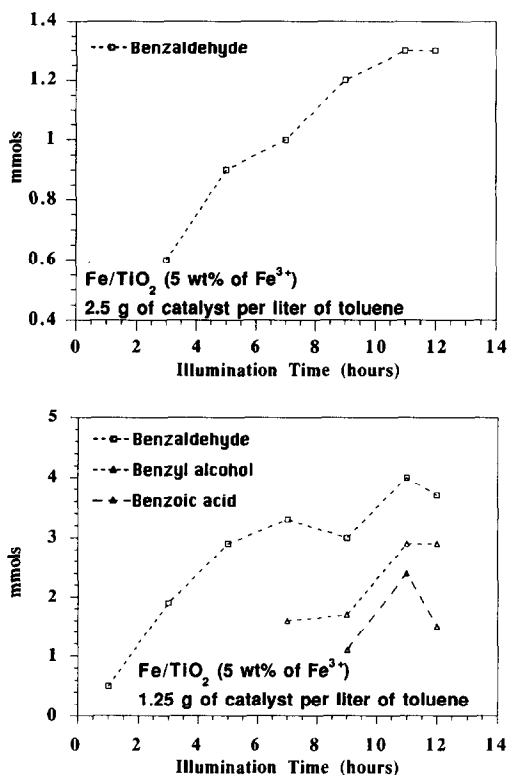


Fig. 3. Evolution of product quantities from heterogeneous photocatalytic oxidation of toluene with Fe/TiO<sub>2</sub> (5 wt.-% Fe<sup>3+</sup>) photocatalyst at the indicated concentrations of catalyst. (Data from experiments 5 and 6 reported in Table 1).

ticle size also having been observed [25]. Results reported by Navio et al. [18] have shown (see Table 1) that, while the undoped TiO<sub>2</sub> used in this work is constituted by small round free individual grains (1–5 μm diameter), the Fe/TiO<sub>2</sub> grains are formed by irregular aggregation of several particles. Thus, for Fe/TiO<sub>2</sub> (0.5 wt.-% in Fe<sup>3+</sup>) the average size of aggregates is about 50 μm diameter, whereas for Fe/TiO<sub>2</sub> (5 wt.-% in Fe<sup>3+</sup>) the average grain size has been estimated to be about 180 μm diameter.

Memming has calculated the transit time necessary for charge carriers formed within the bulk to reach the surface of the semiconductor particles [27]. While in a particle with a diameter of 10<sup>-2</sup> μm it takes only 10<sup>-12</sup> s before electrons and holes can be trapped in energetically favorable sites at the semiconductor/electrolyte interface, a transit time of 10<sup>-10</sup> s is computed for a particle diameter of 1 μm. As lifetimes have been reported

to be in the nanosecond time regime for electron/hole pairs in semiconductor particles [21], recombination within the bulk will be a competitive process in μm-sized particles.

Our results suggest that both morphology and particle size can affect the product distribution and yields, through the concentration of catalyst, apart from its possible effect upon light scattering and reflection by the photocatalyst particles.

At the same time, the photocatalytic efficiency of TiO<sub>2</sub> is governed by its crystal structure. It is known that anatase is a more efficient photocatalyst than rutile [28]. Thus, one additional factor which could be invoked to explain the differences in photoactivity between our catalysts is the difference in anatase/rutile ratios between them. However, looking at Table 1, it does not seem that this effect must be a relevant factor because the observed differences in anatase/rutile ratios between the photocatalysts used here are practically negligible.

#### Selectivity and mechanistic features

For neat liquid toluene, three factors affected the selectivity: the illumination time, the nature and the concentration of the photocatalyst. Except for experiment 2 at prolonged illumination time (> 5 h) in any case, benzaldehyde was by far the main product. After illumination time < 3 h, no noticeable amounts of benzyl alcohol and/or benzoic acid were detected. After prolonged illumination (7–12 h), the selectivity for benzaldehyde was gradually reduced by the progressive appearance of other products of photooxidation such as benzyl alcohol and benzoic acid.

Heterogeneous photocatalytic oxidation of toluene in non-aqueous systems in oxygenated atmosphere has been previously investigated by Fujihira et al. [14] under UV-illumination up to 2 h. A mechanism has been proposed by those authors assuming the possibility that the benzyl radicals formed can readily react either with oxygen (leading to an organic peroxyradicals which is reduced to benzaldehyde) or with superoxide species O<sup>-</sup> (giving benzaldehyde directly) [29]. It is interesting that Fujihira et al. [14] detected

Table 3

Data of the average values of quantum yields<sup>a</sup> for experiments reported on Table 2

Experimental conditions	Quantum yields <sup>a</sup>
1. TiO <sub>2</sub> (2.5 g of catalyst per liter of toluene)	10 <sup>-2</sup>
2. TiO <sub>2</sub> (1.25 g of catalyst per liter of toluene)	5 × 10 <sup>-3</sup>
3. Fe/TiO <sub>2</sub> (0.5 wt.-% of Fe <sup>3+</sup> ) (2.5 g of catalyst per liter of toluene)	3 × 10 <sup>-3</sup>
4. Fe/TiO <sub>2</sub> (0.5 wt.-% of Fe <sup>3+</sup> ) (1.25 g of catalyst per liter of toluene)	10 <sup>-2</sup>
5. Fe/TiO <sub>2</sub> (5 wt.-% of Fe <sup>3+</sup> ) (2.5 g of catalyst per liter of toluene)	5 × 10 <sup>-4</sup>
6. Fe/TiO <sub>2</sub> (5 wt.-% of Fe <sup>3+</sup> ) (1.25 g of catalyst per liter of toluene)	2 × 10 <sup>3</sup>

<sup>a</sup> Values obtained as an average of the quantum yields for each experiment.

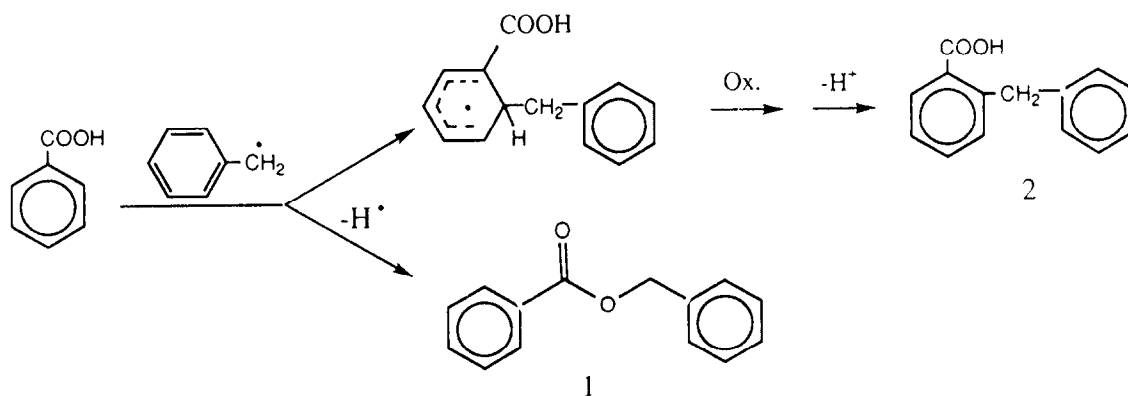
only benzaldehyde when using unloaded titania catalyst after UV-illumination for a period < 2 h. This observation is in accordance with our results for below 3 h of illumination (exps. 1 and 2, Fig. 1), when TiO<sub>2</sub> was used as photocatalyst.

On the other hand, the heterogeneous photocatalytic oxidation of liquid toluene in aqueous suspensions of TiO<sub>2</sub> has been studied in some detail by Fujihira et al. [12,13]. Those authors have reported that, in aqueous media, at a period of illumination < 2 h, benzaldehyde was one of the main products. Although benzyl alcohol was detected as traces, benzoic acid was not detected [12,13]. Under our experimental conditions using neat liquid toluene, only benzaldehyde was detected, as practically the only product, for a period of illumination < 3 h.

However, further oxidation to benzyl alcohol and to benzoic acid and subsequent decarboxyla-

tion occurred progressively for prolonged illuminations.

According to our results, the formation of benzyl alcohol, generated from the photooxidation of benzyl radicals [12], could be associated to the presence of water. Although a neat liquid toluene, previously distilled, was used in this work, the progressive oxidations of benzaldehyde to the other found products might be initiated by the low amount of surface-bound hydroxyl radicals, since in our experimental conditions the photocatalysts were not dehydrated before use. Indeed, after prolonged illumination, qualitative evidence of carbon dioxide together with partial oxidation products was observed and the simultaneous production of water can be considered as allowing the continuous generation of hydroxyl radicals. In the presence of water, several types of oxygen-derived free radical are formed [2–6] from which



(Equation 6)

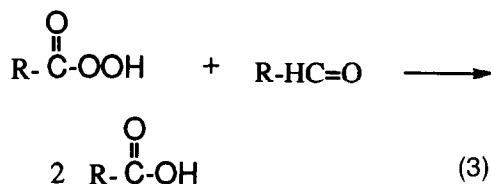
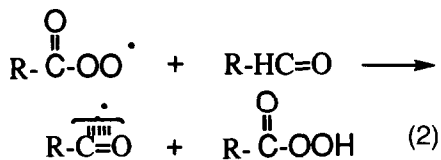
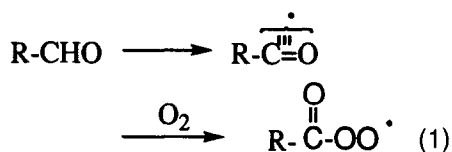
Scheme 1.

most organic molecules are mineralized. It must be considered also that in the aqueous phase, for solubility reasons, benzyl alcohol and benzoic acid must be more readily dissolved than benzaldehyde.

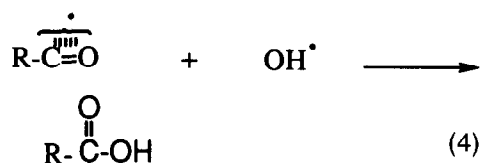
Therefore, benzyl alcohol and benzoic acid in the micro-drops of water could be photocatalytically destroyed by a drastic photooxidation to CO<sub>2</sub> and water. In fact the photocatalytic oxidation of the aromatic ring to CO<sub>2</sub> under UV-illumination in aqueous emulsion of TiO<sub>2</sub> has been observed by Izumi et al. [30,31].

On the other hand it must be mentioned that toluene oxidation on UV-illuminated TiO<sub>2</sub> with and without O<sub>2</sub>, NO<sub>2</sub> or H<sub>2</sub>O, has been reported [32]. From these studies it is concluded that the superoxide species O<sub>2</sub><sup>•-</sup> is very active for mineralization of toluene (CO<sub>2</sub> formation), while O<sup>-</sup> seems to be responsible for the partial oxidation of toluene.

The formation of benzoic acid from benzaldehyde could be via autooxidation of benzaldehyde by direct reaction with molecular oxygen, a reaction which is very well known [33,34]. Autooxidation of aldehydes occurs readily — the formation of a ‘collar’ of benzoic acid on bottles of benzaldehyde is a familiar manifestation. The initial products of reactions with aldehydes are peracids [34].



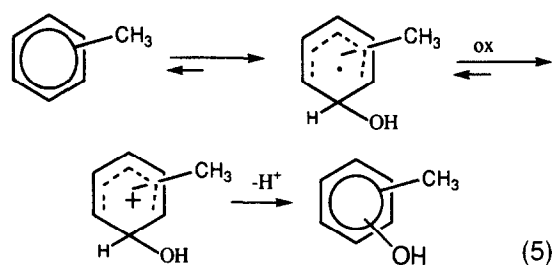
The peracid yields the final product by direct oxidation of the aldehyde, but may be trapped by other very reactive radicals such as OH before this process occurs, giving benzoic acid.



Thus, assuming that such processes can occur, the autooxidation of benzaldehyde to benzoic acid must be considered as an important factor in the chemical yields in benzaldehyde conversion. Under our experimental conditions, benzoic acid is detected only after prolonged illumination time and as mentioned above could also be subsequently photodegraded to CO<sub>2</sub> in the aqueous microphase [31].

Because the surface of the catalysts used exhibits both acid and base properties (Table 1), it is reasonable to propose that the photogenerated benzyl alcohol and benzoic acid molecules could be stabilized on the surface of the catalysts through an acid–base reaction. In such a case, even if benzyl alcohol and benzoic acid molecules are formed at short illuminations they could be adsorbed at the surface of catalysts and appear only after extended illuminations. Thus, benzyl alcohol and/or benzoic acid start to appear after longer illumination times when a concentration of 2.5 g of catalyst per liter of toluene is used; however they are detected at shorter illumination times when lower concentrations are used.





The formation of cresols as traces, is also the consequence of the presence of water either adsorbed at the catalysts surface or generated during the photoprocesses. Hydroxy radicals photo-generated from water can be attached to the aromatic ring of toluene, leading to the formation of an intermediate radical which is further aromatized [12,33] according to Eq. 5.

The formation of cresols, from toluene, in non-aqueous media, has also been observed by other authors [35] but only after extended illumination times. Likewise, the photocatalyzed mineralization of cresols in aqueous media with UV-illuminated titania has been reported [36]; the complete photomineralization of cresols to  $\text{CO}_2$  and water is faster ( $> 2.5$  h) in excess of molecular oxygen. The formation of hydroxyl radicals in UV-illuminated aqueous titanium dioxide suspensions in the presence of *p*-cresol/oxygen has been observed. All these data clearly indicate that the subsequent mineralization of toluene could occur via intermediate cresols and/or hydroxy radicals attacking the partial oxidation products. Indeed, the degradation of benzene and toluene by the  $\text{TiO}_2/\text{UV}$  process has been reported [37].

The formation of products (1) and (2) could be explained by the presence of benzyl radicals which can be attached to the benzoic acid molecules, either to the ring or to the side-chain, according to Eq. 6 – Scheme 1.

We do not exclude the formation of very small amounts of other products which could be formed by benzyl radicals attacking other compounds. In fact, Fujihira et al. [12,13] have found the compound (1) as a product during the UV-illumination of toluene in both aqueous and non-aqueous systems even, in the absence of air [14].

Finally, the poor reactivity found for pure iron oxide,  $\alpha\text{-Fe}_2\text{O}_3$ , can be explained by the electronic and structural properties of the hematite which presents a low mobility of charge carriers and fast surface recombination [21,22,38,39].

### 3.3. Heterogeneous photocatalytic oxidation of 4-picoline

The pyridine nucleus was less stable than the benzene nucleus under  $\text{TiO}_2$  photocatalytic conditions, since the oxidation of methylpyridines in acetonitrile led to inorganic products (complete oxidation), although traces of partial oxidation products were found but only at short illumination times, and were not detected for 4-picoline [17]. These data for the  $\text{TiO}_2$ -photocatalyzed oxidation of methylpyridines contrast with our results for the  $\text{TiO}_2$ -photocatalyzed oxidation of methylbenzene (toluene), which is selectively transformed into benzaldehyde.

The absence of selectivity, found for  $\text{TiO}_2$ -photocatalyzed oxidation of picolines, might be due to the relatively strong adsorption of picolines by the nitrogen atom, which might prevent the desorption of partly oxidized intermediates.

Iron-doped titania samples are less hydroxylated than undoped  $\text{TiO}_2$  showing lesser capacity for pyridine adsorption than the undoped titania sample (Table 1). On the other hand the incorporation of a certain amount of  $\text{Fe}^{3+} < 0.5$  wt.-% into  $\text{TiO}_2$  induces changes in chemical yields and on the selectivities observed for the heterogeneous photocatalytic oxidation of toluene (Table 2). On the basis of these differences we extended our work to the photocatalytic oxidation of 4-picoline using  $\text{Fe}/\text{TiO}_2$  samples with 0.5 wt.-% of  $\text{Fe}^{3+}$ . A concentration of 2.5 g of catalyst per liter was used; illumination time was extended up to 24 h.

No partial oxidation products were found at either short or prolonged illumination times. However, qualitative evidence of a progressive formation of  $\text{CO}_2$  during the course of illumination was found. This suggests the complete photocatalyzed mineralization of 4-picoline under our experimental conditions.

The total discrepancy in the heterogeneous photocatalytic oxidation between toluene and 4-picoline, when compared under the same experimental conditions, can be rationalized in terms of the strength of the bonds between the surface sites of the catalyst and the reactant/product in each case.

Benzene and its derivatives can form a variety of charge-transfer complexes depending on their electron-donating or electron-accepting ability [40].

The formation of charge-transfer complexes has been reported in some systems of metal oxides and benzene derivatives [41–43]. The interaction of benzene with the surface of  $\text{TiO}_2$  has been studied by Suda [44,45]. This author concluded that benzene carrying pi-electrons is absorbed in a flat orientation on the dehydroxylated site, preferentially by surface  $\text{Ti}^{4+}$  ions, through the formation of charge-transfer complexes; a weakly reversible adsorption of benzene on the hydroxylated surface is reported due to the  $\text{OH}\cdots\pi$  interaction. Similar results have been reported for the interaction of toluene molecules with titania catalysts [45]. In contrast, a stronger adsorption of 4-picoline by the nitrogen atom in a vertical orientation is expected. Because recombination of the photogenerated electron and hole is so rapid, interfacial electron transfer is kinetically a competitive process only when the donor or acceptor is preadsorbed at the surface of the catalyst. Indeed, it has been suggested that preliminary and strong adsorption is a prerequisite for highly efficient mineralization. It should be noted that the expected steric hindrance around the nitrogen heteroatom in 2-picoline could induce a lesser capacity for adsorption of this molecule compared with 4-picoline. If such is the case, partial oxidation products of the heterogeneous photocatalytic oxidation of 2-picoline could be expected, as has been reported by Fox et al. [17]. In any case the complete mineralization of picolines seems to be faster than their partial photooxidation. In fact, the total mineralization of pyridine into  $\text{CO}_2$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , etc. has been reported to occur by the  $\text{TiO}_2/\text{UV}$  process [46].

#### 4. Conclusions

Although the heterogeneous photocatalytic oxidation of toluene and picolines has been previously investigated by several authors, our investigation has attempted to correlate structural aspects, surface properties, concentration and chemical nature of the photocatalysts with chemical yields and selectivity of products. In particular, our results show that water plays an important role in the distribution of products.

The important role of adsorption effects in photocatalysis on semiconductors is emphasised. Thus, differences in the affinity and mode of adsorption of different chemical compounds (i.e., toluene and picolines) should give rise to differences for their partial or complete heterogeneous photocatalytic oxidation.

Obviously, all these observations are of interest either for water detoxification or for chemical synthesis.

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#### References

- [1] N. Serpone and E. Pelizzetti, *Photocatalysis-Fundamentals and Applications*, Wiley Interscience, New York, 1989.
- [2] M.A. Fox and M.T. Dulay, *Chem. Rev.*, 93 (1993) 341.
- [3] M.A. Fox and P. Pichat, in M.A. Fox and M. Chanon (Editors), *Photoinduced Electron Transfer*, Vol. D, Elsevier, Amsterdam, 1988, p. 241.
- [4] M.A. Fox, C.C. Chen, K. Park and J.N. Younathan. *Am. Chem. Soc. Symp. Ser.*, 278 (1985) 69.
- [5] P. Pichat, *Catal. Today*, 19 (1994) 313.
- [6] J.M. Herrmann, C. Guillard and P. Pichat, *Catal. Today*, 17 (1993) 7.

- [7] O. Legrini, E. Oliveros and A.M. Braun, *Chem. Rev.*, 93 (1993) 671.
- [8] P. Pichat, C. Guillard, C. Maillard, L. Amalric and J.C. D'Oliveira, in D.F. Ollis and H.A.I. Ekabi (Editors), *TiO<sub>2</sub>-Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, p. 207.
- [9] R.I. Bickley, in *Catalysis*, Vol. 5, Specialist Periodical Reports, R. Soc. Chem., London, 1982, p. 325.
- [10] M. Schiavello, *Photocatalysis and Photoreactors-Fundamentals and Developments*, NATO-ASI, series C, Vol. 146, Dordrecht, 1985.
- [11] J.A. Navio, C. Cerrillos and G. Colón, in *Trends in Photochemistry and Photobiology*, Council of Scientific Research Integration, Research Trends, India (in press).
- [12] M. Fujihira, Y. Satoh and T. Osa, *Nature*, 293 (1981) 206.
- [13] M. Fujihira, Y. Satoh and T. Osa, *Chem. Lett.*, (1981) 1053.
- [14] M. Fujihira, Y. Satoh and T. Osa, *J. Electroanal. Chem.*, 126 (1981) 277.
- [15] P. Pichat, J. Disdier, J.M. Herrmann and P. Vaudano, *Nouv. J. Chim.*, 10 (1986) 545.
- [16] O. Beaume, A. Finiels, P. Geneste, P. Graffin, A. Guida, J.L. Olivé and A. Saedan, in M. Guisnet et al. (Editors), *Heterogeneous Catalysis and Fine Chemicals III*, Studies in Surface Science and Catalysis, Vol. 78, Elsevier, Amsterdam, 1993, p. 401.
- [17] M.A. Fox, H. Ogawa and J. Muzyka, in D.S. Ginley et al. (Editors), *Photoelectrochemistry and Photosynthesis on Semiconducting Materials*, Vol. 14, *Electrochem. Soc.*, 1988, p. 9.
- [18] J.A. Navio, M. Macias, M. Gonzalez-Catalan and A. Justo, *J. Mater. Sci.*, 27 (1992) 3036.
- [19] J.M. Campelo, A. Garcia, J.M. Gutierrez, D. Luna and J.M. Marinas, *J. Colloid Interface Sci.*, 95 (1983) 544, and references cited therein.
- [20] P. Pichat, in M. Schiavello (Editor), *Photoelectrochemistry, Photocatalysis and Photoreactors*, Reidel, Dordrecht, 1985, p. 425.
- [21] G. Rothemberg, J. Moser, M. Grätzel, N. Serpone and D.K. Sharma, *J. Am. Chem. Soc.*, 107 (1985) 8054.
- [22] J. Moser, M. Grätzel and R. Gallay, *Helv. Chim. Acta*, 70 (1987) 1596.
- [23] J.A. Navio, F.J. Marchena, M. Roncel and M.A. de la Rosa, *J. Photochem. Photobiol. A: Chem.*, 55 (1991) 319.
- [24] M. Formenti, F. Juillet, P. Meriaudeau and S.J. Teichner, *Chem. Technol.*, 1 (1971) 680.
- [25] D.W. Bahenemann, in E. Pelizzetti and M. Schiavello (Editors), *Photochemical Conversion and Storage of Solar Energy*, Kluwer, Dordrecht, 1991, p. 251.
- [26] P. Pichat, in E. Pelizzetti and M. Schiavello (Editors), *Photochemical Conversion and Storage of Solar Energy*, Kluwer, Dordrecht, 1991, p. 277.
- [27] R. Memming, *Topics Curr. Chem.*, 143 (1988) 79.
- [28] M.V. Rao, K. Rajeshwar, V.R. Pai Verneker and J. Dubow, *J. Phys. Chem.*, 84 (1980) 1987.
- [29] T. Kanno, T. Ogushi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.*, 21 (1980) 467.
- [30] I. Izumi, W.W. Dunn, K.O. Wilbourn, F.F. Fan and A.J. Bard, *J. Phys. Chem.*, 84 (1980) 3207.
- [31] I. Izumi, W.W. Dunn and A.J. Bard, *J. Phys. Chem.*, 85 (1981) 218.
- [32] Takashi Ibuzuki and Koji Takeuchi, *Atmos. Environ.*, 20(9) (1986) 1711.
- [33] N.S. Isaacs, in *Reactive Intermediates in Organic Chemistry*, John Wiley and Sons, London, 1974, pp. 334–335.
- [34] C.J.M. Stirling, in *Radicals in Organic Chemistry*, Chap. 3, Oldbourne Chemistry Series, Oldbourne Press, London, 1965, p. 59.
- [35] R. Ogushi, T. Kanno, H. Sakuragi and K. Takamuru, *Abstr. Annu. Meet. Chem. Soc. Jpn.*, 1, 1981, p. 256.
- [36] R. Terzian, N. Serpone, C. Minero and E. Pelizzetti, *J. Catal.* 128 (1991) 352.
- [37] R. Beyerle-Pfñür, K. Hustert, P.N. Moza and M. Voget, *Toxicol. Environ. Chem.*, 1980, pp. 20–21 and 129–134.
- [38] J.H. Kennedy and K.W. Frese, *J. Electrochem. Soc.*, 125 (1978) 709.
- [39] H. Nakanishi, G. Sánchez, M. Hendewerk and G.A. Somorjai, *Mater. Res. Bull.*, 21 (1986) 137.
- [40] R.S. Mulliken and W.B. Person, in *Molecular Complexes*, Wiley-Interscience, New York, 1969.
- [41] M.R. Basila, *J. Chem. Phys.*, 35 (1961) 1151.
- [42] J.A. Cusumano and M.J.D. Low, *J. Phys. Chem.*, 74 (1970) 973 and 1950.
- [43] J.A. Cusumano and M.J.D. Low, *J. Colloid Interface Sci.*, 38 (1972) 245.
- [44] Y. Suda, *Langmuir*, 4 (1988) 147.
- [45] M. Nagao and Y. Suda, *Langmuir*, 5 (1989) 42.
- [46] G.K.C. Low, S.R. McEvoy and R.W. Matthews, *Chemosphere*, 19 (10/11) (1989) 1611.