ELSEVIER

Catalysis Today 54 (1999) 131–141

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Photocatalytic degradation of aqueous hydroxy-butandioic acid (malic acid) in contact with powdered and supported titania in water

Jean-Marie Herrmann *, Halima Tahiri, Chantal Guillard, Pierre Pichat

URA au CNRS Photocatalyse, Catalyse et Environnement, Ecole Centrale de Lyon, BP 163, 69131 Ecully Cedex, France

Abstract

Malic acid, a model molecule for partially oxidized products found either in biomass or in various degradative processes, could totally be mineralized by photocatalytic degradation. Laboratory experiments enabled one to determine the identity of 15 intermediates, logically presented in four parallel degradation pathways. The major one is initiated by a decarboxylation ('photo-Kolbe') reaction in the α-position with respect to the OH group. Parallel experiments have been performed in a slurry pilot solar photoreactor at PSA (Almeria, Spain), on a large scale (250 l). The same main intermediate products and the same kinetic laws were observed. TiO_2 has been used either in slurries or supported on several rigid inert plates. Deposition of titania on glass and quartz was carried out by a dip coating procedure and the deposition on stainless steel by an electrophoretic deposition process. The resulting materials have been exhaustively characterized by XPS, SEM/EDX, XRD and UV-vis absorption spectroscopy. Their photocatalytic activity pattern as a function of the nature of the support followed the decreasing order: TiO_2/quartz > TiO_2/steel = TiO_2/glass ≫ photolysis. This decline in activity has been correlated with the presence of cationic impurities (Si^{4+}, Na^+ for glass and Cr^{3+}, Fe^{3+} for stainless steel) in the titania layer as a consequence of the thermal treatment necessary to improve the cohesion of the titania layer and its adhesion onto the support. ©1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Heterogeneous photocatalysis has recently emerged as an efficient method for purifying water and air [1–5] in most of the cases encountered. More than 1200 references have been recently collected on this discipline [6]. Up to now, titania in the form of anatase has always been found to be the best photocatalyst.

Several attempts have been performed to increase photoefficiency either by noble metal deposition or by ion doping. p-type doping was obtained by dissolving in the lattice of titania heterocations of valency lower than that of Ti^{+4} (Al^{+3}, Cr^{+3}, Ga^{+3}), whereas n-type materials were obtained by dissolving heterocations of valency higher than 4+ (Nb^{+5}, Ta^{+5}, Sb^{+5}). In photocatalytic reactions of organic pollutant degradation, which are essentially total oxidation reactions, such modifications did not enhance the photocatalytic activity of titania and were rather detrimental. The inhibiting effect was ascribed to an increase in the electron-hole recombination rate [7]. Actually, p-type doping agents create acceptor centers which trap photo-electrons and then, once negatively charged, attract holes, thus behaving as recombination centers [8]. On the other hand, n-type doping agents create donor centers. By increasing the concentration of conduction electrons in the solid, electron-hole recombination is also favored, which is detrimental for

---

* Corresponding author. Tel.: +33-4-72-18-64-93; fax: +33-4-78-33-03-37
E-mail address: herrmann@ec-lyon.fr (J.-M. Herrmann)

PII: S0920-5861(99)00175-3

photoefficiency [8]. The resulting photocatalytic efficiencies for doped samples have been found to be lower than that of pure titania even when a substantial modification of the absorbance spectrum to the visible region was obtained, as in the case of Cr^{3+} doping [6]. However, despite the narrow UV-fringe absorbable by TiO_2 and the relatively low UV-radiant flux received at the the earth's surface, it is possible to perform solar detoxification of polluted waters [2,9,10].

Water contains numerous organic micropollutants of anthropogenic origin. The photocatalytic destruction of various compounds has already been carried out in our laboratory in order to evaluate the efficiency of the process, to identify the nature of the intermediate products and to elucidate the reaction pathways [3]. The present study concerns the photocatalytic degradation of malic acid (COOH-CHOH-CH_2-COOH, abbreviated MA) which is an example of a polycarboxylic acid containing an alcoholic group. Such a molecule is not toxic since it is present in white wines but it can often be found in fermentation processes and in biomass. The objective was to determine the reaction pathways leading to total mineralization via the production of carboxylic intermediates often found in the degradation chain of organic pollutants [1–6].

2. Experimental

2.1. Materials

Malic acid (MA) and all the other acids were purchased from Aldrich with the highest purity grade (≥99%) and used as received. Only one intermediate product (CHO-CH_2-COOH: formyl-ethanoic or malonaldehydic acid) was not commercial, probably because of its high unstability in air. Its identification required the use of LC/MS. The photocatalyst was TiO_2 Degussa P 25, mainly anatase (ca. 70%) of non-porous polyhedral particles of ca. 30 nm mean size with a surface area of 50 m^2/g.

2.2. Laboratory photoreactor and light source

The batch photoreactor was a cylindrical flask made of Pyrex of ca. 100 ml with a bottom optical window of ca. 4 cm diameter and was open to air. Irradiation was provided by a high pressure mercury lamp (Philips HPK 125 W) and was filtered by a circulating-water cell (thickness 2.2 cm) equipped with a 290 nm cut-off filter made of Pyrex. The water cell was used to remove IR radiation, thus preventing any heating of the suspension.

2.3. Analyses

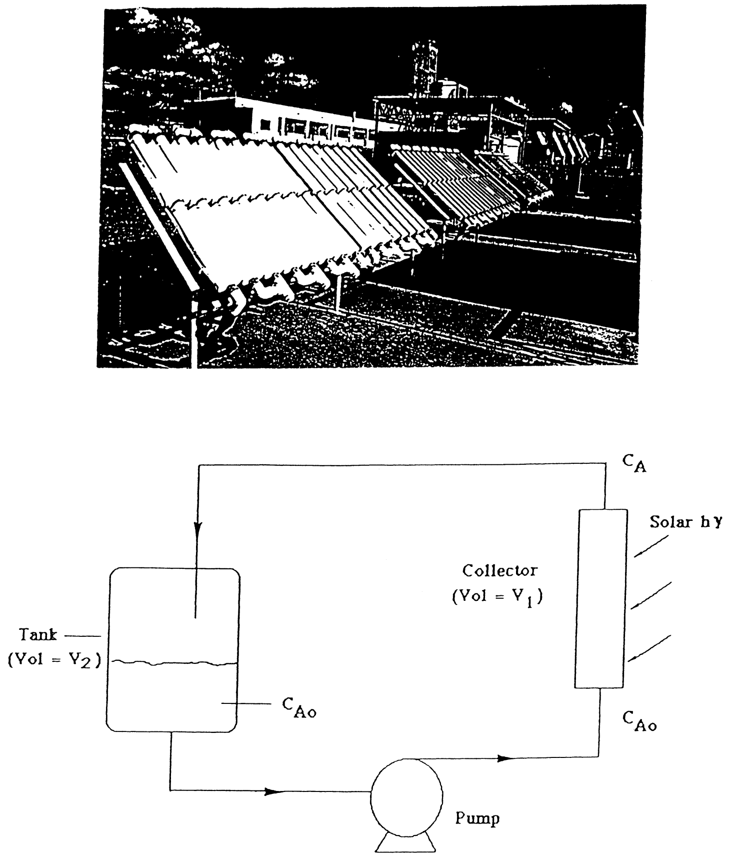
Millipore disks (0.45 mm) were used to remove particulate matter before HPLC analysis. Although non-agglomerated solid particles may pass through these membranes, our experience showed that the performance of the chromatographic column was not impaired for a long period of use. The HPLC system comprised a Varian 9010 pump and a Varian 9065 polychrom detector adjusted at 210 nm. An ion exchange chromatographic column (Aminex HPX-87 H, length, 300 mm; internal diameter, 7.8 mm; particle diameter, 9 μm) was used. The mobile phase was composed of H_2SO_4, 5×10^{-3} mol/l and the flow rate was 0.2 ml/min.

2.4. Procedure

In an ordinary photocatalytic test performed at room temperature (20°C), 70 mg TiO_2 were added under stirring in 20 ml of a millimolar solution of MA (500 ppm) and maintained in the dark during 1 h to reach complete adsorption at equilibrium. At time $t = 0$, a screen was removed from the window of the water cell located in front of the preheated lamp. Samples of the suspension (0.3 ml) were removed at regular intervals for analysis. The quantity of 70 mg of titania was chosen since in our conditions there is full absorption of UV light entering the photoreactor. The oxidation involved oxygen from air dissolved at saturation (≤1.4 mmol).

2.5. Pilot solar photoreactor

The compound parabolic collector (CPC) modules were selected for the present water detoxication study since they provide better solar efficiency than parabolic concentrators because they use both direct and diffuse UV-light [9,10]. The present configuration



Scheme of the CPC photoreactor at PSA

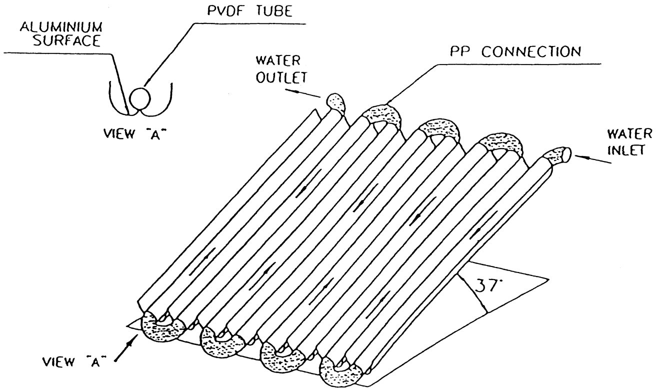


Fig. 1. Photograph and schematic of the CPC photoreactor at PSA, Spain.

of CPC's solar reactor recently settled at Plataforma Solar de Almeria (PSA), Spain, consists of six modules connected in series. Their total reflective surface is 8.9 m^2. Each CPC module purchased from Industrial Solar Technology Corporation, Denver, is 1.22 m wide and 1.22 m long (Fig. 1). Each module consists of eight parallel CPC reflectors (152 mm wide) with UV-transparent tubular receivers (i.d. 48 mm), made of fluoropolymer because this material is chemically inert and has excellent UV stability and transmissivity. Two modules are coupled as a collector which is mounted on a fixed platform inclined at 37° corresponding to the latitude of PSA in Almeria. This provides optimized performance for a fixed solar system. The three sun-light collectors consisting of two CPC modules in series were mounted in series (Fig. 1).

At the beginning of all the experiments, the sun-light collectors were put in the dark by covering them with a canvas sheet, whereas the chemical compound to be destroyed was added to the tank and progressively dissolved by vigorous stirring induced by a high circulation flow-rate (3.5 m^3/h). This was continued until reaching a constant concentration throughout the system. Titania (Degussa P-25) was subsequently added with a total concentration of 0.200 g/l, corresponding to the optimized threshold obtained for CPC reactors [10]. The suspension was then agitated in the dark for 1 h to allow adsorption of the pollutant. The canvas sheets covering the collectors were removed at time $t=0$. Samples were collected at regular intervals. Kinetics were followed as a function of the residence time. According to the procedure described above, the actual time of reaction corresponds to the residence time t_R. At any flow rate, t_R is proportional to the actual time and to the ratio of the illuminated volume to the total volume.

In such conditions, the CPC sun reactor can be considered as a perfectly agitated slurry batch reactor. The high flow rate (3.5 m^3/h) provides (i) a good homogeneous suspension of TiO_2, (ii) a satisfactory homogeneity of the concentration throughout all the volume, (iii) a good saturation of water in oxygen from the air estimated to be 6–7 mg O_2/l in summer time (it can increase to 9 mg O_2/l in winter time) and (iv) an oxygen content high enough to provide an optimum conversion of the reactant in one pass in the CPC photoreactor.

3. Results and discussion

3.1. Photocatalytic degradation of malic acid in the laboratory batch photoreactor

3.1.1. Total mineralization

Under UV-light ($\lambda \geq 290$ nm), without TiO_2, the disappearance of malic acid was negligible. In contact with titania in the dark, ca. 10% of malic acid was adsorbed at equilibrium, which corresponded to a coverage of about 1.2 molecule/nm^2. By irradiating the suspension, malic acid totally disappeared within 90 min with first order kinetics. This corresponded to a Langmuir–Hinshelwood mechanism with the coverage being proportional to [MA] in this concentration range. The total mineralization was followed by measuring (i) the total organic carbon [TOC] in the filtered solution and (ii) the quantity of CO_2 evolved. The TOC became nil at $t=$ ca. 6 h and the evolved CO_2 reached a plateau corresponding to 98% of the expected value for a total mineralization at $t=$ ca. 10 h.

3.1.2. Intermediate products

The time difference between MA disappearance and total evolution of CO_2 reflected the existence of several intermediates. The main intermediate product could only be definitively identified by LC–MS and corresponded to 3-oxopropanoic acid ($HCO\text{-}CH_2\text{-}COOH$). All the 15 intermediate products mentioned were detected using GC,HPLC, GC/MS, capillary electrophhoresis as indicated in in Fig. 2. Most of them were detected as traces (<1%) after preconcentration and a quantitative estimation of their transient yields as a function of MA conversion was not accurate enough for an overall kinetic study. However, the 15 intermediate products were logically inserted into four parallel degradation pathways described in Fig. 2. This presentation is based (i) on the logical progressive degradation of MA (C_4) to formic acid and CO_2 and (ii) on the proper degradation of the main initial intermediates in the first two lines, except that of malonaldehydic acid which is not commercial.

The oxidative photodegradation may involve two oxidizing agents: photoproduced holes h^+ and OH° radicals, known as strong oxidizing agents, generated as follows:

$$(TiO_2) + h\nu \rightarrow e^- + h^+ \tag{1}$$

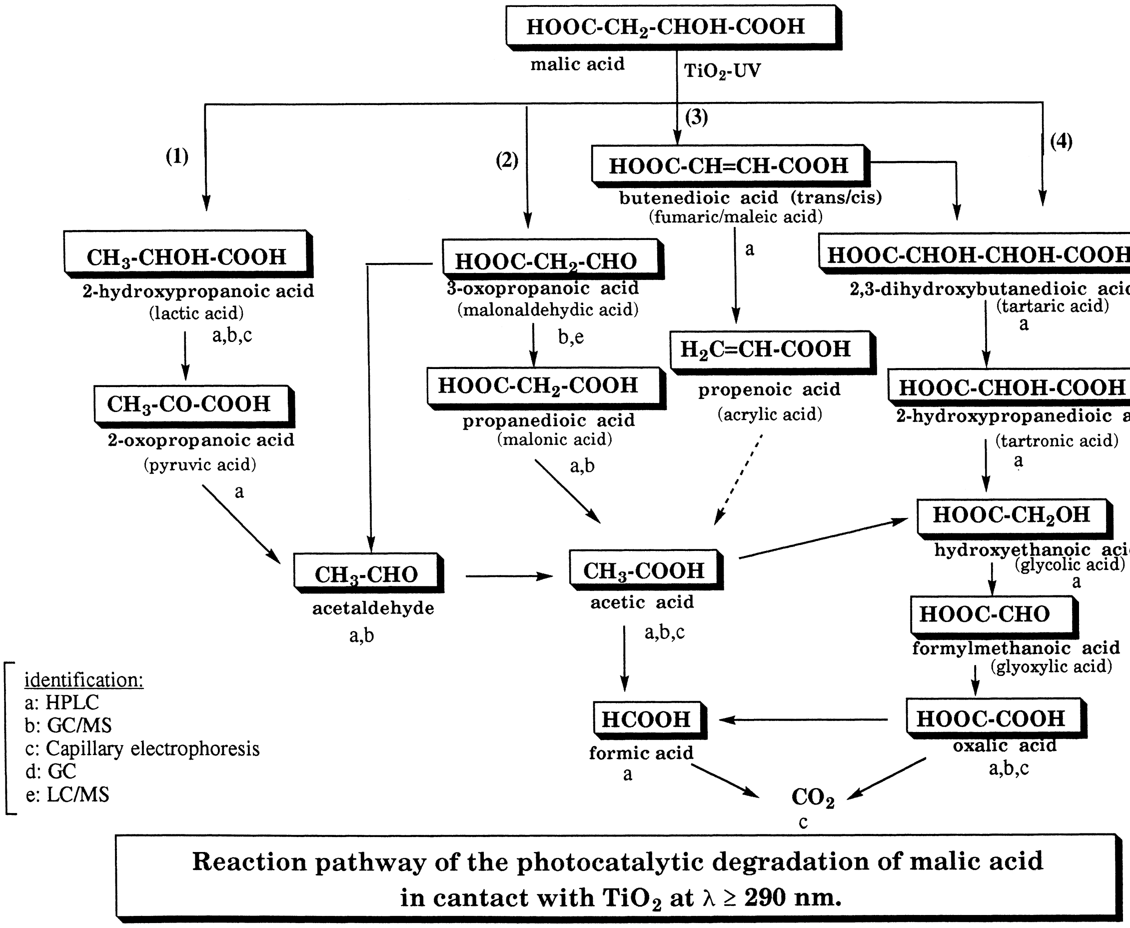


Fig. 2. Photocatalytic degradation pathway of malic acid in contact with titania.

$$(H_2O \leftrightarrow H^+ + OH^-) + h^+ \rightarrow H^+ + OH^\circ \qquad (2)$$

Holes can directly oxidize MA according to a ‘photo-Kolbe’ reaction:

$$RCOO^- + h^+ \rightarrow R^\circ + CO_2 \qquad (3)$$

and OH° radicals are prone to abstract a H atom:

$$RCOO^- + OH^\circ \rightarrow R'^\circ - COO^- + H_2O \qquad (4)$$

The radicals thus formed will add O_2 and finally give rise to the products. However, the photo-Kolbe process (Eq. (3)) seems to be predominant, with decarboxylation in the α-position from the OH group, since Route 2 in Fig. 2 is the main one with the preferential formation of 3-oxopropanoic acid [11]. This indicates that the preferential mode of adsorption of malic acid is related to the binding of the carboxylic group in the α-position from the OH group to the amphoteric hydroxyls at the surface of titania. The other carboxylic group of MA can also be linked to the surface since lactic acid is also formed via the photo-Kolbe process (Fig. 2).

The competitive oxidation route via OH° radicals also intervenes, since two C_4 acids are evolved in solution: fumaric/maleic and tartaric acids (Fig. 2). The two actions of OH° radicals consist in H atom abstraction or in OH addition. These processes are described in Fig. 3.

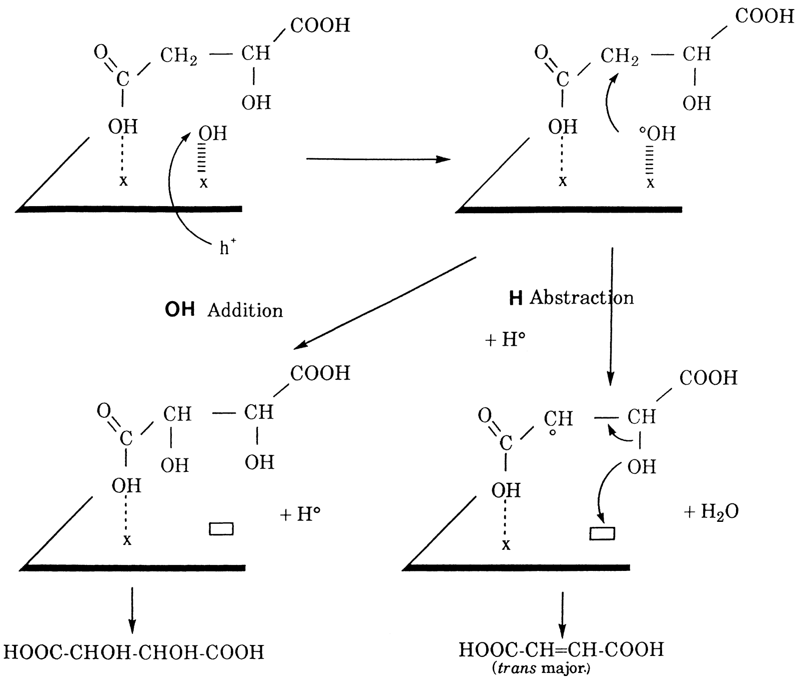


Fig. 3. Reaction routes of OH° radicals with adsorbed malic acid; H abstraction and OH addition.

3.2. *Photocatalytic degradation of malic acid in the CPC solar reactor at PSA*

Malic acid was degraded in the solar CPC photoreactor using first a rather high concentration (3.73 mmol/l; 500 ppm) to have enough sensitivity for detection and quantification the various intermediates. Malic acid totally disappeared after a residence time of 120 min corresponding to a real time of 274 min (Fig. 4 A). The apparent zero-order corresponds to a Langmuir–Hinshelwood mechanism with saturation of adsorption, in line with the very low concentration of titania in suspension and with the relatively high concentration in MA. For an initial concentration of malic acid, that is five-times lower, the order was found equal to one in agreement with laboratory results.

Total degradation was measured by following the TOC. The TOC disappeared within a longer time than that required for the total disappearance of MA (Fig. 4B). For a high initial concentration equal to 3.73×10^{-3} (500 ppm), solar degradation was interrupted at the night and had to wait for the next day for total completion. However, degradation was achieved in a much shorter time than in laboratory experiments. In addition, the intermediate products, although identical, were found in much lower amounts in solution. Both phenomena were ascribed to the design of the solar photoreactor, more adapted to obtaining a final product as shown by Levenspiel [12].

3.3. *Photoactivity of supported titania samples*

3.3.1. *Samples supported on glass and quartz (fused silica)*

The samples were prepared by the well established method of dip coating [13]. The supports were then immersed in a solution of titanium tetraisopropoxide ($Ti(OCH(CH_3)_2)_4$ from Merck) in dry i-PrOH with a concentration of 13 ml of alcoholate in 100 ml of solution. The sheets were removed from solution and then dried in air in a few seconds when a white turbidity appeared in the supports due to the hydrolysis of the alcoholate adsorbed layer by the humidity of ambient air. This procedure was repeated to obtain samples with increasing thickness of titania. Finally, samples

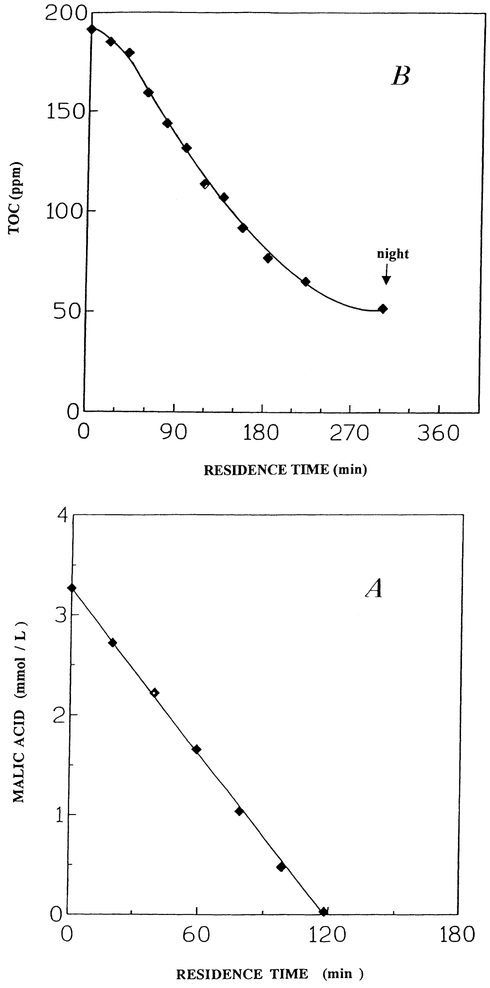


Fig. 4. (A) Apparent zero-order reaction of malic acid disappearance for $C_0 = 500$ ppm in the CPC reactor at PSA (B): simultaneous total organic carbon (TOC) disappearance as a function of the residence time.

were calcined at 673 K during 2 h to fully decompose the alcoholate and to eliminate carbon-containing impurities.

The texture and morphology of the layers were observed by SEM. The layers appeared with a granular morphology that could be interesting for photocatalytic activity. With the SEM, we have also measured by EDX the TiKα fluorescence signal for all the samples and for a pressed pellet of TiO_2 Degussa P-25 used as a reference. From these measurements, and according to the method of Waldo et al., we have evaluated the thickness of the TiO_2 layer (0.2 mm).

The XRD pattern obtained in the low angle incident mode to increase the sensitivity to the surface indicated in all cases, the presence of the anatase phase, which is the most active allotropic form of TiO_2 in photocatalysis. The samples prepared on quartz exhibited a better crystallization than those prepared on glass for the same amount of deposited TiO_2. Finally, the UV-vis absorption spectra of the materials indicated the characteristic band gap of titania as described in Fig. 5.

3.3.2. Samples deposited on stainless steel

The samples were prepared by the method of electrophoretic deposition that has been developed for the preparation of ceramic coatings [13]. The stainless steel foil was placed in a suspension of TiO_2 Degussa P-25 (mainly anatase) in acetone (1 g in 100 ml), homogenized by sonication and stirred magnetically during the time of the deposition. A counter-electrode of platinum was placed in the suspension just in front of the stainless steel substrate with the same size and shape. A potential was applied between both electrodes, the stainless steel foil acting as the cathode. Two samples were prepared by applying 125 and 200 V during 4 and 2 min, respectively. Because of their natural surface charge, the titania particles move to the stainless steel foil forming a layer. Finally, to improve the adhesion, the respective samples were heated in a N_2 flow at 973 K during 48 h.

3.3.3. Photocatalytic activity of supported-titania samples

The kinetic curves representing the photocatalytic degradation of malic acid in contact with the different supported titania samples are given in Fig. 6. The total disappearance of malic acid occurred within 1 h for TiO_2/quartz, whereas it required 3 h for TiO_2/glass and TiO_2/steel. For comparison, the suspension of TiO_2 Degussa P-25 (5 mg) decomposed malic acid within 30 min. The direct photolysis (without catalyst) indicated a disappearance with a much slower kinetics. If malic acid is progressively unstable under UV-light, the presence of a solid catalyst acts as an inner filter and strongly decreases the contribution of homogeneous photolysis.

The comparison of the various systems gives the following decreasing order of photoactivity:

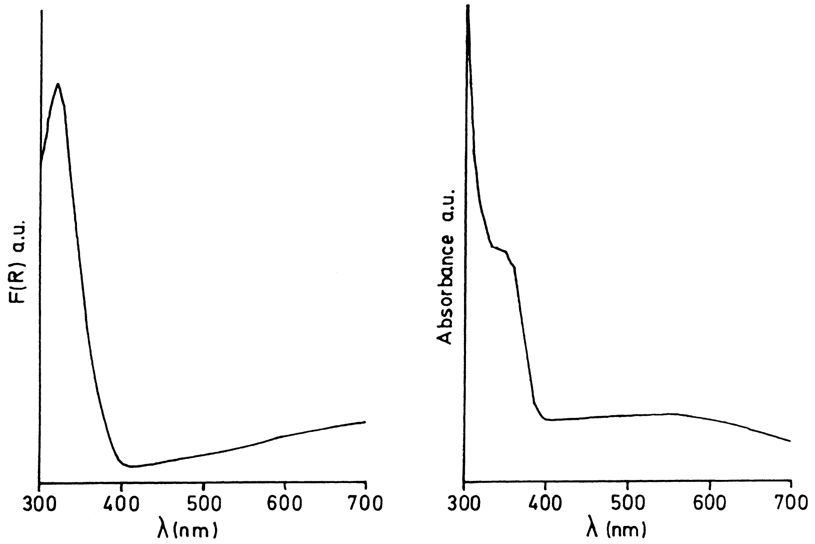


Fig. 5. UV-visible absorption spectra of anatase deposited on steel (left) and on quartz (right).

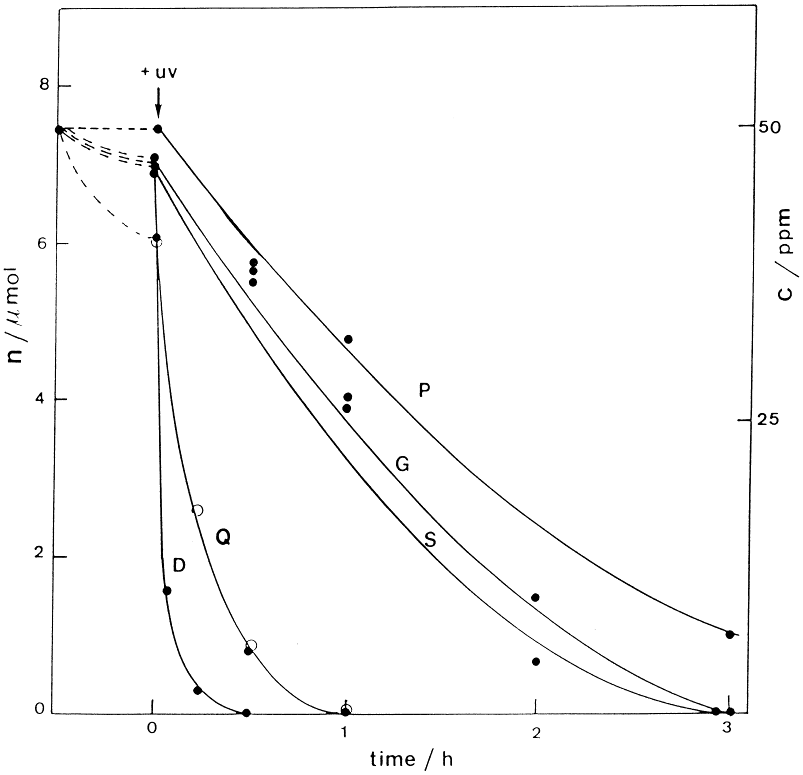


Fig. 6. Apparent first order reaction of MA disappearance (number of micromols of MA as a function of irradiation time) in contact with titania deposited on glass (G); stainless-steel (S) and quartz (fused silica) (Q). Curves (P) and (D) refer to photochemistry (without catalyst) and to suspended titania Degussa (5 mg in 20 ml), respectively. The open circles refer to a duplicated experiment (see text).

Table 1
Rate constants and specific rate constants of malic acid photocatalytic degradation in contact with titania deposited on various supports

Catalyst	Rate constant (apparent first-order, per hour)	Relative activity	Total mass of TiO_2 (mg)	Specific rate constant (per hour/gram)
TiO_2/glass	0.52	1	1.1	$4.73 \times 10^{+2}$
TiO_2/steel	0.58	1.1	4.5	$1.29 \times 10^{+2}$
TiO_2/quartz	4.12	7.9	1.1	$3.745 \times 10^{+3}$
TiO_2-Degussa P-25	12.17	23.4	5	$2.43 \times 10^{+3}$

$$\text{Degussa P25} > TiO_2/\text{quartz} \gg TiO_2/\text{steel} \geq TiO_2/\text{glass} \gg \text{photolysis}$$

A more quantitative comparison can be done by comparing the apparent rate constants. The linear transforms $\ln C_o/C = k_a t$ of the curves in Fig. 6 give the following relative activity pattern, unity being given to the less active sample:

$$7.9\,(TiO_2/\text{quartz}) \gg 1.1\,(TiO_2/\text{steel}) \geq 1(TiO_2/\text{glass})$$

A more quantitative comparison can be made by expressing the rate constant per mass unit of titania. This is given in Table 1, which additionally includes the loadings of titania on the different supports. If the pseudo- first-order reaction rate constants are expressed per mass unit of deposited titania (specific rate constants), the order is slightly different (Table 1, column 4). However, a semiquantitative comparison can only be done with the titania-deposited samples, which have comparable geometries, and hence a comparable incident illumination. In these conditions, quartz appears one order of magnitude more efficient as a support than glass and stainless steel.

The most active of the catalyst (TiO_2/quartz) was washed twice with doubly distilled water, dried in air and then re-used in the same photocatalytic conditions. The reproducibility of the kinetic results was excellent (see curve Q (open circles) in Fig. 6). This clearly indicates that this solid had not been deactivated by a previous test and could be re-utilized by simple washing.

The photocatalytic activity has been expressed by the rate of disappearance of malic acid. Actually, disappearance does not mean total mineralization. However, it has been previously shown by quantitative analysis that malic acid was totally degraded in contact with an illuminated suspension of titania according to the reaction:

$$\text{COOH-CHOH-CH}_2\text{-COOH} + 3O_2 \rightarrow 4CO_2 + 3H_2O$$

This required a reaction time substantially longer than for disappearance. This is due to the progressive carbon-chain degradation. For all the catalysts tested, the intermediates were found in trace amounts, so that it was not possible to make accurate quantitative kinetic studies. However, they were identical to those found for pure P-25 Degussa titania. In particular, 3-oxopropanoic acid was also found as the major intermediate product released. This clearly indicates that the deposition of titania on a rigid support does not change the reaction mechanism nor the reaction pathway found with slurry suspensions of catalysts (Fig. 2).

3.3.4. *Possible origin of the influence of the support upon photoactivity*

Under identical working conditions, quartz appears as a better support than glass and stainless steel. Since these three supports are chemically and photocatalytically inert, the difference in activity for the deposited titania specimens has to be related to TiO_2-support interactions established during the preparation. Heat treatments are necessary for good cohesion of the titania layer and good adhesion onto the support. During these periods of heat treatments, the support at the interface does not remain inactive. This is particularly true for TiO_2/glass samples which are treated up to a point close to the melting point of glass. This induces the diffusion of ions present in glass, clearly evidenced by XPS analysis, which detected the presence of sodium and probably silicon ions in the deposited layer (Fig. 7). Similarly, the heating of stainless steel

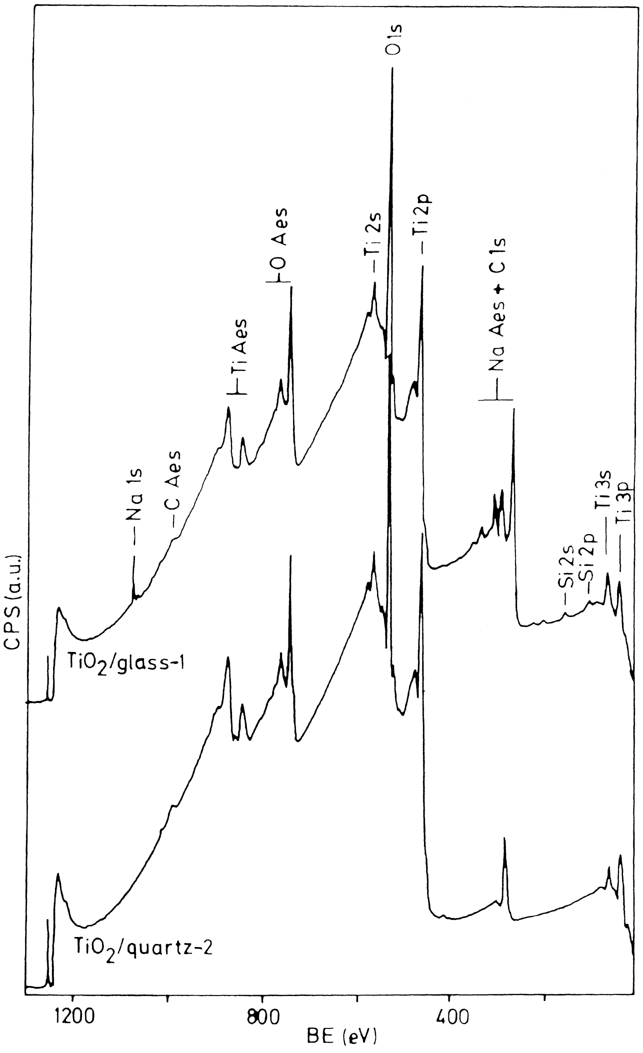


Fig. 7. XPS analyses of glass- and quartz-deposited titania.

at 973 K has probably produced the diffusion of some ions (mainly Fe^{3+} and Cr^{3+}) from the support into titania, as demonstrated by EDX analysis (Fig. 8). The analysis depth for EDX being smaller than the titania layer thickness, the simultaneous presence of certain amounts of Fe and Cr with deposited titania clearly indicates that these ions are dissolved in the oxide. In addition, Fe^{3+} and Cr^{3+} are well known as doping agents for titania, acting as recombination centers [8]. This detrimental doping effect is supported by two facts. First, quartz or fused silica, is quite stable and much more inert at high temperature than the other two supports. Consequently, there is no transfer of heterocations at the interface during preparation as indicated by XPS analysis. There results a higher degree of purity for supported titania, which is a pre-requisite for optimum photocatalytic activity. Secondly, examination of adsorption in the dark indicated that the coverage is about the same for all samples. Initiating the UV-illumination under identical conditions and with similar coverages, one would have expected closer rates. The large differences in photocatalytic activities could, therefore, be mainly ascribed to the doping effect. As a consequence of this work, the deposition of

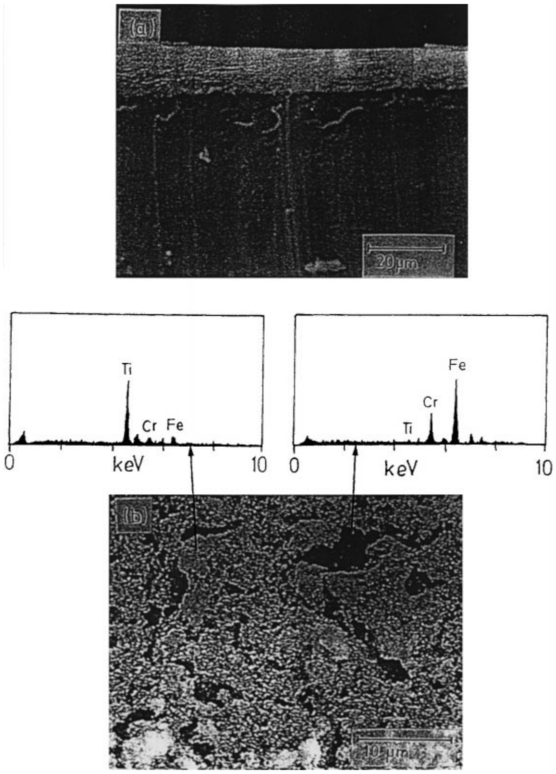


Fig. 8. STEM-EDX analysis of titania deposited on stainless steel (a) cross section view (b) top view.

very photoactive titania on glass for the elaboration of self-cleaning glasses requires a previous deposit of a very pure silica sublayer acting as a barrier for the migration of detrimental sodium ions [14].

4. Conclusions

Malic acid which is representative of molecules present in the biomass and also of oxidized carboxylic intermediates could be totally mineralized by photocatalysis. Identical kinetic results have been obtained either in a laboratory microphotoreactor working with artificial light or in the solar pilot plant at PSA in Almeria (Spain). An efficient deposited titania catalyst requires the absence of contamination by foreign cations originating from the support during the preparative calcination (e.g., Cr^{3+} and Fe^{3+} from stainless steel and Na^{+} and Si^{4+} from glass) since they act as doping agents i.e., as electron-hole recombination centers.

Water pollutant removal appears as the most promising potential application of photocatalysis since (i) many organic pollutants are totally mineralized and (ii) there are interesting advantages: chemical stability of TiO_2 in aqueous media; low cost of the catalyst ($\sim$10 FF/kg or 1.54 EURO/kg); cheap chemicals in use; no additives required (only oxygen from the air); system applicable at low concentrations. As a consequence, solar photocatalysis is a cheap way to purify and recycle (drinking) water in sunny dry places.

References

[1] Photocatalysis and Environment: Trends and Applications, in: M. Schiavello (Ed.), NATO ASI Series C, vol. 238, Kluwer Academic, London, 1987.
[2] Photocatalytic Purification and Treatment of Water and Air, in: D.F. Ollis, H. Al-Ekabi (Eds.), Elsevier, Amsterdam, 1993.
[3] J.M. Herrmann, C. Guillard, P. Pichat, Catal. Today 17 (1993) 7.
[4] O. Legrini, E. Oliveros, A. Braun, Chem. Rev. 93 (1993) 671.
[5] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: G.R. Zepp, D.G. Crosby (Eds.), Aquatic and Surface Photochemistry, Lewis, Boca Raton, FL, 1994, p. 261.
[6] D.M. Blake, in: Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air, NREL/TP-430-22197, National Renewable Energy Laboratory, Golden Co., 1997.
[7] W. Mu, J.M. Herrmann, P. Pichat, Catal. Lett. 3 (1989) 73 .
[8] J.M. Herrmann, J. Didier, P. Pichat, Chem. Phys. Lett. 108 (1984) 618.
[9] S. Malato, Ph.D. Dissertation, Almeria University, Spain, 1997
[10] J.M. Herrmann, J. Disdier, P. Pichat, S. Malato, J. Blanco, Appli. Catal. B: Environmental 17 (1998) 15.
[11] H. Tahiri, Ph.D. Dissertation, Lyon I University, France, 1998
[12] O. Levenspiel, in: Chemical Reaction Engineering, Wiley, New York, 1972, p. 175
[13] A. Fernandez, G. Lassaletta, V.M. Gimenez, A. Justo, A.R. Gonzalez-Elipe, J.M. Herrmann, H. Tahiri, Y. Aitichou, Appl. Catal. B: Environmental 7 (1995) 49.
[14] Y. Paz, A. Heller, J. Mat. Res. 12 (1997) 2759.