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Selective oxidation of phenol and benzoic acid in water via home-prepared TiO₂ photocatalysts: Distribution of hydroxylation products

Marianna Bellardita^{a,*}, Vincenzo Augugliaro^a, Vittorio Loddo^a, Bartolomeo Megna^b, Giovanni Palmisano^a, Leonardo Palmisano^{a,**}, Maria Angela Puma^a

^a "Schiavello-Grillone" Photocatalysis Group, Dipartimento di Ingegneria Elettrica, Elettronica e delle Telecomunicazioni, di tecnologie Chimiche, Automatica e modelli Matematici (DIEETCAM), University of Palermo, Viale delle Scienze, 90128 Palermo, Italy

^a Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, University of Palermo, Viale delle Scienze, 90128 Palermo, Italy

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ABSTRACT

The hydroxylation of phenol (a substrate containing an electron donor group) and of benzoic acid (a substrate containing an electron withdrawing group) has been carried out by the photocatalytic method in aqueous suspensions containing commercial or home prepared TiO₂ samples. The aim of the work was to study the distribution of hydroxylation products when different photocatalysts were used and to correlate the selectivity to some physico-chemical features of the powders. The samples were characterized by X-ray diffraction, thermogravimetry, determination of crystalline phase percentage, specific surface area and zero charge point. The photoreactivity results indicate that the products of the primary oxidation of phenol are the *ortho*- and *para*-mono-hydroxy derivatives while those of benzoic acid are all the mono-hydroxy derivatives independently of the catalyst. The selectivity degrees: the highest selectivity values were obtained by using the commercial samples that resulted the least hydroxylated and the most crystalline ones. A kinetic model, taking into account the mineralization and the partial oxidation reaction routes, is proposed by using the Langmuir–Hinshelwood model.

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1. Introduction

Photocatalysis by TiO₂ has been mainly applied to degrade organic and inorganic pollutants both in vapor and in liquid phases [1-3]. Its main advantage consists not only in the mild experimental conditions under which the process is carried out, but also in the possibility to abate refractory, very toxic and non biodegradable molecules. TiO₂ has been elected as the most reliable photocatalyst due to its low cost, high activity and (photo)stability under irradiation [2].

Investigation on photocatalytic oxidation of aromatic compounds has been focused on the interactions of these species with the catalyst surface, the mechanism of photoreaction and the reaction kinetics [4–19]. The affinity of the aromatic substrates to the TiO_2 surface determines the occurrence of adsorption and photoadsorption in a more or lesser extent. Several papers have been published dealing with the photocatalytic degradation of benzene derivatives such as phenol [14,20–25] and benzoic acid [14,26–28,13] and the reaction mechanism in the presence of TiO₂ dispersion is also well known [4,7,20,27–32]. Only few papers deal with selectivity toward the hydroxylated species [33,34].

In a study of the photocatalytic degradation of phenol and benzoic acid, Vione et al. [14] report indirect evidence of considerably different interactions of these two species with the TiO_2 surface. The principal oxidation route of phenol degradation involve hydroxyl radicals adsorbed on TiO_2 surface, whereas for benzoic acid the main process is the adsorption of substrate on the surface of the catalyst and the degradation of the substrate takes place through electron transfer process involving surface species. This finding suggests that the interaction of benzoic acid with the TiO_2 surface is stronger than that of phenol as the former behaves as a bidentate species. When the surface of the TiO_2 was modified by replacing the hydroxyl groups with fluoride ions, the adsorption phenomena resulted different and the degradation process occurred in the solution bulk.

By considering the intermediates produced during the first oxidation steps, mechanistic studies suggest that hydroxyl radicals are the species involved in oxidation processes carried

^{*} Corresponding author. Tel.: +39 091 23863722; fax: +39 091 23863722.

^{**} Corresponding author. Tel.: +39 091 23863746; fax: +39 091 23863722. *E-mail addresses:* marianna.bellardita@unipa.it (M. Bellardita), leonardo.palmisano@unipa.it (L. Palmisano).

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out in the presence of O_2 [4–8]. In particular, phenol oxidation was studied in the presence of anatase TiO₂ and hydroquinone, catechol and 1,2,4-trihydroxybenzene were found as the main intermediates [4,5,7]. In order to explain the formation of monohydroxy derivatives substituted only in *ortho* (catechol) and *para* (hydroquinone) positions, Peiró et al. [7] proposed that phenol molecule reacts with a hydroxyl radical, giving rise to an adduct that transforms into a phenoxy radical possessing resonant structures only when the attack occurs in *ortho*- and *para*-positions. These resonance structures account for the achievement of the two different mono-hydroxy derivatives and other more complex intermediates deriving from reaction between two phenoxy radicals. Hydroquinone, formed by either phenol or 4-chlorophenol hydroxylation, participates to a keto-enol equilibrium by forming p-benzoquinone, as previously described [8].

Generally many mechanistic studies have been performed by investigating the degradation of only one aromatic compound while only a few investigations have been aimed to determine whether the nature of the substituent group in the aromatic ring influences the production of the hydroxylated intermediates. A study on selectivity of photocatalytic hydroxylation of aromatic species indicates that the electronic nature of the substituent groups is linked to the formation of one or more monohydroxylated species [35]. The study was carried out by using only commercial anatase TiO₂ sample and the general rule that the meta-substituted hydroxy-species is never formed in the presence of an electron donor group (EDG) was found. This feature has been also confirmed by in a lot of research papers where many types of TiO₂ photocatalysts were used while no papers have been published where meta-substituted hydroxy-species were reported to be formed in the presence of an EDG.

It is indeed well known that the oxidation of aromatic species occurs through two main pathways, i.e. direct mineralization (through a series of adsorbed intermediates which do not desorb into the bulk of solution) and partial oxidation giving rise to different aromatic, aliphatic and ionic (both organic and inorganic) species [36,37]. In this paper TiO₂ photocatalysts with different bulk and superficial features have been used for performing the oxidation of two aromatic compounds, i.e. phenol (PH) bearing an EDG and benzoic acid (BA) bearing an electron withdrawing group (EWG). The investigation has been aimed to find a correlation between the photocatalytic selectivity toward the hydroxylated compounds and some physico-chemical property of the different powders. Different kinds of home-prepared anatase, rutile and brookite TiO₂ samples have been used along with Merck and Degussa P25 commercial samples and a SiO₂ supported sample for the sake of comparison. A kinetic study by using the Langmuir-Hinshelwood model has been also performed and the model parameters have been determined.

2. Experimental

2.1. Samples preparation starting from TiCl₄

Titanium tetrachloride (Fluka 98%) was used as the precursor without any further purification. It was slowly added to distilled water (molar ratio Ti/H_2O 1:60; volume ratio 1:10) at room temperature. After ca. 12 h of continuous stirring at room temperature, a clear solution was obtained.

HP0.5 [38]: The clear solution was boiled for 0.5 h under agitation. This treatment produced a milky white TiO_2 dispersion; the solid was dried in a rotary evaporator at 323 K. The code used for this sample is HP0.5.

HP298-673 [39]: 360 mL of 1 M NaOH aqueous solution were added to clear TiCl₄ solution to induce the precipitation of TiO₂. The

resulting solid was filtered and washed until the washing water had a neutral pH. Then it was calcined at 673 K for 3 h and the sample is named HP298-673.

 $1_{-5BS373}$ [40]: 10 mL of TiCl₄ were slowly added to 50 mL of distilled water at room temperature. After ca. 15 min of continuous stirring, a clear transparent solution was obtained. This was heated in a closed bottle and aged at 373 K in an oven for 48 h. The bottle was allowed to cool to room temperature, and the resultant solid was recovered using a rotary evaporator at 323 K. The sample is identified with the notation 1_5BS373.

Brookite [41]: 15 mL of TiCl₄ were added dropwise to a solution containing 630 mL of demineralized water and 240 mL of concentrated hydrochloric acid. The solution obtained after continuous stirring was heated in a closed bottle and aged at 373 K in an oven for 48 h. The resultant precipitate contained a mixture of brookite and rutile. Pure brookite nanoparticles were separated by peptization by removing many times the supernatant and adding water to restore the initial solution volume. After few washes, a dispersion of brookite particles was obtained whilst the rutile phase remained as a precipitate. The dispersions containing the brookite particles were collected and dried in a rotary evaporator at 673 K.

S5 [42]: A commercial SiO₂ (Cabot) was used as support. 10 g of silica were added to 110 mL of the TiCl₄ solution and the obtained suspension was boiled for 2 h. The final suspension was dried in a rotary evaporator. The code used for this sample is S5.

2.2. Preparation of the home prepared samples starting from TiOSO₄

Titanium (IV) oxysulfate (Sigma–Aldrich) was used as the precursor. 20 g of $TiOSO_4$ were added to 90 mL of distilled water. After ca. 2 h of continuous stirring at room temperature, a clear solution was obtained. This solution was heated in a closed bottle and aged at 373 K in an oven for 48 h. The resultant precipitate was washed by withdrawing many times the supernatant liquid and by adding pure water to restore the initial solution volume and to eliminate most of the sulfate ions. The resultant solid was recovered using a rotary evaporator at 323 K and calcined at 873 K for 10 h. The code used for this sample is HP873S.

2.3. Catalysts characterization and reactivity set up

X-ray diffractometry (XRD) patterns of the powders were recorded by a Philips diffractometer (operating at a voltage of 40 kV and a current of 30 mA) using the Cu K α radiation and a 2 θ scan rate of 1.28° min⁻¹. The crystalline sizes of the samples were determined by using the Scherrer equation [43]. The specific surface areas (SSA) of the powders were determined in a FlowSorb 2300 apparatus (Micromeritics) by using the single-point BET method. The samples were degassed for 0.5 h at 523 K prior to the measurement by using a N₂/He mixture 30/70 (v/v).

The crystallinity of all the samples was evaluated following the procedure reported by Jensen et al. [44]. XRD diffractograms were recorded for mixtures of TiO_2 and CaF_2 (50%, w/w) and the areas of the 100% peaks of anatase (101), rutile (110) and CaF_2 (220) were determined. By comparing the ratio between the areas of (101) and (220) peaks or of (110) and (220) peaks to the ratios obtained by using the pure phases (1.25 for anatase and 0.90 for rutile), the amount of crystalline and amorphous phases present in the samples was determined. No reference values are reported for brookite TiO_2 crystalline phase.

The zero charge point (ZCP) of the various catalyst samples was calculated by using the method of mass titration [45–47] which involves finding the limiting pH value of an oxide/water slurry as the oxide mass content is increased. Varying amounts of powders were added to water and the resulting pH values were measured

B

R

Intensity (a. u.)

R

after 24 h of equilibration. For Degussa P25 sample the determination of the ZCP value was repeated three times by preventively washing the sample under UV-irradiation in order to clean the surface from all impurities.

Simultaneous thermal gravimetric (TG/DTG) and differential thermal analysis (DTA) measurements were performed on catalysts by using a PerkinElmer STA 6000 system, in the 30–750 °C range in a nitrogen flux of ca. 20 mL min⁻¹. The temperature program consists of three steps: temperature scan from 30 to 120 °C at 10 °C min⁻¹, 15 min in isothermal condition at 120 °C, temperature scan from 120 to 750 at 10 °C min⁻¹.

A Pyrex batch photoreactor of cylindrical shape, containing 0.5 L of aqueous suspension, was used for performing the reactivity experiments. The photoreactor was provided with ports in its upper section for the inlet and outlet of gases and for sampling. A magnetic stirrer guaranteed a satisfactory suspension of the photocatalyst and the uniformity of the reacting mixture. A 125 W medium pressure Hg lamp (Helios Italquartz) was axially immersed within the photoreactor and it was cooled by water circulating through a Pyrex thimble; the temperature of the suspension had an average value of 10 mW cm⁻²; it was measured by using a radiometer UVX Digital, at $\lambda = 360$ nm.

Different amounts of the catalysts (ranging from 0.2 to $0.8 \, g \, L^{-1}$) were used for the reactivity runs; they were determined in order to get the same photon flux absorbed by the suspension for each catalyst. That amount was determined by slowly adding the powder to the suspension and by measuring the photon flux transmitted by the suspension; when the transmitted radiation was less than 10% with respect to the incident one, catalyst addition was stopped. The starting concentrations of PH and BA ranged from 0.1 to 5 mM. The initial pH of the suspensions was ca. 6 for PH and ca. 3 for BA. When necessary, pH was adjusted by adding some drops of NaOH 1 M solution. The suspensions were saturated by bubbling O₂ at atmospheric pressure for 0.5 h in the dark and throughout all the runs.

Samples for analyses were withdrawn at fixed intervals of time; the catalyst was immediately separated from the aqueous solution by filtering through 0.2 μ m Millex Millipore filters. For each sample a particular care was devoted to determine the concentrations of hydroxylation products (*ortho, meta* and *para*). The substrates and the intermediates produced during the reactions were analyzed with a HPLC Beckman Coulter (System Gold 126 Solvent Module and 168 Diode Array Detector), equipped with a Phenomenex Synergi 4 μ Hydro-RP column (250 mm long × 4.60 mm i.d.). The HPLC eluent consisted of 45% (v/v) 1 mM aqueous solution of trifluoroacetic acid and 55% (v/v) methanol. The flow rate was 0.4 mL min⁻¹ and the identification was carried out by comparison with authentical standard samples.

Total organic carbon (TOC) analyses were carried out by using a 5000A Shimadzu TOC analyzer. These analyses allowed to determine the amount of organic carbon mineralized to CO_2 in the course of the reaction.

The quantitative determination of oxalate, acetate and formate ions was performed with a Dionex DX 120 ionic chromatograph, using a Dionex Ion Pac AS14 column (250 mm long \times 4 mm i.d.). The eluent was an aqueous solution of NaHCO₃ (1 mM) and Na₂CO₃ (8 mM) at a flow rate of 1 mL min⁻¹.

3. Results and discussion

3.1. Catalysts characterization

Fig. 1 reports the X-ray diffractograms of all the samples used in this work; Table 1 summarizes the main features of the catalysts



Fig. 1. X-Ray diffractograms of the used samples: (a) Merck; (b) P25; (c) HP0.5; (d) HP298-673; (e) 1_5BS373; (f) Brookite; (g) HP873S; (h) S5.

with the references where the detailed preparation methods can be found. The various peaks corresponding to the three main phases of TiO₂ have been identified. HP0.5 and S5 are the least crystallized samples with the smallest crystallite size. Both catalysts show the presence of anatase as the main phase; they were not subjected to a strong thermal treatment, but were only warmed at 100 °C for 0.5 or 2 h. Experimental evidence of the virtual absence of anatase and rutile in brookite sample has been confirmed by Raman spectroscopy [41]. It can be noticed that the specific surface areas of the home prepared samples are higher than those of the commercial samples, whereas the crystallite sizes are smaller. The SSA of Merck is the lowest among all the samples, indicating a strong particle agglomeration.

The commercial samples showed an amorphous phase percentage of 10% (P25) and 26% (Merck). Among the home prepared samples, the highest crystallinity values were found for calcined samples HP298-673 and HP873S, indicating that the crystallinity increases by increasing the temperature of the thermal treatment. All the other samples revealed a low percentage of crystalline phase. The percentage of crystalline phase in the brookite sample was not determined because no reference values are reported in literature and it is not a trivial task to prepare a pure brookite sample with a high degree of crystallinity (hopefully near to 100%) since calcination treatments easily transform brookite into rutile.

Zero charge points of catalysts ranged from 0 to 4.5, the highest figures being those of commercial samples; it must be reported that the ZPC value of the used P25 sample resulted lower than that reported in the literature [47]. The difference found can be probably ascribed to differences between P25 batches that are also characterized by different ratios between anatase and rutile.

According to literature [48] the weight losses of hydroxylated TiO_2 samples in the 30–120 °C range are due to the physically adsorbed water and they mainly depend on residual humidity after the preparation of the powders. The losses in the 120–300 °C and

(h)

(g)

(f)

(e)

(d)

(c)

(b)

Photocatalyst	Phases	$SSA^{a} (m^{2} g^{-1})$	Crystallinity ^b (%)	Crystallite size (nm)	$T_{\max,p}^{c}(K)$	ZCP ^d	Reference ^e
Merck	А	10.0	74	60.0 (A)	-	4.5	-
P25	A, R	50.0	72 (A) 18 (R)	25.0 (A) 33.0 (R)	-	4.0	-
HP0.5	A, R	235	6.8 (A)–(R)	4.60 (A) 2.10 (R)	373	0.30	[38]
HP298-673	Α	35.0	26	8.80	673	3.7	[39]
1_5BS373	R	87.0	12	3.50	373	0.45	[40]
Brookite	В	82.0	_	6.60	373	0.70	[41]
S5	A, R, S	177	6 (A)–(R)	12.7 (A) 2.80 (R)	373	0	[42]
HP873S	Α	44.0	40	23.6	873	1.5	-

Some morphological, structural and surface features of the used catalysts.

A: anatase; R: rutile; B: brookite; S: silica.

^a BET specific surface area.

^b Percentage of crystallinity

^c Highest temperature to which the photocatalysts were heated during their preparation.

^d Zero charge point.

^e References reporting details of the preparation method.

300-600 °C ranges can be related to weakly bonded OH groups and strongly bonded OH groups, respectively. In this work the thermal analysis of P25 sample has been taken as reference for the other catalysts. The P25 graph, reported in Fig. 2(a), shows that two clear steps in weight loss are present in relation to the different OH groups: the first one at ca. 300 °C and the second one at ca. 600 °C. Table 2 reports the OH groups weight losses together with the humidity loss for all the catalysts; the values of global losses of OH groups are also reported. It can be seen that the two commercial samples are the least hydroxylated ones with values ranging between 0.1 and 0.78% (w/w), whereas the home-prepared ones are the most hydroxylated ones with the highest value equal to 10.76% (w/w) for HP0.5. It can be noticed that S5 sample is characterized



Fig. 2. Weight percentage as a function of temperature for samples (a) P25 and (b) HP05.

by a high amount of humidity, probably due to the high porosity of silica used as the support. Home-prepared samples calcined at high temperature have a low OH content, which decreases by increasing the calcination temperature and HP873S shows values close to those found for P25.

3.2. Photoreactivity

Before performing the photocatalytic runs, the extent of adsorption of the substrate was measured after 0.5 h mixing, keeping the reactor under dark conditions. The differences between the initial concentration value (0.5 mM for both substrates) and that measured after adsorption were negligible in the presence of commercial TiO₂ samples, whereas in the presence of HP873S and HP298-673 samples, adsorption was negligible only for PH. Conversely, adsorption of both PH and BA in the presence of homeprepared samples was significant, ranging from 2% to 21%. The highest values were recorded with BA in the presence of HP0.5 (12%), 1_5BS373 (19%) and HP873S (21%). These data indicate that the adsorption is neither straightforwardly related to the SSA and ZCP values nor to the hydroxyl groups content and that PH has a week affinity with the catalysts surface, although all of the above parameters can in principle influence the adsorption phenomena. It is known [35] that the additional electron density, induced in the aromatic ring by the presence of -OH substituent, is not beneficial for the adsorption of the molecule, while the presence of -COOH, by reducing the electron density of the aromatic ring and by imparting the property of a bidentate species to BA, favors the adsorption of this molecule onto the catalyst surface. In our opinion the above effects should be taken into account rather than the slight difference between the 1-octanol-water partition coefficients (K_{ow}) reported by Gumy et al. [49] for PH (1.46) and BA (1.50). Notably a higher K_{ow} value should suggest a stronger affinity of the molecule to the TiO₂ particles.

The photoreactivity runs indicated that PH and BA were oxidized in all cases and the concentrations of their oxidation products increased with irradiation time. Two parallel routes

Table 2 OH groups weight percentage (%, w/w) determined by TGA.

Sample	Humidity	OHweak	OH _{strong}	OH _{total}
Merck	0.3000	0.060	0.0400	0.1000
P25	0.7500	0.420	0.360	0.7800
HP873S	1.300	0.370	0.350	0.7200
HP298-673	3.440	0.890	0.920	1.810
S5	50.45	2.90	0.940	3.840
Brookite	4.720	2.01	2.29	4.300
1_5BS373	5.430	2.40	2.22	4.620
HP0.5	7.990	6.66	4.10	10.76

Table 1

Table 3	
Photoreactivity in the	presence of PH and BA.

Photocatalyst	<i>с</i> _{РН} (mM) ^а	$t_{X=15\%} (\min)^{\rm b}$	Min _{X=15%} (%) ^c	$Min_{t=90}$ (%) ^d	$c_{BA} (mM)^{a}$	$t_{X=15\%} (\min)^{\rm b}$	Min _{X=15%} (%) ^c	$\operatorname{Min}_{t=90}(\%)^{\mathrm{d}}$
Merck 0.8 g L^{-1}	0.10	7.40	1.80	25.0	0.10	9.20	2.00	23.5
	0.25	13.0	1.60	6.60	0.25	17.1	1.20	13.5
	0.50	22.0	Negligible	Negligible	0.50	25.3	3.20	9.00
	1.0	38.2	Negligible	1.00	1.0	64.6	1.00	1.00
	3.0	81.5	1.00	0.500				
	5.0	120	0.500	0.500	5.0	144	2.50	0.200
P25 $0.2 g L^{-1}$	0.10	5.00	6.70	92.0	0.10	4.50	8.30	100
-	0.25	7.30	6.20	82.0	0.25	5.20	4.80	83.7
	0.50	11.0	6.00	47.6	0.50	10.5	3.70	50.0
	1.0	17.6	2.10	9.60	1.0	15.0	3.30	20.6
	5.0	133	3.80	2.60	5.0	108	7.60	6.50
HP0.5 $0.4 \text{g} \text{L}^{-1}$	0.10	30.0	7.00	14.0	0.10	10.0	8.60	77.4
, i i i i i i i i i i i i i i i i i i i	0.25	57.5	5.00	13.0	0.25	12.7	6.50	44.5
	0.50	95.0	12.0	11.0	0.50	15.0	4.50	23.0
	1.0	145	10.0	7.00	1.0	70.0	9.80	14.0
	5.0	780	12.5	2.00	5.0	300	8.60	3.10
HP298-673	0.50	60.0	7.60	31.0	0.50	16.4	4.90	27.0
$0.6 \mathrm{g} \mathrm{L}^{-1}$	1.0	78.3	4.70	24.0				
$1_5BS373 \ 0.6 \ g \ L^{-1}$	0.50	65.0	8.50	19.0	0.50	9.50	5.90	55.0
Brookite 0.6 g L ⁻¹	0.50	41.7	5.00	13.0	0.50	12.8	4.60	26.0
S5 0.8 g L ⁻¹	0.50	60.0	7.80	8.30	0.50	38.0	12.2	29.0
HP873S 0.6 g L ⁻¹	0.50	15.0	4.50	26.0	0.50	10.5	4.20	37.6

^a Substrate initial concentration.

^b Time needed to reach 15% conversion.

^c Mineralization at 15% conversion.

^d Mineralization at t = 90 min.

[35] were operative from the starting of irradiation: the first one giving rise to the direct mineralization of the substrate through adsorbed intermediates that do not desorb into the bulk of solution and the second one leading to partial oxidation to aromatic and aliphatic molecular and ionic species. Times required to reach 15% conversion ($t_{X=15\%}$) along with mineralization percentages for the same conversion ($Min_{X=15\%}$) and for reaction time of 90 min ($Min_{t=90}$) are reported in Table 3.

The $t_{X=15\%}$ parameter refers to the disappearance rate of the substrate, regardless of what the produced species are; conversely the Min_{X=15\%} and Min_{t=90} ones have been calculated by considering the TOC decrease in the reacting solutions. Provided that no organic volatile compounds were formed during the reaction, TOC measurement amounts to the formed CO₂. This assumption has been supported by gas-chromatographic analyses carried out with a flame ionization (FID) detector, that showed the absence of any peaks.

The PH photodegradation rate was higher than that of BA in the presence of Merck, whereas it was lower in the presence of all the other catalysts (see the longer and the shorter times, respectively, in the $t_{X=15\%}$ column). This insight can be correlated to the poor surface hydroxylation [50] and to the low SSA of Merck.

Merck, Degussa P25 and HP873S are the most oxidizing catalysts with the shortest times needed to reach 15% conversion. Accordingly all these catalysts are well crystallized as shown by Fig. 1 and contain anatase as the main phase.

The highest degree of mineralization is observed in the presence of P25 for PH and of 1_5BS373 for BA (by taking the value of 0.5 mM for the substrates starting concentration and 90 min as reaction time). The other home prepared samples showed a mineralization power between P25 and Merck. TiO₂ Merck indeed gave rise to a low extent of mineralization both in the presence of PH and BA.

Apart from CO₂, other species found during PH oxidation were the monohydroxylated derivatives, formed by insertion of an OH group into the aromatic ring, the p-benzoquinone, the dihydroxylated species 1,2,4-trihydroxybenzene and traces of some polyaromatic species (2,2'-biphenol, 4,4'-dihydroxybiphenol) in accord to previous studies [7]. Aliphatic compounds deriving from breakage of aromatic ring (mucic, malonic and oxalic acid) were detected during the oxidation of both PH and BA in the present study.

3.3. Selectivity

Selectivity determination was aimed to analyze the regioselectivity corresponding to the formation of ortho-, meta- and para-monohydroxy derivatives upon oxidation. During phenol oxidation, hydroquinone, that is the para-monohydroxy derivative, gives rise to p-benzoquinone since it participates to a keto-enol equilibrium as previously reported [8]. Some photocatalytic runs (not reported for the sake of brevity) were carried out by using hydroquinone or p-benzoquinone as the starting substrate: in both cases the two species were found in the irradiated solutions. In the present investigation we consider the para-monohydroxy phenol derivative as the sum of hydroquinone and p-benzoquinone. Notably the latter compound was present in relevant amount in the runs carried out by using home prepared catalysts whereas only traces were detected in the presence of Merck and P25. The low quantity of p-benzoguinone detected in the presence of commercial catalysts could be explained by the high degradation rate shown by these catalysts. This hypothesis was corroborated by photocatalytic runs carried out starting from p-benzoquinone in the presence of P25 and HP0.5 samples: from the beginning of irradiation an aliquot of the substrate was degraded while the remaining one was transformed to hydroquinone and 2hydroxy-benzoquinone. The degradation rate of p-benzoquinone and hydroquinone by P25 was two times higher than that by HP0.5. Moreover other oxidation derivatives came from PH, as previously highlighted.

Table 4 shows the selectivity values at 15% conversion and the o-m-p distribution of the monohydroxylated compounds. In particular, selectivity ranged from 1.9% to 74%. Phenol oxidation did not give rise to attack of hydroxyl radical in *meta*-position. This behavior, independent of the used catalyst, has been reported for all

84	

Table 4	
Coloctivi	

Selectivity to mono-hydroxylated derivatives in the presence of PH and BA.

Photocatalyst	<i>c</i> _{PH} (mM) ^a	$S_{X=15\%}$ (%) ^b	o-m-p ^c	<i>c</i> _{BA} (mM) ^a	$S_{X=15\%}$ (%) ^b	<i>о-т-р</i> с
Merck 0.8 g L^{-1}	0.1	65	55-0-45	0.1	43	41-31-28
0	0.25	64	54-0-46	0.25	46	30-36-34
	0.5	74	56-0-44	0.5	39	37-35-28
	1	59.8	55-0-45	1	57	40-34-26
	3	72	56-0-44			
	5	74	50-0-50	5	34	35-36-28
$P25 0.2 g L^{-1}$	0.1	50	22-0-78	0.1	21	21-43-36
	0.25	48	27-0-73	0.25	24	14-47-39
	0.5	50	43-0-57	0.5	27.4	22-43-35
	1	39.7	42-0-58	1	27.5	23-45-32
	5	65	42-0-58	5	33.4	23-51-26
HP0.5 $0.4 \text{g} \text{L}^{-1}$	0.1	30	0-0-100	0.1	3.2	0-42-58
-	0.25	25	0-0-100	0.25	1.9	0-39-61
	0.5	26.8	0-0-100	0.5	2.32	0-41-59
	1	14.5	6-0-94	1	4.5	0-40-60
	5	12.7	11-0-89	5	8.9	14-33-53
HP298-673	0.5	27	0-0-100	0.5	22	17-43-40
$0.6\mathrm{g}\mathrm{L}^{-1}$	1	19.4	5-0-95			
1_5BS373 0.6 g L ⁻¹	0.5	23.2	8-0-92	0.5	3.2	12-60-38
Brookite 0.6 g L ⁻¹	0.5	25.4	6-0-94	0.5	9.1	15-40-45
S5 0.8 g L ⁻¹	0.5	35.6	2-0-98	0.5	9.8	12-42-46
HP873S $0.6 g L^{-1}$	0.5	54	3-0-97	0.5	33.3	19-44-37

^a Substrate initial concentration.

^b Selectivity at 15% conversion.

^c *o*-*m*-*p* distribution of monohydroxylated oxidation compounds at 15% conversion.

substituted benzenes bearing an electron donor group (EDG), such as PH [15,35]. In the case of electron withdrawing groups (EWGs), instead, all the three regio-isomers are obtained, as confirmed during the oxidation of BA regardless of the catalysts used.

The highest selectivity values were obtained with commercial well crystallized samples for both substrates, accordingly to the results of partial oxidation of glycerol [51]. Conversely, in the partial oxidation of aromatic para-substituted alcohols to the corresponding aldehydes [38,39] an opposite behavior was observed, with the highest selectivities obtained in the presence of home-prepared catalysts. In the last cases the highly crystalline powders degrade both the substrate and its intermediates owing to their elevated oxidant power. The substrates nature and their interaction with catalyst surface determine different adsorption degree and reaction routes and it is not possible to generalize the catalyst behavior with respect to selectivity without considering the type of photoreaction and the experimental conditions used. In particular Merck, which is less oxidant than P25 (as showed in Table 3, columns $t_{X=15\%}$), was more selective. HP873S was the most selective catalyst among the home prepared ones for both the substrates (Table 4), and it was also more selective than P25. The selectivity was quite low in the presence of the other poorly crystalline home-prepared powders. Fig. 3 reports the selectivity data as a function of the crystallinity degree: it may be noted that by increasing the crystallinity, the selectivity increases. The higher is the percentage of amorphous phase, the greater is the amount of defects and therefore the probability of entrapment of the hole-electron pairs, thus reducing the photocatalytic activity.

TGA analysis allowed to correlate the amount of total hydroxylation of catalysts (Table 2) with selectivity toward monohydroxylated derivatives. A sharp decrease in selectivity was found by increasing the total hydroxylation degree, as shown in Fig. 4. A similar correlation was found independently of the two different OH groups (weekly and strongly adsorbed), indicating that the kind of interaction between OH and TiO_2 is not essential in determining reaction selectivity, whereas the total amount is a crucial parameter. On this ground TiO₂ Merck, that is the least hydroxylated sample, and HPO.5, that is the most hydroxylated one, are the most and the least selective catalysts, respectively. This finding is corroborated by a previous study [22] showing that a higher hydroxylation degree of the catalyst leads to a lesser oxidation of PH, because of limited surface coverage and hole transfer to the organic molecule. Moreover PH oxidation produced higher amounts of *ortho*-isomer with respect to the *para*-one when Merck was used. Conversely P25 gave rise to an opposite trend. By increasing the initial PH concentration, however, the selectivity difference between *ortho*- and *para*-monohydroxy derivatives, especially in the presence of P25, decreased to a few percentage units. This behavior can be ascribed to the high coverage of catalytic sites by PH molecules, causing a lower selectivity of the hydroxyl radical attack.

The *ortho*-isomer was absent or its concentration was much lower than that of the *para*-one in the presence of home prepared catalysts especially when the PH initial concentration was lower than 1 mM. The maximum regio-selectivity recorded was 11% in the presence of HP0.5 and an initial concentration of 5 mM. Such values can be explained by considering the strong interaction of *ortho*-monohydroxy PH derivative, i.e. catechol, with catalyst surface, determining a fast degradation before desorption. An increase of PH initial concentration favors desorption because of the greater competition on the catalytic sites. Hence, selection of appropriate catalyst and initial concentration can avoid the release of *ortho*monohydroxy derivative into the solution bulk.

BA oxidation carried out by commercial TiO₂ samples gave rise to a quite uniform distribution in *ortho-*, *meta-* and *para-*isomers. A slight predominance of *ortho-*derivative was observed in the presence of Merck, whereas P25 produced prevalently the *meta*derivative. Home prepared HP0.5 sample gave rise to the only *meta*and *para-*isomers with total absence of the *ortho-*isomer up to an initial substrate concentration of 1 mM, whereas 14% *ortho-*isomer appeared when 5 mM initial concentration was used. An analogous explanation to that given for *ortho-*monohydroxy PH derivative can be provided. Using all the other home prepared catalysts yields BA *ortho-*monohydroxy derivative in minor amounts, ranging from



Fig. 3. Selectivity to mono-hydroxylated species vs. crystallinity of the used photocatalysts. (a) PH 0.5 mM; (b) BA 0.5 mM.

12% to 19%. A possible reason which may account for difference in selectivity to *ortho*-isomer is that molecules can adsorb on different TiO_2 surface centers and the used catalysts contain a diverse distribution of these various sites.

Interestingly, dark adsorption of catechol (20H-PH) and 2hydroxy-benzoic acid (2OH-BA) showed to be significant for both compounds only on HP0.5: an experimental run carried out in this study showed that starting with a concentration of 0.5 mM and catalyst amount of 0.4 g L^{-1} , 20% of the initial 2OH-PH was adsorbed on TiO₂ surface, whereas starting with 0.5 mM 2OH-BA and 0.4 gL^{-1} catalyst, 33.3% of substrate was adsorbed. This strong interaction can be explained by considering the affinity of -OH and -COOH groups with the hydroxylated high surface area of HP0.5. The spatial proximity of two of these groups on the aromatic ring can be probably responsible for the measured strong adsorption on the catalyst. In fact, the meta- and para-hydroxy derivatives did not show analogous behavior. Araña et al. [52,53] studied the photocatalytic degradation of phenol and phenolic compounds by using P25 as the catalyst. They observed a different way of adsorption of the various molecules onto TiO₂ surface. Catechol adsorption was much higher with respect to other compounds and its interaction occurred mainly through the formation of a catecholate monodentate. Starting from a 0.5 mM concentration, the percentage of adsorbed catechol on P25 and Merck surface was only 3.8%.

Figs. 5 and 6 show the evolution of TOC, concentration of PH, BA and their monohydroxy-derivatives in the course of photocatalytic runs carried out by using P25 and HP873S. Moreover p-benzoquinone concentration was reported when significant. CO_2 concentration has been divided by the carbon atoms present in PH (6) and BA(7) in order to be easily comparable with the disappeared substrate expressed in molar concentration. The results indicate that the production of monohydroxy derivatives coming from PH usually is higher than that from BA, suggesting that the presence of either EDG or EWG influences not only the regioselectivity of hydroxyl radical, but also the relative amount of the monohydroxy derivatives. There was a lack in the carbon mass balance when the concentration of the species reported in the figures was considered and compared with the TOC values, experimentally determined. This is due to the presence of unknown compounds deriving from the aromatic ring opening.

3.4. Kinetics

The data obtained in this work indicate that all the three monohydroxy derivatives were obtained starting from BA, whereas the main monohydroxylated compounds from PH were *ortho-* and *para-*isomers being the *meta-*isomer totally absent.

The kinetics were studied considering the two parallel pathways previously discussed, as already highlighted in literature for other substrates [54]. Photoreactivity results modeling was based on the assumption that all the elementary reactions of BA and PH oxidation, both partial and total, occur on the catalyst surface and involve adsorbed species, which can interact with hydroxyl groups. The rate-determining step of the photooxidation process on the catalyst surface is hypothesized to be the second order reaction between the hydroxyl radical and the aromatic molecule adsorbed onto the catalyst surface. This model is commonly used to analyze the kinetics of photocatalytic reactions and it generally provides a satisfactory prediction of the progress of the species concentration in liquid [55] or gas [56] phase.

The different kinds of sites hypothesized to exist onto the catalyst surface are the following: the first one adsorbing O_2 , the



Fig. 4. Selectivity to mono-hydroxylated species vs. samples global hydroxylation determined by TGA for the used photocatalysts. (a) PH 0.5 mM; (b) BA 0.5 mM.



Fig. 5. PH (a) and BA (b) photocatalytic oxidation runs by using Degussa P25. (a) ◊ TOC, ♦ phenol, hydroquinone, and h catechol; (b) ◊ TOC, ♦ benzoic acid, here 2-hydroxy benzoic acid, here 3-hydroxy benzoic acid, and 4-hydroxy benzoic acid.

second one adsorbing substrates by producing mono-hydroxylated species and the third one adsorbing the substrates and their intermediate products by eventually producing their mineralization. As the adsorbed oxygen acts as an electron trap thus hindering the electron-hole recombination, the hydroxyl radical concentration depends on the fractional sites coverage by O₂ [54].

Under these assumptions the disappearance rate of substrate for second order surface reactions in parallel (monohydroxylation and mineralization) may be written in terms of Langmuir–Hinshelwood kinetics as [54]:

$$(-r_{\rm S}) \equiv -\frac{1}{S} \frac{\mathrm{d}N_{\rm S}}{\mathrm{d}t} = k_1 \theta_{\rm OX} \theta_1 + k_2 \theta_{\rm OX} \theta_2 \tag{1}$$

where *S* is the surface area of the catalyst, N_S the substrate moles, *t* the irradiation time and θ_{OX} the fractional site coverage of oxygen. k_1 and k_2 are the second order rate constants and θ_1 and θ_2 the fractional site coverages of the substrate evolving to monohydroxy derivatives and of the substrate that is directly oxidized to CO₂, respectively.

It is reasonable to hypothesise that the monohydroxy intermediates, once formed, compete with the starting substrates for the adsorption on the mineralizing sites, thus the fractional site coverages, given by the Langmuir relationship, are [54]:

$$\theta_{\rm Ox} = \frac{K_{\rm Ox}C_{\rm Ox}}{1 + K_{\rm Ox}C_{\rm Ox}} \tag{2}$$

$$\theta_1 = \frac{K_{\rm MH}C_{\rm S}}{1 + K_{\rm MH}\left(C_{\rm S} + \sum_I C_I\right)} \tag{3}$$

$$\theta_2 = \frac{K_{\rm Min}C_{\rm S}}{1 + K_{\rm Min}\left(C_{\rm S} + \sum_I C_I\right)} \tag{4}$$



Fig. 6. PH (a) and BA (b) photocatalytic oxidation runs by using HP873S. (a) ◊ TOC, ♦ phenol, hydroquinone, catechol, and p-benzoquinone; (b) ◊ TOC, ♦ benzoic acid, 2-hydroxy benzoic acid, 3-hydroxy benzoic acid, and 4-hydroxy benzoic acid.

in which C_{OX} , C_{S} and C_{l} are the oxygen, the substrates and the monohydroxy derivatives concentrations in the aqueous phase, whereas K_{OX} , K_{MH} and K_{Min} are the equilibrium adsorption constants of oxygen and of substrate on monohydroxylating and mineralizing sites, respectively. Eqs. (3) and (4) are written under the hypothesis that the values of equilibrium adsorption constants of the substrates and monohydroxy derivatives are similar, both for the hydroxylation site and for the mineralization one.

Owing to the fact that all the experiments were carried out in a batch reactor by continuously bubbling oxygen into the liquid phase, the fractional site coverage of oxygen is constant during the occurrence of the run. By substituting Eqs. (3) and (4) in Eq. (1), one obtains:

$$-\frac{V}{S}\frac{\mathrm{d}C_{\mathrm{S}}}{\mathrm{d}t} = k^{\mathrm{I}}\frac{K_{\mathrm{MH}}C_{\mathrm{S}}}{1+K_{\mathrm{MH}}\left(C_{\mathrm{S}}+\sum_{I}C_{I}\right)} + k^{\mathrm{II}}\frac{K_{\mathrm{Min}}C_{\mathrm{S}}}{1+K_{\mathrm{Min}}\left(C_{\mathrm{S}}+\sum_{I}C_{I}\right)} \quad (5)$$

where *V* is the reaction volume, $k^{l} = k_{1}\theta_{Ox}$ and $k^{ll} = k_{2}\theta_{Ox}$.

The production rate of intermediates can be expressed as follows:

$$\frac{V}{S}\frac{\mathrm{d}\sum_{I}C_{I}}{\mathrm{d}t} = k^{\mathrm{I}}\frac{K_{\mathrm{MH}}C_{\mathrm{S}}}{1+K_{\mathrm{MH}}\left(C_{\mathrm{S}}+\sum_{I}C_{I}\right)} - k^{\mathrm{II}}\frac{K_{\mathrm{Min}}\sum_{I}C_{I}}{1+K_{\mathrm{Min}}\left(C_{\mathrm{S}}+\sum_{I}C_{I}\right)}$$
(6)

The production rate of CO₂, normalizing its concentration to the substrates one, can be expressed as:

$$\frac{V}{S}\frac{\mathsf{d}(C')}{\mathsf{d}t} = k^{\mathrm{II}}\frac{K_{\mathrm{Min}}\left(C_{\mathrm{S}} + \sum_{l}C_{l}\right)}{1 + K_{\mathrm{Min}}\left(C_{\mathrm{S}} + \sum_{l}C_{l}\right)}$$
(7)

where C' is the normalized carbon dioxide, i.e. it is equal to $C_{CD}/6$ in the case of PH and to $C_{CD}/7$ in the case of BA, C_{CD} being the

Table 5

Equilibrium adsorption constants and kinetic constants for phenol and benzoic acid photocatalytic partial oxidation (K_{MH} , k^{I}) and mineralization (K_{Min} , k^{II}).

	Phenol	Benzoic acid
P25		
$K_{\rm MH}~({\rm m}{\rm M}^{-1})$	2.0	1.8
$K_{\rm Min} ({ m m}{ m M}^{-1})$	25	30
$k^{\rm I} \times 10^6 ({\rm mmol}{\rm m}^{-2}{\rm s}^{-1})$	5.1	0.11
$k^{\rm II} \times 10^6 ({\rm mmol}{\rm m}^{-2}{\rm s}^{-1})$	2.83	4.3
Merck		
$K_{\rm MH}~({\rm m}{\rm M}^{-1})$	1.1	0.23
$K_{\rm Min} ({ m m}{ m M}^{-1})$	15	2.5
$k^{\rm I} \times 10^6 ({\rm mmol}{\rm m}^{-2}{\rm s}^{-1})$	5.0	15
$k^{\rm II} \times 10^6 ({\rm mmol}{\rm m}^{-2}{\rm s}^{-1})$	0.83	1.4
HP0.5		
$K_{\rm MH}~({\rm m}{\rm M}^{-1})$	0.38	9.1
$K_{\rm Min} ({ m m}{ m M}^{-1})$	2.8	8.2
$k^{\rm I} \times 10^6 ({\rm mmol}{\rm m}^{-2}{\rm s}^{-1})$	0.052	0.033
$k^{\rm II} \times 10^{6} \ ({\rm mmol} \ {\rm m}^{-2} \ {\rm s}^{-1})$	0.15	0.28

measured carbon dioxide concentration. The global molar balance can be described by the following relationship:

$$C_{S,0} = C_S + \sum_I C_I + C'$$
 (8)

$$C_{\rm S} + \sum_{I} C_{I} = C_{{\rm S},0} - C' \equiv y$$
 (9)

in which $C_{S,0}$ is the initial substrate concentration. By substituting Eq. (9) in Eq. (7), the following differential equation is obtained:

$$-\frac{V}{S}\frac{\mathrm{d}y}{\mathrm{d}t} = k^{\mathrm{II}}\frac{K_{\mathrm{Min}}y}{1+K_{\mathrm{Min}}y} \tag{10}$$

Integration of Eq. (10) with the limiting conditions that $y = C_{S,0}$ at t = 0 and $y = C_{S,0} - C'$ at t = t gives:

$$t = \frac{V}{S} \frac{1}{k^{II} K_{\text{Min}}} \left(\ln \frac{C_{S,0}}{C_{S,0} - C'} + K_{\text{Min}} C' \right)$$
(11)

A least square best fitting procedure of Eq. (11) to all the experimental data of C' versus t yields the values of k^{II} and K_{Min} ($R^2 > 0.95$) for BA and PH. This non linear fit was carried out by using the curvefitting function available in TK Solver 5.0. These values are reported in Table 5 together with the 90% confidence intervals. In order to compare the experimental data with the kinetic model (Eq. (11)) which gives t as a variable dependent on C, for some representative runs, Fig. 7 shows the experimental values of t versus C' in the case of P25, Merck and HP0.5 samples. The lines drawn through the experimental points represent Eq. (11) in which the fitted parameters have been substituted: a satisfactory fitting of the model to the experimental data may be noted. Moreover, the obtained results suggest that the mineralization pathway is similar for both substrates. In fact the lines indicating the kinetic model are very close each other, thus suggesting that the nature of substituent group does not influence the mineralization reaction.

In order to determine k^{l} and K_{MH} , Eq. (10) has been divided by Eq. (5) giving rise to the following relation:

$$\frac{dy}{dC_S} = \frac{Ay(1 + K_{MH}y)}{C_S[(1 + K_{Min}y) + A(1 + K_{MH}y)]}$$
(12)
where

$$A = \frac{K_{\rm Min}k^{\rm H}}{K_{\rm MH}k^{\rm I}}$$

By integrating Eq. (12) with the limit conditions that $y = y_0$ for $C_S = C_{S,0}$ and y = y for $C_S = C_S$, one obtains the following equation:

$$\ln\left(\frac{C_{S,0}}{C_S}\frac{y}{y^0}\right) = \frac{K_{Min}}{AK_{MH}}\ln\frac{1+K_{MH}y^0}{1+K_{MH}y} + \frac{1}{A}\ln\left(\frac{y^0}{y}\frac{1+K_{MH}y}{1+K_{MH}y^0}\right)$$
(13)



Fig. 7. Experimental values of irradiation times versus $C: \blacksquare$, BA; \Box , PH. The continuous and dotted lines represent the kinetic model (Eq. (11)) for BA and PH runs, respectively. (a) P25; (b) Merck; (c) HP0.5.

By substituting the values of k^{II} and K_{Min} in Eq. (13), the least square best fitting procedure for all the runs, at different initial concentrations, yielded the values of k^{I} and K_{MH} for BA and PH. They are reported in Table 5 for P25, Merck and HP0.5 catalysts together with the 90% confidence intervals. Partial oxidation kinetic constants (k^{I}) are higher by using Merck sample for both PH and BA, conversely k^{II} figures are higher when using HP0.5. P25 shows different kinetic behavior for PH and BA oxidation: in the former case, k^{I} is higher than k^{II} , contrarily to values obtained with BA. The last insight is in agreement with the stronger mineralization generally obtained from BA oxidation with respect to PH oxidation in the presence of P25 (see Table 3). By using the same catalyst sample, moreover, selectivity to mono-hydroxy derivatives was higher starting from PH, in accord with the kinetic constants figures.

As far as the equilibrium adsorption constants are concerned, the highest ones are those referring to PH and BA mineralization carried out by P25 sample. The lowest figures are instead the ones



Fig. 8. Experimental values of C_S versus y (defined in Eq. (9)): \blacksquare , BA; \Box , PH. The continuous and dotted lines represent the kinetic model (Eq. (13)) for BA and PH runs, respectively. (a) P25; (b) Merck; (c) HP0.5.

corresponding to mono-hydroxylation of BA and PH by using P25 and HP0.5, respectively.

For some representative runs, Fig. 8 reports the values of C_S as a function of y; the lines drawn through the experimental points represent the kinetic model (Eq. (13)) in which the fitted parameters have been substituted; also in this case a satisfactory fitting of the model to the experimental data may be noted. The results indicate that the production of monohydroxy derivatives is higher for PH than for BA suggesting that the presence of either EDG or EWG influences not only the regio-selectivity of hydroxyl radical, but also the relative amount of the monohydroxy derivatives.

4. Conclusions

The photocatalytic hydroxylation of a substrate containing an electron donor group (phenol) and one containing an electron withdrawing group (benzoic acid) in the presence of commercial and home prepared TiO_2 photocatalysts has been reported.

The photocatalytic results indicate that the products of the primary oxidation of phenol were the *ortho* and *para*-mono-hydroxy derivatives while those of benzoic acid were all the mono-hydroxy derivatives. For both the substrates the ortho-isomer was absent or its concentration was much lower than that of the *para*-one in the presence of home prepared catalysts because of the strong interaction of ortho-monohydroxy derivative with catalyst surface, especially when the substrate initial concentration was lower than 1 mM. Hence the selection of the appropriate catalyst and of the substrate concentration avoid the release of ortho isomer in the solution facilitating the separation operations. The highest selectivity values were obtained with the commercial sample Merck for both substrates. As expected, the selectivity toward mono-hydroxy derivatives and the distribution of the regio-isomers are strongly influenced by the photocatalyst properties. In particular, a dependence of the selectivity on the percentage of catalyst crystallinity and on the total amount of OH groups present on the catalyst surface has been observed. Crystalline and poorly hydroxylated TiO₂ Merck sample, and HP0.5, the most hydroxylated one, are the most and the least selective catalysts, respectively.

A kinetic Langmuir–Hinshelwood model, taking into account the two parallel pathways of mineralization and of partial oxidation, was developed for P25, Merck and HP0.5 samples. Equilibrium adsorption constants and kinetic constants found for the mineralization route were similar for both substrates, thus indicating that the nature of the substituent group does not influence the mineralization reaction. Opposite trends were observed for the partial oxidation constants. Finally it can be stated that the fitting of experimental data to the kinetic model is generally satisfactory.

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