

# **Aqueous selective photocatalytic oxidation of salicyl alcohol by TiO<sub>2</sub> catalysts: influence of some physico-chemical features**

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## **Abstract**

Partial photocatalytic oxidation of salicyl alcohol (2-hydroxybenzyl alcohol) to salicylaldehyde in water was investigated under environmental friendly conditions in the presence of home prepared and commercial TiO<sub>2</sub> (Merck and Aeroxide P25) samples under UVA irradiation. The photocatalysts were characterized by using BET, XRD and SEM (or TEM) techniques. The effects of crystallinity degree, pH (3-11) and presence of a hole trap (ethanol) on the photocatalytic activity and product selectivity were investigated. 4-Hydroxybenzyl alcohol was also used to study the influence of the position of the substituent group in the aromatic ring. High alcohols conversion and product selectivity values were obtained at pH=11 by using well crystallized TiO<sub>2</sub> samples. The conversion values significantly decreased by increasing the hole trap concentration, whereas the selectivity

values increased slightly. The selectivity towards the corresponding aldehyde after 30% of alcohol conversion was significantly higher for 4-HBA (48%) than for 2-HBA (32%), due to the para position of the substituent group. In order to clarify the different selectivity of the products, we have also performed various experiments starting from the products; these results indicate that the selectivity is also strongly dependent on the stability of the products under the experimental conditions used. By concluding, this article reports that the influence on conversion and selectivity for the studied reaction, under various experimental conditions, depends both on the TiO<sub>2</sub> type and on the substrate.

**Keywords:** Photocatalysis, salicyl alcohol, salicylaldehyde, salicylic acid, selective oxidation, TiO<sub>2</sub>, environmental friendly conditions.

## 1. Introduction

Heterogeneous photocatalysis is a “green” and economic technology, which can be carried out under mild experimental conditions of pressure and temperature in the presence of inexpensive and nontoxic semiconductors as photocatalysts, and generally by using water as the solvent. Moreover, O<sub>2</sub> present in air can be used as the oxidizing agent, and solar light or artificial light with low-energy consumption as the irradiation sources [1-6]. Due to the mild operative conditions and inexpensiveness, the photocatalytic method can compete with the classical technologies that require usually more drastic conditions. However, photocatalysis has some drawbacks such as the need for UV light irradiation to activate most semiconductors, the low selectivity towards partial oxidation products (when water is used as the solvent) and the difficulty of working with highly concentrated solutions.

Heterogeneous photocatalysis has been generally used for wastewater treatment to degrade harmful compounds as pesticides, dyes, drugs, and their intermediates [4]. Photocatalytic reactions involve fast attack of strong oxidizing agents as hydroxyl radicals, which

unselectively degrade and mineralize almost all organic compounds especially in water. However, the method can be also used for selective oxidation and reduction reactions to produce chemicals with high added value starting from various organic substrates such as alcohols [6-10].

On the irradiated surface of a solid photocatalyst, in fact, oxidizing and reducing species form simultaneously making the photocatalytic method suitable for organic synthesis through oxidative or reductive pathways or through the combination of both. It is possible to find in the pertinent literature examples of organic synthesis via oxidative [10-16] or via reductive pathways [17-21].

The efficiency of photocatalytic organic synthesis can be improved by optimizing some characteristics of the solid photocatalysts such as type of polymorph, degree of crystallinity, surface acid-base properties, exposure of particular crystalline facets, coupling of different semiconductors, position of the valence and conduction bands, and addition of dopants. Moreover, also parameters related to the reaction system such as reactor geometry, setup configuration, type of solvent, presence of gas, temperature, type and quantity of photocatalyst, and initial pH appear to be essential [8,9,22].

TiO<sub>2</sub> is the most used photocatalyst, since it is highly photoactive, cheap, and resistant to photocorrosion. The most common polymorphs of TiO<sub>2</sub> are anatase, rutile and brookite which have different intrinsic electronic and surface physicochemical properties [23-28] resulting in a different photocatalytic activity and selectivity. From a photocatalytic point of view, anatase is generally considered the most active phase and rutile the least active, while, until a few years ago, brookite activity was less studied due to the difficulty in obtaining it as a pure phase.

Salicylaldehyde (2-hydroxybenzaldehyde) is a key precursor for a variety of chelating agents, by condensation with amines, some of which are commercially important [29]. Salicylic acid, derived from the metabolism of salicin (an alcoholic  $\beta$ -glucoside), is widely used in organic

synthesis and functions as a plant hormone. Salicylic acid is also a starting molecule for synthesis of acetylsalicylic acid (aspirin) [30].

In this work, the photocatalytic oxidation of salicyl alcohol (2-hydroxybenzyl alcohol) to salicylaldehyde and salicylic acid is reported. The reaction was performed under environmental friendly conditions in the presence of home prepared and commercial TiO<sub>2</sub> samples. The photocatalysts were characterized and the effects of crystallinity degree, pH and the presence of a hole trap (ethanol) on the photocatalytic activity and product selectivity were studied. 4-Hydroxybenzyl alcohol was also used to study the influence of the substituent group on the aromatic ring.

## **2. Experimental**

### **2.1 Materials**

Titanium oxysulfate hydrate (TiOSO<sub>4</sub>·xH<sub>2</sub>O 29% Sigma), 2-hydroxybenzyl alcohol (>98% Aldrich), 2-hydroxybenzyl aldehyde (99.8% Aldrich), 2-hydroxybenzoic acid (98% Sigma-Aldrich), 4-hydroxybenzyl alcohol (>98% Aldrich), 4-hydroxybenzyl aldehyde (99.8% Aldrich), 4-hydroxybenzoic acid (98% Sigma-Aldrich) and ethanol were used without further purification. Commercial TiO<sub>2</sub> samples (Merck and Aeroxide P25) were used as reference photocatalysts.

### **2.2 Samples preparation**

25 g of TiOSO<sub>4</sub>·xH<sub>2</sub>O were added to 100 mL of distilled water in a Teflon vessel. The solution was heated at 180 °C for 2h inside a stainless-steel autoclave. After the thermal treatment, the precipitate was washed three times with distilled water, and then dried overnight at 60 °C. The powder was labelled as HPA, where A refers to anatase TiO<sub>2</sub> polymorphic phase. In

order to promote the powder crystallization, two different aliquots were calcined at 600 °C for 2h and 8h respectively. These samples were named HPA-600-2h and HPA-600-8h.

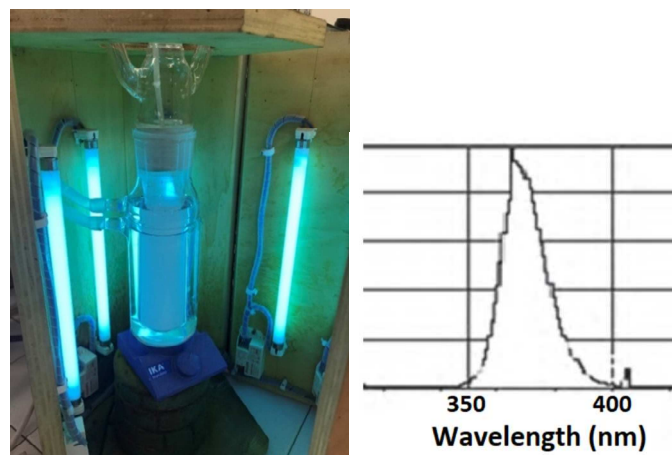
### **2.3 Samples characterization**

The X-ray diffraction (XRD) analysis of the samples was performed by a Philips diffractometer using the Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation at 40 kV and a current of 30 mA with a  $2\theta$  scan rate of  $1.28^\circ \text{ min}^{-1}$ . The crystalline size and the crystallinity of the samples were determined by using the Scherrer equation [31] and the Bellardita et al. method [32], respectively. The specific surface areas (SSA) were measured in a FlowSorb 2300 apparatus (Micromeritics) by using the single-point BET method. Before the measurement the samples were degassed by flowing a N<sub>2</sub>/He mixture 30/70 (v/v) for 0.5 h at 523 K. SEM (Scanning electron microscopy) images were obtained using a FEI Quanta 200 ESEM microscope, operating at 30 kV on specimens upon which a thin layer of gold had been evaporated. TEM images were acquired by using a Tecnai G2 transmission electron microscope operating at 200 kV.

### **2.4 Photocatalytic runs**

Aqueous partial oxidation of 2-hydroxybenzyl alcohol (2-HBA) and 4-hydroxybenzyl alcohol (4-HBA) along with additional runs starting from the products was carried out in liquid-solid regime in a Pyrex reactor externally irradiated by six Actinic BL TL MINI 15 W/10 Philips lamps. The main emission peak was in the near-UV region at 365 nm (Figure 1). The volume of solution was 150 mL, the alcohols initial concentration was 0.5 mM and the used photocatalyst amount was 0.2 g/L. The pH of the suspension was adjusted by using 0.1 M HCl or NaOH solutions. The runs were carried out at ca. 30 °C and atmospheric air was used as the oxygen source. The lamps were switched on 30 minutes after the TiO<sub>2</sub> introduction inside the reactor to ensure the achievement of the adsorption-desorption equilibrium of the

substrate on the catalyst surface. Samples were withdrawn at fixed time intervals and filtered through 0.2  $\mu\text{m}$  membranes for the quantitative determination of the substrates and their intermediates.



**Fig. 1.** The photoreactor and the spectrum of the lamp (Actinic BL TL MINI 15 W/10 Philips Neon).

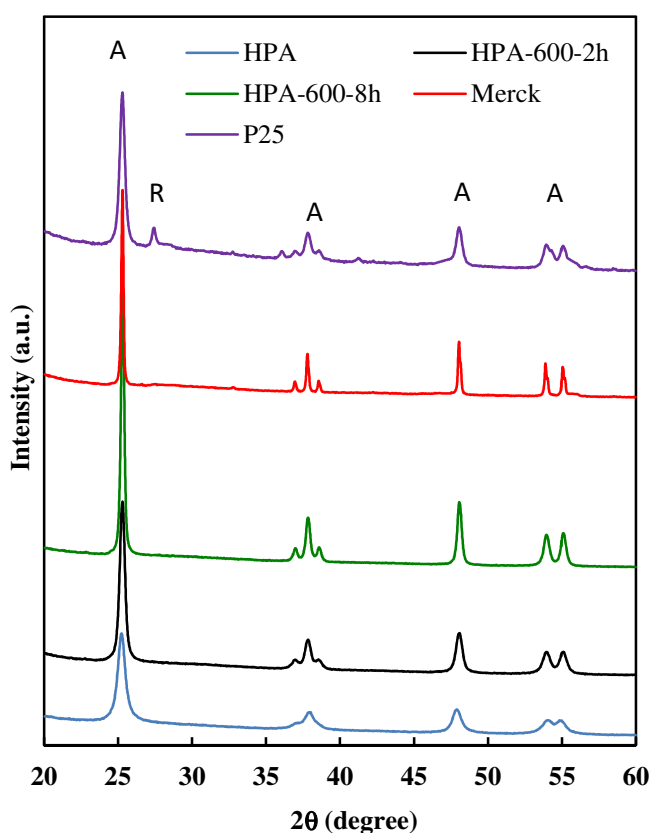
## 2.5 Analytical techniques

A Beckman Coulter HPLC (System Gold 126 Solvent Module and 168 Diode Array Detector) equipped with a Phenomenex Kinetex 5 mm C18 100A column (4.6 mm x 150 mm) was used for the analysis of the reaction solution after irradiation. The eluent consisted of a mixture of acetonitrile and 13 mM trifluoroacetic acid aqueous solution (30:70 volumetric ratio), and the flow rate was  $0.8 \text{ mL}\cdot\text{min}^{-1}$ . Total Organic Carbon (TOC) analyses were performed by using a Total Organic Carbon analyser (Shimadzu, TOC-LCPN model) to evaluate amount of substrates that mineralized to  $\text{CO}_2$ .

## 3. Results and discussion

Figure 2 shows XRD patterns of Aeroxide P25, Merck and home prepared (HPA) photocatalysts. In Table 1 are reported crystal phase, BET specific surface area, and crystallinity of the used samples. The XRD peaks at  $2\theta = 25.58^\circ, 38.08^\circ, 48.08^\circ, 54.58^\circ$  can be attributed to the anatase  $\text{TiO}_2$  phase, while those at  $2\theta = 27.5^\circ, 36.5^\circ, 41.0^\circ, 54.1^\circ, 56.5^\circ$

to the rutile one. All of the catalysts are in the anatase phase, however P25 also includes a fraction of rutile (ca. 80% A, 20% R). P25 and Merck samples presented the highest crystallinity percentage (90 and 80%, respectively), while the HP ones exhibited low crystallinity values that increased by calcination and/or duration of the thermal treatment. HPA showed the highest surface area (169 m<sup>2</sup>/g) and a significant decrease was observed after calcination. On the contrary, the crystallites size increased with the thermal treatment, as expected.



**Fig. 2.** XRD patterns of Aerioxide P25, Merck and home prepared (HPA) photocatalysts. A= Anatase. R = Rutile.

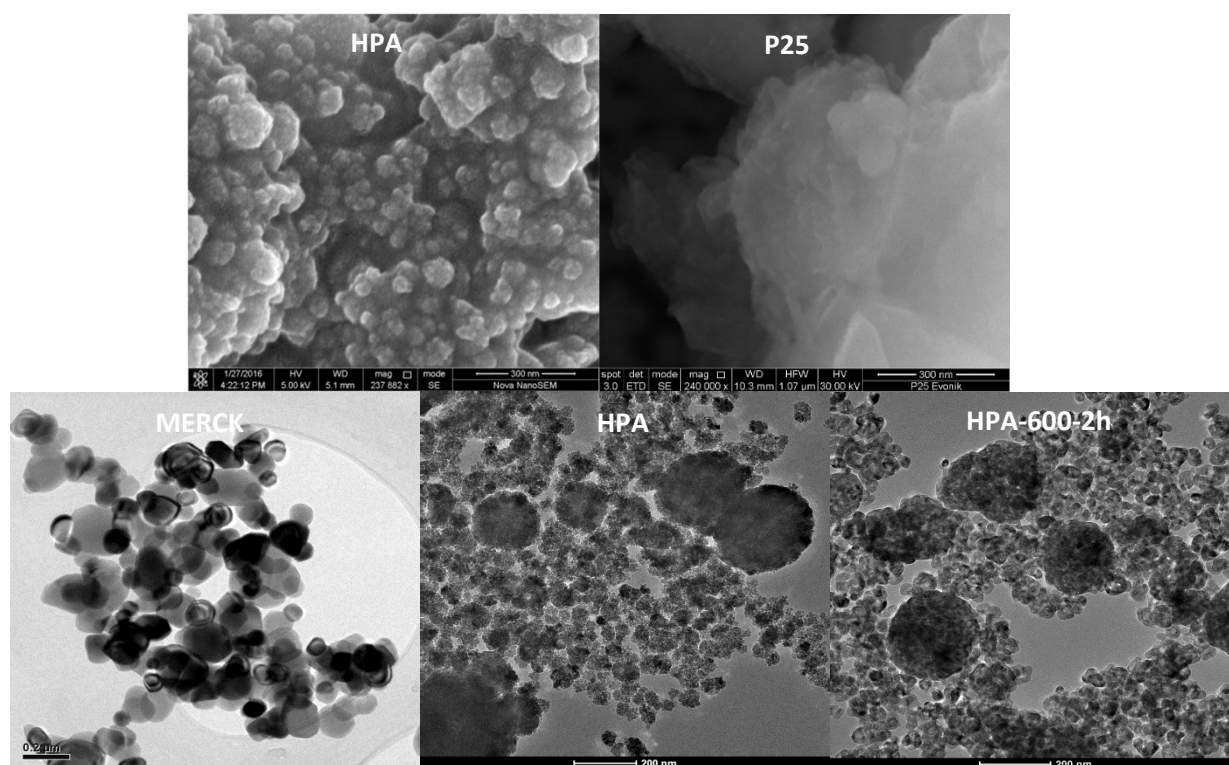
**Table 1.** Crystal phase, BET specific surface area, and crystallinity of the catalysts.

A= Anatase, R = rutile.

Catalyst	Phase	Primary particle	Crystallinity	A.S.S.
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		size (nm)	(%)	(m <sup>2</sup> g <sup>-1</sup> )
Merck	A	60	79	10
P25	A+R	25.0 (A) 33.0 (R)	37 (A) 62 (R)	50
HPA	A	35	24	169
HPA-600-2h	A	139	35	43
HPA-600-8h	A	150	46	34

Figure 3 shows selected SEM and TEM images of the used samples. HPA samples exhibit clusters of small roundish particles, whilst P25 irregular shaped agglomerates. For the commercial TiO<sub>2</sub> samples spherical particles whose size ranges from 100 to 200 nm can be observed by TEM analysis, whilst the home prepared HPA samples consist of agglomerates with lower dimensions. A slight increase in particle size can be observed for the HPA-600-2h sample due to sintering of the aggregates after heat treatment.





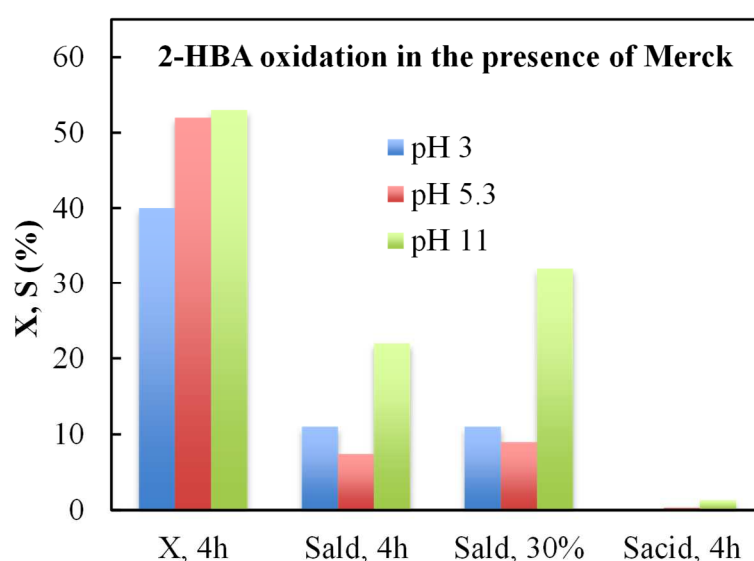
**Fig. 3.** SEM (HPA, Aeroxide P25) and TEM (Merck, HPA, HPA-600-2h) images of TiO<sub>2</sub> samples, respectively.

Figure 4 reports the photocatalytic activity results of 2-HBA oxidation by using TiO<sub>2</sub> Merck at different pH's. At pH's 5.3 and 11, significant alcohol conversion was observed (ca. 52%), whilst at pH 3 just 40% conversion was obtained after 4h of irradiation. Different factors contribute to the higher activity observed at basic pH conditions. Dark adsorption percentages of the alcohol were quite similar at pH's 5.3 and 11 (5 and 8%, respectively); on the contrary almost no adsorption occurred at pH 3. Therefore, it can be concluded that a slight higher interaction between the alcohol and the TiO<sub>2</sub> surface occurred by increasing the pH.

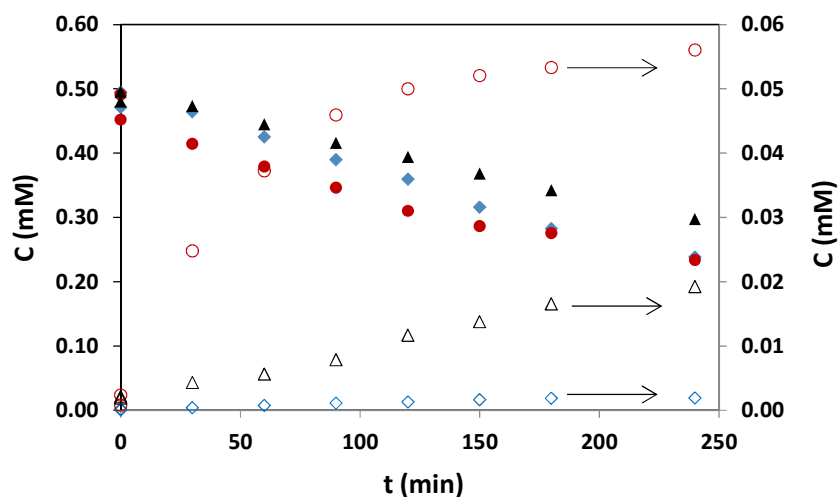
The variation of pH of the reaction medium can give rise to various effects depending both on the preparation of the photocatalyst and the molecular structure of the substrate. In the latter case, the higher activity under basic conditions cannot be attributed to electrostatic factors. However, although an interaction between the deprotonated fraction of 2-HBA and the low fraction of positively charged catalyst surface (with respect to the lower pH value) cannot be excluded at pH = 11, that interaction can not be considered important. Indeed, at pH = 11 the concentration of the deprotonated form of 2-HBA (negatively charged) is higher than that of its protonated form, but the surface of TiO<sub>2</sub> is predominantly negatively charged. A more significant role in increasing the degradation rate of the substrate, in the basic system, is probably played by the hydroxide ions adsorbed on the surface of the catalyst, since their significant quantity can induce a greater formation of OH radicals mainly by reaction with the photo-produced holes. On the other hand, 2-HBA is present almost as protonated form (and then neutral) at pH 3 being its pK<sub>a</sub> = 9.92, whilst the TiO<sub>2</sub> surface is positively charged being the pH value of 3 below the zero charge point [15]. Therefore, the interaction between 2-HBA

and TiO<sub>2</sub> surface was possibly very weak, the OH<sup>-</sup> species concentration low and consequently the activity less significant than at pH=11. Moreover, at acidic pH=3 an intramolecular hydrogen bonding can be formed between the two adjacent –OH groups that stabilizes the molecule.

The selectivity was also surprisingly the highest at pH 11. This trend is opposite to what was observed in a previous work concerning the partial oxidation of benzyl alcohol and p-methoxybenzyl alcohol to the corresponding aldehydes [7], where it was reported that higher selectivity was obtained at lower conversion degrees. The most important factor addressing the selectivity is the stability of the produced intermediate under the working conditions. In this case, the high selectivity values obtained at basic pH indicate that salicylic aldehyde was very stable in water and therefore it underwent a low degradation. It can be noticed that almost no selectivity to salicylic acid was found. Probably, the produced acid is easily decomposed to open ring products and CO<sub>2</sub>. 2-HBA and salicylic aldehyde concentrations during irradiation time at different pH's are plotted in Figure 5. The maximum aldehyde concentration (ca. 0.057 mM) was obtained at pH 11.



**Fig. 4.** X=conversion; S=selectivity.  $X_{4h}$ : conversion after 4h irradiation.  $S_{ald, 4h}$  and  $S_{ald, 30\%}$ : salicylic aldehyde selectivity after 4h of irradiation and at 30% conversion, respectively.  $S_{acid, 4h}$ : salicylic acid selectivity after 4h of irradiation.



**Fig. 5.** Photocatalytic oxidation of 2-HBA (full symbols) to salicylic aldehyde (empty symbols) at pH 3 ( $\blacktriangle$ ), 5.3 ( $\blacklozenge$ ) and 11 ( $\bullet$ ) by using Merck. Aldehyde concentrations are reported in the right ordinate.

In Table 2 the photocatalytic activity results of 2-HBA in the presence of ethanol as hole trap are reported. By increasing the ethanol concentration, the activity values considerably decreased due to the competition for holes between the substrate and ethanol. However, the selectivity values increased slightly. By considering both activity and selectivity, the yield decreased by adding ethanol. Therefore, the presence of ethanol as a hole trap was detrimental for the oxidation of 2-HBA, unlike what was reported in our previous work for the oxidation of benzyl alcohol [33].

**Table 2.** Photocatalytic activity results of 2-HBA (0.5 mM) under UV irradiation in the presence of ethanol as hole trap at pH 11.

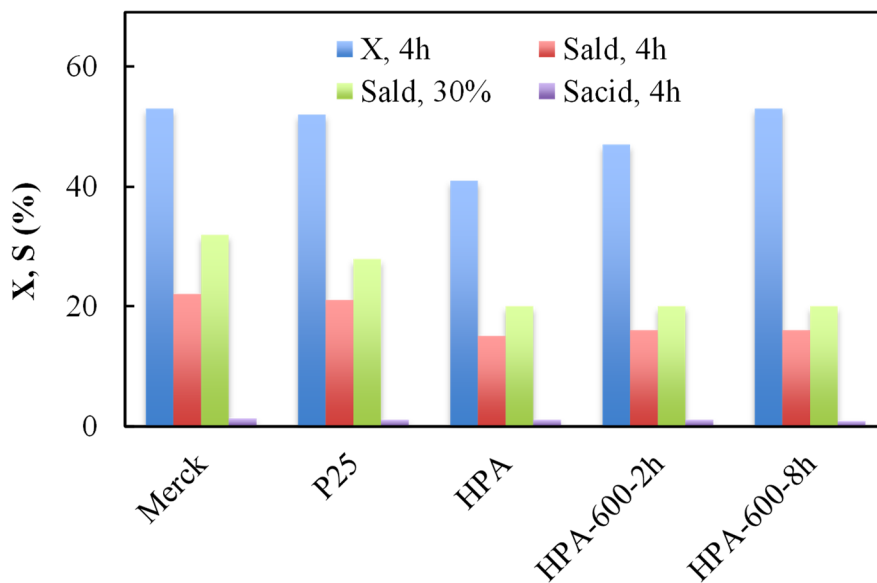
Catalyst	$X_{4h}$	$S_{ald, 4h}$	$S_{ald, 30\%}$	$S_{acid, 4h}$	Ethanol
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	(%)	(%)	(%)	(%)	(mM)
Merck	53	22	32	1.3	-
Merck	48	18	24	1.4	0.10
Merck	38	29	33	1.6	0.50
Merck	10	32	-	3.5	5.0

X=conversion; S=selectivity.  $X_{4h}$ : conversion after 4h irradiation.  $S_{ald, 4h}$  and  $S_{ald, 30\%}$ : salicylic aldehyde selectivity after 4h of irradiation and at 30% conversion, respectively.  $S_{acid, 4h}$ : salicylic acid selectivity after 4h of irradiation.

Figure 6 shows the photocatalytic activity results of 2-HBA performed at pH 11 by using HP and commercial samples. Merck, P25 and HP-600-8h samples showed the highest conversion values, but the selectivity was maximum with the Merck one. For the HP samples, by increasing the crystallinity, the photocatalytic activity also increased. Indeed, the most crystalline HPA sample (HPA-600-8h) showed a high conversion (53 vs 41%) but the selectivity towards 2-hydroxybenzaldehyde (20% at 30% conversion) was virtually the same as for the other HP samples. In this case, the most crystalline sample showed the maximum conversion, in accordance with the general observation that the oxidant power of a photocatalyst increases with the crystallinity due to a lower defects amount [32].

In the presence of Merck, the most crystalline sample, both the conversion and the selectivity presented the highest values, and this result was different from that observed with other monohydroxylated aromatic alcohols [7], but in agreement with what reported for the photocatalytic partial oxidation of glycerol [34].



**Fig.6.** Photocatalytic oxidation of 2-HBA. X=conversion; S=selectivity.  $X_{4h}$ : the conversion after 4h irradiation.  $S_{ald, 4h}$  and  $S_{ald, 30\%}$ : salicylic aldehyde selectivity after 4h of irradiation and at 30% conversion, respectively.  $S_{acid, 4h}$ : salicylic acid selectivity after 4h of irradiation.

Table 3 shows the conversion and selectivity values measured during the partial oxidation of 4-HBA. The conversion values were slightly lower than those obtained for 2-HBA when commercial samples were used, whilst a more evident decrease was observed with the HP samples. As far as the selectivity is concerned, higher values than those of 2-HBA were obtained for all of the photocatalysts, in particular towards the acid (1.3% starting from 2-HBA and 9.1% starting from 4-HBA). Probably, both 2-HBA and its oxidation products decomposed more easily than 4-HBA and its derivatives, due probably to a higher affinity with the  $TiO_2$  surface (see Fig. 6 and Table 3). In particular, a good interaction can occur for 2-hydroxybenzoic acid in which hydroxyl and acid functional groups are in ortho position. On the contrary, the experimental results indicate that the two groups in para position in the 4-hydroxybenzoic acid, make it more stable under the working condition with respect to salicylic acid. The adsorption of the two starting molecules and consequently the attack by radicals could be different (for instance the greater symmetry of 4-HBA could favour its plate

adsorption on the surface of the photocatalyst) Nevertheless, it is very difficult to understand clearly this phenomenon by a spectroscopic investigation (for instance by IR spectroscopy) due to the presence of OH groups both in the TiO<sub>2</sub> surface and in the substrates which give rise to strong absorption covering a large part of the spectrum.

An important influence on the photoactivity is that of the crystallinity degree of the photocatalyst. In fact, the photocatalytic activity (in terms of 4-HBA conversion) of HP samples significantly increased by increasing the crystallinity from 19 to 42%, whilst the selectivity decreased at the high conversion values. These results are in agreement with those obtained previously with 4-methoxybenzyl alcohol [34], and indicate that the least crystalline samples were less oxidant and more selective. The highest product selectivity value for 4-HBA, after 4h of irradiation, was obtained by using the HPA sample (40%), which afforded the lowest conversion (19%). By considering the same degree of conversion (30%), however, the highest selectivity values were measured with the commercial samples, even if the data were not dramatically different from those found in the presence of the calcined HPA samples (see Table 3). Therefore, even for 4-HBA, in the presence of commercial samples, the most crystalline photocatalysts were more oxidant and more selective.

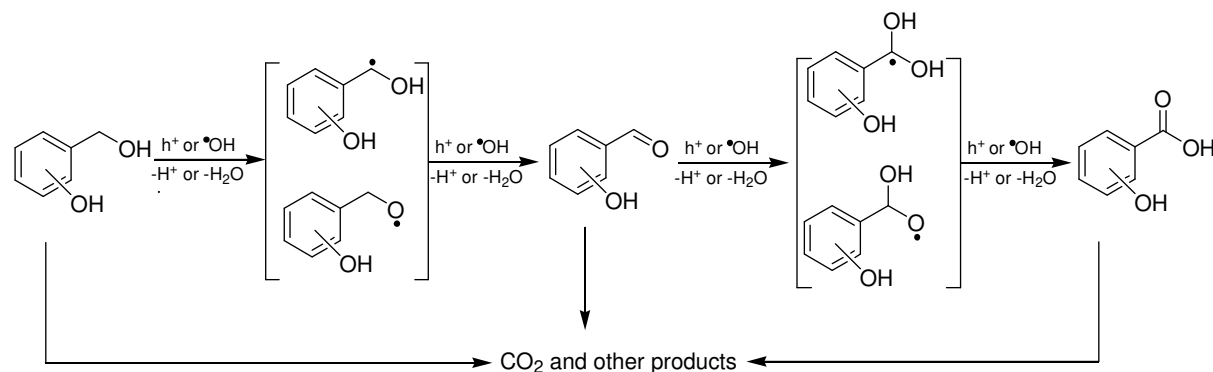
**Table 3.** Photocatalytic activity results of 4-HBA (0.5 mM) under UV irradiation at pH 11.

<b>Catalyst</b>	<b>X<sub>4h</sub></b> (%)	<b>S<sub>Ald, 4h</sub></b> (%)	<b>S<sub>Ald, 30%</sub></b> (%)	<b>S<sub>acid, 4h</sub></b> (%)
Merck	48	38	48	9.1
P25	48	36	40	8.5
HPA	19	40		0
HPA-600-2h	38	33	35	3.8
HPA-600-8h	42	35	37	5.5

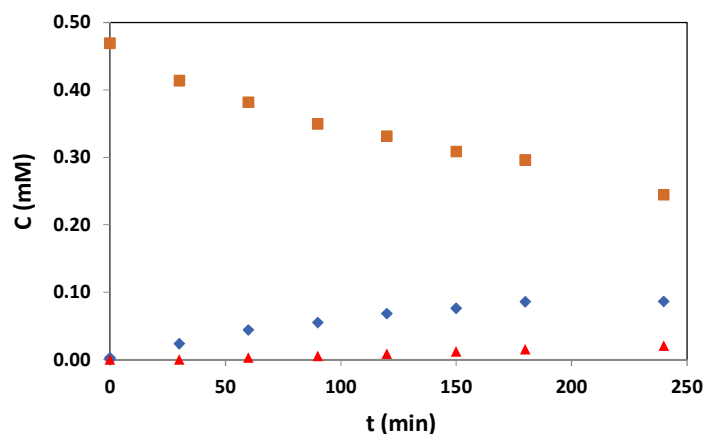
X=conversion; S=selectivity. X<sub>4h</sub>: the conversion for 4h irradiation. S<sub>4h</sub> and S<sub>Ald, 30%</sub>: 4-hydroxybenzyl aldehyde selectivity after 4 h at 30% conversion, respectively. S<sub>acid</sub> for 4h: 4-hydroxybenzoic acid selectivity after 4h irradiation.

Scheme 1 shows a proposed mechanism for the photocatalytic oxidation of 2-HBA and 4-HBA. The initial steps could be the interaction of  $h^+$  or hydroxyl radicals with the substrate (2-HBA or 4-HBA) producing hydroxybenzaldehyde that is successively oxidized to hydroxybenzoic acid. The over-oxidation products of these valuable molecules are mainly aliphatic species and  $CO_2$ .

Figure 7 shows a representative run of 4-HBA oxidation to 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid performed at pH 11 by using Merck  $TiO_2$ . Throughout the run, the substrate concentration decreased, while that of both products increased, although the variation of concentration for both aldehyde and acid between ca. 200 and 250 minutes was virtually negligible. It is very likely, as observed usually in photocatalysis, that long irradiation times favor formation of open ring unidentified products with their subsequent mineralization.



**Scheme 1.** The proposed mechanism for photocatalytic oxidation of 2-HBA and 4-HBA.



**Fig. 7.** Photocatalytic oxidation of 4-HBA (■) to 4-hydroxybenzaldehyde (◆) and 4-hydroxybenzoic acid (▲) at pH 11 in the presence of Merck.

Further experiments were performed (Table 4) to highlight the stability/instability of 2-HBA, salicylic aldehyde, salicylic acid and 4-hydroxybenzoic acid under neutral and basic conditions. The results show that both the partial oxidation of 2-HBA and mineralization were more significant at pH 6, justifying the lower selectivity values. Salicylic aldehyde oxidation was much higher at pH 6 than at pH 11 (conversion after 3h of irradiation equal to 85 vs 33%, see Fig. 8). These results point out that 2-HBA partial oxidation product is less stable at low pH and a better performance can be achieved at higher pH values. In addition, almost the same activity results were obtained for salicylic acid oxidation at pH 3, 6 and 11.

The comparison of salicylic acid and 4-hydroxybenzoic acid oxidation at pH 11 showed that the conversion of salicylic acid is almost twice higher than that of 4-hydroxybenzoic acid. For this reason, ca. 9% selectivity towards 4-hydroxybenzoic acid was obtained starting from 4-hydroxybenzyl alcohol, whilst almost no salicylic acid was formed during the partial oxidation of 2-HBA. These results indicate that the selectivity is strongly dependent on the stability of the products under the experimental conditions used.

By comparing the resonance structures of each couple of 2- and 4- substituted phenols isomers (2-HBA and 4-HBA) and those of the corresponding partial oxidation products, i.e. 2-



and 4- aldehydes and the related 2-and 4-acids (see Fig. 9), the number and the position of the charges are the same. Consequently, their stability appears virtually the same. Therefore, it must be stressed that in heterogeneous photocatalysis, considerations on the reacting molecules without considering their interaction with the catalyst surface are not informative and cannot be related straightforwardly to the observed photoreactivity. For these reasons, we conclude that the major conversion and minor selectivity observed for 2-HBA isomer, when compared to the 4-HBA isomer, is probably due to its major interaction with the catalyst surface, due to the proximity of phenolic –OH to the alcohol/aldehyde/acid moieties. A thorough investigation on this specific point could be useful to try to understand more, but this is not the aim of this work.

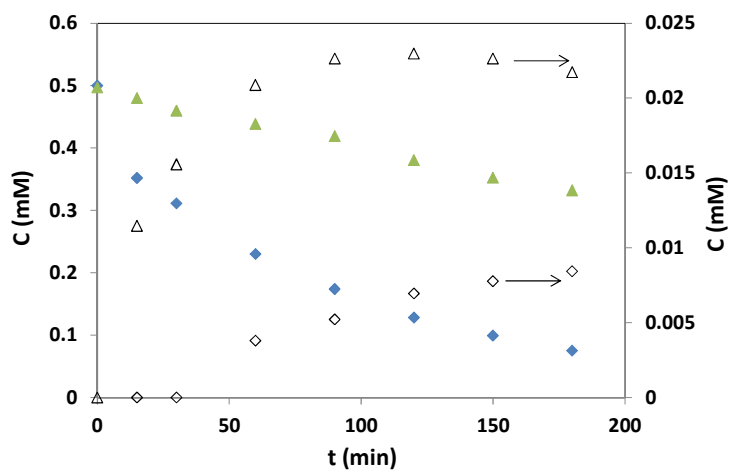
In order to compare the mineralization pathways, the CO<sub>2</sub> selectivity values, divided by 6 for stoichiometric normalization, after 3h irradiation were also determined. Notably, the highest CO<sub>2</sub> selectivity values were obtained for salicylic aldehyde oxidation (ca. 41-52%), whilst low figures were found for salicylic acid and 4-hydroxybenzoic acid oxidation. Moreover, the selectivity values towards salicylic acid from salicylic aldehyde oxidation (up to 8%, for 30% conversion) were also low. The above finding suggests that the salicylic aldehyde reaction pathway from 2-HBA preferentially proceeds towards mineralization rather than further partial oxidation to salicylic acid.

**Table 4** . Photocatalytic activity results (substrates initial concentration 0.5 mM) in water under UV irradiation for different pH's by using Merck TiO<sub>2</sub>.

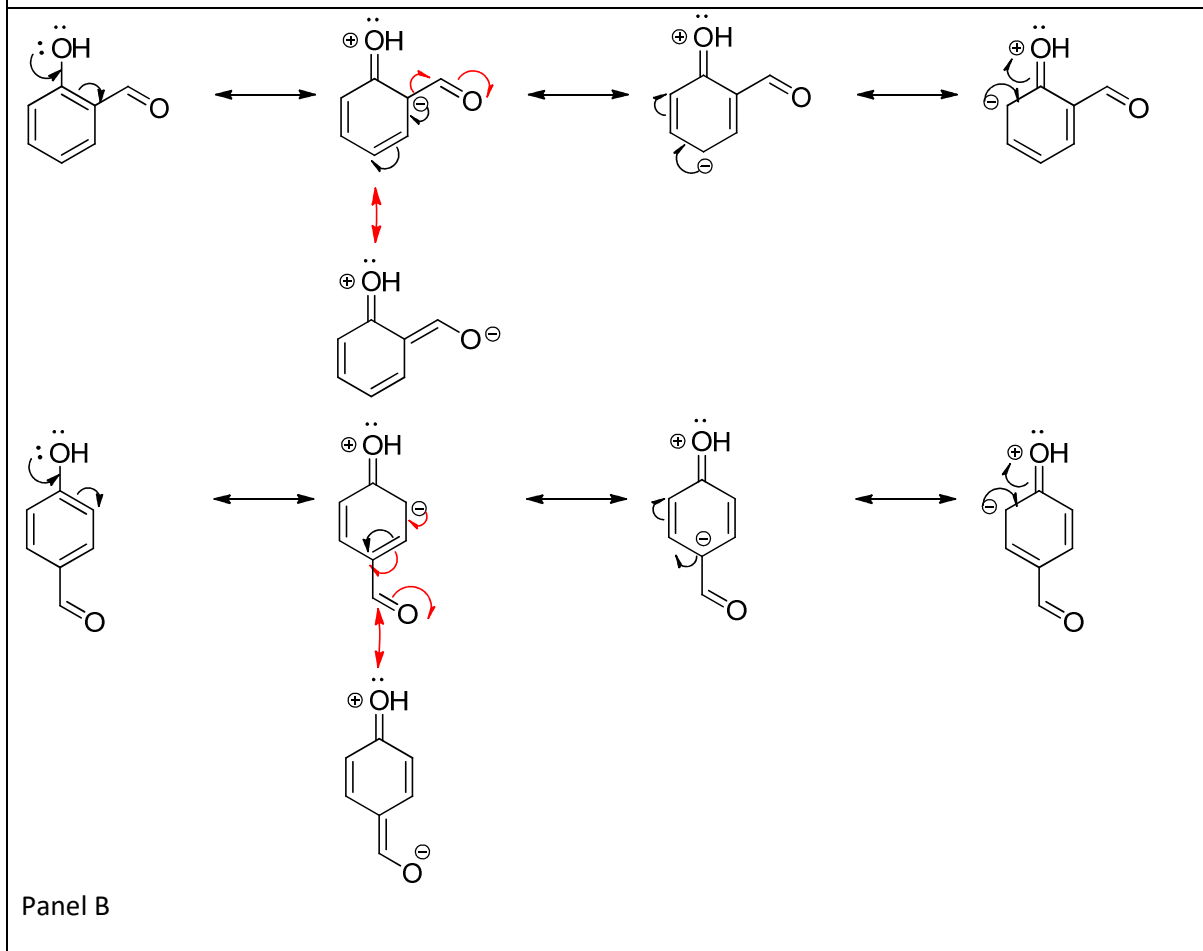
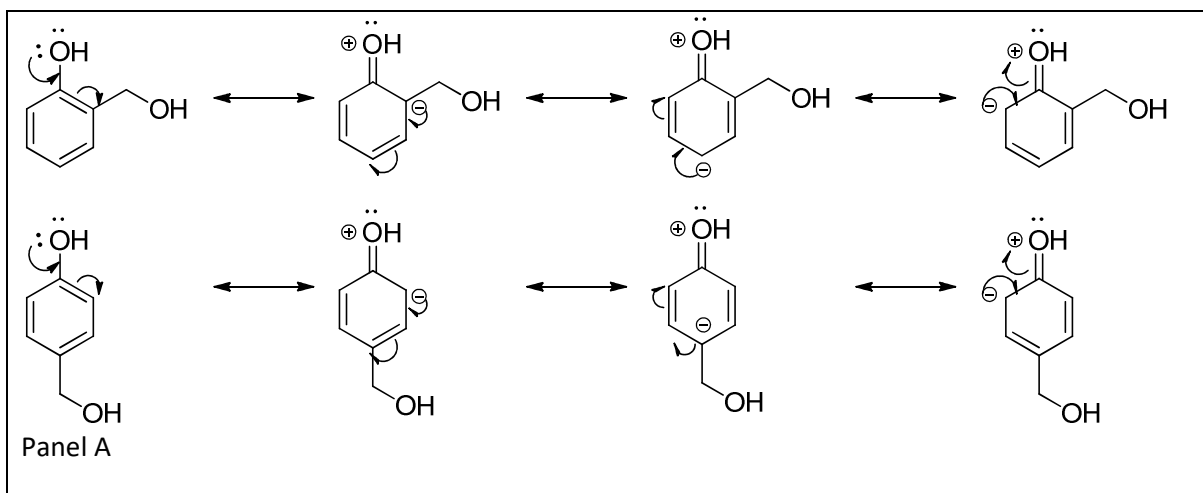
<b>Substrate</b>	<b>pH</b>	<b>X<sub>3h</sub></b>	<b>S<sub>Ald, 30%</sub></b>	<b>S<sub>Acid, 30%</sub></b>	<b>SCO<sub>2</sub>/6, X<sub>3h</sub></b>
		(%)	(%)	(%)	(%)
2-HBA	6	55	9	<b>0</b>	9.7
2-HBA	11	41	28	<b>0</b>	low

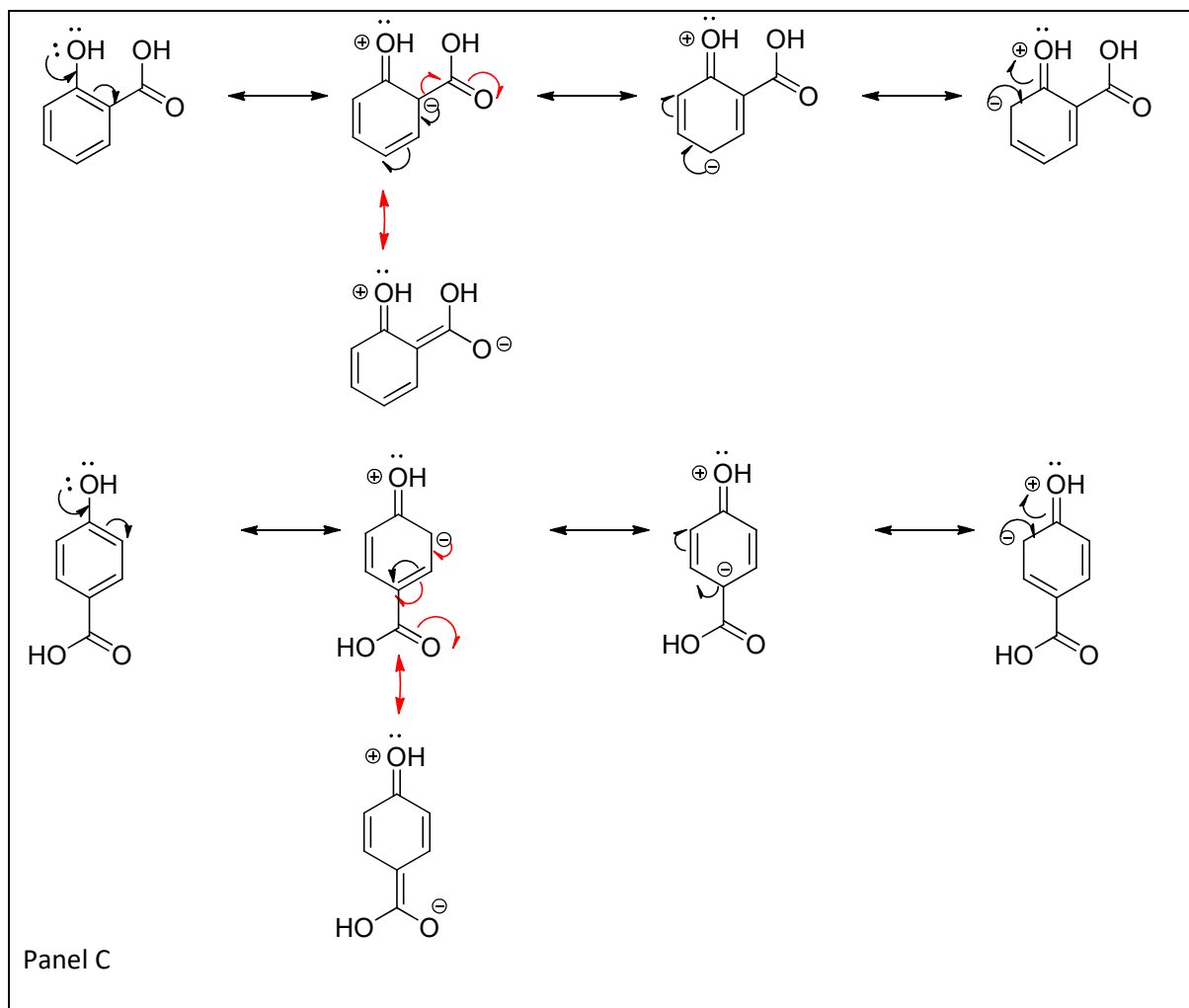
salicylic aldehyde	6	85	8	41
salicylic aldehyde	11	33	5	52
salicylic acid	3.6	45		8.7
salicylic acid	6	45		3.9
salicylic acid	11	46		1.2
4-hydroxybenzoic acid	11	26		2.5

X=conversion; S=selectivity.  $X_{3h}$ : conversion after 3h irradiation.  $S_{Ald, 30\%}$ : aldehyde selectivity after 30% conversion.  $S_{Acid, 30\%}$ : salicylic acid selectivity after 30% conversion. The  $CO_2$  selectivities were considered after 3h of reaction ( $X_{3h}$ ).



**Fig. 8.** Photocatalytic oxidation of salicylic aldehyde (full symbols) to salicylic acid (empty symbols) at pH 6 (◆) and 11 (▲). Salicylic acid concentrations are reported in the right ordinate.





**Fig. 9.** A comparison between 2-HBA and 4-HBA, corresponding partial oxidation products 2- and 4- aldehydes and related 2-and 4-acids resonance structures respectively.

## Conclusions

In this work selective photocatalytic oxidation of salicyl alcohol was investigated under environmental friendly conditions in the presence of some home prepared and commercial  $\text{TiO}_2$  samples. The photocatalysts were characterized and the effects of crystallinity degree, pH and hole trap presence (ethanol) on the photocatalytic activity and product selectivity were studied. High alcohols conversion and product selectivity values were obtained at basic conditions, and by using well crystalline  $\text{TiO}_2$  samples. By increasing the added concentration of ethanol as a hole trap, the activity values considerably decreased while the selectivity values increased slightly. 4-Hydroxybenzyl alcohol was also used as the starting substrate to

study the influence of the position of the substituent group. Selectivity to the corresponding aldehyde and acid was much higher for 4-HBA than 2-HBA due to the less tendency of the first substrate (more stable to the oxidant attacks) to give rise to a complete mineralization and probably to open ring intermediates products. This work demonstrates that the selectivity depends on both the photocatalyst and substrate, and the different photocatalyst parameters (as crystallinity degree) can play a different role in the presence of different substrates. It would be useful as future work to attempt a spectroscopic investigation, that could be difficult due to the presence of OH groups both in the substrates and on the surface of the photocatalysts, to correlate conversion and selectivity of 2-hydroxybenzyl alcohol and 4-hydroxybenzyl alcohol to the position of the OH substituent.

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#### **References**

- [1] M. Schiavello, *Photocatalysis and Environment. Trends and Applications*; Kluwer: Dordrecht, The Netherlands, 1988.
- [2] M. A. Fox, M. Dulay, *Heterogeneous Photocatalysis*, *Chem. Rev.* 93 (1993) 341-357.
- [3] A. Mills, S. Le Hunte, *An Overview of Semiconductor Photocatalysis*, *J. Photochem. Photobiol. A* 108 (1997) 1-35.
- [4] J.-M. Herrmann, *Heterogeneous Photocatalysis: Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants*, *Catal. Today* 53 (1999) 115-129.

- [5] J.-M. Herrmann, Fundamentals and Misconceptions in Photocatalysis, *J. Photochem. Photobiol. A* 216 (2010) 85-93.
- [6] V. Augugliaro, G. Camera-Roda, V. Loddo, G. Palmisano, L. Palmisano, J. Soria, S. Yurdakal, Heterogeneous photocatalysis and photoelectrocatalysis: From unselective abatement of noxious species to selective production of high-value chemicals, *J. Phys. Chem. Lett.* 6 (2015) 1968-1981.
- [7] S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro, L. Palmisano, Nanostructured rutile TiO<sub>2</sub> for selective photocatalytic oxidation of aromatic alcohols to aldehydes in water, *J. Am. Chem. Soc.* 130 (2008) 1568-1569.
- [8] F. Parrino, M. Bellardita, E.I. García-López, G. Marcì, V. Loddo, L. Palmisano, Heterogeneous photocatalysis for selective formation of high value-added molecules: some chemical and engineering aspects, *ACS Catal.* 8 (2018) 11191-11225.
- [9] J. Kou, C. Lu, J. Wang, Y. Chen, Z. Xu, R. S. Varma, Selectivity Enhancement in Heterogeneous Photocatalytic Transformations, *Chem. Rev.* 117 (2017) 1445-1514.
- [10] M. Bellardita, V. Loddo, G. Palmisano, I. Pibiri, L. Palmisano and V. Augugliaro, Photocatalytic green synthesis of piperonal in aqueous TiO<sub>2</sub> suspension, *Appl. Catal. B* 144 (2014) 607-613.
- [11] S. Higashida, A. Harada, R. Kawakatsu, N. Fujiwara, M. Matsumura, Synthesis of a coumarin compound from phenanthrene by a TiO<sub>2</sub>-photocatalyzed reaction, *Chem. Commun.* (2006) 2804-2806.
- [12] M. Bellardita, E. García-López, G. Marcì, B. Megna, F.R. Pomilla, L. Palmisano, Photocatalytic conversion of glucose in aqueous suspensions of heteropolyacid-TiO<sub>2</sub> composites, *RSC Adv.* 5 (2015) 59037-59047.
- [13] H. Yoshida, H. Yuzawa, M. Aoki, K. Otake, H. Itoh, T. Hattori, Photocatalytic hydroxylation of aromatic ring by using water as an oxidant, *Chem. Commun.* (2008) 4634-4636.

- [14] X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao, Selective Formation of Imines by Aerobic Photocatalytic Oxidation of Amines on TiO<sub>2</sub>, *Angew. Chem. Int. Ed.* 50 (2011) 3934-3937.
- [15] M. Bellardita, V. Augugliaro, V. Loddo, B. Megna, G. Palmisano, L. Palmisano, M.A. Puma, Selective oxidation of phenol and benzoic acid in water via home-prepared TiO<sub>2</sub> photocatalysts: distribution of hydroxylation products, *Appl. Catal. A* 441- 442 (2012) 79- 89.
- [16] C. Pruden, J. Pross, Y. Li, Photoinduced reduction of aldehydes on titanium dioxide, *J. Org. Chem.* 57 (1992) 5087-5091.
- [17] M. Bellardita, G. Camera-Roda, F. Parrino, V. Loddo, G. Palmisano, Coupling of membrane and photocatalytic technologies for selective formation of high added value chemicals, *Catal. Today* 340 (2020) 128-144.
- [18] K. Park, H. Joo, K. Ahn, K. Jun, One Step Synthesis of 4-Ethoxy-1,2,3,4-Tetrahydroquinoline from Nitroarene and Ethanol: A TiO<sub>2</sub> Mediated Photocatalytic Reaction *Tetrahedron Lett.* 36 (1995) 5943-5946.
- [19] M. Bellardita, A. Di Paola, E. García-López, V. Loddo, G. Marcì, L. Palmisano, Photocatalytic CO<sub>2</sub> Reduction in Gas-Solid Regime in the Presence of Bare, SiO<sub>2</sub> Supported or Cu-Loaded TiO<sub>2</sub> Samples, *Curr. Organic Chem.* 17 (2013) 2440-2448.
- [20] S.O. Flores, O. Rios-Bernij, M.A. Valenzuela, I. Córdova, R. Gómez, R. Gutiérrez, Photocatalytic reduction of nitrobenzene over titanium dioxide: by-product identification and possible pathways, *Top. Catal.* 44 (2007) 507-511.
- [21] A. Hakki, R. Dillert, D. Bahnemann, Photocatalytic conversion of nitroaromatic compounds in the presence of TiO<sub>2</sub>, *Catal. Today* 144 (2009) 154-159.
- [22] F. Parrino, V. Loddo, V. Augugliaro, G. Camera-Roda, G. Palmisano, L. Palmisano, S. Yurdakal, Heterogeneous photocatalysis: Guidelines on experimental setup, catalyst

- characterization, interpretation and assessment of reactivity, *Catal. Rev. Sci. Eng.* 61 (2019) 163-213.
- [23] M. Bellardita, E. García-López, G. Marci, L. Palmisano, Photocatalytic formation of H<sub>2</sub> and value-added chemicals in aqueous glucose (Pt)-TiO<sub>2</sub> suspension, *Int. J. Hydrogen Energ.* 41 (2016) 5934-5947.
- [24] O. Carp, C.L. Huisman, A. Reller, Photoinduced Reactivity of Titanium Dioxide. *Prog. Solid State Chem.* 32 (2004) 33-177.
- [25] S.-D. Mo, W.Y. Ching, Electronic and Optical Properties of Three Phases of Titanium Dioxide: Rutile, Anatase, and Brookite, *Phys. Rev. B Condens. Matter.* 51 (1995) 13023-13032.
- [26] X. L. Wang, A. Kafizas, X.O. Li, S.J.A. Moniz, P.J.T. Reardon, J.W. Tang, I.P. Parkin, J.R. Durrant, Transient Absorption Spectroscopy of Anatase and Rutile: The Impact of Morphology and Phase on Photocatalytic Activity, *J. Phys. Chem. C* 119 (2015) 10439-10447.
- [27] Y.-F. Li, U. Aschauer, J. Chen, A. Selloni, Adsorption and Reactions of O<sub>2</sub> on Anatase TiO<sub>2</sub>, *Acc. Chem. Res.* 47 (2014) 3361-3368.
- [28] M. Buchalska, M. Kobielski, A. Matuszek, M. Pacia, S. Wojtyła, W. Macyk, On Oxygen Activation at Rutile and Anatase-TiO<sub>2</sub>, *ACS Catal.* 5 (2015) 7424-7431.
- [29] D. Janež, S. Kreft, Salicylaldehyde is a characteristic aroma component of buckwheat groats, *Food Chem.* 109 (2008) 293–298.
- [30] D.R. Palleros (2000). *Experimental organic chemistry*. New York: John Wiley & Sons. p. 494. ISBN 978-0-471-28250-1.
- [31] P. Scherrer, *Nachr. Ges. W. Gottingen*, Determination of the size and internal structure of colloidal particles using X-rays, *Math. Phys. Kl.* 2 (1918) 96–100.
- [32] M. Bellardita, A. Di Paola, B. Megna, L. Palmisano, Determination of the crystallinity of TiO<sub>2</sub> photocatalysts, *J. Photochem. Photobiol. A*, 367 (2018) 312-320.



- [33] V. Augugliaro, H. Kisch, V. Loddo, M.J. López-Muñoz, C. Márquez-Álvarez, G. Palmisano, L. Palmisano, F. Parrino, S. Yurdakal, Photocatalytic oxidation of aromatic alcohols to aldehydes in aqueous suspension of home prepared titanium dioxide. 1. Selectivity enhancement by hole traps, *Appl. Catal. A* 349 (2008) 182-188.
- [34] V. Augugliaro, H.A. Hamed El Nazer, V. Loddo, A. Mele, G. Palmisano, L. Palmisano, S. Yurdakal, Partial photocatalytic oxidation of glycerol in TiO<sub>2</sub> water suspensions. *Catal. Today* 151 (2010) 21-28.