Catalysis Today xxx (xxxx) xxx



Contents lists available at ScienceDirect

Catalysis Today



journal homepage: www.elsevier.com/locate/cattod

Aqueous selective photocatalytic oxidation of salicyl alcohol by TiO₂ catalysts: Influence of some physico-chemical features

Sedat Yurdakal^a, Marianna Bellardita^{b,*}, Ivana Pibiri^c, Leonardo Palmisano^b, Vittorio Loddo^b

^a Kimya Bölümü, Fen-Edebiyat Fakültesi, Afyon Kocatepe Üniversitesi, Ahmet Necdet Sezer Kampüsü, 03200 Afyonkarahisar, Turkey

^b Dipartimento di Ingegneria, University of Palermo, Viale delle Scienze Ed. 6, Palermo 90128, Italy

^c Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche (STEBICEF), University of Palermo, Viale delle Scienze Ed. 16-17, Palermo 90128, Italy

ARTICLE INFO

Keywords: Photocatalysis Salicyl alcohol Salicylaldehyde Salicylic acid Selective oxidation TiO₂ Environmental friendly conditions

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_2 (Merck and Aeroxide P25) samples under UVA irradiation. The photocatalysts were characterized by using BET, XRD, SEM and/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_2 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 role of the para position of the substituent group. In order to clarify the different selectivity of the products, various experiments have been also performed starting from the products; these results indicate that the selectivity is also strongly dependent on the stability of the formed products under the experimental conditions used. By concluding, this article reports that the conversion and selectivity values for the studied reaction depend both on the TiO₂ type and on the substrate.

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_2 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 [10–17] or via reductive pathways [18–22].

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

* Corresponding author. *E-mail address:* marianna.bellardita@unipa.it (M. Bellardita).

https://doi.org/10.1016/j.cattod.2021.06.030

Received 5 October 2020; Received in revised form 11 May 2021; Accepted 25 June 2021 Available online 10 July 2021 0920-5861/© 2021 Elsevier B.V. All rights reserved.



Fig. 1. XRD patterns of Aeroxide P25, Merck and home prepared (HPA) photocatalysts. A = Anatase. R = Rutile.

 Table 1

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

Catalyst	Phase	Primary particle size (nm)	Crystallinity (%)	A.S.S. (m ² g ⁻¹)
Merck	А	60	79	10
P25	$\mathbf{A} + \mathbf{R}$	25.0 (A) 33.0 (R)	37 (A) 62 (R)	50
HPA	Α	35	24	165
HPA-600-2 h	А	139	35	43
HPA-600-8 h	А	150	46	34

A = Anatase, R = rutile.

of gas, temperature, type and quantity of photocatalyst, and initial pH appear to be essential [8,9,23].

 TiO_2 is the most used photocatalyst, since it is highly photoactive, cheap, and resistant to photocorrosion. The most common polymorphs of TiO_2 are anatase, rutile and brookite which have different intrinsic electronic and surface physicochemical properties [24–29] 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 [30]. Salicylic acid, derived from the metabolism of salicin (an alcoholic β -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) [31].

Photocatalytic oxidation of 4-hydroxybenzyl alcohol using a commercial ZnO in water under UVA irradiation was investigated [32]. The effect of substrate concentration and absence/presence of isopropyl

alcohol in the product distribution was examined. The main oxidation products were 4-hydroxybenzaldehyde, 3,4-dihydroxybenzyl alcohol, and hydroquinone. By increasing the substrate concentration, 3,4-dihydroxybenzyl alcohol yield decreased significantly. Moreover, in the presence of isopropyl alcohol, no 3,4-dihydroxybenzyl alcohol as a product was detected, and hydroquinone yields increased by increasing the substrate concentration. Also, the reaction rate decreased significantly but 4-hydroxybenzaldehyde selectivity increased. 4-Hydroxybenzyl alcohol was oxidized to 4-hydroxybenzaldehyde in the presence of a commercial (Sigma Aldrich, rutile) and home-prepared rutile TiO2 photocatalysts in water at neutral pH and under UV-Vis irradiation [33]. Only 13% and 8.5% 4-hydroxybenzaldehyde selectivity values were obtained using home-prepared and Sigma-Aldrich catalysts, respectively. Marotta and co-workers [34] studied the photocatalytic oxidation of benzyl alcohols (i.e., 2-HBA and 4-HBA) in water under UV irradiation using a commercial TiO₂ catalyst (Sigma Aldrich, anatase). This work [34], different from the present investigation, was performed in deaerated and very acidic conditions (pH = 2) in the presence of Cu^{2+} ion (0.5 mM) as electron trap instead of oxygen (usually used by other researchers). After 2 h of irradiation, conversions of 42% and 39% were obtained for 2-HBA and 4-HBA, respectively. The selectivity values after 2 h towards the corresponding aldehvde and acid were ca. 43% and 12% for 2-HBA and 56% and 20% for 4-HBA.

Homogeneous photocatalytic oxidation of 2-HBA was also investigated using 2-methoxybenzaldehyde as a catalyst, and almost no 2hydroxybenzaldehyde selectivity (0.6% for 50% conversion) was obtained [35]. The same reaction was also performed by using Degussa P25 and a home-prepared anatase TiO_2 catalyst in water under UV–Vis irradiation and at neutral conditions. Only 7.5% and 8% selectivity values (for 50% conversion) towards aldehyde were obtained using Degussa P25 and the home-prepared sample, respectively.

In this work, the photocatalytic oxidation of salicyl alcohol (2hydroxybenzyl alcohol) to salicylaldehyde and salicylic acid is reported. The reaction was performed under environmental friendly conditions in the presence of home-prepared (HP) and commercial TiO₂ 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, and photocatalytic experiments using the partial oxidation product of 2-hydroxybenzyl alcohol and 4-hydroxybenzyl alcohol as the starting substrates were performed to explain the obtained results.

2. Experimental

2.1. Materials

Titanium oxysulfate hydrate (TiOSO₄·xH₂O 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 TiO₂ samples (Merck and Aeroxide P25) were used as reference photocatalysts.

2.2. Samples preparation

25 g of TiOSO₄xH₂O were added to 100 mL of distilled water in a Teflon vessel. The solution was heated at 180 °C for 2 h 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 labeled as HPA, where A refers to anatase TiO₂ polymorphic phase. In order to promote the powder crystallization, two different aliquots were calcined at 600 °C for 2 h and 8 h respectively. These samples were named HPA-600-2 h and HPA-600-8 h.



Fig. 2. SEM (HPA, Aeroxide P25) and TEM (Merck, HPA, HPA-600-2 h) images of TiO₂ samples, respectively.

Table 2

Photocatalytic activity results of 2-HBA (0.5 mM) under UV irradiation for different pH's in the presence of the commercial TiO₂ sample Merck. X = conversion; S = selectivity. X₃₄ h: conversion after 4 h irradiation. S_{ald,30%}: salicylaldehyde selectivity after 4 h of irradiation and at 30% conversion, respectively. S_{acid,4} h: salicylic acid selectivity after 4 h of irradiation.

pН	$X_{4 h}$	S _{Ald,4 h}	S _{Ald,30%}	S _{acid,4 h}
3.0	37	11	12	0.0
5.3	52	7.4	9.0	0.3
11	53	22	32	1.3

2.3. Samples characterization

The X-ray diffraction (XRD) analysis of the samples was performed by a Philips diffractometer using the Cu K α (k = 1.5406 Å) radiation at 40 kV and a current of 30 mA with a 20 scan rate of 1.28° min⁻¹. The primary particle size and the crystallinity of the samples were

determined by using the Scherrer equation [36] and the Bellardita et al. method [37], 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 N₂/He mixture 30/70 (v/v) for 0.5 h at 523 K.

Nitrogen adsorption-desorption measurements were acquired by using a Micromeritics ASAP 2020 apparatus. The samples were degassed below 1.3 Pa at 200 °C prior to the measurement. The pore size distributions (PSD's) were obtained by using the Barrett Joyner Halenda (BJH) method applied both on the adsorption and desorption branches of the isotherms.

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.



Fig. 3. Photocatalytic oxidation of 2-HBA (full symbols) to salicylaldehyde (empty symbols) at pH 3 (**A**), 5.3 (**♦**) and 11 (**●**) by using Merck. Aldehyde concentrations are reported in the right ordinate.

Table 3

Photocatalytic activity results of 2-HBA (0.5 mM) under UV irradiation in the presence of ethanol as hole trap at pH 11 by using commercial TiO₂ sample Merck. X = conversion; S = selectivity. X_{4 h}: conversion after 4 h irradiation. S_{ald,4 h} and S_{ald,30%}: salicylaldehyde selectivity after 4 h of irradiation and at 30% conversion, respectively. S_{acid,4 h}: salicylic acid selectivity after 4 h of irradiation.

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



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

Table 4

Photocatalytic activity results of 4-HBA (0.5 mM) under UV irradiation at pH 11. X = conversion; S = selectivity. X₄ h: the conversion after 4 h irradiation. S₄ h and S_{Ald,30%}: 4-hydroxybenzyl aldehyde selectivity after 4 h and at 30% conversion, respectively. S_{acid,4} h: 4-hydroxybenzoic acid selectivity after 4 h irradiation.

Catalyst	$X_{4 h}$ (%)	S _{Ald,4 h} (%)	S _{Ald,30%} (%)	S _{acid,4 h} (%)
Merck	48	38	48	9.1
P25	48	36	40	8.5
HPA	19	40		0
HPA-600-2 h	38	33	35	3.8
HPA-600-8 h	42	35	37	5.5

2.4. Photocatalytic experiments

Aqueous partial oxidation of 2-hydroxybenzyl alcohol (2-HBA) and 4-hydroxybenzyl alcohol (4-HBA) along with additional selected tests starting from the products were 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 (Fig. S1). 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 experiments were carried out at ca. 30 °C and atmospheric air was used as the oxygen source. The lamps were switched on 30 min after the TiO₂ 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 μ m membranes for the quantitative determination of the substrates and their intermediates. The experiments were carried out twice, and the differences between two of them were about 2%.

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 \times 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 mL 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 CO₂.

3. Results and discussion

Fig. 1 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° , 48.08° , 54.58° can be attributed to the anatase TiO₂ phase, while those at $2\Theta = 27.5^{\circ}$, 36.5° , 41.0° , 54.1° , 56.5° 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 ($169 \text{ m}^2/\text{g}$) and a significant decrease was observed after calcination. On the contrary, the crystallites size increased with the thermal treatment, as expected.

In Fig. S2 are reported the nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves (inset) of the HPA and HPA-600-2 h samples. They display Type IV isotherms with hysteresis loops at relative pressure between 0.5 and 1.0 and between 0.7 and 1, suggesting the contemporaneous presence of mesopores (2–50 nm) for HPA and macropores (> 50 nm) for HPA-600-2 h, respectively [38]. The hysteresis curve is type H3 and can been associated to slit-like pores formed by plate-like particles. After the thermal treatment an increase in the pore size distribution is observed.

XPS spectra of similar samples (the TiO₂ samples were prepared starting from TiOSO₄ by thermal treatment in a Pyrex bottle at 100 °C and successively calcined at different temperatures) were acquired in a previous study [39]. The spectra revealed the Ti 2p peak at 459.5 \pm 0.2 eV which is typical of Ti⁴⁺ and the presence of residual sulfur quantities. In fact, the amount of residual sulfur was low in all of the samples (S/Ti atomic ratio equal to ca. 0.1) and scarcely influenced by temperature and duration of calcination. The spectra of the samples calcined at 600 °C for 3 h and 10 h were similar to those of the non-calcined sample.

Fig. 2 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_2 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-600-2 h sample due to sintering of the aggregates after heat treatment.

Many commercial and home-prepared TiO_2 samples were tested for the partial oxidation of 2-HBA at pH 11 with the aim to compare their photoactivity as far as both the conversion of the substrate and the selectivity towards the aldehyde are concerned. The results are reported in Table S1. The best results were obtained in the presence of two commercial samples (Merck and P25) and only one of the home prepared (HPA).

In Table 2 (Fig. S3) the photocatalytic activity results of 2-HBA oxidation by using TiO_2 Merck are reported at different pH's. At pH's



Fig. 5. Photocatalytic oxidation of 4-HBA (
to 4-hydroxybenzaldehyde (
) and 4-hydroxybenzoic acid (
) at pH 11 in the presence of Merck.



Scheme 1. The scheme of photocatalytic oxidation of 2-HBA and 4-HBA.

Table 5

Photocatalytic activity results (substrates initial concentration 0.5 mM) in water under UV irradiation for different pH's by using Merck TiO₂. X = conversion; S = selectivity. X_{3 h}: conversion after 3 h irradiation. S_{Ald,30%}: aldehyde selectivity after 30% conversion. S_{Acid,30%}: salicylic acid selectivity after 30% conversion. The CO₂ selectivity's was considered after 3 h of reaction (X_{3 h}).

Substrate	pН	X _{3 h} (%)	S _{Ald,30%} (%)	S _{Acid,30%} (%)	S _{CO2} /6, X _{3 h} (%)
2-HBA	6	55	9	0	9.7
2-HBA	11	41	28	0	low
salicylaldehyde	6	85		8	41
salicylaldehyde	11	33		5	52
salicylic acid	3	45			8.7
salicylic acid	6	45			3.9
salicylic acid	11	46			1.2
4-hydroxybenzoic acid	11	26			2.5

5.3 and 11, significant alcohol conversion was observed (ca. 52%), whilst at pH 3 just 40% conversion was obtained after 4 h 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 TiO₂ 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 cannot 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 TiO₂ 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 $pK_a = 9.92$, whilst the TiO₂ surface is positively charged being the pH value of 3 below the zero charge point [16]. Therefore, the interaction between 2-HBA and TiO2 surface was possibly very weak, the OH⁻ species concentration low and consequently the activity less significant than at pH 11. Moreover, at 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 observed in a previous work concerning the partial oxidation of 4-methoxybenzyl alcohol to the corresponding aldehyde [7], where it was reported that higher activity and product selectivity were obtained at low pH's. Therefore, the pH effect on the activity and product selectivity depends also on the structure of the substrate.

The most important factor addressing the product 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 salicylaldehyde was very stable in a basic water environment in the presence of TiO_2 and irradiation, and therefore it underwent a low



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

degradation (see Table 5). It can be noticed that almost no selectivity to salicylic acid was found. Probably, the produced acid was easily decomposed to open ring products and CO₂. 2-HBA and salicylaldehyde concentrations during irradiation time at different pH's are plotted in Fig. 3. As the irradiation time increases, a progressive decrease in 2-HBA concentration and a simultaneous increase in salicylaldehyde can be noted. At pH = 3 the degradation of alcohol is slower, and increases at higher pH values. The maximum aldehyde concentration (ca. 0.057 mM) was obtained at pH 11.

In Table 3 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. Therefore, the presence of ethanol as a hole trap was detrimental for the oxidation of 2-HBA and beneficial for selectivity in accordance to what reported in our previous work for the oxidation of benzyl alcohol [33]. When high amount of ethanol was added (i.e., 5 mM), a drastic reduction of the 2-HBA oxidation occurred as it competed with the main substrate for the holes.

Fig. 4 shows the photocatalytic activity results of 2-HBA performed at pH 11 by using HP and commercial samples. In particular the 2-HBA conversion and the selectivity to the corresponding aldehyde and acid after 4 h of irradiation are compared. Furthermore, to allow a more direct comparison between the different samples, the selectivity towards aldehyde was also calculated for the same alcohol conversion (30%). Merck, P25 and HP-600-8 h samples showed the highest conversion values, but the selectivity was maximum with the Merck one (Table S2). For the HP samples, the photocatalytic activity also increased by increasing the crystallinity. Indeed, the most crystalline HPA sample (HPA-600-8 h) showed a higher conversion with respect to HPA (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 [40].

In the presence of Merck, one of the most crystalline samples, 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 [41].

Table 4 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. 5 and Table 4). In particular, a good interaction on the titania surface can occur for salicylaldehyde and 2-hydroxybenzoic acid in which the functional groups are in the ortho position. Furthermore, these molecules show intramolecular hydrogen bonds, while —OH functional groups in the para position give rise to intermolecular hydrogen bonds (which can lead to dimerization) [42].

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 favor its planar 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_2 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 slightly decreased at the high conversion values. The conversion values obtained with 4-HBA are in agreement with those previously found for 4-methoxybenzyl alcohol [40], and indicate that the least crystalline samples were less oxidant. On the contrary, during the partial oxidation of 4-methoxybenzyl alcohol, the selectivity towards the corresponding aldehyde strongly depended on TiO₂ crystallinity [40]. In particular, the highest selectivity values were obtained with the less crystalline catalysts. The highest product selectivity value for 4-HBA, after 4 h 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 4). Therefore, even for 4-HBA, in the presence of commercial samples, the most crystalline photocatalysts were more oxidant and more selective.

Scheme 1 shows a sketch of 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 CO₂.

Catalysis Today xxx (xxxx) xxx



Fig. 7. A comparison between 2-HBA and 4-HBA, corresponding 2- and 4-aldehydes partial oxidation products and related 2-and 4-acids resonance structures respectively.

S. Yurdakal et al.

Catalysis Today xxx (xxxx) xxx

Fig. 5 shows a representative run of 4-HBA oxidation to 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid performed at pH 11 by using Merck TiO₂. 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 min was virtually negligible. It is very likely, as observed usually in photocatalysis, that long irradiation times favor the formation of open ring unidentified products which subsequently can be mineralized.

Further experiments were performed (Table 5) to highlight the stability/instability of 2-HBA, salicylaldehyde, salicylic acid and 4-hydroxybenzoic acid under neutral and basic conditions. The results show that both the oxidation of 2-HBA and mineralization to CO_2 were more significant at pH 6, evidencing higher tendency to the oxidation at this pH and justifying the lower selectivity values to aldehyde. Salicylaldehyde oxidation was much higher at pH 6 than at pH 11 (conversion after 3 h of irradiation equal to 85 vs 33%, see Fig. 6). These results point out that the 2-HBA partial oxidation product is less stable at low pH and explains the enhanced selectivity to salicylaldehyde at higher pH values. Runs carried out by starting from salicylic acid showed almost the same activity results 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 at pH 11 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. This behavior can be due to a different interaction of the two substrates with the photocatalyst surface probably ascribable to a different adsorption way and/or a different strength of adsorption.

By comparing the resonance structures of each couple of 2- and 4substituted 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. 7), the number and the position of the charges are the same. Consequently, their stability appears virtually the same. Nevertheless, 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 CO₂ selectivity values, divided by 6 for stoichiometric normalization, after 3 h irradiation were also determined. Notably, the highest CO₂ selectivity values were obtained for salicylaldehyde 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 salicylaldehyde oxidation (up to 8%, for 30% conversion) were also low. The above finding suggests that the salicylaldehyde reaction pathway from 2-HBA preferentially proceeds towards mineralization rather than further partial oxidation to salicylic acid.

Although the reported conversion and selectivity values are not very high, the obtained results can be useful to understand the key catalysts physico-chemical features and how they can influence the conversion and selectivity values. A possible future development could be the use of a continuous reactor in the presence of a selective membrane to separate and recover the product formed preventing its further transformation and/or the use of composites TiO_2 based photocatalysts containing specific functionalities to address the formation of the desired compounds.

4. 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 TiO₂ 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 TiO₂ 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 (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 4hydroxybenzyl alcohol to the position of the OH substituent.

CRediT authorship contribution statement

Sedat Yurdakal: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. Marianna Bellardita: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. Ivana Pibiri: Investigation. Leonardo Palmisano: Conceptualization, Writing – review & editing. Vittorio Loddo: Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors thank Dr. Melike Kalkan (University of Ankara, Turkey) for her help in carrying out some photocatalytic tests and Professor Giovanni Palmisano (Department of Chemical Engineering, Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates) for TEM analysis.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2021.06.030.

References

- 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

S. Yurdakal et al.

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 TiO₂ 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, V. Augugliaro, Photocatalytic green synthesis of piperonal in aqueous TiO₂ suspension, Appl. Catal. B 144 (2014) 607–613.
- [11] M. Bellardita, V. Loddo, L. Palmisano, Formation of high added value chemicals by photocatalytic treatment of biomass, Mini Rev. Org. Chem. 17 (2020) 884–901.
- [12] S. Higashida, A. Harada, R. Kawakatsu, N. Fujiwara, M. Matsumura, Synthesis of a coumarin compound from phenanthrene by a TiO₂-photocatalyzed reaction, Chem. Commun. (2006) 2804–2806 (Camb.).
- [13] M. Bellardita, E. García-López, G. Marcì, B. Megna, F.R. Pomilla, L. Palmisano, Photocatalytic conversion of glucose in aqueous suspensions of heteropolyacid–TiO₂ composites, RSC Adv. 5 (2015) 59037–59047.
- [14] 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 (Camb.).
- [15] X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao, Selective formation of imines by aerobic photocatalytic oxidation of amines on TiO₂, Angew. Chem. Int. Ed. 50 (2011) 3934–3937.
- [16] 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 TiO₂ photocatalysts: distribution of hydroxylation products, Appl. Catal. A 441–442 (2012) 79–89.
- [17] C. Pruden, J. Pross, Y. Li, Photoinduced reduction of aldehydes on titanium dioxide, J. Org. Chem. 57 (1992) 5087–5091.
- [18] 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.
- [19] K. Park, H. Joo, K. Ahn, K. Jun, One step synthesis of 4-ethoxy-1,2,3,4-tetrahydroquinoline from nitroarene and ethanol: a TiO2 mediated photocatalytic reaction, Tetrahedron Lett. 36 (1995) 5943–5946.
- [20] M. Bellardita, A. Di Paola, E. García-López, V. Loddo, G. Marcì, L. Palmisano, Photocatalytic CO₂ reduction in gas-solid regime in the presence of bare, SiO₂ supported or Cu-loaded TiO₂ samples, Curr. Org. Chem. 17 (2013) 2440–2448.
- [21] 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.
- [22] A. Hakki, R. Dillert, D. Bahnemann, Photocatalytic conversion of nitroaromatic compounds in the presence of TiO₂, Catal. Today 144 (2009) 154–159.
- [23] 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.
- [24] M. Bellardita, E. García-López, G. Marcì, L. Palmisano, Photocatalytic formation of H₂ and value-added chemicals in aqueous glucose (Pt)-TiO₂ suspension, Int. J. Hydrog. Energy 41 (2016) 5934–5947.

- [25] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, Prog. Solid State Chem. 32 (2004) 33–177.
- [26] 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.
- [27] 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.
- [28] Y.-F. Li, U. Aschauer, J. Chen, A.S. elloni, Adsorption and reactions of O₂ on anatase TiO₂, Acc. Chem. Res. 47 (2014) 3361–3368.
- M. Buchalska, M. Kobielusz, A. Matuszek, M. Pacia, S. Wojtyła, W. Macyk, On oxygen activation at rutile and anatase-TiO₂, ACS Catal. 5 (2015) 7424–7431.
 D. Janeš, S. Kreft, Salicylaldehyde is a characteristic aroma component of
- [30] D. R. Palleros, Experimental Organic Chemistry, John Wiley & Sons, New York,
 [31] D.R. Palleros, Experimental Organic Chemistry, John Wiley & Sons, New York,
- [31] D.R. Palleros, Experimental Organic Chemistry, John Wiley & Sons, New York, 2000, p. 494. ISBN 978-0-471-28250-1.
- [32] C. Richard, F. Bosquet, J.-F. Pilichowski, Photocatalytic transformation of aromatic compounds in aqueous zinc oxide suspensions" effect of substrate concentration on the distribution of products, J. Photochem. Photobiol. A 108 (1997) 45–49.
- [33] S. Yurdakal, V. Augugliaro, Partial oxidation of aromatic alcohols via TiO₂ photocatalysis: the influence of substituent groups on the activity and selectivity, RSC Adv. 2 (2012) 8375–8380.
- [34] R. Marotta, I. Di Somma, D. Spasiano, R. Andreozzi, V. Caprio, An evaluation of the application of a TiO₂/Cu(II)/solar simulated radiation system for selective oxidation of benzyl alcohol derivatives, J. Chem. Technol. Biotechnol. 88 (2013) 864–872.
- [35] G. Scandura, G. Palmisano, S. Yurdakal, B.S. Tek, L. Özcan, V. Loddo, V. Augugliaro, Selective photooxidation of ortho-substituted benzyl alcohols and the catalytic role of ortho-methoxybenzaldehyde, J. Photochem. Photobiol. A 328 (2016) 122–128.
- [36] 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.
- [37] M. Bellardita, A. Di Paola, B. Megna, L. Palmisano, Determination of the crystallinity of TiO₂ photocatalysts, J. Photochem. Photobiol. A 367 (2018) 312–320.
- [38] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure Appl. Chem. 57 (1985) 603–619.
- [39] A. Di Paola, M. Bellardita, L. Palmisano, R. Amadelli, L. Samiolo, Preparation and photoactivity of nanocrystalline TiO₂ powders obtained by thermohydrolysis of TiOSO₄, Catal. Lett. 143 (2013) 844–852.
- [40] 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.
- [41] V. Augugliaro, H.A. Hamed El Nazer, V. Loddo, A. Mele, G. Palmisano, L. Palmisano, S. Yurdakal, Partial photocatalytic oxidation of glycerol in TiO₂ water suspensions, Catal. Today 151 (2010) 21–28.
- [42] A. Katritzky, C.A. Ramsden, J. Joule. Handbook of Heterocyclic Chemistry, 3rd ed., Elsevier, Amsterdam, 2010.