Surface processes in selective photocatalytic oxidation of hydroxybenzyl alcohols by TiO₂ P25

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Abstract

Aryl aldehydes and acids are important industrial intermediates, but their synthesis from the corresponding alcohols often requires the use of high temperatures and harmful solvents and oxidant agents. Heterogeneous photocatalysis represents an interesting option for the partial oxidation of alcohols to aldehydes at room temperature using water as solvent. In this work, the partial photocatalytic oxidation of 2-hydroxybenzyl alcohol (salicyl alcohol) and 4-hydroxybenzyl alcohol to the corresponding aldehydes and acids has been compared, under environmental-friendly conditions, employing TiO₂ P25 as photocatalyst in water. The selectivity to the corresponding aldehydes and acids, under the same experimental conditions, was higher for 4-hydroxybenzyl alcohol than for 2-hydroxybenzyl alcohol owing to its greater stability with respect to oxidant attacks and to the lower adsorption of 4-hydroxybelzaldehyde and 4-hydroxybenzoic acid on the photocatalyst surface. The processes occurring at the oxide surface during the reaction were monitored at the molecular level by FT-IR spectroscopy under *in situ* UV irradiation to get deeper insights into the different behavior of the two alcohols.

Keywords: FT-IR spectroscopy, salicyl alcohol, salicylaldehyde, salicylic acid, environment-friendly oxidation, adsorption.

1. Introduction

Aryl aldehydes are widely employed as intermediates for the production of pharmaceuticals, dyes, and plasticizers. The industrial synthesis of these compounds is based on the selective catalytic oxidation of the corresponding alcohols. In general, the industrial processes are carried out with harmful organic solvents at high temperature and pressure employing oxidant agents, thus producing dangerous wastes {Kantlehner, 2003 #315}. Therefore, it would be highly desirable to develop alternative strategies to carry out these syntheses in more sustainable conditions. In this scenario, photocatalysis could represent an interesting option to obtain the desired products at room temperature using water as solvent {Palmisano, 2011 #325;Chen, 2019 #309;Bellardita, 2021 #324}. However, up to now, semiconductor photocatalysts have been widely employed for the complete degradation of organic molecules to water and carbon dioxide {Konstantinou, 2004 #312;Mino, 2016 #228}, while their use for synthetic purposes is more limited {Chen, 2019 #309;Wang, 2022 #310;Rangarajan, 2020 #308}.

The photocatalytic approach has been already explored for different partial oxidation reactions involving for instance 4-methoxybenzyl alcohol {Tsukamoto, 2011 #332}{Palmisano, 2007 #306}, p-methoxytoluene {Heggo, 2020 #311}, hydroxybenzyl alcohols {Richard, 1997 #318;Yurdakal, 2021 #302}, benzene {Yoshida, 2008 #317}, benzyl alcohol {Feng, 2011 #331}{Colmenares, 2016 #323;Luong, 2021 #307} and 4-methylbenzyl alcohol {Kasap, 2016 #314;Xu, 2018 #313}. In particular, selective oxidation of salicyl alcohol (2-hydroxybenzyl alcohol) produces salicylaldehyde, which is a key precursor for several chelating agents, obtained after condensation with amines, which are interesting for commercial applications. Moreover, further oxidation leads to salicylic acid, which is commonly used in organic synthesis and employed as a food preservative, a bactericide, and an antiseptic. Salicylic acid is also the starting molecule for the synthesis of different pharmaceuticals, including acetylsalicylic acid (aspirin) {Ekinci, 2011 #316}.

In this contribution, we investigated an environmental-friendly process based on the partial photocatalytic oxidation in water of salicyl alcohol (2-hydroxybenzyl alcohol, 2-HBAlc) and 4-hydroxybenzyl alcohol (4-HBAlc) to the corresponding aldehydes and acids, employing TiO_2 P25. The aim was to understand, at the molecular level, why the same catalyst, in identical experimental conditions, can exhibit a remarkably different catalytic behavior with structurally very similar substrates. TiO_2 P25 was chosen because it is considered a benchmark in the field of photocatalysis {Mino, 2012 #140;Ohno, 2001 #305} and was reported to ensure good activity and selectivity in this kind of reactions owing to its excellent crystallinity {Yurdakal, 2021 #302}.

As different photocatalytic results were found with the two starting substrates {Marotta, 2013 #330}{Yurdakal, 2021 #302}, we tried to understand the reason of these experimental findings. In

particular, we studied the interaction of the two alcohols and corresponding aldehydes and acids with the catalyst combining adsorption experiments in solid-liquid regime and FT-IR experiments in controlled atmosphere. Moreover, we tried to disclose the molecular processes occurring at the catalyst surface during the photocatalytic reactions employing a recently developed experimental setup, which allows the acquisition of FT-IR spectra in transmission while simultaneously irradiating the sample with a UV-Vis beam {Mino, 2016 #227;Mino, 2019 #303}.

2. Materials and Methods

2.1 Materials

The TiO_2 used in these experiments was commercial Evonik P25, which is considered a benchmark in the field of photocatalysis owing to its excellent activity. TiO_2 P25 is prepared by flame hydrolysis of $TiCl_4$ and contains a mixture of about 85% anatase and 15% rutile with a specific surface area of about 60 m^2/g {Mino, 2013 #172}.

2-hydroxybenzyl alcohol (salicyl alcohol) (purity > 98%), 2-hydroxybenzyl aldehyde (salicylaldeyde) (99.8%), 2-hydroxybenzoic acid (salicylic acid) (98%), 4-hydroxybenzyl alcohol (> 98%), 4-hydroxybenzyl aldehyde (99.8%) and 4-hydroxybenzoic acid (98%) were purchased from Sigma-Aldrich and used without further purification.

2.2 Adsorption and photocatalytic tests

Adsorption tests were done to evaluate the interaction of the different substrates with the catalyst. 1 g of TiO_2 P25 was added to 100 mL of a 2 mM aqueous solution of the different compounds and the dispersions were left in the dark under stirring for 2 hours to allow the adsorption of the organic compounds onto the catalyst surface. The concentration of the substrate still present in solution after reaching the adsorption-desorption equilibrium was evaluated by HPLC (*vide infra*).

The photocatalytic runs were carried out in a Pyrex cylindric reactor irradiated from the outside by 6 Actinic BL TL MINI 15 W UV Philips lamps. The TiO_2 P25 (concentration 0.2 g L^{-1}) was added to 150 mL of 2-hydroxybenzyl alcohol or 4-hydroxybenzyl alcohol aqueous 0.5 mM solutions and after 30 minutes of stirring in the dark, necessary to allow the adsorption-desorption equilibrium, the lamps were switched on. The pH of the suspension was adjusted to 11 by adding NaOH. Water was circulated on a thimble surrounding the reactor to cut the IR irradiation and avoid the temperature increase. The reactor during the tests was left open to allow the solubilization of the oxygen present in the air; the runs lasted 4 h. Aliquots of the reaction mixture were withdrawn at fixed time and filtered through 0.25 μm membranes to separate the catalyst before the HPLC analyses by a Beckman

Coulter System Gold apparatus. A mixture of 13 mM trifluoroacetic acid aqueous solution and acetonitrile was used as eluent and a Phenomenex Kinetex 5 mm C18 100A column for the quantitative determination of all the compounds.

2.3 FT-IR spectroscopy

Before starting the IR experiments, a solution at 1 mg/mL of the substrate to be investigated was prepared and 200 µL were deposited on 20 mg of TiO_2 P25 powder. Subsequently, the powder was dried at room temperature for 12 hours. Once the powder was dried, the material was pressed into a self-supporting pellet to perform the FT-IR measurements. The pellets were placed in quartz cells equipped with KBr windows designed to carry out spectroscopic measurements in controlled atmosphere and connected to a conventional vacuum line (residual pressure: 1×10^{-5} mbar). A Bruker Equinox 55 spectrometer (resolution: 4 cm^{-1}; detector: DTGS) was employed for the spectra collection, averaging 128 scans.

For *in situ* UV-Vis irradiation during the FT-IR experiments, a Newport 500 W Hg(Xe) arc lamp was employed with a water filter to eliminate the infrared portion of the spectrum. The UV-Vis radiation was focused on the TiO_2 P25 pellet using an aspherical fiber bundle focusing assembly and a large core liquid light guide {Mino, 2016 #227}.

The resulting IR spectra were normalized to the pellet 'optical density' (weight of pellet in mg / area of pellet in cm^2) in order to make differences in absorbance independent from differences in the thickness of the pellets.

3. Results and discussion

### 3.1 Adsorption and photocatalytic experiments in liquid-solid regime

A scheme of the reactions involved in the photocatalytic oxidation of 2-HBAlc and 4-HBAlc occurring in aqueous solutions in presence of O_2 is reported in Figure 1. The initial reaction step could be the interaction of photogenerated holes (h^+) or hydroxyl radicals (•OH) with the substrates producing hydroxybenzaldehyde which is successively oxidized to hydroxybenzoic acid. The over-oxidation products of these industrially relevant molecules are mainly aliphatic species and CO_2.
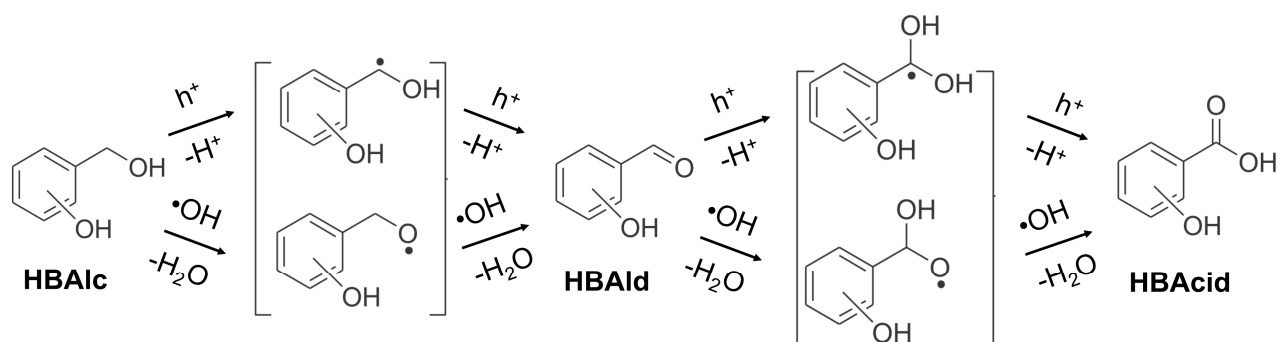
Figure 1. Reaction scheme for the partial photocatalytic oxidation of 2-HBAlc and 4-HBAlc.

The effect of the solution pH on the reaction rate was investigated in detail in a previous publication, which concluded that higher alcohol conversion and product selectivity values could be obtained in basic conditions (i.e. pH = 11) {Yurdakal, 2021 #302}. Therefore, we performed our photocatalytic partial oxidation tests in solid-liquid regime in similar conditions. As visible in Figure 2, we observed a gradual conversion of both hydroxybenzyl alcohols to hydroxybenzaldehyde and, to a smaller extent, to hydroxybenzoic acid. Comparing the results after 4 hours of UV irradiation (Table 1), we can note that the conversion was similar for both alcohols. Conversely, the selectivity to the corresponding aldehyde and acid was much higher for 4-HBAlc than for 2-HBAlc. These data could be rationalized considering the different adsorption properties and stability to photo-oxidation of the reactants and intermediates with substituents in para or ortho positions.

To get deeper insight into this issue, we investigated the adsorption on the TiO_2 P25 surface of the different molecules in dark conditions. As shown in Table 1, the surface concentration (molecules/nm^2) of the substrates with substituents in ortho position was always much higher (i.e. close to the monolayer coverage) than for the corresponding compounds with the OH group in para, being even one order of magnitude higher for the aldehydes and acids. The adsorption mechanisms which explain these remarkably different behaviors will be better discussed while describing the IR results (section 3.2).
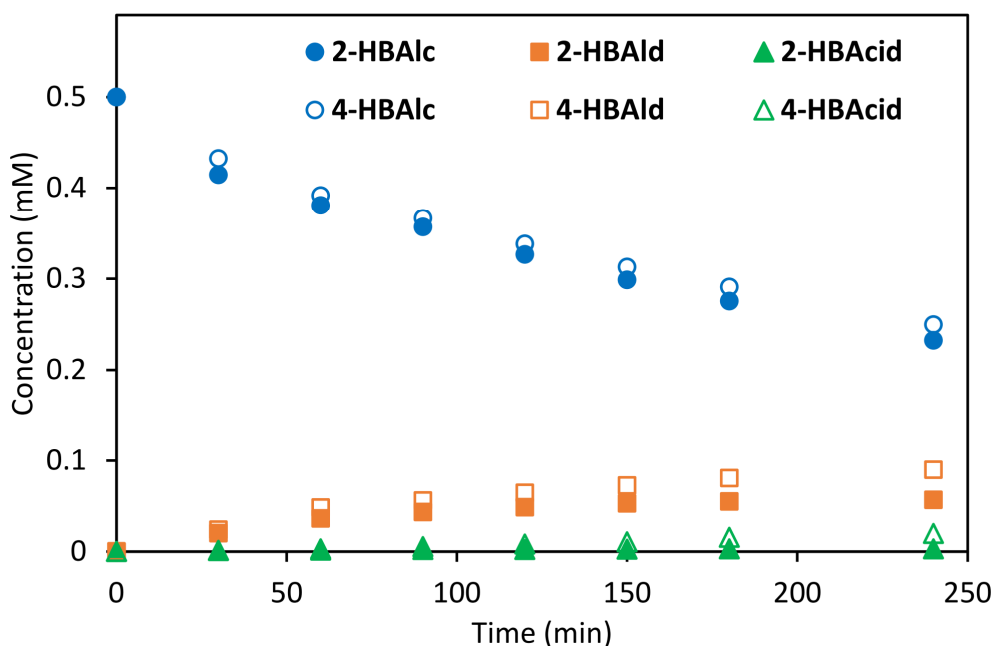
Figure 2. Photocatalytic oxidation of 2-HBAlc to salicylaldehyde and salicylic acid (full symbols) and of 4-HBAlc to 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid (empty symbols) at pH = 11 by using TiO_2 P25.

Table 1. Upper part: photocatalytic activity results for the conversion of 2-HBAlc and 4-HBAlc at pH = 11 after 4 h of UV irradiation. X: conversion; S_{Ald}: selectivity to aldehydes; S_{Acid}: selectivity to acids. Bottom part: adsorption data, as percentage of adsorbed molecules or number of adsorbed molecules per nm^2, for the different substrates in dark conditions.

| Photocatalytic conversion results			
Substrate	**X (%)**	**S_{Ald} (%)**	**S_{Acid} (%)**
2-HBAlc	52	21	1.1
4-HBAlc	48	36	8.5
Dark adsorption results			
Substrate	**Ads (%)**	**Ads (molec/nm^2)**	
2-HBAlc	19	0.46	
4-HBAlc	4.1	0.10	
2-HBAld	80	1.93	
4-HBAld	5.8	0.14	
2-HBAcid	70	1.69	
4-HBAcid	5.4	0.13	

3.2 Investigation of the surface processes by FT-IR spectroscopy

In order to get deeper insight into the surface process occurring at the oxide surface, the photocatalytic reactions have been investigated by FT-IR spectroscopy in controlled atmosphere under *in situ* UV irradiation, after adsorbing on the TiO_2 P25 pellet the target molecule from the aqueous phase (see Materials and Methods section). To mimic the conditions employed in the experiments in liquid-solid regime (section 3.1), during the irradiation the samples were kept in contact with a 20% O_2 – 80% N_2 mixture at 800 mbar and with water vapor at 10 mbar, i.e. a condition which ensures the presence of a multilayer of adsorbed water at the catalyst surface {Mino, 2016 #227}.

Figure 3A shows the IR spectrum of 2-HBAlc adsorbed on TiO_2 P25 (red curve) and the effect of increasing UV irradiation times up to 4 hours (grey to blue curves). In the initial spectrum we can recognize the stretching modes of the aromatic ring centered at 1600 and 1483 cm^{-1}. The latter signal shows a small bathochromic shift with respect to the free molecule in gas phase, suggesting a reduction of the electrodonation from the substituent groups upon surface adsorption {Arana, 2007 #195}. The doublet of bands at 1276 and 1264 and cm^{-1} is due to ν(C-O) stretching modes: they are observed in similar spectral positions also for the strong dissociative adsorption of phenol on TiO_2 P25 {Mino, 2016 #227} and in the spectra of adsorbed catechol {Arana, 2005 #329}. The presence of a multilayer of co-adsorbed water is testified by the intense band at 1635 cm^{-1} ascribed to the δ(H_2O) bending mode {Mino, 2020 #304}. The observed spectral features suggest that 2-HBAlc is strongly adsorbed at the TiO_2 surface, likely in a bidentate configuration, as proposed for catechol (1,2-dihydroxybenzene) on the basis of combined DFT and STM studies {Liu, 2011 #322;Giorgi, 2013 #320}.

During the UV irradiation we can note the progressive decrease of the vibrational features of the alcohol, in particular of the ν(C-O) stretching mode connected to the benzyl moiety, which nearly completely disappears after 4 hours of irradiation. In parallel, we observe the rise of the bands ascribed to the aldehyde, like the ν(C=O) signal at ca. 1655 cm^{-1}.

Moving now to the photoreactivity of 2-HBAld (Figure 3B), we can see that the spectral modifications are more limited with respect to the case of 2-HBAlc. However, after 4 hours of UV irradiation, we can note the presence of some bands typical of the salicylic acid, like the two signal at ca. 1515 and 1350 cm^{-1}, assigned to ν_{as}(COO⁻) and ν_s(COO⁻) vibrations {Borah, 2011 #327;Hu, 2016 #326}. Finally, we can consider the photo-oxidation of 2-HBAcid (Figure 3C), which gives rise to open-ring intermediates, responsible for the appearance of the ν(C=O) signal at ca. 1715 cm^{-1}, likely ascribed to adsorbed oxalates {Hug, 2006 #328;Mino, 2016 #227}. This band could be recognized also in the IR spectra collected after UV irradiation of 2-HBAlc (blue curve in Figure 3A).
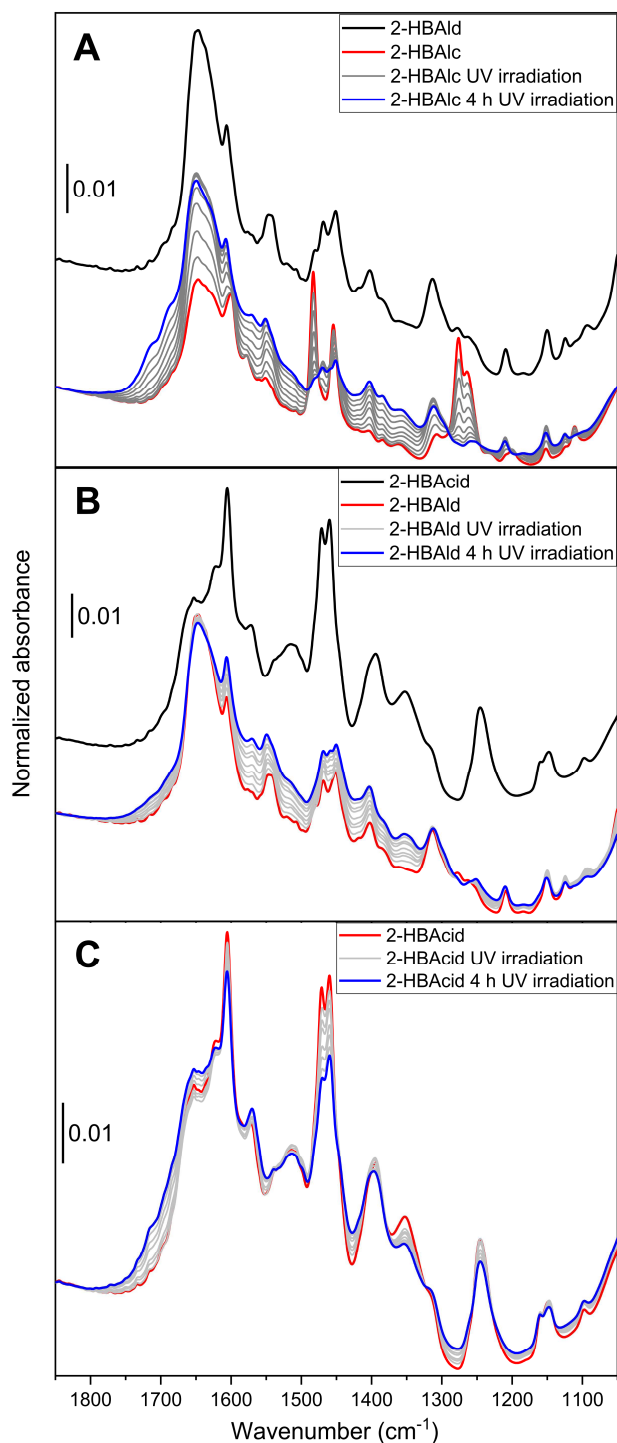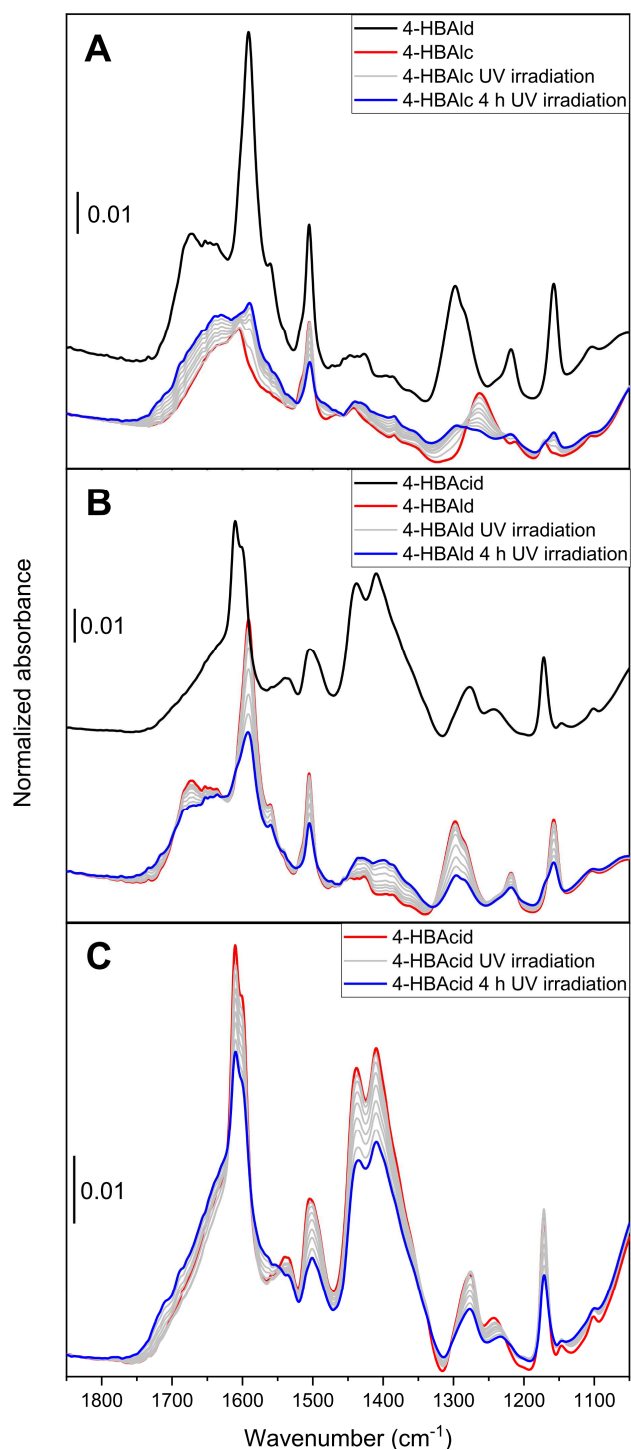
Figure 3. FT-IR spectra of the selected molecules adsorbed on TiO_2 P25 and effect of increasing UV irradiation times up to 4 hours: (A) 2-HBAlc, (B) 2-HBAld and (C) 2-HBAcid.

Figure 4 displays the same IR experiments performed for the molecules with the substituent in para position. The spectrum of adsorbed 4-HBAlc (red curve in Figure 4A) shows the stretching modes of the aromatic ring centered at 1605 and 1505 cm^{-1}. The former signal is gradually converted into the

typical ν(C=C) stretching signal of the 4-HBAld at 1590 cm^{-1} upon UV irradiation. The ν(C-O) vibration gives rise to a single broad band at ca. 1260 cm^{-1}. This spectroscopic feature suggests a possible monodentate adsorption of the molecule on the surface, as proposed in the literature for the interaction of hydroquinone (1,4-dihydroxybenzene) on TiO$_2$ {Arana, 2005 #329}. We can, thus, infer that 4-HBAlc shows a weaker interaction with the catalyst than 2-HBAlc: this conclusion explains the much higher surface adsorption observed in the experiments in liquid-solid regime for the substrates with the substituents in ortho position (see Table 1). A higher adsorption both of the starting alcohol and the corresponding aldehyde and acid (see Table 1) favors the oxidant attack and the complete decomposition to CO$_2$ and H$_2$O, resulting in lower selectivity.

As in the case of salicylaldehyde and salicylic acid, the conversion of 4-HBAld (Figure 4B) and 4-HBAcid (Figure 4C) after 4 hours of UV irradiation in the IR cell is not complete as observed for the alcohols. During the photo-oxidation of 4-HBAld (Figure 4B), we can note the decrease of the ν(C=O) signal at ca. 1670 cm^{-1} and the growth of the bands at ca. 1535 and 1400 cm^{-1}, ascribed to ν_{as}(COO$^-$) and ν_s(COO$^-$) vibrations {Borah, 2011 #327;Hu, 2016 #326}. Concerning the photoreactivity of 4-HBAcid (Figure 4C), we can see the appearance of the ν(C=O) signal at ca. 1715 cm^{-1}, observed also in the oxidation of 2-HBAcid and associated to adsorbed oxalates. This kind of short-chain organic acids has been already observed as reaction intermediate in the photodegradation of different aromatic carboxylic acids {Velegraki, 2008 #333}.

Figure 4. FT-IR spectra of the selected molecules adsorbed on TiO$_2$ P25 and effect of increasing UV irradiation times up to 4 hours: (A) 4-HBAlc, (B) 4-HBAld and (C) 4-HBAcid.

4. Conclusions

The combination of experiments in liquid-solid regime and of IR spectroscopy measurements under *in situ* UV irradiation allowed us to rationalize the different results obtained for the partial photocatalytic oxidation of hydroxybenzyl alcohols with substituents in different positions. In

particular, we observed a similar conversion of both 2-hydroxybenzyl alcohol and 4-hydroxybenzyl alcohol after 4 hours of UV irradiation in water in presence of TiO_2 P25, but the selectivity to the corresponding aldehydes and acids was higher for 4-HBAlc than for 2-HBAlc.

Adsorption experiments in the dark showed a considerably higher adsorption for the compounds with the substituents in ortho position (even more than one order of magnitude higher for the aldehydes and acids). These findings were explained by the spectroscopic data, which showed that 2-HBAlc is strongly adsorbed in a bidentate way, while the interaction of 4-HBAlc is monodentate and weaker. The IR measurements allowed us also to follow the evolution of the surface intermediates formed during the photo-oxidation reactions. The weaker adsorption of the substrates with the substituents in para position favors a greater stability of the reaction intermediates with respect to further oxidant attacks and, thus, ensures a higher selectivity.

References