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# Role of TiO<sub>2</sub>-based photocatalysts on the synthesis of the pharmaceutical precursor benzhydrol by UVA-LED radiation

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#### **Graphical abstract**

#### Highlights

- Benzhydrol formation was evaluated.by photochemical and photocatalytic routes.
- TiO<sub>2</sub>-based materials were synthesized and characterized.

- The photocatalysts were studied under UVA-LED radiation.
- Efficient formation of benzhydrol was achieved using Pd/TiO<sub>2</sub> as photocatalyst.
- Photoluminescence analyses suggest effective electron transfer between TiO<sub>2</sub> and Pd particles.

#### Abstract

The influence of several reactional parameters was investigated on the photocatalytic reduction of benzophenone to the pharmaceutical precursor benzhydrol under UVA-LED radiation. The optical semiconductor titanium dioxide was loaded with 1.0 *wt*.% of noble metals (Pd, Pt and Au) by incipient wetness impregnation method. The TiO<sub>2</sub>-based materials were characterized by various techniques. Results showed that the benzhydrol selectivity is highly influenced by the nature of the solvent and the presence of KOH (acting as nucleophilic agent) The most efficient system was obtained using 2-propanol, 5.0 mM of KOH, and 0.1 g L<sup>-1</sup> of catalyst, achieving 100% selectivity of benzhydrol after 10 min reaction. Among the TiO<sub>2</sub>-based materials, the Pd/TiO<sub>2</sub> showed high efficiency for benzhydrol formation (in absence KOH) with an enhancing of *c.a.* 49% compared with neat TiO<sub>2</sub>. The decrease of photoluminescence intensity observed for Pd/TiO<sub>2</sub> material suggests an effective electron transfer from TiO<sub>2</sub> to Pd nanoparticles.

*Keywords: Photocatalysis; optical semiconductor; fine organic chemicals; Redox reactions; noble metals.* 

#### **1. Introduction**

The high demand of fine organic chemicals including fragrances and flavours, agrochemicals and pharmaceuticals are driving worldwide industry and researchers to

developing new processes affording high selectivity of these chemicals. New perspectives on the development of alternative industrial processes that can be safe, environmentally friendly, and profitable have been attempted [1-4]. Heterogeneous photocatalysis appeared as a promising technology by providing a green alternative to conventional thermal catalytic organic synthesis processes [5-9]. Advantages of photocatalytic processes include the possibility of operating under mild conditions of temperature and pressure, exempt of using hazardous reagents and the prospect of using low energy consumption irradiation sources for reaction activation [10-12]. Benzhydrol (diphenylmethanol, BH) is a precursor commonly used in the pharmaceutical industry for the production of drugs such as antihistamine, antihypertensive and antiallergenic agents[13]. In general, the synthesis of benzhydrol may occur through Grignard reaction (e.g., using ethylmagnesium or phenylmagnesium bromide [14] or by catalytic reduction of benzophenone (BP) using catalysts such as sodium or aluminum amalgams [15, 16]. In organic photochemistry, the reduction of benzophenone by UV irradiation, in the presence of alcohols, is generally considered as a model ketone photoreduction reaction [17, 18]. In such conditions, the formation of benzhydrol, acetone and other intermediates (e.g., benzopinacol and benzopinacolone) occur by hydrogen abstraction from the photoexcited benzophenone in the presence of an alcohol [18]. Schuster et al. [19], described the photoreduction of BP in 2-propanol under UV irradiation, being benzopinacol the main product and BH detected in very low concentrations. Bochet et al. [20] reported the formation of BH by photoreduction of BP in 2-propanol, using potassium hydroxide (KOH) as reaction promoter. The use of TiO<sub>2</sub> as heterogeneous photocatalyst for the reduction of benzophenone was also reported by Escobar et al. [21]. The novelty of this work relies on the application of heterogeneous photocatalysis technology using noble metals-TiO<sub>2</sub> as catalysts, avoiding in this way the addition of

strong bases (such as KOH). The present work explored systematic aspects of the photocatalytic synthesis of the pharmaceutical precursor benzhydrol from benzophenone reduction under an energy-efficient and low-cost light UVA-LEDs as irradiation source.

#### 2. Experimental

#### 2.1 Chemical and methods

Benzophenone (BP,  $(C_6H_5)_2CO \ge 99\%$ ) and 2-propanol ((CH<sub>3</sub>)<sub>2</sub>CHOH, 99.5%) were purchased from Sigma-Aldrich. Potassium hydroxide (KOH,  $\ge$  86%) and benzhydrol (BH,  $(C_6H_5)_2CHOH$ ,  $\ge 99\%$ ) were supplied from Fluka. Benzopinacol (BPC,  $(C_6H_5)_2C(OH)C(C_6H_5)_2OH$ , 99%) was purchased from Alfa Aesar. Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH,  $\ge 99.5\%$ ) was obtained from Panreac. Methanol (CH<sub>3</sub>OH,  $\ge 99\%$ ) was supplied from VWR. Ultrapure water was produced in a Direct-Q Millipore system. TiO<sub>2</sub> Aeroxide<sup>®</sup> P25 (P25, 80% anatase and 20% rutile) powder was obtained from Evonik Degussa Corporation (Essen, Germany). Gold (III) chloride trihydrate (HAuCl<sub>4</sub>.3H<sub>2</sub>O,  $\ge 49\%$ ), palladium (II) chloride (PdCl<sub>2</sub>,  $\ge 99\%$ ) and chloroplatinic acid solution (H<sub>2</sub>PtCl<sub>6</sub>, 8 *wt*.% in H<sub>2</sub>O) were supplied from Sigma-Aldrich.

#### 2.2 Preparation and characterization of the catalysts

Noble metals were loaded on  $TiO_2$  by incipient wetness impregnation method. Briefly, the  $TiO_2$  was placed in a flask, and was sonicated for 30 min. Then, an aqueous solution with the noble metal precursor (1.0 *wt*.%) was added drop by drop into the flask containing the  $TiO_2$  under sonication for 90 min. The final catalysts were calcined under N<sub>2</sub> flow at 200 °C for 1h followed by a H<sub>2</sub> flow at the same temperature for 3 h. The catalysts were labeled as M/TiO<sub>2</sub>, where M corresponds to Au, Pt or Pd.

The specific surface area of the resulting materials was monitored by multipoint analysis of  $N_2$  adsorption isotherms at -196 °C using the Brunauer-Emmett-Teller (BET) method

in a Quantachrome NOVA 4200e apparatus. Transmission electron microscopy (TEM) images were obtained using a LEO 906E instrument operating at 120 kV, equipped with a 4 M pixel 28x28 CCD camera from TRS.

X-ray diffraction (XRD) analysis was conducted in a PANalytical X'Pert MPD apparatus equipped with an X'Celerator detector and secondary monochromator (Cu K $\alpha \lambda = 0.154$ nm, 50 kV, 40 mA; data recorded at a 0.017° step size, 100 s/step). Rietveld refinement with a PowderCell software was applied for identification of the crystallographic phases. X-ray photoelectron spectroscopy (XPS) analysis was performed in a Kratos AXIS Ultra HAS apparatus, using the VISION software for data acquisition and CASAXPS software for data analysis. The analyses were carried out with a monochromatic Al K $\alpha$  X-ray source (1486.7 eV), operating at 15kV (90 W), in FAT (Fixed Analyser Transmission) mode, with a pass energy of 40 eV for regions ROI and 80 eV for survey.

Diffuse reflectance UV–Vis spectra (DRUV-Vis) were conducted in a JASCO V-560 spectrophotometer equipped with an integrating sphere attachment (JASCO ISV-469). The spectra were recorded in diffuse reflectance mode and transformed by the JASCO software to equivalent absorption Kubelka–Munk units.

Photoluminescence (PL) measurements were carried out at room temperature on a JASCO (FP-82000) fluorescence spectrometer with a 150W Xenon lamp as light source.

#### 2.3 Photocatalytic setup

In a typical photocatalytic experiment, a glass-immersion reactor was filled with 100 mL of a 2-propanol solution containing a certain concentration of benzophenone as subtract for benzhydrol synthesis. The solution was magnetically stirred and continuously purged

with argon. The photocatalytic reactions were performed in the absence of KOH and using 1 g L<sup>-1</sup> of catalyst. For comparison purposes, photochemical experiments under homogeneous conditions were also performed, using KOH as a promoter to hydrogen transfer. The reactions were performed under UV light irradiation using four 10 W LEDs with an emission line at 385 nm located axially at a 3.5 cm distance from the reactor walls. The irradiation power of each LED reaching the reactor was  $c.a. 400 \text{ W m}^{-2}$ , which was determined using a UV-Vis spectroradiometer (USB2000+, OceanOptics, USA). Before turning the illumination on, the benzophenone solution was saturated with argon and the first sample was taken after 1h. Then, the solution was irradiated for 1 h and samples were withdrawn regularly from the reactor and analyzed by High Performance Liquid Chromatography (HPLC) using a Hitachi Elite LaChrom instrument equipped with a Diode Array Detector (L-2450), a Purospher Star RP-18 column (250 mm x 4.6 mm, 5 mm particles), and a solvent delivery pump (L-2130) at a fixed flow rate of 1 mL min<sup>-1</sup>. The method starts with an equilibrated mixture of water (A):methanol (B) (20:80) followed by a linear gradient step to A:B (10:90) in 6 min; finally the initial conditions were re-established in a 9 min gradient step and the A:B (20:80) mixture was isocratically eluted for 4 min. The production of benzhydrol and benzophenone consumption during the photocatalytic reactions was followed as function of conversion (X), selectivity (S) and the reaction yield (Y).

#### 3. Results and discussion

#### 3.1 Catalyst characterization

The specific surface area ( $S_{BET}$ ) of the catalysts was determined by N<sub>2</sub> adsorption at -196 °C. As already reported in the literature the  $S_{BET}$  of the commercial Aeroxide<sup>®</sup>

TiO<sub>2</sub> P25 is *c.a.*  $53 \pm 3 \text{ m}^2 \text{g}^{-1}$ . Some reports have also been showed that the deposition of noble metals may improve the adsorption ability of optical semiconductors by promote an enhancing on their specific surface area [22-24]. Yet, in most cases the surface area of the metal-loaded materials is increase by change the textural properties of the semiconductors (*e.g.*, by thermal treatments). In the present study the thermal treatment used for the reduction of the noble metal phase was maintained at 200 °C, which did not interfere with the textural properties of the TiO<sub>2</sub>, *i.e.*, it wasn't notice any change on the S<sub>BET</sub> of the resulted photocatalysts. This observation could be also explain due to the low loading of the noble metal added during the photocatalysts preparation.

Fig. 1 shows representative TEM images of the TiO<sub>2</sub> based photocatalysts used in this study (~ 1 wt.% of each noble metal on TiO<sub>2</sub> P25) and the particles size distribution of the noble metal used in this study. The mean of the each noble metal was investigated by TEM analysis and was based on a count of more than 200 individual nanoparticles. The characteristic structure of TiO<sub>2</sub> P25 particles is shown (Fig. 1a), revealing the presence of spheroidal TiO<sub>2</sub> nanoparticles with an average size near to that of metal particles (30-50 nm). Regarding the results TiO<sub>2</sub> based materials was noticed that the mean of particle size of the noble metals loaded on TiO<sub>2</sub> present a narrow size when compared with the TiO<sub>2</sub> particles size, which difficult their detection. Yet, some spots ranging 20-25 nm are observed on the TiO<sub>2</sub> based materials, which seems to indicate the presence of the noble metals particles on the surface of the photocatalysts. Additionally, elemental mapping obtained by EDXS analysis (Fig. SD1) revealed a good dispersion of the noble metals on the TiO<sub>2</sub> surface.

The X-ray powder diffractograms of neat  $TiO_2$  P25 and noble metals/ $TiO_2$  materials are shown in Figure 2. The presence of crystalline phases (anatase and rutile) of the  $TiO_2$  was

confirmed by XRD measurements, in which the typical diffraction lines such as 25.4° and 27.5°, corresponding to the lattice planes of (101) and (110), respectively can be observed. In addition, comparing the patterns of the neat  $TiO_2$  with the synthesized noble metals/TiO<sub>2</sub> (Fig. 2) no diffraction peaks corresponding to the respective noble metal were detected. This could be attributed to the low amount of noble metals loaded on the TiO<sub>2</sub> surface, which could be beyond the detection limit of the diffractometer.

The surface chemical composition of the noble metal/TiO<sub>2</sub> materials was investigated by deconvolution of the XPS profiles. As displayed in Fig. 3a, the Au/TiO<sub>2</sub> material shows two peaks at binding energy (BE) 87.96 eV and 84.26 eV corresponding to Au  $4f_{5/2}$  and Au  $4f_{7/2}$ , respectively, with spin-orbital splitting photoelectrons at 3.70 eV, which is in agreement with the literature [25, 26]. Regarding the Pt/TiO<sub>2</sub> catalyst (Fig. 3b), it was observed the presence of two peaks in the region of Pt  $4f_{7/2}$  at 71.56 eV and 72.90 eV, corresponding to reduced Pt nanoparticles (Pt<sup>0</sup>) and to Pt<sup>2+</sup> ions, respectively [26-28]. The same evidence was verified at the Pt  $4f_{5/2}$  region, in which two peaks at 74.81 eV and 75.89 eV were also detected (Pt<sup>0</sup> and Pt<sup>2+</sup>, respectively).

The Pd/TiO<sub>2</sub> sample was analyzed before and after (fresh and used samples) the photocatalytic reduction of BP to BH (Fig. 3c and 3d, respectively). Concerning the fresh sample, the XPS deconvolution profiles revealed three Pd species in the Pd  $3d_{5/2}$  region located at 335.30, 336.08 and 338.18 eV, which are generally assigned to Pd<sup>0</sup>, palladium oxide (PdO) and Pd<sup>2+</sup>, respectively [26, 29]. Moreover, in the Pd  $3d_{3/2}$  region the peaks corresponding to the same Pd species (Pd<sup>0</sup>, PdO and Pd<sup>2+</sup>) were also observed with BE of 340.51, 341.30 and 343.19 eV, respectively.

Similar peaks were observed in both sub regions (Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$ ) in the sample collected after the reutilization studies (Fig. 3d), however with different proportions of

the Pd species. From the XPS analyses it was found that the fresh sample only contains 28% of Pd in its reduced form, whereas after the photocatalytic reuse reactions a high amount of Pd<sup>0</sup> species was detected (~68%). This increase in the metallic Pd content may be ascribed to the photoreduction of palladium species during the photocatalytic experiments [30]. In fact, it has been reported that Pd<sup>2+</sup> species may suffer reduction by solvated electrons and 2-propanol when exposed to a light source [31], which corroborate the XPS results obtained for the used photocatalyst sample (Fig. 3d).

Additionally, from DRUV-Vis (Fig. 4a) can be noticed the characteristic plasmon resonance band spectra of the noble metals such as Pt and Pd, corroborate with the TEM images.Moreover, the strong absorption band with onset around 400 nm is observed for TiO<sub>2</sub> being attributed to the bandgap transition of the semiconductor. The Pd/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts a second absorption band is observed in the visible range at 470 nm and 576 nm, respectively, which indicates the capacity of these materials to harvest the light from UV to the visible range. Moreover, in the case of the Pd/TiO<sub>2</sub> catalyst the maximum peak at 470 nm is commonly attributed to d–d transition of Pd<sup>2+</sup> [32], which is in agreement with XPS analysis (Fig. 3c), where these Pd species are well noticed.

The wavelength position of surface plasmon resonance band is commonly related with the size and shape of noble metals particles, however was noticed from TEM images that the size and shape of the particles is maintain independently of the noble metal deposited in TiO<sub>2</sub> surface. Additionally, from Tauc plot obtained by diffuse reflectance UV-Vis spectra (Fig. 4 inset) was observed that a presence of noble metals on TiO<sub>2</sub> particles induce a slight decrease in the bandgap energy of the resulted materials comparing with the bare TiO<sub>2</sub> (3.23 eV). A similar bandgaps were obtained for the TiO<sub>2</sub>-based catalysts Au/TiO<sub>2</sub> (3.10 eV), Pt/TiO<sub>2</sub> (3.08 eV) and Pd/TiO<sub>2</sub> (3.05 eV). These results corroborate

the previous observations by TEM images, which was observed a good distribution and similar particle size of noble metals on TiO<sub>2</sub> surface.

The materials were characterized by photoluminescence (PL) spectroscopy in order to explore the effect of noble metals particles on  $TiO_2$  particles. The PL spectra at room temperature of neat  $TiO_2$  and  $TiO_2$ -based materials under an excitation energy fixed a 280 nm (4.43 eV) are shown in Fig. 5.

The direct bandgap found for TiO<sub>2</sub> (3.23 eV) was confirmed by PL analysis with the presence of intense emission both in the UV and visible range. For the TiO<sub>2</sub>-based materials the bandgap energy was slight decrease, nevertheless an intense quenching of the characteristic bands of TiO<sub>2</sub> was observed, being more pronounced for Pd/TiO<sub>2</sub> material. The extensive quenching of luminescence intensity shows that the noble metals may act as efficient scavengers of photogenerated electrons produced in TiO<sub>2</sub> particles under UV irradiation. Additionally, the PL spectra quenching indicate a decrease on the recombination of photogenerated electron-hole pairs [33], which may lead to higher efficiencies in the photocatalytic reduction process.

#### 3.2 Photo-induced production of benzhydrol

In general, heterogeneous photocatalysis are widely dependent from the reactional parameters, such as catalyst load, initial substrate concentration, solvent used, presence of oxidant/reductant agents, irradiation source, among others. Concerning the photo-induced reduction of benzophenone, the selection of the type of solvent is an important step that need to be considered, due to the ability of the solvent works as a source of hydrogen. Moreover, to achieve the desirable products the photo-reduction of

benzophenone requires the presence of KOH as a promoter of hydrogen transfer [20]. Thus, the effect of selected operation parameters was evaluated for optimization of the benzhydrol production from the photocatalytic reduction of benzophenone. In this sense, to evaluate the photochemical and the heterogeneous photocatalytic regimes for benzhydrol formation a couple of reactions were performed in the absence of KOH. During those experiments, 2-propanol was used as a solvent and the initial concentration of the substrate (benzophenone) was fixed at 1.5 mM. During the heterogeneous photocatalytic reaction, the amount of catalyst was set as 1.0 g L<sup>-1</sup>. The results in terms of photochemical and photocatalytic regimes are displayed in Fig. 6.

Results show that BP is easily converted to produce mainly benzopinacol (BPC) under photochemical (Fig. 6a, filled symbols). The presence of TiO<sub>2</sub> during the photocatalytic reaction tends to increase the selectivity to benzhydrol formation (Fig. 6b), nevertheless BPC remains as a main product (Fig. 6a, open symbols). The photochemical reduction of benzophenone in 2-propanol yielding in benzopinacol and acetone as stable products is well discussed in literature [21, 34, 35]. Briefly, the mechanism start with the molecule of benzophenone absorbing energy (photons) reaching the triplet state, which is the responsible for the intermolecular hydrogen abstraction reaction of photoexcited benzophenone from 2-propanol. In order to obtain high yields of benzhydrol refuting the photochemical regime, a study of catalyst amount (0.05 g L<sup>-1</sup> – 1.25 g L<sup>-1</sup>) and concentration of substrate (0.5 mM – 1.75 mM) was performed (SD2a and SD2b, respectively). It was found higher selectivity and yield for benzhydrol production when the reaction were performed with a catalysts amount of 0.1 g L<sup>-1</sup>, and using an initial concentration of BP of 1.5 mM, therefore the following experiments were performed using these concentrations of catalyst and substrate concentration.

The effect of using 2-propanol (iPrOH), methanol (MeOH) and ethanol (EtOH) as solvents under alkaline medium using a selected concentration of KOH (5.0 mM) as a promoter of hydrogen transfer is depicted in Fig. 7.

The results show 100% of selectivity for BH production after 10 min reaction when iPrOH was used as solvent (Fig. 7b) in the presence of KOH, which indicate that the efficiency of the process is highly influenced by the solvent nature and from the presence of KOH. On the other hand, when MeOH and EtOH were used as solvents the process showed high selectivity for benzopinacol production, however in small concentrations when compared with the results obtained from BP photochemical reduction in iPrOH in the absence of KOH (Fig. 6a). Weiner et al. showed that 2-propanol holds special features due to effective hydrogen bonding for photochemical reduction of benzophenone, however the main product obtained from this reaction was benzopinacol. In a similar study, Waldemar et al. [36] studied the effect of the same alcohol solvents for benzophenone reduction during laser-jet photolysis. Analogous results were obtained, the benzophenone photoreduction in 2-propanol was more selective for benzopinacol production. The same authors describe that effective photoreduction of benzophenone follows the order ability iPrOH > EtOH > MeOH due to the quenching rate constants of triplet-excited benzophenone through intermolecular hydrogen transfer, which are  $7.5 \times 10^6$ ,  $1.9 \times 10^6$  and  $0.21 \times 10^6$  s<sup>-1</sup> M<sup>-1</sup>, respectively [21].

These studies proved that the selection of the alcohol solvents for benzophenone photochemical reduction is crucial. In addition, during this study it was found that the presence of homogeneous (KOH) and heterogeneous (TiO<sub>2</sub>) catalysts led to an increase of on yield BH production. These results seems to be ascribed at two main factors: i) the addition of KOH acting as nucleophilic agent (rich in electron species  $OH^{-}$ ), which will

reacts with the electrophilic species poor in electrons (C=O of the benzophenone), leading to the protonation of the intermediate alkoxide to give an alcohol derivative (in this case benzhydrol) and ketones derivatives; ii) the deoxygenated suspension of  $TiO_2$  in benzophenone in iPrOH is followed by simultaneous oxidation and reduction of adsorbed reactants (Scheme 1).

The photochemical and photocatalytic reduction of benzophenone in 2-propanol show higher formation of benzopinacol (Fig. 6a), which corroborate with the earlier studies [17, 21]. Thus, the effect of KOH as a hydrogen promoter on the photocatalytic reduction of benzophenone was studied by varying the KOH concentration from 1.0 - 10 mM (Fig. 8). No further addition of this agent was conducted during the photocatalytic experiment. For comparison propose the results obtained in absence of KOH (Fig. 6) are also shown.

As expected, the introduction of KOH leads to an increase of the efficiency of the photocatalytic reduction of BP into BH (Fig. 8). Even for the lowest concentration of KOH (1.0 mM), a significant enhancement for BH production was observed with respect to the reaction in the absence of this hydrogen promoter transfer. The optimal concentration of KOH found was 5 mM, which corresponds to the highest selectivity for benzhydrol production, and in this case was not detected the formation of the intermediate benzopinacol.

The present work showed that the photocatalytic regime could be a good candidate for benzophenone reduction to benzhydrol. Nevertheless, in order to obtain higher yield of BH is always required the addition of a nucleophilic agent such as KOH.

As described previously, the photocatalytic activity of TiO<sub>2</sub> can be enhanced by loading of noble metals nanoparticles, seeking for charge separation efficiency. The introduction of noble metal nanoparticles in metal oxide semiconductors is considered one of the most efficient techniques for enhancing their photocatalytic activity. Depending of the wavelength of irradiation and the type of metal, noble metal nanoparticles may improve charge separation as a result of localized electromagnetic field, store electrons driving the Fermi level to more negative potentials, promote electron transfer to adsorbed species and/or increase the light absorption due to surface plasmon and light-trapping effects [37-39]. Moreover, several studies have demonstrated that noble metal nanoparticles can be highly chemoselective for the hydrogenation of molecules containing carbonyl group [15, 40, 41]. Therefore, the study was followed by the loading the Au, Pt and Pd particles into TiO<sub>2</sub>. It has also been reported that in photocatalytic hydrogenation reactions using noble metals are very influenced by the nature and concentration of alcohol, the solution pH and reaction temperature [42]. Thus, in order to understand the effect of noble metals loading on TiO<sub>2</sub> the following results were conducted in absence of KOH, using iPrOH as solvent, and with an amount of catalyst of 0.1 g  $L^{-1}$ . This catalyst concentration was selected based on the previously studies on the effect of catalyst amount for BH formation (Fig. SD2a). In Fig. 9 are depicted the results using noble metals based TiO<sub>2</sub> photocatalysts.

In general the results show that highest selectivity for BH production is obtained in the presence of noble metals, with exception for Au/TiO<sub>2</sub> material in which the yield is similar to the obtained with neat  $TiO_2$  (Fig. 9b). Moreover, the results suggest the existence of different activation mechanisms depending on the type of noble metal used.

It is generally accepted that semiconductor loading with noble metals may enhance the amount and lifetime of photogenerated electron-hole pair avoiding charge recombination [42, 43]. This effect was observed by photoluminescence analysis were  $Pd/TiO_2$  being the material with higher quenching of the luminescence intensity.

Additionally, the plasmonic effect of noble metals nanoparticles is often as the main contribute for enhanced photoactivity in semiconductors such TiO<sub>2</sub> under visible light irradiation [44], however this effect was not expected to occur since the irradiation source used was UVA-LEDs with an emission line at 385 nm. The main reasonable rationalization of photocatalytic mechanism under UV light assumes the direct photoexcitation of TiO<sub>2</sub>, in which photo-excited hot electrons may be transferred via a Schottky junction from the conduction of TiO<sub>2</sub> to noble metal particles deposited on its surface, while photogenerated holes remains on TiO<sub>2</sub>, being available for oxidation of adsorbed reactants (Scheme 1). Moreover, the higher photoelectric work function of Pt (5.7 eV) compared with Pd (5.2 eV) and Au (5.1 eV) [45] could suggest higher efficiency for Pt/TiO<sub>2</sub> catalyst by facilitating electron transfer from the conduction band of TiO<sub>2</sub> to the noble metals extending the lifetime of charge carriers. Thus, the photocatalytic reduction of the BP can be ascribed to the presence of an excess amount of electrons at the noble metal surface. Yet, more photogenerated holes will accumulate at the interface thus increasing the formation of hydroxyl radicals, which may favor oxidation reactions. Regarding the photocatalytic results was found that Pd/TiO<sub>2</sub> material shows high efficiency for BH production, being observed an increase of  $\sim 49\%$  on the concentration compared with neat TiO<sub>2</sub> after 1 h reaction. Although TiO<sub>2</sub> based materials show similar bandgaps, the main driving force involved in the production of BH from BP photocatalytic reduction may be attributed to the significant depression quenching of the PL emission spectrum observed for Pd/TiO<sub>2</sub> (Fig. 5), suggesting an effective electron

transfer from TiO<sub>2</sub> and Pd nanoparticles favoring the reduction of BP at catalyst surface. The benefits of loaded Pd nanoparticles on TiO<sub>2</sub> was already demonstrated by Li et al. [46] in this case for the photocatalytic reduction of CO<sub>2</sub> into high-value-added products. The authors found that palladium nanoparticles on TiO<sub>2</sub> not only prevent the electron-hole recombination but may also promote the adsorption and activation of the substrate forming active sites for the desired products. Moreover, as described above the noble metals/TiO<sub>2</sub> materials were calcined under an H<sub>2</sub> stream. In general, during the calcination treatment the H<sub>2</sub> molecules are firstly adsorbed and dissociated into hydrogen atoms over the metal surface, and then migrate onto the TiO<sub>2</sub> support [28, 47]. This phenomenon is known as hydrogen spillover, in which the combination of noble metals and TiO<sub>2</sub> materials, and thus may promote an enhancement on the activity of the resulting photocatalysts.

Additionally, the photostability of the Pd/TiO<sub>2</sub> was investigated by reusing the catalyst in consecutive experiments for BH production. Before each reaction cycle, the photocatalyst was washed with deionized water and dried at 100 °C. As shown in Fig. 10, the efficiency of Pd/TiO<sub>2</sub>, in terms of selectivity for BH formation, decrease (from 28.5% to 20.0%) after the first run, yet it remains constant after the next cycles. This slightly activity loss can be ascribed to the decrease of Pd nanoparticles during the first recycling reaction. In fact, as revealed by XPS analyses (Fig. 3) the relative amounts of palladium species (Pd<sup>0</sup>, Pd<sup>2+</sup> and PdO) present in the fresh sample and after several reuses changed. Since XPS analysis is considered a surface quantitative spectroscopic technique, it is difficult to infer about the amount of each species in the bulk catalyst. From XPS it was found that the atomic percentage of Pd species before and after reuse decrease from 1.6 at.% to 0.6 at.%,

respectively. These results may rationalize the slight decrease on the efficiency of the  $Pd/TiO_2$  after the first run.

Overall, the present work shows that noble metals based  $TiO_2$  materials can be used for the synthesis of benzhydrol by photocatalytic reduction of benzophenone without adding KOH, however further improvements on the photocatalysts to increase the benzhydrol yield has to be attempted. An example, is the preparation of bimetallic  $TiO_2$  based catalysts using transition metals which are already been used as efficient materials for photocatalytic hydrogenation reactions [48].

#### Conclusions

Heterogeneous photocatalysis was used as efficient technology for benzhydrol production. The photoreduction of benzophenone for benzhydrol production is mainly dependent of the solvent and of the presence of a promotor of hydrogen transfer such as KOH. Using 2-propanol as solvent benzophenone was easily converted into benzopinacol under UVA-LED irradiation. By using a certain concentration of KOH, benzhydrol was the main product obtained, achieving 100% selectivity after 10 min reaction.

In general, noble metal deposition on  $TiO_2$  particles increased the efficiency of the photocatalysts. Among all the photocatalysts, the Pd/TiO<sub>2</sub> material showed the higher efficiency for benzhydrol production. The reaction reuses showed slight decrease after the first run however, the photostability remained in the following cycles. The enhance activity was ascribed to the action of noble metals acting as electron sinks, thus increasing the efficiency and lifetime of charge separation in the semiconductor.

The highest quenching observed for  $Pd/TiO_2$  material by PL measurements suggests an effective electron transfer from  $TiO_2$  to Pd particles, preventing the recombination of

photogenerated electron-hole pairs, and thus improve the photoactivity for benzhydrol formation.

#### **Declaration of interests**

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.

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Figure 1 – TEM micrographs of bare  $TiO_2$  (a), Au/TiO<sub>2</sub> (b), Pt/TiO<sub>2</sub> (c) and Pd/TiO<sub>2</sub> (d), and metal nanoparticle size distribution (inset).



Figure 2 - XRD diffractograms of neat TiO<sub>2</sub> and noble metals/TiO<sub>2</sub> materials; anatase

(A) and rutile (R).



Figure 3 – XPS patterns of fresh Au/TiO<sub>2</sub> (a), Pt/TiO<sub>2</sub> (b) and Pd/TiO<sub>2</sub> (c) catalysts and used Pd/TiO<sub>2</sub> (d).



Figure 4 – DRUV-Vis spectra and Tauc plot (inset) of TiO<sub>2</sub> based photocatalysts.



Figure 5 – Photoluminescence spectra of neat  $TiO_2$  and noble metals/ $TiO_2$  materials.



Figure 6 – (a) Concentration profiles of BH and BCP under photochemical and photocatalytic regimes (filled and open symbols, respectively); and (b) BP conversion, selectivity and yield towards BH production after 10 min of reaction.



Figure 7 – (a) Concentration profiles of BH (filled symbols) and BPC (open symbols) varying the solvent nature; and (b) BP conversion, selectivity and yield towards BH production after 10 min of reaction.



Figure 8 – (a) Concentration profiles of BH varying the concentration of KOH. (b) BP conversion, selectivity and yield towards BH production after 10 min of reaction.



Figure 9 – (a) Concentration profiles of BH using noble metals/TiO<sub>2</sub> catalysts. (b) BP conversion, selectivity and yield towards BH production after 10 min of reaction.



Figure 10 – Reusability assessment of Pd/TiO2 as photocatalyst for BP conversion, selectivity and yield towards BH production after 10 min of reaction.



$$2\text{TiO}_2 \xrightarrow{h\nu} 2e^- + 2h^+ \tag{1}$$

$$\begin{array}{c} OH \\ \downarrow \\ + 2h^{+} \\ \end{array} \begin{array}{c} hv \\ \downarrow \\ + 2H^{+} \\ \end{array} \begin{array}{c} O \\ + 2H^{+} \\ \end{array}$$
 (2)

$$2e^{-} + 2H^{+} +$$
  $hv$   $hv$   $(3)$ 



Scheme 1 – Photocatalytic production of benzhydrol using 2-propanol as a solvent [21].