

Photocatalytic Reduction of Benzophenone on TiO₂: Effect of Preparation Method and Reaction Conditions

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Dedicated to Silvia Bulbulian

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Abstract. The photocatalytic reduction of benzophenone was studied focusing on improving the yield to benzhydrol. TiO₂ was synthesized by means of a hydrothermal technique. TiO₂ (Degussa TiO₂-P25) was used as a reference. Catalysts were characterized by XRD and nitrogen physisorption. The photocatalytic reduction was carried out in a batch reactor at 25 °C under nitrogen atmosphere, acetonitrile as solvent and isopropanol as electron donor. A 200 W Xe-Hg lamp ($\lambda = 360$ nm) was employed as irradiation source. The chemical composition of the reaction system was determined by HPLC. Structural and textural properties of the synthesized TiO₂ depended on the type of acid used during sol formation step. Using HCl, a higher specific surface area and narrower pore size distribution of TiO₂ was obtained in comparison with acetic acid. As expected, the photochemical reduction of benzophenone yielded benzopinacol as main product, whereas, benzhydrol is only produced in presence of TiO₂ (i.e. photocatalytic route). In general, the hydrothermally synthesized catalysts were less active and with a lower yield to benzhydrol. The optimal reaction conditions to highest values of benzhydrol yield (70-80%) were found at 2 g/L (catalyst loading) and 0.5 mM of initial concentration of benzophenone, using commercial TiO₂-P25.

Keywords: Benzophenone, Photocatalytic Reduction, Titanium Dioxide.

Resumen. Se estudió la reducción fotocatalítica de benzofenona enfocándose en mejorar el rendimiento hacia bencidrol. El TiO₂ se sintetizó empleando el método hidrotérmico y el comercial (Degussa TiO₂-P25) se empleó como catalizador de referencia. Los catalizadores se caracterizaron mediante difracción de rayos-X y fisisorción de nitrógeno. La reducción fotocatalítica se llevó a cabo en un reactor discontinuo a 25 °C en atmósfera de nitrógeno, acetonitrilo como disolvente e isopropanol como agente donador de electrones. Se utilizó una lámpara de Xe-Hg ($\lambda = 30$ nm) de 200 W como fuente de irradiación. La composición química del sistema reaccionante se determinó mediante cromatografía de líquidos. Las propiedades estructurales y texturales de los catalizadores sintetizados dependieron del tipo de ácido utilizado durante la etapa de formación del sol. Con HCl se obtuvo la mayor superficie específica y una distribución estrecha de tamaño de poro del TiO₂ en comparación con el ácido acético. Como se esperaba, la reducción fotoquímica de la benzofenona produce benzopinacol, mientras que el bencidrol sólo se obtiene mediante la ruta fotocatalítica. En general, los catalizadores sintetizados por la ruta hidrotérmica fueron menos activos y con un bajo rendimiento hacia bencidrol. Las condiciones óptimas de reacción para obtener el mayor rendimiento a bencidrol se obtuvieron con 2 g/L (concentración de catalizador) y una concentración inicial de benzofenona de 0.5 mM, empleando el catalizador comercial de TiO₂-P-25.

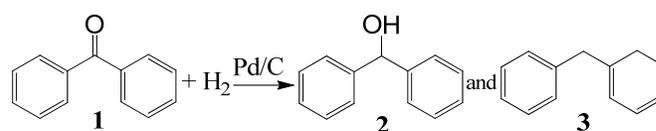
Palabras clave: Benzofenona, reducción fotocatalítica, dióxido de titanio.

Introduction

Benzhydrol (hydroxydiphenyl methane, (C₆H₅)₂CHOH) and its derivatives are important intermediates in the pharmaceutical industry [1]. For instance, antihistamines, antihypertensive agents and antiallergenic agents, among others, are the main drugs obtained from benzhydrol. Other applications of benzhydrol are in the synthesis of agrochemicals (e.g. hexachlorophene and dichlorophen), as a fixative in perfumery and as a terminating group in polymerizations reactions [2]. The conventional route to produce benzhydrol is the catalytic reduction of benzophenone. Catalysts such as sodium or aluminium amalgams, sodium borohydride, LiAlH₄, and Al(OiPr)₃/iPrOH have been tested for reduction of benzophenone [3]. However, catalytic hydrogenation [4], electrochemical [5] and electrocatalytic hydrogenation [6], ultrasound irradiation reduction [3] as well as photochemical [7] and photocatalytic reduction [8] represent alternative routes to the synthesis of benzhydrol.

Catalytic hydrogenation of benzophenone (**1**) can be utilized as a single technical route to benzhydrol (**2**) as shown in scheme 1.

However, high pressure, pure hydrogen, solvent, separation of byproducts (e.g. diphenylmethane (**3**)) and expensive Pd catalysts are required [9]. Therefore, a green method, according to the well-known principles, must reduce or eliminate dangerous conditions and generation of hazardous substances [10]. In this sense, photocatalytical reactions (i.e. semiconductor photochemistry or heterogeneous photocatalysis) are the most attractive and significant targets of research in organic syntheses [11]. The fundamental principles of



Scheme 1. Catalytic hydrogenation of benzophenone.

heterogeneous photocatalysis have been extensively studied [12], which involve transfer phenomena, adsorption, surface reactions, desorption and removal of the products from the interface region. In short, when a semiconductor is illuminated with photons whose energy is equal to or greater than its band-gap energy, free photoelectrons (e^-) in the conduction band and photoholes (p^+) in the valence band are formed. After the adsorption of reactants occurs, and according to their redox potential, and electron transfer takes place towards acceptor (A) molecules, whereas a positive photohole is transferred to a donor (D) molecule (Scheme 2).

Each ion formed in steps II and III reacts to form the intermediate and final products. Specifically, in the field of photocatalytic organic syntheses, oxidation of organic compounds have been largely studied because the most common metal oxides and metal chalcogenide semiconductors have valence band edges that lie positive of the oxidation potentials of most organic functional groups [13]. In contrast, photocatalytic reductions are less frequently found because the reducing power of a conduction band electron is significantly lower than the oxidizing power of a valence band hole [14]. In previous works, our group has reported the photocatalytic reduction of nitrobenzene [15] and benzaldehyde [16] to obtain the corresponding aniline or benzyl alcohol as target products. However, we have found that the chemistry of dark reactions, after radicals are formed, follows a complex mechanisms and the selectivity can be drastically changed [17].

In particular, the photocatalytic reduction of benzophenone has been scarcely studied [8, 17, 18] in comparison with the photochemical route which has a long history [7]. The first work concerning the photocatalytic reduction of several aromatic ketones, using acetonitrile and triethylamine as sacrificial electron donor and cadmium sulphide as catalyst, was published in 1989 [8]. It was found, although, higher conversions of ketones, the yield to benzhydrol was at around 47%, and the results were explained in terms of direct electron transfer from the conduction band to the adsorbed ketones.

In the present work, we prepared titanium dioxide by a hydrothermal method to get higher specific surface area than the commercial TiO_2 (anatase, rutile or mixtures) and test them in the photocatalytic reduction of benzophenone to benzhydrol. The obtained catalysts were characterized by XRD and nitrogen physisorption. We mainly studied the effect of type of catalyst, initial concentration of benzophenone and mass of catalyst on the conversion and yield to benzhydrol.

Results and Discussion

Figure 1 displays the XRD patterns of the samples synthesized using different acids and calcined at 350 °C, as well as the ref-

erence catalyst without any thermal treatment. It is shown for sample TiO_2 -H (Fig. 1b, using HCl during synthesis), that the diffraction peaks are wide indicating that the sample has small crystallite size. The average crystallite size of this sample was 7.2 nm, determined via the Scherrer equation. In addition, the identified phases were 72% anatase, 18% brookite and 10% rutile according to JCPDS= 78-2486, 29-1360 and 82-0514 cards, respectively. When acetic acid is used in the synthesis (sample TiO_2 -A, Figure 1c) almost 100% anatase phase is obtained with an average crystallite size of 9.5 nm. As reported earlier, acetic acid does not behave only as an inhibitor for hydrolysis-condensation reaction but also as a ligand of the polymeric precursor enhancing the formation of single phases, i.e. anatase [19]. The XRD pattern of commercial TiO_2 -P25 is shown in Fig. 1a. As expected, this sample presented two phases, 75% anatase and 25% rutile, with an average particle size of 20 nm.

Table 1 shows the textural properties of the calcined catalysts from the nitrogen adsorption isotherms. TiO_2 -A catalyst had higher values of pore size and pore volume, than TiO_2 -H catalyst, and its specific surface area was lower than TiO_2 -H. One explanation to this behavior can be given in terms of phase composition of each sample. Indeed, TiO_2 -H presented three different phases, anatase, rutile and brookite and each one has a particular structure such as tetragonal, octahedral and orthorhombic, respectively. In this case, this material is denser with narrow pore size distribution and a smaller pore size and, as a consequence, a higher specific surface area than TiO_2 -A, which only had anatase (Fig. 2). These results evidence that the hydrothermal synthesis of TiO_2 improves the specific surface area compared with that of TiO_2 -P25 (50 m²/g).

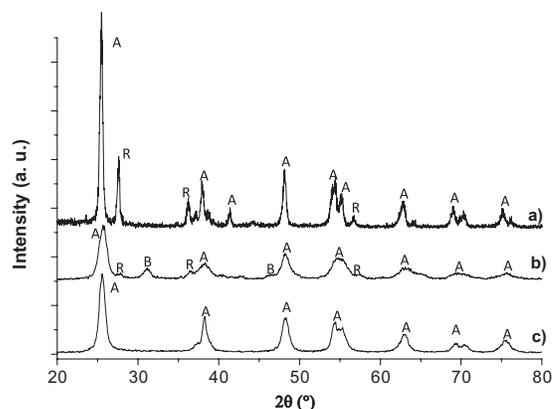
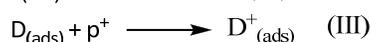


Fig. 1. X ray diffraction patterns of the samples: a) TiO_2 -P25, b) TiO_2 -H, c) TiO_2 -A.

Table 1. Textural properties of the catalysts.

Catalyst	Average Pore Diameter (BJH, nm)	Specific surface area (m ² /g)	Pore Volume (cm ³ /g)
TiO_2 -H	8.0	141	0.315
TiO_2 -A	15.2	114	0.513



Scheme 2. Steps of the photocatalytic process.

The liquid phase photochemical reduction of benzophenone in N₂ atmosphere was carried under UV light irradiation. Figure 3 shows the chromatogram after 45 min of reaction time using an initial concentration of benzophenone of 1 mM and an excess of isopropanol as reduction agent. As can be seen, the reactant is almost converted to benzopinacol in a short time; however, several unidentified products were also detected in an elution time range from 0 to 11 min. The concentration profile at different reaction times is shown in Fig. 4. The conversion of benzophenone was 93% and was well fitted as a first order kinetics (pseudo rate constant, $k' = 0.063 \text{ min}^{-1}$ and $R^2 = 0.99$). As is well known, the electronically excited benzophenone forms hydroxydiphenylmethyl and solvent-derived radicals. The ground-state hydroxydiphenylmethyl radicals may dimerize to benzopinacol (**4**) [20] (Scheme 3); however, a cross-coupled reaction with hydroxyalkyl radicals (from isopropanol) can occur [21] (Scheme 4), which could explain the formation of several byproducts (e.g. asymmetric pinacols (**5**)) as shown in Fig. 3.

On the contrary, the photocatalytic reduction of benzophenone showed a high conversion of benzophenone with selectivity to benzhydrol nearly to the selectivity to benzopinacol (Figure 5). Blank experiments were carried out in order to study the effect of the presence of TiO₂ or UV-light or isopropanol on the photocatalytic reduction of benzophe-

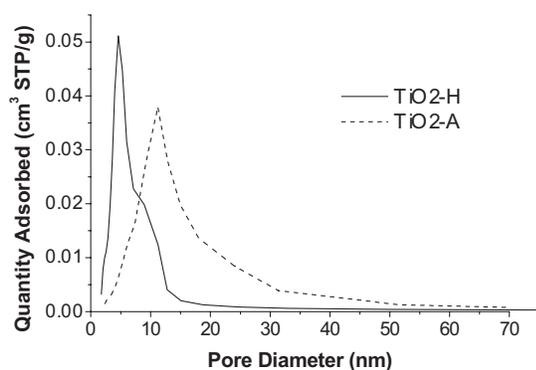


Fig. 2. Pore size distribution of the calcined catalysts.

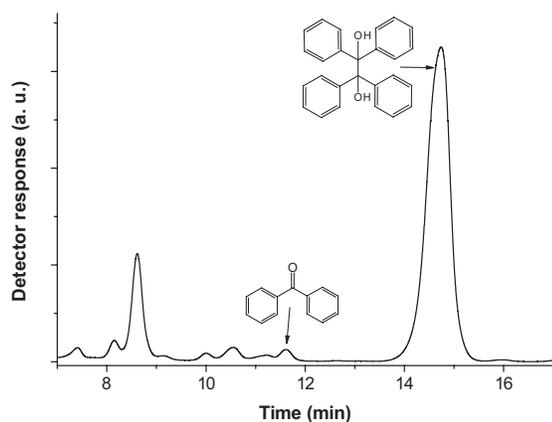


Fig. 3. Chromatogram of the photochemical reaction after 45 min of irradiation.

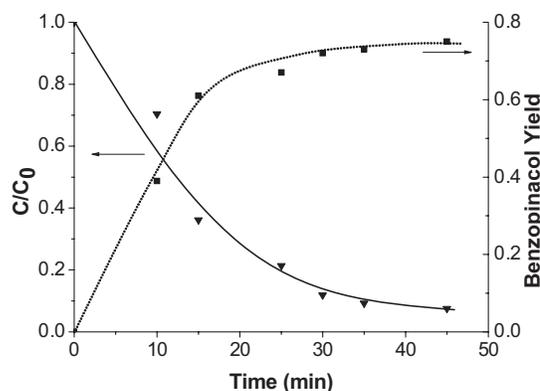
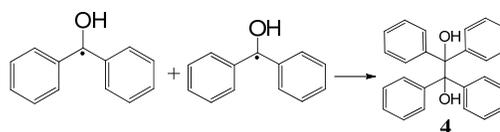
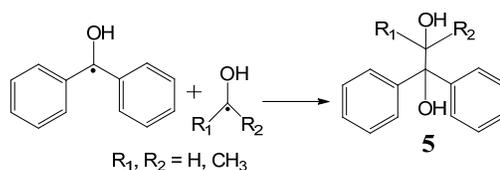


Fig. 4. Relative concentration of benzophenone and yield of benzopinacol vs. time of the photochemical reaction.



Scheme 3. Benzopinacol formation through the dimerization of 2 hydroxydiphenylmethyl radicals.



Scheme 4. Formation of asymmetric pinacols.

none. The reduction was only accomplished in the presence of: TiO₂+benzophenone+isopropanol+UV-light in a deoxygenated suspension. The photocatalytic reduction of benzophenone is followed by simultaneous oxidation and reduction of the absorbed reactants in presence of isopropanol (Scheme 5):

The product distribution of the photocatalytic reduction of benzophenone with the TiO₂ hydrothermal catalysts and TiO₂-

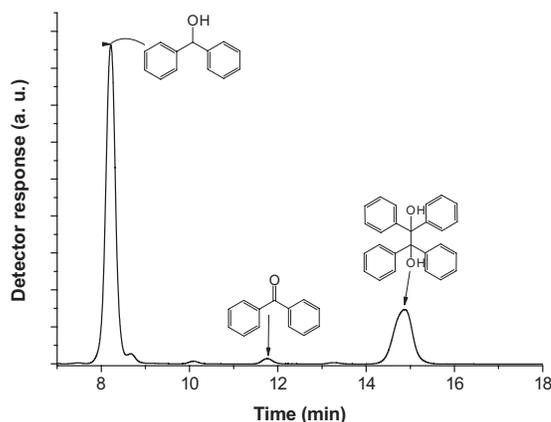
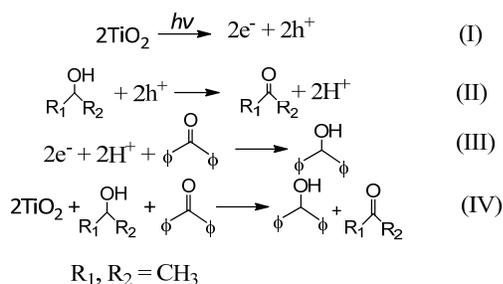


Fig. 5. Chromatogram of the photocatalytic reaction using TiO₂-P25 as photocatalyst (2 g/L) after 45 min of irradiation. Same conditions as figure 3.

P25 is presented in Fig. 6. All these catalysts were compared at the same reaction conditions. TiO₂-P25 showed the higher conversion and selectivity to benzhydrol. On the other hand, TiO₂-H and TiO₂-A exhibited a low conversion of benzophenone and low selectivity to benzhydrol. In these reactions, the photocatalyst and benzophenone are competing for the photons so, if the semiconductor has a lower photocatalytic activity, the amount of benzophenone converted to benzhydrol is lower than the amount converted to benzopinacol through the photochemical pathway. These results indicate that even though hydrothermal catalysts showed a higher specific surface area and low crystallite size compared with TiO₂-P25, there are other factors that may affect the photocatalytic activity [22].

The effect of initial concentration of benzophenone on the conversion using TiO₂-P25 is shown in Fig. 7. At high concentration of benzophenone, 6-10 mM, a straight line of concentration profile is followed, which corresponds to zero order kinetics. However, at small initial concentration, 1-0.5 mM, a different behavior is observed following a first order kinetics with long induction periods (20 min) where the conversion is insignificant. Figure 7 is also related with the competition between the photochemical reaction, favored at high concentration of benzophenone and the photocatalytic reaction, which is higher at low concentration.

The influence of the amount of TiO₂-P25 on the conversion and yield to benzhydrol was studied maintaining the concentration of benzophenone in 0.5 mM. The amount of TiO₂ was varied from 1 to 4 g/L for the same volume of a fixed concentration of the solution (Fig. 8). An increase in the



Scheme 5. Photocatalytic reduction of benzophenone.

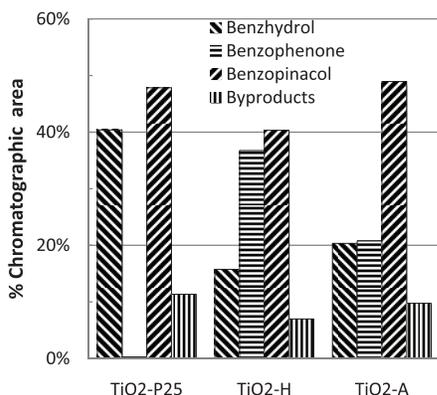


Fig. 6. Product distribution of the photocatalytic reactions using different TiO₂ photocatalysts.

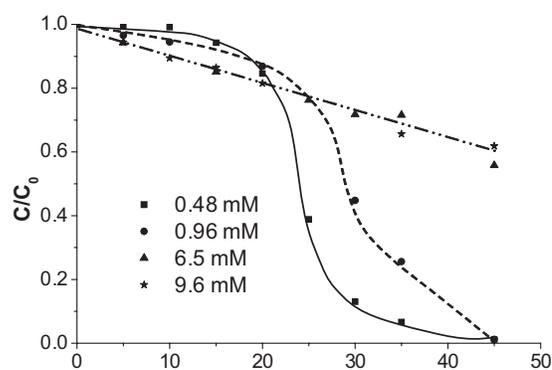


Fig. 7. Relative concentration of benzophenone vs. time in function of the initial concentration.

conversion of benzophenone was observed with increasing amount of TiO₂. However, after 30 min of reaction time the conversion was almost the same for 2-4 g/L of TiO₂. In addition, it is clearly noted that the induction period, which was also observed at low concentration of benzophenone (Fig. 7), is drastically decreased with the concentration 3 g/L of TiO₂. Note that a linear decrease of benzophenone concentration is followed with a 3 g/L catalyst concentration, indicating that the photocatalytic cycle is performed at optimal conditions avoiding induction periods, which delay the photoreduction of benzophenone.

Tables 2 and 3 summarize the effect of the concentration of benzophenone and the amount of TiO₂ on the conversion and yield. In general, the lower concentration of benzophenone the higher conversion and yield to benzhydrol, whereas increasing the amount of catalyst, no significant changes in conversion occur, but the highest yield to benzhydrol is obtained.

The photochemical reduction tends to be highly selective to benzopinacol (yield = 90%) while the photocatalytic reduction is most selective to benzhydrol (yield = 70%) as shown in scheme 6. Furthermore, several byproducts were detected by both routes which have not been identified yet and it will be very useful to propose a reduction/oxidation pathway occurring at dark conditions.

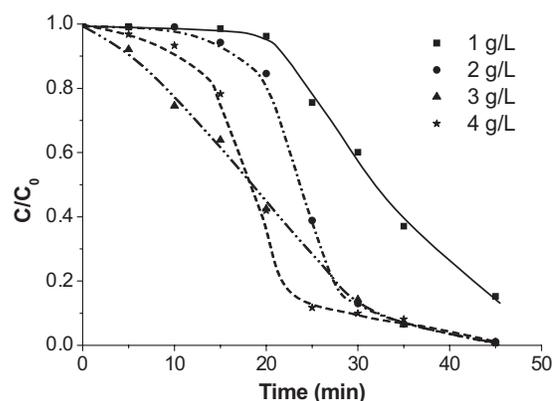


Fig. 8. Relative concentration of benzophenone vs. Time in function of catalyst concentration.

Table 2. Conversion and yield as a function of initial concentration of benzophenone (catalyst TiO₂-P25, t = 45 min).

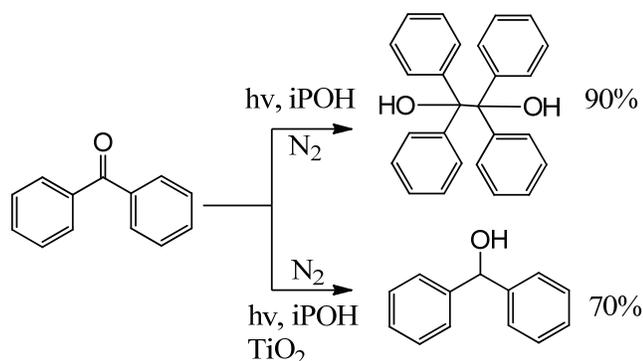
Initial concentration of benzophenone (mM)	Conversion (%)	Yield to benzhydrol (%)
0.48	98	70
0.96	98	52
6.50	44	37
9.06	38	29

Table 3. Conversion and yield as a function of catalyst concentration (catalyst TiO₂-P25, t = 45 min, [benzophenone]₀ = 0.48 mM).

Catalyst concentration (g/L)	Conversion %	Yield of benzhydrol (%)
1	85	47
2	98	70
3	99	62
4	99	63

Conclusions

Hydrothermally synthesized TiO₂ catalysts presented superior values of specific surface area, compared with that of TiO₂-P25, and a different phase composition depending of the type of acid used in the synthesis. Using acetic acid (114 m²/g) only anatase of 9.5 nm of crystal size is obtained. In contrast, with hydrochloric acid (141 m²/g) and a mixture of anatase, brookite and rutile with an average crystal size of 7.2 nm is obtained. Both catalysts showed a lower conversion of benzophenone and yield to benzhydrol than TiO₂-P25, despite the improvement of the specific surface area. A high conversion of benzophenone was detected by the photochemical route; however, benzopinacol was the main product. On the other hand, the photocatalytic reduction only occurred with the presence of TiO₂ + isopropanol (electron donor) + solvent (acetonitrile) and UV light, and the conversion and selectivity depended of the

**Scheme 6.** Photochemical and photocatalytic reduction of benzophenone.

initial concentration of benzophenone and the amount of catalysts. The optimal conditions to obtain high selectivity to benzhydrol were observed at the lowest concentration of benzophenone (0.5 mM) and catalyst concentration (TiO₂-P25) of 2 g/L.

Experimental Section

Synthesis of catalyst base TiO₂ using hydrothermal method:

In one flask, a solution containing cetyl trimethyl ammonium bromide (CTAB, 0.16 mol), ethyl alcohol (10 mol) and water (17 mol) was prepared and homogenized by magnetic stirring at room temperature. A second solution was prepared with titanium tetra isopropoxide (1 mol), ethyl alcohol (10 mol) and acetic acid (3 mol). The second solution was poured drop by drop into the first solution to begin the reaction under vigorous stirring and was aged for 24 h. The mixture was then transferred to a Teflon-lined stainless steel autoclave with a volume of 100 mL and kept at 100 °C for 24 h under static conditions in a convection oven. The obtained catalyst powder was rinsed five times with a mixed solution of water and ethyl alcohol (molar ratio 1:1). The solid was dried at 80 °C during 12 h. Finally, the catalyst was calcined in two steps, first at 150 °C for 3 h, then at 350 °C for 6 h, to remove the excess of surfactant occluded inside the pores. The rate temperature in both cases was of 1 °C/min.

Characterization of catalyst of TiO₂:

The crystalline phases of prepared and commercial TiO₂ were identified by XRD. The specific surface area, pore volume and pore size distribution were obtained by nitrogen physisorption. X-ray powder diffraction (XRD) patterns were collected on a Siemens D500 diffractometer coupled to a copper anode tube (K α , λ = 1.5405 Å). The physisorption experiments were carried out on an Autochem ASAP 2020, and the pore size distribution were determined using the desorption branch. The samples were heated at 300 °C during 4 h.

Reactions

Porous TiO₂ synthesized by hydrothermal method and commercial TiO₂ (Degussa, TiO₂-P25) were used as catalysts for the photocatalytic reduction of benzophenone to produce benzhydrol. The reaction system containing all reagents (benzophenone, isopropanol, acetonitrile and TiO₂) was maintained at room temperature (25 °C) and irradiated with UV- light from a 200 W Xe-Hg lamp (λ_{max} = 360 nm) for 45 min. The chemical composition of the reactor was determined by liquid chromatography using a GBC HPLC equipped with an isocratic pump and a UV-Vis detector (λ = 205 nm).

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