TiO$_2$ and Pd/TiO$_2$ as Photocatalysts for Hydrogenation of Ketones and Perspective of Membrane Application

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Abstract: *Photocatalytic transfer hydrogenation of aromatic and aliphaticketones by using TiO$_2$ and home-made TiO$_2$ doped with palladium by deposition-precipitation method (Pd/TiO$_2$) in a batch reactor under UV light has been studied. Different photocatalytic tests have been performed by using ethanol as electron and hydrogen donor and water/ethanol solution to obtain data on the reaction parameters. The results found, using the ethanol solution, showed acetophenone conversion, selectivity and yield higher than in the in water/ethanol solution (50/50 v/v). The highest acetophenone conversion was obtained by using Pd/TiO$_2$ under UV light. For butanone the best results (as conversion, selectivity and yield) were obtained by using Pd/TiO$_2$.The values of butanone conversion and the yield to butanol increased almost six times more than the commercial TiO$_2$. Pure ethanol was better than the water-formic acid as both solvent and electron-hydrogen donor. Some considerations on using in perspective these data on a photocatalytic membrane reactor are also reported.*

Keywords: *Photocatalysis, Ketone hydrogenation, Titanium dioxide, Palladium doped titanium dioxide, Photocatalytic membrane reactor, Photocatalytic membrane.*

1. INTRODUCTION

Among the main chemical transformations, currently applied in industrial practices, reduction processes, such as the reduction of carbonyl compounds in the corresponding alcohols, play an important role in organic synthesis [1-3]. In particular, acetophenone (AP) hydrogenation has been widely studied since the resultant reduction product, 1-phenylethyl alcohol or also phenyl ethanol (PE), is a common precursor for the preparation of analgesic and anti-inflammatory drugs as well as fragrances and perfumes [4-6].

Homogeneous (e.g. Ru, Ir) and heterogeneous catalysts (e.g. Pd, Pt, Ru and Au) have been reported to be effective for ketones reduction [7-13]. Recently Shimura el al. [14] reported the use of Ni-loaded CeO$_2$ as catalyst for the transfer hydrogenation of aliphatic and aromatic ketones to the corresponding alcohols by using 2-propanol.

In our previous work [5]Pd-loaded hierarchical FAU (Pd-FAU) membranes, containing an intrinsic secondarynon-zeolitic (meso)porosity, were prepared and tested in the catalytic transfer hydrogenation of acetophenone (AP) to produce phenylethanol (PE). The best experimental conditions were selected and applied to the Pd-loaded FAU membrane. It was found enhanced catalytic performance such as a five-fold higher productivity than with the unsupported Pd-FAU crystals (11.0 vs. 2.2 mg product gcat^{-1}h^{-1}). The catalytic performance of the membrane on the alumina support was also tested in a tangential flow system obtaining productivity higher than that of the batch system (22.0 vs. 11.0 mg product gcat^{-1}h^{-1}).

The above approaches are of catalytic type but exploitation of photocatalytic reactions in the design of efficient and environment-friendly technologies has attracted great attention[1].The most widely used photocatalyst is titanium dioxide (TiO$_2$).The main problems of using TiO$_2$are the electron/hole recombination and the spectrum of absorbance mainly in the UV region. Noble metals doping of TiO$_2$ have been reported to be very effective to overcome previous limitations [1, 15, 16].

Our previous study [4] was focused on the photocatalytic transfer hydrogenation of acetophenone to phenylethanol using water as solvent and formic acid as hydrogen and electron donor. This same reaction was studied very recently by Lavorato et al. [6] evaluating the photocatalytic properties of TiO$_2$-loaded faujasite (FAU) zeolite and Pd/TiO$_2$/FAU as photocatalysts.

Another class of electron and hydrogen donor largely used for photocatalytic reductions are alcohols. They are used in large excess (e.g. as solvent) to shift the reaction to the desired product, because during the transfer hydrogenation alcohols are oxidized to ketones or aldehydes that can compete with the substrate. Kohtani et al. [17] reported the photocatalytic activity of polycrystalline P25 TiO$_2$ powder to hydrogenate acetophenone and others aromatic ketones using methanol, ethanol, and propan-2-ol as solvent and electron donor under UV light. Escobar et al.[18] reported the photocatalytic transfer hydrogenation of ketones using titanium dioxide as photocatalyst and 2-propanol as hydrogen donor.

In the present work, the hydrogenation of aromatic (acetophenone) and aliphatic (butanone) ketones was investigated using commercial TiO$_2$ and home-prepared Pd/TiO$_2$ in ethanol or ethanol/water as solvent in a photocatalytic batch reactor. Ethanol was used as both solvent and electron-hydrogen donor and different aspects were investigated: (i) TiO$_2$ amount, (ii) UV light activity of titanium dioxide doped with palladium, (iii) different intensity and distribution of irradiation source, (iv) mixture of water ethanol (1:1).

Some considerations on using in perspective a membrane photoreactor are also reported.

2. EXPERIMENTAL SECTION

2.1. Apparatus and Methods

Preliminary experimental tests on photocatalytic hydrogenation of acetophenone and butanone, using ethanol as solvent, were conducted in the batch reactor described in our previous works [4,6]. The system consists of a cylindrical pyrex glass reactor (V = 500 mL) with an immersed mercury lamp (medium pressure Hg lamp, 125 W, emitting mainly in the UV region, with an emission peak at 366 nm). The system was maintained at a temperature of 32°C.

Samples were withdrawn from the reacting solution each hour during all photocatalytic tests to identify concentrations of species involved in the chemical reaction. Each test had duration of 7 hours. The samples were filtered through a hydrophobic membrane made of polypropylene (GH-Polypro, pore size 0.2 μm) to remove the catalyst before the analysis.

The photocatalytic tests conducted in the batch photoreactor with ethanol as solvent were carried out using 50 mmol of acetophenone or butanone as substrate and an appropriate amount of TiO$_2$ and Pd/TiO$_2$ as photocatalyst.

Detection of possible reaction products was performed by a Gas Chromatograph, Agilent model 6890N equipped with a FID detector and a capillary column SupelcowaxTM 10 (Fused silica, 10m × 0.1mm ×0.1μm film thickness).

The results of the experimental tests were elaborated using the following parameters:

$$\text{Reactant conversion} = \frac{\text{moles reacted of reactant}}{\text{initial moles of reactant}} \times 100 \tag{1}$$

$$\text{Product selectivity} = \frac{\text{moles of product produced}}{\text{moles of reacted reactant}} \times 100 \tag{2}$$

$$\text{Product yield} = \frac{\text{moles of product produced}}{\text{initial moles of reactant}} \times 100 \tag{3}$$

where reactant is acetophenone and product is phenylethanol or butanone and butanol, respectively.

2.2. Materials

Titanium dioxide P25 (TiO$_2$) from Degussa was used as photocatalyst. Palladium (II) chloride, (PdCl$_2$, 99% purity) from Aldrich, was used to synthetize Pd/TiO$_2$. Ethanol absolute (C$_2$H$_6$O$_2$, 99.8% purity) from Panreac, was used as solvent and electron and hydrogen donors. Acetophenone Reagent Plus (C$_8$H$_8$O, 99% purity) from Sigma Aldrich and Butanone Analytical Reagent (C$_4$H$_8$O, 99.5% purity) from Riedel-de Haen were used as substrates.

2.3. Synthesis and Characterization of Pd/TiO$_2$

Pd/TiO$_2$ was synthesized by deposition-precipitation method. More details are reported in supporting information in our previous work [4]. During this preparation the required amount of Pd was added as 0.056 M PdCl$_2$ acidic solution drop wise to a basic TiO$_2$ solution under vigorous stirring. The resulting solution was centrifuged at 15000 rpm for 30 minutes to recover the solid fraction, which was the modified photocatalyst. This solid was washed with water to remove ammonia and chloride ions that can alter the properties of the catalyst. The resulting catalyst was chemically reduced by adding NaBH$_4$.

The Pd/TiO$_2$ sample was characterized by X-ray photoelectron spectroscopy (XPS) analysis that was performed using a VG-Escalab 210 photoelectron spectrometer with an Mg Kα X-ray resource [4].

3. RESULTS AND DISCUSSION

3.1. Pd/TiO$_2$ Characterization

The XPS analysis [4], showed that there are Ti, O, C and Pd elements on all the surface of the Pd/TiO$_2$ samples. The Ti element results from the TiO$_2$. The O element is assigned to TiO$_2$ and CO. The C element is assigned to the C pollution in the instrument. The percentage of Pd loaded on the TiO$_2$ surface corresponds to 0.65%.

3.2. Photocatalytic Hydrogenation of Acetophenone in Ethanol

Experimental tests on photocatalytic hydrogenation of acetophenone were conducted in a batch reactor, using ethanol as both solvent and electron-hydrogen donor, in order to investigate different aspects: TiO$_2$ amount, influence of solvent and addition of 50% of water, type of photocatalyst, different intensity and distribution of irradiation source.

3.2.1. Titanium Dioxide Amount

To optimize the operative conditions for photocatalytic hydrogenation of acetophenone in ethanol, tests with different amounts of TiO$_2$ as photocatalyst were carried out. In particular, the following amounts were considered: 0.1, 0.8, 1.5 and 3.0 g L^{-1}.

The results show a general increase of the conversion in the time, but increasing the amount of the catalyst, acetophenone conversion decreases (Figure 1) while the selectivity to phenylethanol increases (Table 1). This trend can be explained considering that increasing the catalyst amount a screening effect (increase in opacity and light scattering) of particles occurs. This phenomenon leads to a decreased passage of radiation through the suspension thus limiting the reactivity of the system. The yield has a maximum value for the amount of TiO$_2$ equal to 1.5 g L^{-1} (Table 1).
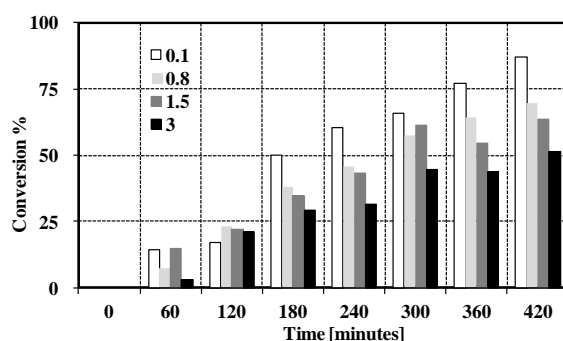

Fig1. *Acetophenone conversion vs. time using different catalyst amount (from 0.1 to 3.0 g L^{-1}). Operative conditions: 500 mL ethanol, 50 mmol acetophenone, T = 32°C, reaction time =7h.*

Table1. *Comparison of acetophenone conversion, phenylethanol selectivity and yield in the photocatalytic tests by using different TiO$_2$ amounts. Operative conditions: 500 mL ethanol, 50 mmol acetophenone, T = 32 °C, time = 7h.*

TiO$_2$ (g L^{-1})	Conversion (%)	Selectivity (%)	Yield (%)
0.1	87.0	4.7	4.1
0.8	69.8	16.8	11.7
1.5	63.5	26.6	16.9
3.0	51.3	29.4	15.1

3.2.2. Influence of Solvent and Water Addition

Khan et al. [19], studied photocatalytic hydrogenation of cyclohexene in aqueous ethanolic solution (80:20). Thus, in order to study the influence of the solvent on the photocatalytic transfer hydrogenation of the acetophenone, tests in ethanol and water (50:50) were carried out.

The results showed lower conversion, yield and selectivity compared to pure ethanol (Figure 2 and Table 2).
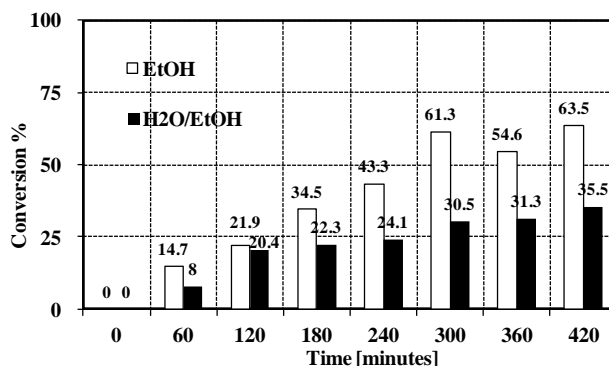

Fig2. *Acetophenone conversion vs. time in ethanol and ethanol/water solution. Operative conditions: V = 500 mL, 50 mmol acetophenone, TiO$_2$ amount = 1.5 g L^{-1}, T = 32 °C, time = 7 h.*

Table2. *Acetophenone conversion, phenylethanol selectivity and yield in the photocatalytic tests by using in ethanol and ethanol/water solution. Operative conditions: V = 500 mL, 50 mmol acetophenone, TiO$_2$ amount = 1.5 g L^{-1}, T = 32 °C, time = 7 h.*

Solvent	Conversion (%)	Selectivity (%)	Yield (%)
Ethanol	63.5	26.6	16.9
Ethanol/water	35.5	6.3	2.2

Acetophenone conversion in aqueous ethanol solution is about half compared to those obtained in pure ethanol. Therefore it can be affirmed that almost all hydrogen used to reduce acetophenone is from ethanol, not from water. Moreover, acetophenone is very slightly soluble in water, thus, the solubilization of the substrate in aqueous/ethanolic solution is more difficult than in pure ethanol. Consequently, acetophenone adsorption on the photocatalyst dissolved in the liquid phase was lower in the aqueous solution than the pure ethanol causing a lower conversion, selectivity and yield (Table 2).

3.2.3. Type of Photocatalyst: Pd/TiO2 Photocatalytic Activity

Experiments conducted in ethanol using Pd/TiO$_2$ were carried out to study the effect of Pd deposited on TiO$_2$. It has been largely reported that noble metals are very effective for enhancing TiO$_2$ photocatalytic activity reducing the electron/hole recombination [1, 4, 6]. Figure 3 shows that acetophenone conversion with TiO$_2$ and Pd/TiO$_2$ were 63.5% and 96.2%, respectively, at 7 hours. As expected, acetophenone conversion increases using Pd/TiO$_2$ because noble metals reduce the possibility of electron-hole recombination, resulting in a stronger photocatalytic activity.
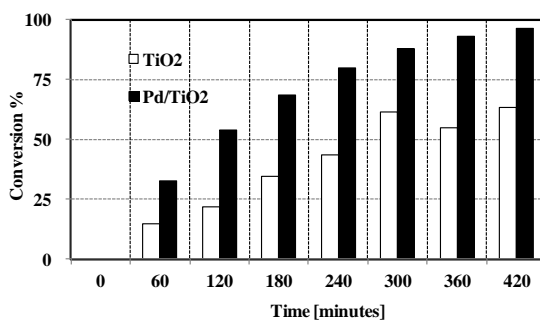

Fig3. *Acetophenone conversion vs. time using TiO$_2$ and Pd/TiO$_2$ as photocatalysts. Operative conditions: 500 mL ethanol, 50 mmol acetophenone, 1.5 g L^{-1} of photocatalyst, T = 32 °C, reaction time =7 h.*

Moreover a higher production of acetaldehyde from ethanol, almost three times more, using Pd/TiO$_2$ in comparison to the tests carried out with TiO$_2$, was observed (Figure 4).
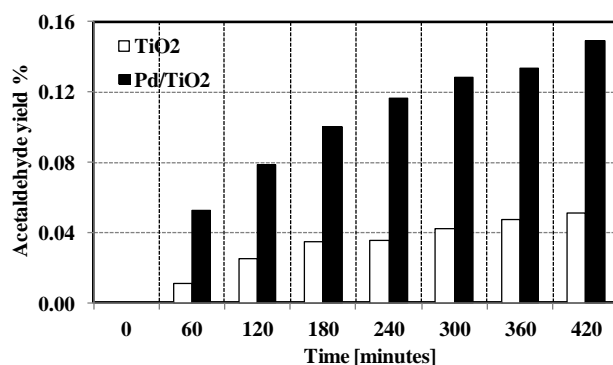

Fig4. *Acetaldehyde yield% vs. time using TiO$_2$ and Pd/TiO$_2$ as photocatalysts. Operative conditions: 500 mL ethanol, 50 mmol acetophenone, 1.5 g L^{-1} of photocatalyst, T = 32 °C, reaction time =7 h.*

This behavior can be explained by considering the following photocatalytic transfer hydrogenation mechanism.TiO$_2$ absorbs light with separation of the electron–hole couple:

$$Pd/TiO_2 + hv \rightarrow e^- + h^+ \tag{4}$$

Holes that migrate to the surface of the semiconductor can oxidize the ethanol adsorbed on photocatalyst with formation of acetaldehyde and H$^+$:

$$CH_3CH_2OH + 2\ h^+ \rightarrow CH_3CHO + 2H^+ \tag{5}$$

Electrons that migrate on the surface of the semiconductor can reduce H$^+$ to atomic hydrogen [20]:

$$2\ H^+ + 2\ e^- \rightarrow 2\ H\bullet \tag{6}$$

Atomic hydrogen can both recombine and desorbs:

$$2\ H \bullet \rightarrow H_2 \tag{7}$$

or reacts with a substrate such as acetophenone reducing it:

$$(C_6H_5)COCH_3 + 2\ H \bullet \rightarrow (C_6H_5)HCOHCH_3 \tag{8}$$

The high production of acetaldehyde previously observed implicates a significant atomic hydrogen production (eq. 6) that can both recombine and desorb (eq. 7) or reduce acetophenone (eq. 8). Indeed, during the photocatalytic tests with Pd/TiO$_2$ an evolution of gas, from the reaction environment, was observed. This high hydrogen ion production from eq. (5) causes an increase of the reactivity of the system. Indeed, a high H$\bullet$ concentration from eq. (6) means also a high probability of its recombination. Furthermore, the aromatic ring of acetophenone makes it a reactive molecule under light irradiation. Consequently it shows good reactivity also using bare TiO$_2$ as photocatalyst. By using Pd/TiO$_2$ the system became excessively reactive causing a decrease in selectivity (3.2% vs 26.6%) and yield (3.1% vs 16.9%) to phenylethanol with respect to bare TiO$_2$.

3.2.4. Influence of The Intensity and Distribution of Irradiation Source

Photocatalytic tests were conducted using two medium pressure Hg lamps, indicated as lamp A (used in the previous tests) and lamp B. These lamps were characterized by different average intensity of light irradiation (I$_A$=35mW/cm^2, I$_B$=55mW/cm^2) and light irradiation distribution of lamp A higher than that of lamp B.

The tests permitted to study the influence of these parameters on the photocatalytic transfer hydrogenation of acetophenone using both TiO$_2$ and Pd/TiO$_2$ catalyst. Best results in terms of acetophenone conversion and phenylethanol yield were obtained by using the lamp A, with lower irradiation intensity, during the tests conducted with both the photocatalysts (Fig.5 and Table 3). Contrariwise the photocatalytic selectivity increased using TiO$_2$ as photocatalyst with lamp B (Table 3).
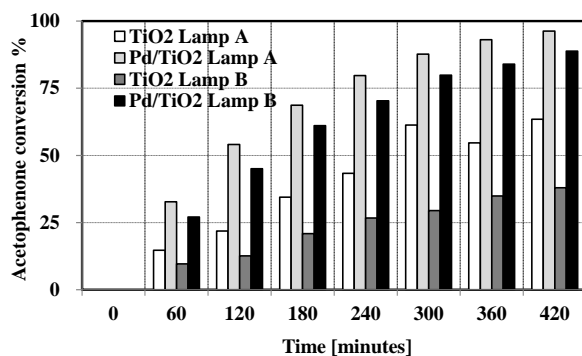
Fig5. *Comparison of acetophenone conversion vs. time using TiO$_2$ and Pd/TiO$_2$ as photocatalysts changing the intensity distribution of the light. Operative conditions: 500mL ethanol, 50 mmol acetophenone, 1.5 g L^{-1} of photocatalyst, T = 32 °C, reaction time =7 h.*

Table3. *Comparison of acetophenone conversion, phenylethanol selectivity and yield using TiO$_2$and Pd/TiO$_2$ as photocatalysts changing intensity and distribution of the light. Operative conditions: 500 mL ethanol, 50 mmol acetophenone, 1.5 g L^{-1} of photocatalyst, T = 32 °C, reaction time =7 h.*

Lamp	Photocatalyst	Light intensity	Conversion (%)	Selectivity (%)	Yield (%)
A	TiO$_2$	35mW/cm^2	63.5	26.6	16.9
B	TiO$_2$	55 mW/cm^2	38.0	37.4	14.2
A	Pd/TiO$_2$	35mW/cm^2	96.3	3.2	3.1
B	Pd/TiO$_2$	55 mW/cm^2	88.8	3.2	2.8

Probably, this behavior is caused by the wider distribution of the light irradiation, despite the lower light intensity, of lamp A with respect to lamp B. Besides at high light intensities, the effect of this parameter on the reaction rate is almost negligible. Indeed, both Konstantinou et al. [21] and Coleman et al. [22], reported that at high light intensities (I > 25 mW/cm^2) the photocatalytic reaction rate becomes independent of the light intensity [23]. As reported in the previous paragraph, by using Pd/TiO$_2$ the system became excessively reactive causing a decrease in selectivity and yield with respect to bare TiO$_2$ by using both lamps A and B.

3.3. Photocatalytic hydrogenation of butanone in ethanol

Butanone was used as a model substrate for photocatalytic transfer hydrogenation of aliphatic ketones in batch reactor, using ethanol as solvent and electron-hydrogen donor. These photocatalytic tests were carried out under the operating conditions found in the previous tests with acetophenone. Commercial TiO$_2$ photocatalyst and the home-prepared Pd/TiO$_2$ were used to compare their behavior.

In contrast to the excessive reactivity of the system described in the previous paragraph, the results on butanone hydrogenation showed very low system reactivity by using bare TiO$_2$ as photocatalyst. As reported in literature [1, 15, 16], noble metals, including Pt, Au, Pd, Rh, Ni, Cu and Ag, are very effective for enhancement of TiO$_2$ photocatalysis. Indeed, by using TiO$_2$ doped with Pd as photocatalyst, butanone conversion and butanol yield increased more than six times than by using bare TiO$_2$ (Fig. 6).
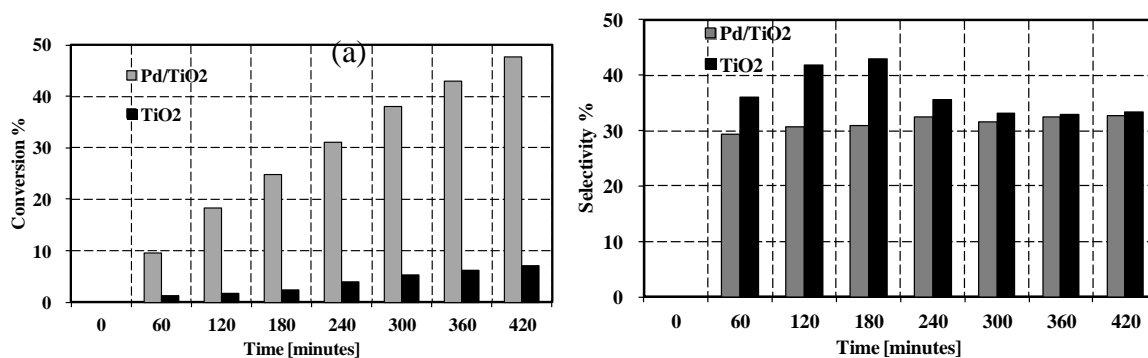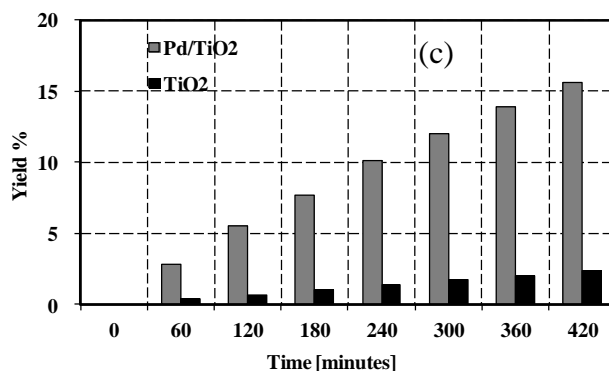
Fig6. *Comparison of butanone conversion (a), selectivity (b) and yield (c) to butanol vs. time using TiO₂ and Pd/TiO₂as photocatalysts. Operative conditions: 500 mL ethanol, 50 mmol butanone, 1.5 g L⁻¹ of photocatalyst, T = 32 °C, reaction time =7 h.*

3.4. Comparison of Photocatalytic Activity between our Previous Works and Future Perspective

For carrying out the photocatalytic transfer hydrogenation of organic molecules the choice of solvent and electron-hydrogen donor are important factors.

In our previous works [4, 6] we synthesized different titanium based photocatalysts and tested them in photocatalytic hydrogenation of acetophenone using water as solvent and formic acid as electron-hydrogen donor also in a PMR. In the present work we tested the photocatalytic activity of TiO₂ and Pd/TiO₂ using ethanol as both solvent and hydrogen-electron donor and a water/ethanol solution for coupling, in perspective, photocatalysis and membrane separation. By comparing the results obtained in batch in our previous work [4] with that of the present work, it can be observed that the yield obtained using water as solvent with 7.5% of formic acid (1.9 M) is double than that obtained using water/ethanol 50/50, but it is lower than that using pure ethanol. Therefore the best solvent for the reaction is found to be ethanol. However, ethanol is not the best solvent for all type of polymeric membranes for coupling in perspective photocatalysis with membrane separations.

The above data can be used as preliminary knowledge of the reacting systems to use them in photocatalytic membrane reactors because they combine the advantages of classical photoreactors and those of membrane processes with a synergy of both technologies. The membrane allows not only the recovery of the catalyst, immobilizing it on the membrane or using the membrane to maintain the catalyst in suspension, but also the selective separation of the desired product from the reaction mixture permitting to obtain improvements of yield and selectivity limiting side catalytic reactions. A fundamental aspect in planning the type of membrane to use for this type of reactions is the type of the solvent of the reacting system. In this case solvent (ethanol) resistant membranes should be used, e.g zeolite membranes [24] or others. Furthermore a configuration of photocatalytic membrane, rather than a slurry photocatalytic reactor, seems more suitable for this case.

However experimental tests will indicate the way to carry out these reactions to take advantages in using a combination of photocatalysis and membrane.

4. CONCLUSIONS

The results on the photocatalytic transfer hydrogenation of acetophenone, dissolved in ethanol in batch reactor, presented in this work, showed that phenylethanol yield had a value of 16.9% at 1.5 g L⁻¹ of photocatalyst amount. Water/ethanol solution (50/50 v/v) showed acetophenone conversion (35.5%), yield (2.2%) and selectivity (6.3%) lower than in pure ethanol. The highest acetophenone conversion (96.2%), accompanied by low yield and selectivity, was obtained by using Pd/TiO₂ as photocatalyst indicating a highly reactive but low selective system.

Comparing the photocatalytic transfer hydrogenation of acetophenone and butanone the results showed an high reactivity of the system using Pd/TiO₂ as photocatalyst for the reduction of acetophenone. In contrast, butanone showed very low system reactivity by using bare TiO₂ as photocatalyst but it increased using Pd/TiO₂. The reduction of butanone with Pd/TiO₂ gave a yield of 15.6 % which was six times more than that bare TiO₂.

Comparing the results obtained in our previous work [4], it can be observed that the yield obtained using water as solvent with 7.5% of formic acid (1.9M), is double than that obtained using water with 50% of ethanol as both hydrogen and electron donors, but it is lower than that using 100% of ethanol. Therefore the best solvent for the reaction is found to be ethanol.

This findings means that solvent-resistant membranes and suitable configuration of photocatalytic membranes should be used to take advantage of the combination of photocatalysis and membrane to carry out photocatalytic transfer hydrogenation of ketones.

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