Synthesis of TiO$_2$-based Photocatalysts in Supercritical CO$_2$

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1. INTRODUCTION

Nowadays, **titanium dioxide** is among the semiconductors mainly used in processes such as photocatalysis, because it brings together a set of properties that make it a very suitable candidate for this type of oxidation-reduction reactions. Among the abovementioned features, TiO$_2$ has a wide *band-gap* (**Table 1**), which results in high negative and positive redox potentials in the *conduction* and *valence bands*, respectively (**Figure 1**). Also, this material is resistant to corrosion, nontoxic, low cost and it possesses physicochemical characteristics that allow it to act as a catalyst [1].

Table 1. Band-gap energies of semiconductors used for photocatalytic processes [2].

Photocatalyst	Band-gap energy (eV)	Photocatalyst	Band-gap energy (eV)
Si	1.10	TiO$_2$ rutile	3.02
WSe$_2$	1.20	Fe$_2$O$_3$	3.10
α-Fe$_2$O$_3$	2.20	**TiO$_2$ anatase**	**3.23**
CdS	2.40	ZnO	3.20
V$_2$O$_5$	2.70	SrTiO$_3$	3.40
WO$_3$	2.80	SnO$_2$	3.50
SiC	3.00	ZnS	3.70

The idea of applying **supercritical fluids (SCFs)** technology to the synthesis of TiO$_2$ arises because to date, the study of CO$_2$ photoreduction, the final stage of this project, has not been developed with photocatalysts synthesized in supercritical media. Moreover, it is well known that the synthesis conditions under which a photocatalyst is prepared influence their properties strongly [3]. To this we must add the results of a recently published work [4], showing a higher photocatalytic activity in the photooxidation of methyl orange aqueous solutions by TiO$_2$ synthesized in **supercritical CO$_2$ (SC-CO$_2$)** compared to commercial TiO$_2$ synthesized in a traditional way.

The properties of SCFs, mainly water and CO$_2$, are very attractive to both the generation of particles and its use in support impregnation and substance microencapsulation [5-7]. This is because they combine a density and solvent power similar to those of liquids, and transport properties (viscosity and diffusivity) similar to those of gases. Furthermore, properties above mentioned can be tuned by simply changing the operating conditions of pressure and temperature [8, 9]. Moreover, SCFs allow the synthesis of particles with specific well-defined

properties (morphology, structure, particle size, or size distribution), which are very important for the final application of the product [5].
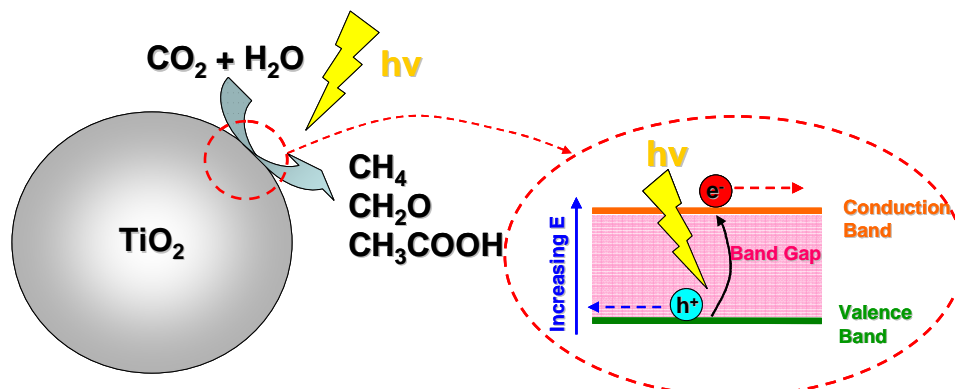

Figure 1. Scheme of the *band-gap* of a semiconductor.

In particular, SC-CO_2 is a very interesting reaction medium for ceramic particles synthesis, since it is non-toxic or flammable, has a low critical temperature, a high degree of compressibility, and low cost. Recent research [5, 6, 10] found that, compared with conventional preparation methods (gel-gel, SGP, and chemical vapor deposition, CVD), the synthesis of TiO_2 in SC-CO_2 can be performed in milder conditions of temperature, and more quickly.

Finally, this work includes the implementation of TiO_2-based photocatalysts synthesized in SCFs in **photocatalytic carbon dioxide reduction** in order to obtain liquid fuels, easy to store and transport. As ultimate goal of this research line, it is considered the production of these photocatalytic reactions with energy intake from sunlight, for which a reactor similar to those used in the literature will be used in future stages of the project.

2. EXPERIMENTAL

2.1 Laboratory plant for the synthesis process

Synthesis of TiO_2 is performed in a semi-continuous pilot plant capable of operating at pressure (150-200 bar) and temperature intervals (250-300 °C) that are necessary to carry out this reaction. The experimental setup consists of 3 subsystems: the impulsion module, comprising a high pressure pump supported by a pressure regulating valve (BPR); the reaction chamber, and the separation system, solid-liquid and liquid-gas (**Figure 2**). The experimental time required is 2 hours [5].

2.2 Supercritical synthesis of TiO_2 and metal-doped TiO_2

The methodology followed to carry out the photocatalyst synthesis is a process of *thermal hydrolysis* of the organometallic compound, which acts as a titanium precursor, by a hydrolytic agent (alcohol) in SC-CO_2.
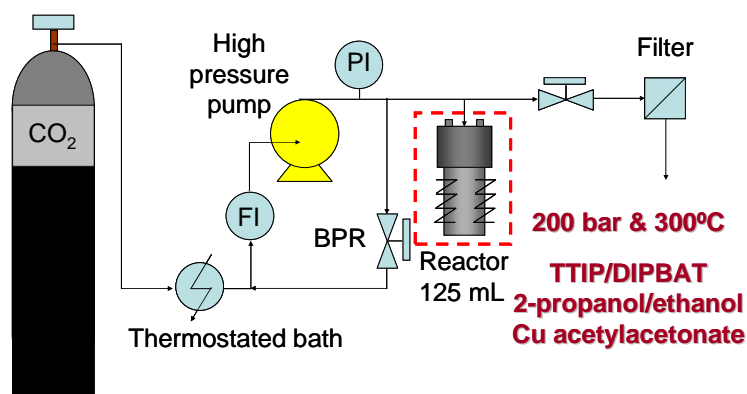
Figure 2. Flow diagram of the high pressure experimental setup used for the synthesis of TiO_2 particles in SC-CO_2. FI, mass flow indicator. PI, pressure indicator. BPR, pressure regulating valve.

Thus, the four possible combinations of two precursors, namely titanium tetraisopropoxide (TTIP) and diisopropoxititanium bis(acetilacetonate) (DIPBAT), and two different hydrolytic agents, isopropanol and ethanol, are used to synthesize TiO_2 [5, 11].

Moreover, the catalyst doping with metallic elements such as copper can be developed in the supercritical synthesis process itself. The procedure for this is based on literature [12], and a maximum content of copper of 1 wt. % has been reached in the photocatalysts.

2.3 Photocatalysts characterization equipments

The characterization of the synthesized catalysts is done using standard analytical procedures. The degree of crystallinity and the presence of different crystalline phases are determined by X-ray diffraction (XRD); the semiconductor structure, by Fourier transform infrared spectroscopy (FTIR); the particle size, with a high resolution laser analyzer; the semiconductor absorbance spectrum and the *band-gap*, by UV-vis diffuse reflectance spectroscopy (DRS); the specific surface and pore size distribution, by BET technique; the number, type and strength of active acid centers present on the catalyst surface, by TPD technique; and the TPR technique (with the same equipment), to measure metal dispersion by pulse chemisorption and the degree of reduction. Chemical analysis was carried out by atomic absorption spectrophotometry.

2.4 Photocatalytic carbon dioxide conversion

After characterization, we proceed to evaluate the photocatalytic activity of the catalyst in the reduction of CO_2, using UV light as energy source, and deionized water as reducing agent.

The experimental setup comprises a photocatalytic reactor made of glass (770 ml approx.), equipped with an UV radiation internal device (150 W), and a cooling system to keep the temperature constant during the course of the reaction (**Figure 3**). In addition, the vessel has several sampling ports for both gas and liquid phases [13].

Figure 3. Photocatalysis reaction experimental setup.

The test conditions consist of a continuous CO_2 stream bubbling in an aqueous suspension of TiO_2 nanoparticles (either ®P25 Aeroxide commercial product, or synthesized), concentration 0.5-1 g/L [13, 14]. Throughout the experimental time, 6-7 hours [15, 16], the reaction mixture is irradiated with light from a medium pressure UV lamp, whose spectral distribution partially fits the photocatalyst absorption spectrum [17].

Samples taken from liquid and gas phases at different times are analyzed in a gas chromatograph (GC) with flame ionization detector (FID).

3. RESULTS AND DISCUSSION

3.1 Supercritical synthesis of TiO_2

The yields of various TiO_2 synthesis experiments, including the two precursors of titanium and the two alcohols mentioned in the previous section, have been calculated (see **Table 2**). Similarly, this operation has been performed for those tests that include a copper-doping process. To obtain these values, the ratio of produced TiO_2 moles and used titanium precursor moles is calculated.

Yield values reached are considerably higher when TTIP is used as titanium precursor, with respect to those experiments that include DIPBAT. It can not be stated that there are significant differences between the use of one or other hydrolytic agent. However, the results of the photocatalytic tests are necessary to choose one of the two precursors as ideal, because recent studies show that DIPBAT results in photocatalysts with larger surface area for adsorption and catalysis [5].

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Table 2. Yield values obtained in different TiO_2 supercritical synthesis reactions, using SC-CO_2 as reaction medium.

Precursor	Alcohol	Doping Metal	Average Yield (%)	Number of Experiments	STDEV (%)
TTIP	Isopropanol		**96**	2	4.99
TTIP	Ethanol		**100**	1	
DIPBAT	Isopropanol		**63**	4	4.11
DIPBAT	Ethanol		**55**	2	14.85
TTIP	Isopropanol	Cu (0.5 wt. %)	**53**	1	
TTIP	Isopropanol	Cu (1.0 wt. %)	**93**	1	
TTIP	Ethanol	Cu (0.5 wt. %)	**95**	1	

3.2 Photocatalysts characterization

I. <u>Commercial TiO$_2$</u>

Firstly, we have studied physical and chemical properties of interest in the commercial catalyst (**Figure 4**). These results are used as reference for comparing commercial TiO$_2$ with the new synthesized photocatalysts.

Thus, this figure shows the results of XRD (a), FTIR (b), particle size distribution (PSD) (c), DRS (d), and BET isotherm (e).

II. <u>Synthesized photocatalysts</u>

In the following lines, the properties studied to date in synthesized semiconductors will be discussed, since they provide information of great interest with regard to its use in photocatalysis.

a. *UV-vis diffuse reflectance spectroscopy (DRS)*

The study of this property of the photocatalysts has an enormous importance with respect to its use under sunlight, which is the final goal of this research project.

By analyzing the obtained results (**Figure 5**), a clear shift of the right branch of the absorbance curve to the visible range, in the case of photocatalysts synthesized from DIPBAT precursor compared to those synthesized with TTIP, can be detected. This is the same effect observed in previous works for photocatalysts doped with nonmetals such as nitrogen [18], and also for catalysts obtained by other synthesis methods such as *solution combustion* (*TSC*) [19]. This result would add value to DIPBAT-catalysts, not only because of the possibility to operate under sunlight, but also thanks to the improvement of the efficiency in the conversion

of CO_2 with UV light from the lamp used in this project, which shows a series of emission peaks in the visible region [20].
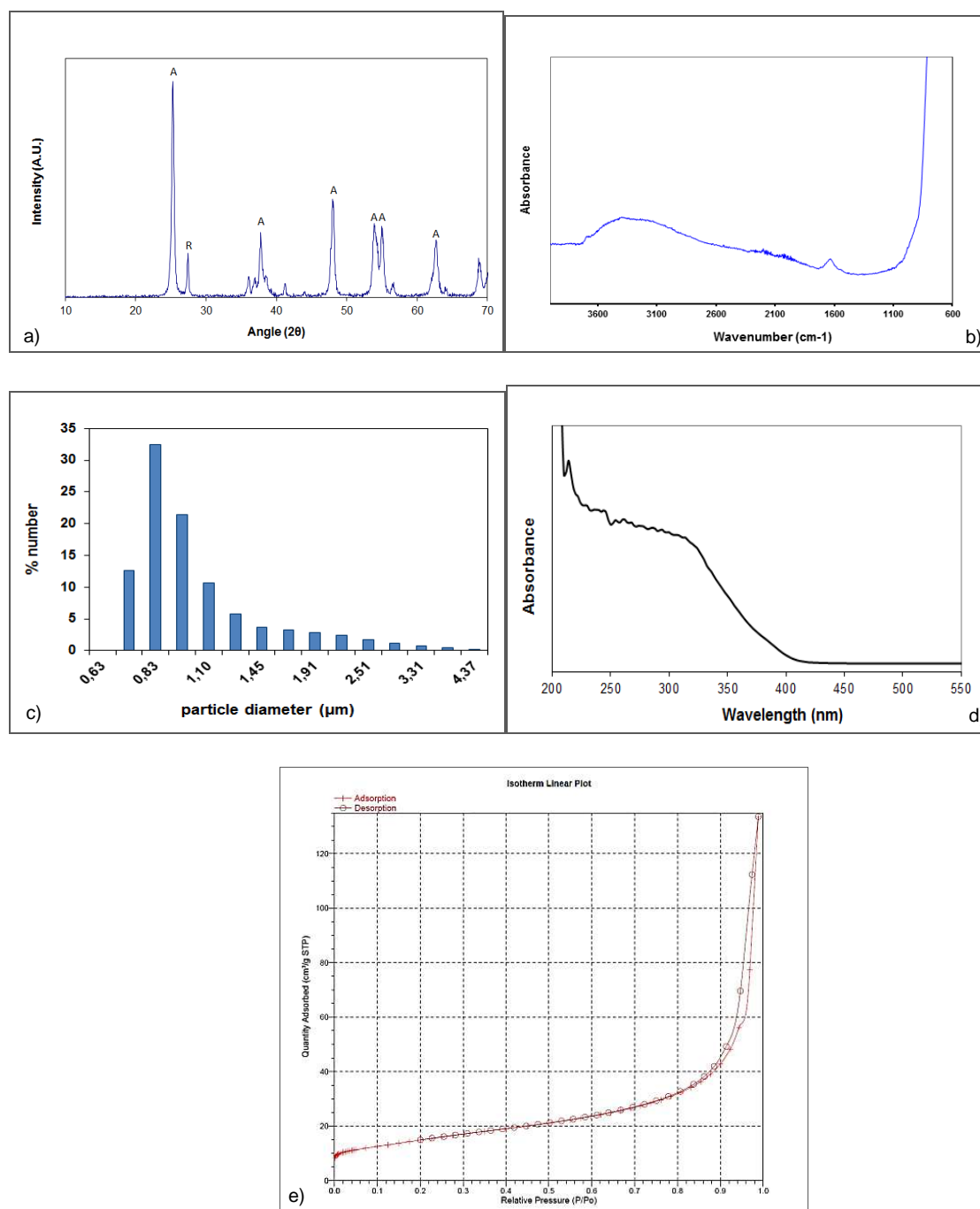

Figure 4. Results of commercial TiO_2 characterization. X-ray diffractogram (a), IR spectrum (b), particle size distribution (c), absorbance spectrum (d) and adsorption-desorption isotherm curves (e).

On the other hand, the absorbance spectrum of a copper-doped catalyst has been compared to that of the same synthesized photocatalyst in absence of metallic element. Thus, the curve for the doped photocatalyst is slightly shifted toward the visible region (see **Figure 6**). Further

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research with catalysts with higher metal content (up to 10 wt. % [14]) will be required to determine if this modification of the semiconductor certainly leads to raise the absorbance in that region of the spectrum.
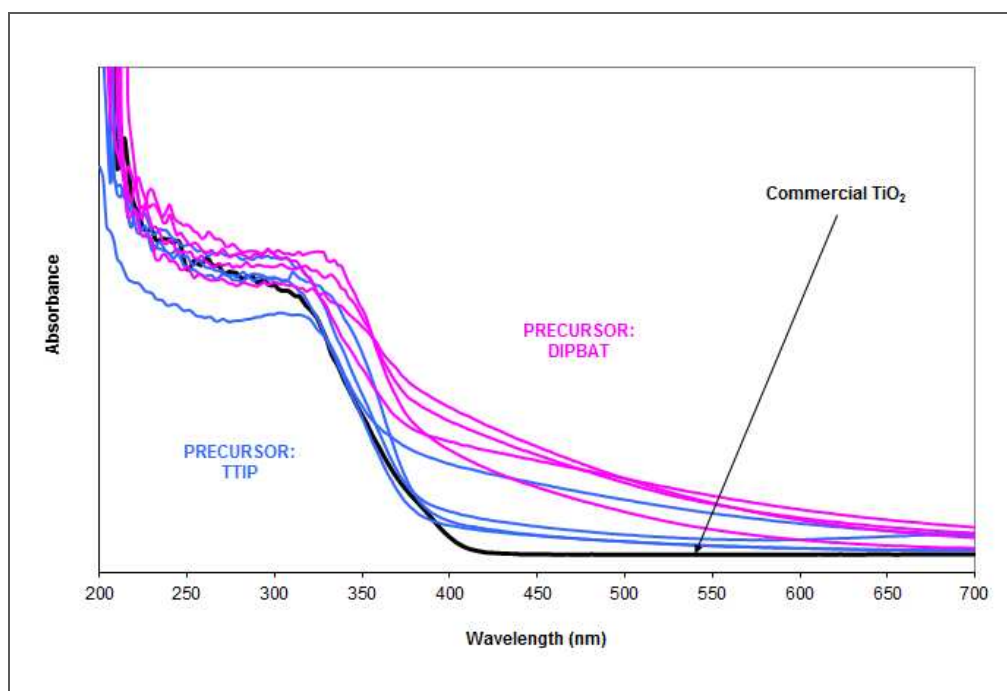

Figure 5. DR/UV-vis spectra of the photocatalysts synthesized from TTIP and DIPBAT titanium precursors, and of commercial TiO_2.
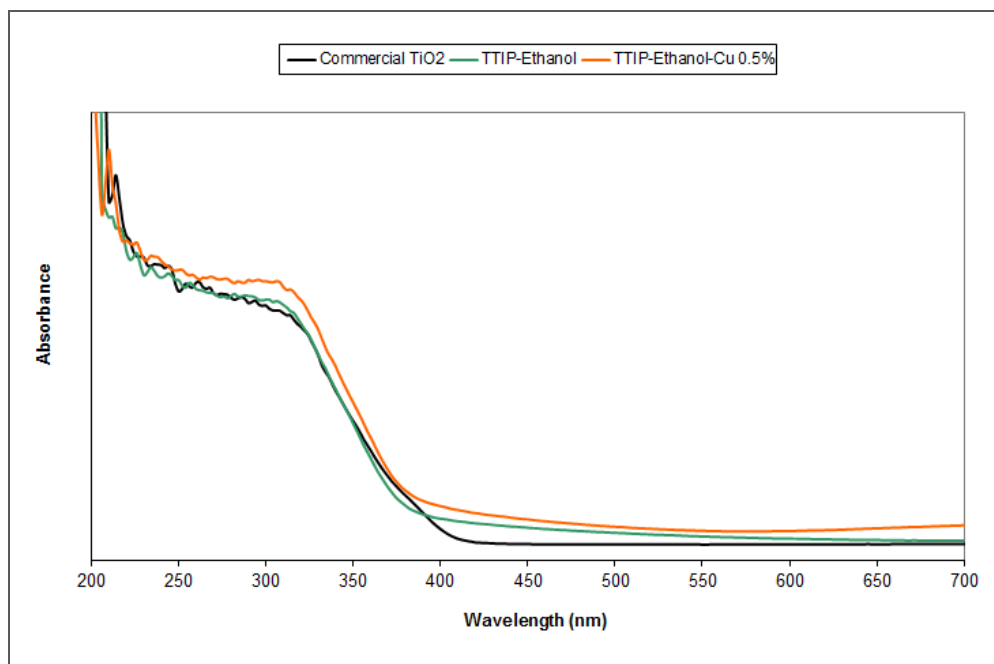

Figure 6. DR/UV-vis spectra of two synthesized photocatalysts, copper-doped and undoped, and of commercial TiO_2.

b. *X-ray diffraction (XRD)*

Another measured property of the catalysts is the XRD pattern. This analysis reports the presence of different allotropic forms of TiO_2, namely anatase and rutile, by means of the distribution of the peaks, as well as the photocatalyst crystallinity, related to the height and resolution of these peaks. Both the predominance of anatase phase and the observation of high well-resolved peaks will promote the photocatalytic process. Firstly, due to the provision of greater specific surface and higher density of active sites in the anatase form [21], and secondly, because of a better behavior under the absorbed radiation associated with a good crystallinity. As shown in **Figure 7**, all the synthesized catalysts exhibit XRD patterns similar to that of commercial TiO_2, and all the observed peaks in these diffractograms are related to anatase phase, not to rutile.
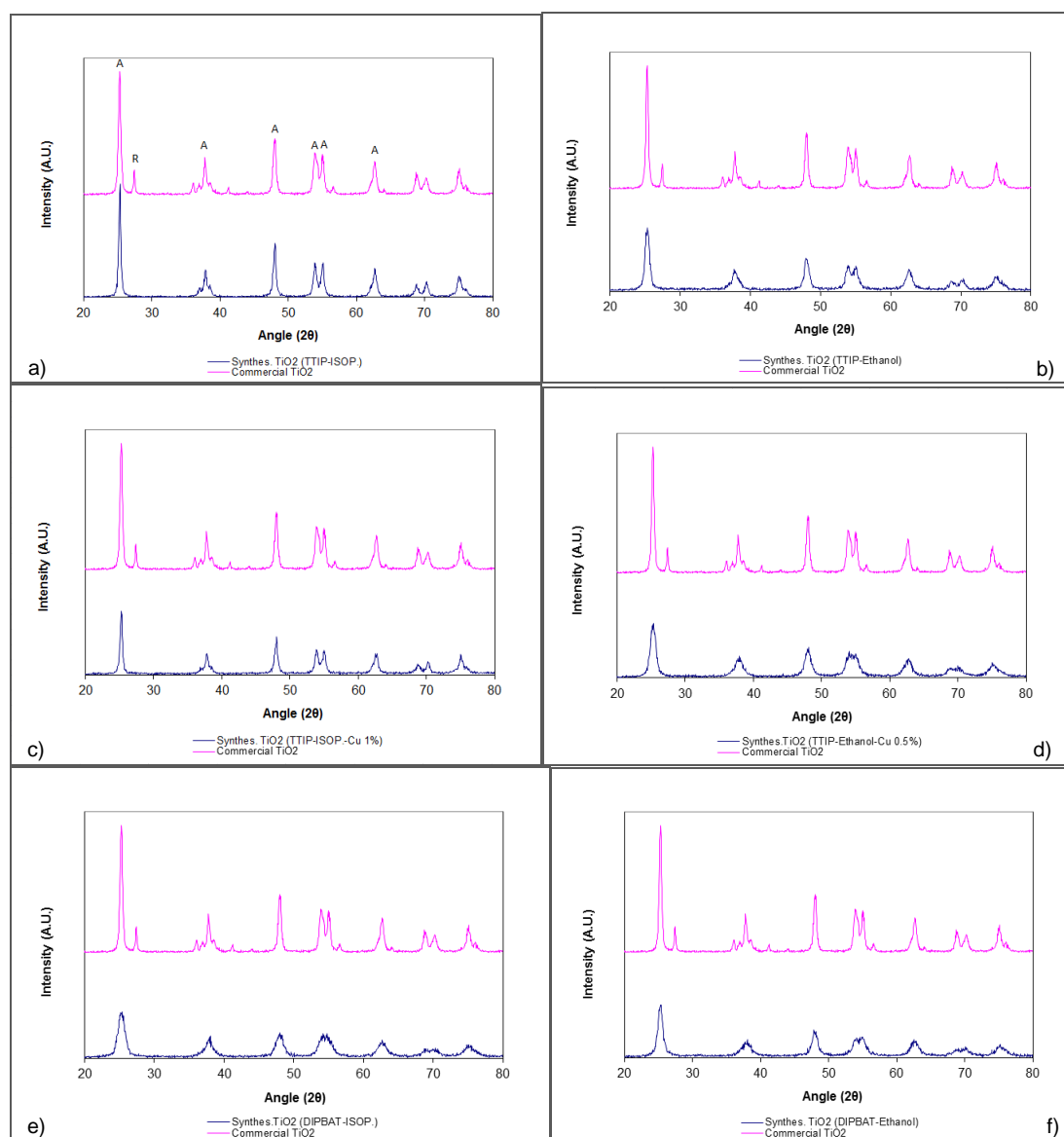

Figure 7. XRD patterns of (a) TTIP-isopropanol, (b) TTIP-ethanol, (c) TTIP-isopropanol-Cu 1.0 wt.%, (d) TTIP-ethanol-Cu 0.5 wt. %, (e) DIPBAT-isopropanol, and (f) DIPBAT-ethanol synthesis combinations. A: anatase phase. R: rutile phase.

Moreover, the best peak resolution and peak height with respect to the pattern of commercial TiO_2, is shown by the synthesis combination undoped TTIP-isopropanol, whereas TTIP-ethanol and copper-doped TTIP-isopropanol combinations exhibit worse results. Copper-doped TTIP-ethanol combination shows lower peak resolution and peak height with regard to its equivalent undoped. Finally, DIPBAT combinations result in poorer resolution peaks than those which include TTIP, and significant differences between the various hydrolytic agents cannot be appreciated.

3.3 Photocatalytic activity evaluation of synthesized catalysts

The experiments of CO_2 photocatalytic reduction have allowed to obtain results for both copper-doped and undoped catalysts, and thus, to compare these curves with that achieved using the commercial catalyst (see **Figure 8**).
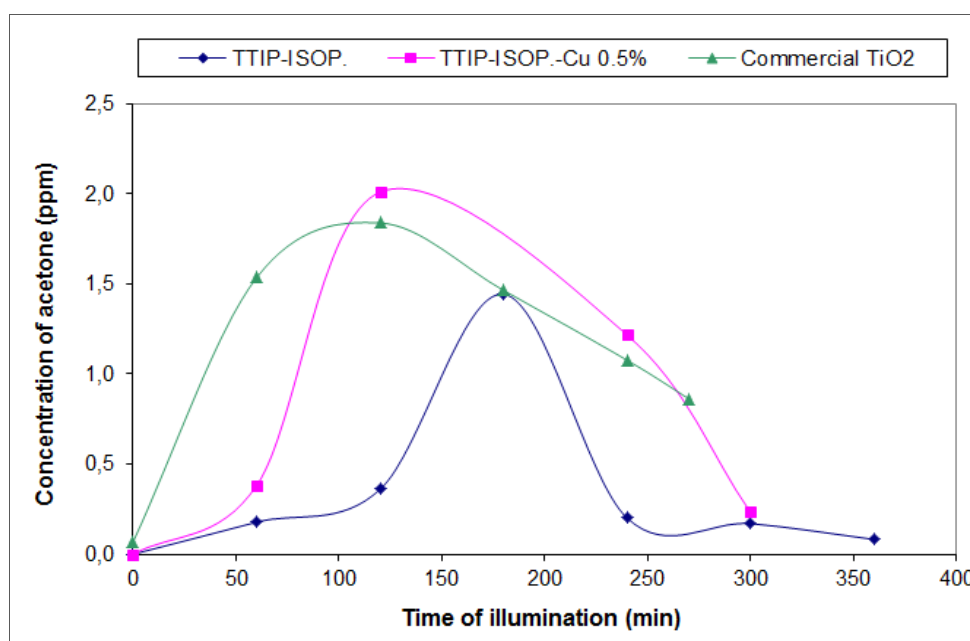

Figure 8. Acetone production in different experiments of CO_2 photocatalytic conversion, with photocatalyst synthesized from TTIP-isopropanol (◊), the previous doped with 0.5 wt. % copper (□), and commercial TiO_2 (Δ).

As shown in the graph, a slightly higher maximum concentration of the main product in CO_2 conversion (acetone) is observed when the photocatalyst is doped with the metallic element. If commercial TiO_2 is used, the maximum concentration of acetone in this case exceeds the one appreciated with the undoped catalyst, and it approaches that of the copper-doped photocatalyst. It is necessary to remark that the doping element content used is not the highest within the range considered in the literature [14, 22, 23], so these results could be still improved.

4. CONCLUSIONS

- It is feasible to obtain photocatalysts whose properties are very similar to the commercial TiO_2 by means of SCFs technology, with some advantages like the possibility of tuning these properties to the requirements of the research with simple changes in the synthesis process. In addition, it is possible to incorporate both metallic and nonmetal elements into the semiconductor during the synthesis reaction, which will provide interesting characteristics to the product.

- Supercritical synthesis assays have resulted in higher yields when TTIP is used as titanium precursor. However, it is necessary to consider the advantages of DIPBAT precursor demonstrated in previous studies, and to experimentally verify if there are differences in their photocatalytic activity, in order to make decisions about the use of one or other compound in the synthesis of TiO_2.

- By analyzing the absorbance spectra of the photocatalysts, it has been observed that the curves obtained from DIPBAT-catalysts show the right branch clearly shifted to the visible range, with respect to those of the commercial catalyst, and the synthesis combinations including TTIP. On the other hand, comparing the absorbance curves of doped and undoped catalysts obtained from the same synthesis combination, it has been possible to appreciate that the curve for the copper-doped photocatalyst is slightly shifted to the visible range. It will be necessary to increase the proportion of doping metal to verify that this effect is due to the metallic element incorporated.

- After carrying out the measurement of XRD patterns to the synthesized catalysts, it has been concluded that in all cases the obtained peaks correspond with the anatase phase, and the synthesis combination that shows the best crystallinity is TTIP-isopropanol. The last mentioned property, in general, is not improved by doping, and gets worse with the replacement of hydrolytic agent with ethanol. If DIPBAT precursor is used, crystallinity appears to be even lower.

- Finally, after several experiments of photocatalytic reduction of CO_2 using a synthesized catalyst doped with copper and its equivalent in absence of metallic element, it can be stated that the major product generated in the reaction (acetone) reaches a slightly higher concentration when the catalyst is doped with respect to commercial TiO_2. Both concentrations are clearly higher than the maximum reached by the photocatalyst without copper. It will be required a greater proportion of metal to confirm that doping leads to better conversion results.

5. ACKNOWLEDGEMENTS

6. REFERENCES

[1] DIEBOLS, U., Surf. Sci. Reports, Vol. 48, **2003**, p. 53.

[2] KABRA, K., CHAUDHARY, R., SAWHNEY, R. L., Ind. Eng. Chem. Res., Vol. 43, **2004**, p. 7683.

[3] AGUADO, J., VAN GRIEKEN, R., LÓPEZ-MUÑOZ, M. J., MARUGÁN, J., Appl. Catal. A: General, Vol. 312, **2006**, p. 202.

[4] MARUGÁN, J., LÓPEZ-MUÑOZ, M. J., VAN GRIEKEN, R., AGUADO, J., Ind. Eng. Chem. Res., Vol. 46, **2007**, p. 7605.

[5] ALONSO, E., MONTEQUI, I., LUCAS, S., COCERO, M. J., J. of Supercrit. Fluids, Vol. 39, **2007**, p. 453.

[6] ALONSO, E., MONTEQUI, I., COCERO, M. J., 5th International Symposium on High Pressure Process Technology and Chemical Engineering, Segovia (Spain), **2007**.

[7] LÓPEZ-PERIAGO, A. M., RIUS, J., REY, F., SABATER, M. J., DOMINGO, C., 5th International Symposium on High Pressure Process Technology and Chemical Engineering, Segovia (Spain), **2007**.

[8] STAHL, E., QUIRIN, K. W., GERARD, D. (Eds.), *Dense gases for extraction and refining.* Springer-Verlag Publishing. Berlin, **1988**.

[9] LUQUE DE CASTRO, M. D., VALCÁRCEL, M., TENA, M. T. *Extracción con Fluidos Supercríticos*. Reverté, Barcelona, **1993**.

[10] ALONSO, E., MONTEQUI, I., COCERO, M. J., J. of Supercrit. Fluids, Vol. 49, **2009**, p. 233.

[11] CHHOR, K., BOCQUET, J.F., POMMIER, C., Mater. Chem. Phys., Vol. 32, **1992**, p. 249.

[12] ALONSO, E., FERNÁNDEZ-RODRÍGUEZ, H., COCERO, M. J., FLUCOMP 2010: IV Reunión de Expertos en Tecnologías de Fluidos Comprimidos, Ciudad Real (Spain), **2010**.

[13] SASIREKHA, N., BASHA, S. J. S., SHANTHI, K., Appl. Catal. B: Environ., Vol. 62, **2006**, p. 169.

[14] SLAMET, NASUTION, H.W., PURNAMA, E., KOSELA, S., GUNLAZUARDI, J., Catal. Commun. Vol. 6, **2005**, p. 313.

[15] YAMASHITA, H., FUJI, Y., ICHIHASHI, Y., ZHANG, S. G., IKEUE, K., PARK, D. R., KOYANO, K., TATSUMI, T., ANPO, M., Catal. Today, Vol. 45, **1998**, p. 221.

[16] SUBRAHMANYAM, M., KANECO, S., ALONSO-VANTE, N., Appl. Catal. B: Environ. Vol. 23, **1999**, p. 169.

[17] LEI, L., HU, X., YUE, P. L., BOSSMAN, S. H., GÖB, S., BRAUN, A. M., Photochem. Photobiol. A: Chem., Vol. 116, **1998**, p. 159.

[18] VARGHESE, O. K., PAULOSE, M., LA TEMPA, T. J., GRIMES, C. A., Nano Lett. Vol. 9(2), **2009**, p. 731.

[19] HUSSAIN, M., CECCARELLI, R., MARCHISIO, D. L., FINO, D., RUSSO, N., GEOBALDO, F., Chem. Eng. J., Vol. 157, **2010**, p. 45.

[20] VILANÓ, M., PADRÓ, A., RUBIO, R.M., RAURET, G., J. Chromatography A, Vol. 819, **1998**, p. 211.

[21] USUBHARATANA, P., MCMARTIN, D., VEAWAB, A., TONTIWACHWUTHIKUL, P., Ind. Eng. Chem. Res., Vol. 45, **2006**, p. 2558.

[22] WU, J.C.S., LIN, H. M., LAI, C. L., Appl. Catal. A: General, Vol. 296, **2005**, p 194.

[23] ANPO, M., YAMASHITA, H., ICHIHASHI, Y., EHARA, S., J. Electroanalyt. Chem. Vol. 396, **1995**, p. 21.