Photocatalityc reduction of CO2 with Cu/TiO2/carbonaceous support synthesized in supercritical conditions

V. Rodríguez , R. Camarillo, F. Martínez, C. Jiménez, I. Asencio, J. Rincón.

Department of Chemical Engineering of University of Castilla-La Mancha. Faculty of Environmental Sciences and Biochemistry. Av. Carlos III s/n (45071) Toledo, Spain.

1. Introduction – The objective of this work is the optimization of conversion of carbon dioxide (one of the most important greenhouse gases) in fuels or others high value components such as methane. Our research is focused on the simulation of an "artificial process of photosynthesis", where the photoreduction of CO2 takes place with a photocatalyst and a reducing agent (water). The catalysts synthesized are based on the semiconductor titanium dioxide (TiO2). Despite the excellent characteristics of TiO2 for CO2 reduction, catalysts could be improved when TiO2 is doped with Cu particles and when they are supported on carbonaceous material such as carbon nanotubes (CNT) or reduced graphene oxide (rGO). The main change with respect to traditional synthesis of these catalysts is the introduction of a supercritical fluid. The advantages of supercritical synthesis in comparison to traditional synthesis is the elimination of conventional solvents, which would make it a more environmental-friendly process. Supercritical CO2 is used due to its abundance, low flammability, low toxicity and cost [1]. Several studies report that TiO2 particles obtained with supercritical fluids exhibit larger surface areas, less agglomeration degree [2], good porosity, high crystallinity and purity, better morphology for charges separation in photoreduction and decreases of band gap energy, which may affect the absorption in wavelengths corresponding to visible light and photocatalytic activity [3].

2. Experimental - The use of supercritical fluids in the synthesis allow to make several procedures in a single reaction: the thermohydrolysis of TiO2 precursor, the metal doping, supporting it on the carbon structure and the reduction of graphene oxide to reduced graphene oxide. The reactions conditions are among 80-200 bar and 60-300 ºC. The INQUIME group of Department of Chemical Engineering at UCLM have designed an ad hoc installation which can resist these reactions conditions. The same occurs with the photoreduction equipment, which was also designed by the INQUIME group. It is composed of a cell (where the photocatalyst, CO2 and the reducing agent are in contact), a Xenon arc lamp that simulates sunlight and a gas chromatograph to quantify the reaction products.

3. Results and Discussion - The photocatalytic activities of catalysts synthesized in supercritical conditions are compared with those corresponding to a commercial TiO2 catalyst (Degussa P25). In most cases, the results obtained are better than P25. In all cases, the majority reaction product is CO and sometimes CH4 can be observed.

4. Conclusions - The supercritical synthesis of TiO2 particles improves the photoreduction of CO2, but it is necessary to optimize the amount of the carbonaceous material and the metal used to achieve results applicable to industrial sector.

5. References [1] C-H. Huang y C-S. Tang, Aerosol Air Qual. Res., 14, (2014) p. 480. [2] J. Yu, J. Jin, B. Cheng y M. Jaroniec, J. Mater. Chem., 2, (2014) p. 3407. [3] R. Camarillo, S. Tostón, F. Martínez, C. Jiménez, J. Rincón, J. Chem. Technol. Biot., 92, (2017) p. 1710.