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Photocatalytic Approaches to Circular Economy: CO_2 Photoreduction to Regenerated Fuels in a three-phase photoreactor

Francesco Conte[1], Antonio Tripodi[1], Gianguido Ramis[2], Ilenia Rossetti[1]*
1 Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, CNR-ISTM and INSTM Unit Milano-Università, via C. Golgi 19, 20133 Milano, Italy; 2 DICCA, Università degli Studi di Genova and INSTM Unit-Genova, via all'Opera Pia 15A, 16100 Genoa, Italy

**Corresponding author E-Mail: ilenia.rossetti@unimi.it*

1. Introduction

CO_2 photocatalytic conversion towards marketable chemicals such as hydrogen, methanol, methane, formaldehyde and formic acid seems to represent a valid and green method to reduce atmospheric concentration of carbon dioxide [1]. It is less energy demanding than traditional processes and does not produce harmful byproducts. For all these reasons photocatalysis appears to be a smart alternative for effective CO_2 conversion. Furthermore, the possibility to exploit solar energy represents a free energy source available worldwide.

We have recently proposed an innovative photoreactor, able to operate up to 20 bar and 100°C for the photoreduction of CO_2. The advantage of the approach is found in the possibility to enhance CO_2 solubility in water (one of the main physical limitations of the process) and the surface adsorption of the reactant over the heterogeneous catalyst [2-4]. High pressure also allows to increase temperature of operation (while keeping sufficiently high concentration of CO_2 in liquid phase), with beneficial effects on all the auxiliary steps of the reaction, i.e. mass transfer, sticking probability, etc. Therefore, the development of a unique high pressure device allows to explore unconventional reaction conditions for both applications, to boost the productivity.

Therefore, in this work, we are reporting some high productivity results for the photoreduction of CO_2, collected using simple and inexpensive photocatalysts, trying to focus on the expected efficiency under solar light irradiation. The case study is represented by irradiation in Northern Italy (3.7 kWh/m^2), specifically Milan, located on the 45.5° parallel, which is an intermediate situation with respect to the maximum and minimum values across Europe, ranging from 5.0 in Southern Europe to 2.6 in Northern Europe.

2. Methods

The innovative photoreactor used for activity testing has been widely described in previous publications [2-4]. An AISI 316 stainless steel, batch type photoreactor was used, with co-axial immersion lamp and bottom stirrer. Testing is done on 1.2 L of solution, allowing *ca*. 0.1 L of head space for the gas. A thermal bath circulates water around the external heating wall, setting the operating temperature. A 125 W medium pressure Hg lamp was used as light source, emitting between 254 and 364 nm (main emission peak). A detailed mapping of the irradiance through the reactor is supplied by a radiometer. Irradiance ranged between 133 and 157 W/m^2 for different tests. This datum is used as comparison with the sunlight irradiance. The catalyst, 0.03 g/cm^3, was suspended in demineralized and outgassed water. The suspension has been saturated with CO_2 at 7 bar pressure overnight before starting irradiation. Tests lasted 24 h at 7 bar pressure and 80°C. Na_2SO_3 0.85 g L^{-1} has been

used as hole scavenger. Sulfite conversion was determined by iodometric titration. The liquid phase products (HCOOH, HCHO and CH_3OH) were analysed by HPLC (Agilent 1220 Infinity, column Alltech OA-10308, 300 mm-7.8 mm), with UV and refractive index (Agilent 1260 Infinity) detectors. HCHO, critical to analyse was also quantified in parallel by UV-Vis spectrophotometry through the Nash reactant and UV-Vis analysis (Perkin Elmer, Lambda 35). The gas phase products (H_2, CH_4 and polar/non polar light gases) were analysed by a gas chromatograph (Agilent 7890) equipped with HP Plot Q and MS columns through a TCD detector.

3. Results and discussion

From preliminary screening on a wide array of samples, we have identified the best results as for productivity of different liquid or gas phase products. In particular, by using commercial TiO_2 Evonik P25, with average UVA irradiance of 150 W/m^2 (365 nm), we obtained a maximum productivity of HCOOH 39.3 mol / h kg_{cat}.

Data of daily irradiance have been collected for the Metropolitan City of Milan (Northern Italy) relative to year 2018. With an average value of 0.156 kW/m^2 day of solar irradiation (of which only a ca. 5% portion can be exploited), the distribution shows a broad variance not only during the seasons, but also within the same time period, depending mainly on weather conditions. This is a first issue with plant sizing, since the huge variability of the primary source induces not only a variable output of the products, but also control problems for the plant, which hardly reaches a stationary condition.

The expected daily and yearly productivity upon solar light exposure has been calculated according to [5] referring to 1 m^3 photoreactor volume distributed in a reactor 0.2 m deep and with the extension of 5 m^2. Stored power ranging from ca. 1.2 to 1.5 MJ/year kg_{cat} were calculated, corresponding to a yearly productivity of ca. 250 kg/year kg_{cat} of HCOOH. These results refer to a very simple, commercial, inexpensive and durable catalyst. The efficiency of the process is still very low when referred to the whole incident radiation, while it increases to *ca*. 10% when referred to the useful fraction of radiation exploitable by the photocatalyst. This suggests on one hand the need for improvement of the light harvesting ability of the sample. On the other hand, it leaves wide room for improvement of the intrinsic catalyst efficiency.

4. Conclusions

The photoreduction of CO_2 has been investigated in a three-phase high pressure photoreactor. The productivity to HCOOH over-performed most literature data and was set as the basis to check the feasibility of a pilot unit 1 m^3/5 m^2. The amount of stored energy yearly, though in an almost continental climate region and with a very basic commercial photocatalyst revealed very promising, but suggested further improvement in the light harvesting properties of the material.

References

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