

## A novel high-pressure photoreactor for CO<sub>2</sub> photoconversion to fuels

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One of the limitations for CO<sub>2</sub> photoreduction in the liquid phase is due to its low solubility in water. This point has been here addressed by designing a fully innovative concept of pressurised photoreactor, allowing operation up to 20 bar and applied for the first time to improve the productivity of this very challenging process.

CO<sub>2</sub> is among the most stable molecules, requiring high amounts of energy to be activated. Photosynthesis allows the conversion of CO<sub>2</sub> and H<sub>2</sub>O, the major products of combustion, into useful organic compounds and represents one of the most efficient ways for CO<sub>2</sub> capture, besides its absorption in oceanic water. This is a natural but complex process leading to a regenerated fuel by photo-irradiation. The natural process has never been mimicked in laboratory, due to the complexity of the enzymatic reactions involved. In spite of this, the topic is intriguing and it raised interest in the late 70s with the first attempts to fix CO<sub>2</sub> at least by partially reducing it to CO. However, the results were not satisfactory for different reasons. The first was a lack of knowledge on the basics of materials science for photocatalysis at that time, now partly overcome by many reports, although for different applications (*e.g.* photo-degradation of pollutants).<sup>1</sup> Another reason was that the limited solubility of CO<sub>2</sub> in water (0.03 M at 25 °C, 1 atm CO<sub>2</sub>), especially at relatively high temperature which could improve the kinetics, always led to very poor productivity. Some attempts with different solvents, *e.g.* methanol or acetonitrile (solubility 0.2 M and 0.3 M, respectively), allowed to increase solubility, but at the expenses of a less sustainable solution. However, no impressive increase of CO<sub>2</sub> conversion was observed.

Some researchers tried to develop catalytic solutions based on supramolecular chemistry and homogeneous catalysis through *e.g.* metalloporphyrins and Re or Ru complexes,<sup>2</sup> which however suffer of many drawbacks: difficult synthesis of the

catalyst, instability during photo-irradiation, often the use of organic solvents and separation problems. Furthermore, the most abundant products were CO and formic acid or formiates, which are toxic and suspect mutagenic products, hard to recycle as renewable fuels. Some attempts to immobilize such complexes over solid surfaces were also done more recently by using dye-sensitized semiconductors, useful also to increase light absorption in the visible region. Indeed, Grätzel's group prepared dye-sensitized porous TiO<sub>2</sub> solar cells (not for this application) with excellent solar power conversion efficiency (about 11%).<sup>3</sup> The dyes absorb visible light to form electronically excited states from which electrons are injected into the conduction band of the semiconductor, producing photo-sensitized catalysts which are able to work under visible light.<sup>4</sup> However, these photosensitizing dyes are not thermally nor photochemically stable. Formiates have been evidenced as the only product also with Au and Pt functionalised carbon based nanoparticles<sup>5</sup> and with Cu- and Ga-loaded TiO<sub>2</sub> nanocomposites.<sup>6</sup> Therefore, after such explorative tests the attention towards this reaction decreased, so that only a few papers on this topic may be found till that time.

Concerning inorganic semiconductors most researchers focused on TiO<sub>2</sub>, recently obtained in nanostructured form. Nanostructuring improved the surface area and the catalytic performance, though unacceptably depressing photo-absorption in the visible region due to blue shift of the absorption edge.<sup>7–9</sup> Indeed, it was proved for different applications that the band gap was tightly related to particle size due to size quantization effects.<sup>10</sup> Absorption in the visible region of the solar spectrum is one of the most pressing problems to solve in order to adopt solar light for CO<sub>2</sub> photoactivation, since the visible portion of the solar spectrum is predominant with respect to the UV one, so far used for this application (the latter representing up to 2–3% of the solar spectrum, only<sup>11</sup>). Attempts to improve Vis light response have been variously proposed. For instance, the selective CO<sub>2</sub> photoreduction to CH<sub>3</sub>OH has been tested in homogeneous phase with Mo complexes.<sup>12</sup> Maximum 0.17 mmol h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup> of CH<sub>4</sub> has been obtained over multiwalled

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carbon nanotubes/TiO<sub>2</sub> core-shell systems.<sup>13</sup> The addition of transition metals or metal oxides to TiO<sub>2</sub> also extends the absorption range towards visible light. Different Cu<sub>2</sub>O facets are differently selective to H<sub>2</sub> or CO (partial CO<sub>2</sub> reduction).<sup>14</sup> Ag decoration of TiO<sub>2</sub> improves CH<sub>4</sub> yield under UV irradiation up to 2.64 mmol h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>.<sup>15</sup> By contrast, CH<sub>4</sub> is not observed in the case of Ni/TiO<sub>2</sub>, hydrogen, methanol, ethanol and acetaldehyde being the main products under both UV or Vis irradiation, with maximum H<sub>2</sub> productivity up to 50–60 mmol h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup> under UV irradiation.

To sum up, the best productivities reported up to now in the literature for fuels regenerated from CO<sub>2</sub> are attested on few mmol kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, mainly under UV irradiation, a value clearly inappropriate for any further development.

Therefore, the following key problems may be evidenced and were addressed in the present work:

- (1) Solubility limitations of CO<sub>2</sub> in liquid solvents, actually depressing productivity;
- (2) Inadequate visible light absorption to be enhanced (keeping flat band potentials compatible with the redox potentials of the reactants);
- (3) Low efficiency in separation of photoproducted charges, to be enhanced;
- (4) Back-oxidation of methanol (product in liquid phase) by holes, limiting the yield of liquid fuels;
- (5) Inadequate knowledge of competitive/consecutive reactions.

To answer such criticisms, we developed a new concept of photoreactor, proposed by our group for the first time<sup>16</sup> and never tested for this application. It is represented by a stainless steel reactor working under high pressure (up to 20 bar), in order to improve CO<sub>2</sub> solubility in a liquid solvent even at relatively high temperature.

Preliminary testing for this application has been carried out with titanium dioxide (Degussa P25) loaded with 0.1%wt of Au catalyst. Au was chosen in order to improve visible light absorption thanks to the formation of a plasmonic band, as shown in Fig. 1 between 500 and 700 nm, besides the typical TiO<sub>2</sub> absorption edge below 400 nm. Furthermore, metals with appropriate work function may act as electron scavengers favouring the separation of photoproducted charges and improving their lifetime or pumping electrons into the conduction band of the semiconductor.

Au has been loaded by deposition-precipitation at pH 9–10 from a NaAuCl<sub>4</sub> solution. The addition of NaBH<sub>4</sub> allowed gold reduction.

The catalyst, *ca.* 0.5 g, has been dispersed in demineralised and outgassed water (1–1.2 L). The suspension has been saturated with CO<sub>2</sub> at different temperature and pressure before starting irradiation with a 125 W medium-pressure Hg vapour lamp with a range of emission wavelengths from 254 nm to 364 nm.

Na<sub>2</sub>SO<sub>3</sub> has been employed in some cases as hole scavenger. Its consumption has been evaluated by iodometric titration. The liquid mixture has been analysed after different reaction time by means of a Total Organic Carbon (TOC) analyser and a gas chromatograph equipped with a FID detector. The gas

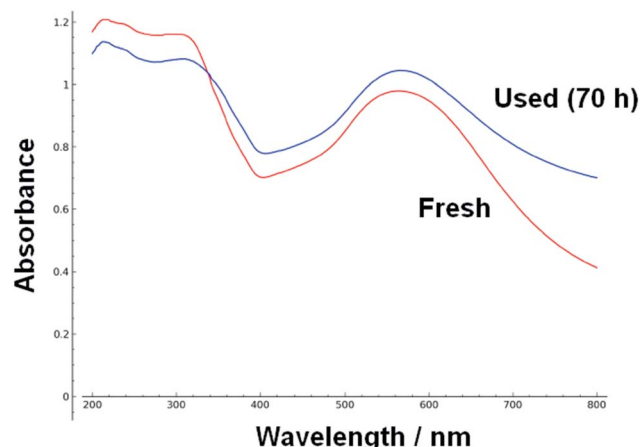


Fig. 1 Diffuse reflectance absorbance spectrum of the photocatalyst fresh and used after 70 h irradiation time.

phase over the liquid has been analysed by a gas chromatograph equipped with a TCD detector and proper set up for the quantification of H<sub>2</sub>, CH<sub>4</sub> and polar/non polar light gases.

The selected catalyst allowed to produce 120 mmol CH<sub>4</sub> kg<sub>cat</sub><sup>-1</sup> at 25 °C, 10 bar after 6 h irradiation.

Further testing at 20 bar, 85 °C allowed to obtain a complex gaseous mixture including *ca.* 6 vol% H<sub>2</sub>, 0.6 vol% CH<sub>4</sub> and different C1–C2 products in liquid phase. Such values corresponded to 51.2 mmol h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup> (1.14 NL h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>) and 1.73 mmol h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup> (0.038 NL h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>) for H<sub>2</sub> and CH<sub>4</sub>, respectively. This would suggest combined CO<sub>2</sub> photoreduction and photoreforming of the liquid phase products. Furthermore, the maximum observed productivity of organic material in liquid phase was *ca.* 110 gC h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>. We observed the presence of both C1 and C2 organic compounds, among which methanol, ethanol and in some cases traces of acetaldehyde. We may also hypothesise the presence of formaldehyde and/or formic acid, which are poorly detectable with a FID detector.

Such productivity to liquid organic products is comparable to that reported for a Cu/Ga-loaded TiO<sub>2</sub> sample<sup>6</sup> towards HCOOH, only. Different liquid products have been evidenced elsewhere,<sup>4</sup> with overall productivity <2 mgC h<sup>-1</sup> (with respect

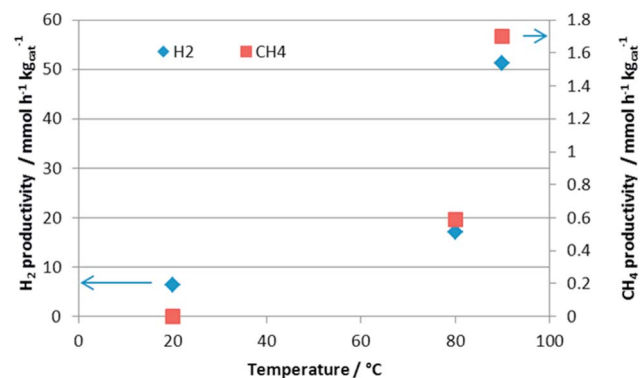


Fig. 2 H<sub>2</sub> and CH<sub>4</sub> productivities at variable temperature, 11 bar, Na<sub>2</sub>SO<sub>3</sub> concentration 1 g L<sup>-1</sup>. Hole scavenger conversion between 88 and 99.9%.



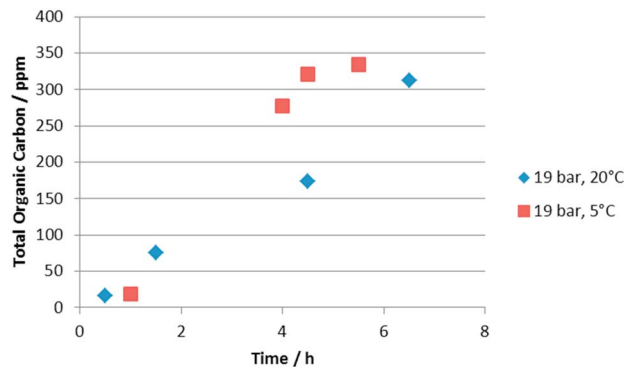


Fig. 3 Evolution with time of the organic products in liquid phase at different temperature.

to the present value  $>60 \text{ mgC h}^{-1}$ ). As for gas phase products, the present results overperform by two orders of magnitude the ones reported by M. Anpo *et al.*<sup>11,16–18</sup> for  $\text{CH}_4$  (up to  $0.02 \text{ mmol h}^{-1} \text{ kg}_{\text{cat}}^{-1}$ ) in their pioneering investigations, who did not quantify any additional contribution of  $\text{H}_2$  in gas phase. The here reported combined production of liquid and gaseous fuels in so high productivity has never been reported, confirming the validity of a high pressure approach to improve  $\text{CO}_2$  photoreduction.

In general, we observed a tight dependence of products distribution on pressure and temperature. An increase of pressure allowed to increase  $\text{CO}_2$  concentration in the liquid phase and favoured the formation of liquid fuels, mainly in form of  $\text{CH}_3\text{OH}$  and  $\text{HCOOH}$ , although a more complex products mixture may be sometimes obtained. This confirms the validity of the approach and the importance of the development of this innovative pressurised reactor.

By contrast, the formation of  $\text{CH}_4$  seems favoured by intermediate pressure, favouring on one hand solubility of the reactant and evolution of the product in gas phase.  $\text{H}_2$  is formed by a consecutive reaction leading to the photoreforming of the organic materials produced by  $\text{CO}_2$  photoreduction. Its concentration, as well as that of  $\text{CH}_4$  is maximised at intermediate pressure. In any case, the application of  $\text{CO}_2$  pressure above ambient is beneficial. For instance, testing at  $80^\circ\text{C}$ , 5 bar led to  $\text{H}_2$  productivity of  $8.0 \text{ mmol h}^{-1} \text{ kg}_{\text{cat}}^{-1}$ , which increased to  $18.7 \text{ mmol h}^{-1} \text{ kg}_{\text{cat}}^{-1}$  at 10 bar.

Temperature has more a complex effect. Indeed it decreases  $\text{CO}_2$  solubility at a given pressure, but it favours kinetics, so that an increase of temperature usually favoured the formation of a  $\text{H}_2/\text{CH}_4$  gas mixture. This occurs at the expenses of liquid phase products, which concentration decreases with temperature confirming. Such preliminary information may confirm that  $\text{H}_2$  is produced by photoreforming of the organic compounds formed in liquid phase. This conclusion seems also supported by the absence of  $\text{H}_2$  during gas phase  $\text{CO}_2$  photoreduction.<sup>19</sup> An example of results obtained at variable temperature is reported in the following Fig. 2 and 3 for the gas and liquid phases, respectively.

The catalyst also proved very stable (Fig. 1). Repeated tests over recycled samples were reproducible up to 5 cycles of *ca.* 70 h each.

## Conclusions

An innovative concept of photoreactor was set up, allowing to operate under pressure up to 20 bar. This system was effectively employed to improve the solubility of  $\text{CO}_2$  in water, thus allowing to overcome one of the main limitations for  $\text{CO}_2$  photoreduction. Higher productivity for both liquid and gas phase photogenerated fuels has been achieved by using a  $\text{Au}/\text{TiO}_2$  catalyst with respect to most literature reports.

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