

Conceptual design and feasibility assessment of photoreactors for solar energy storage

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ABSTRACT

The experimental results of testing with different irradiation power are compared and used as a basis for the feasibility assessment and conceptual design of a photoreforming reactor. The highest H₂ productivity (0.276 mol H₂/h kg_{cat}) was achieved with 1 g/L of 1 wt% Au/TiO₂ P25 catalyst by using a 113 W/m² UVA irradiation. Insufficient hydrogen productivity for practical deployment was achieved, following reactor design. However, the comparison with the state of the art evidenced that also the energy storage potential of the literature photocatalysts do not allow a short term feasibility of the proposed technology. The potential productivity of hydrogen, as well as solar energy storage efficiency are discussed both for the present experimental values and for the best results in the literature.

On the other hand, solar energy can be used to artificially fix CO₂, e.g. captured and stored from combustion processes that can be converted back to chemicals or regenerated fuels. The production of H₂, HCOOH, HCHO and CH₃OH by photoreduction of CO₂ has been evaluated as for daily production potential. CO₂ photoconversion to formaldehyde can be envisaged as solar energy storage mean with 13.3% efficiency, whereas for the other products the solar energy storage efficiency was below 1%.

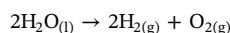
1. Introduction

Solar energy is the most abundant primary source on Earth, which intercepts 180 10⁶ GW of the total emitted power. The incident radiation is mainly constituted by visible ($\lambda = 400\text{--}700$ nm) and infrared components of the spectrum, with a low but not negligible portion of UV rays, amounting to ca. 6% of the total incident radiation at sea level. UV radiation can be further classified into the UVA, UVB and UVC components, whose intensity varies widely depending on altitude, latitude, ozone layer depth and meteorological conditions. The UVA component ($\lambda = 320\text{--}400$ nm) is by far the most abundant, being 10 to 100 times more intense than the UVB component ($\lambda = 280\text{--}320$ nm) (Wald, n.d.).

In the last fifteen years, hydrogen has been proposed as promising energy vector, due to its possible use as clean fuel, characterised by high combustion enthalpy, whose combustion leads to water as only product. Nevertheless, it is currently produced at most from fossil sources, leading to net CO₂ emissions during its production. To improve the environmental sustainability of hydrogen production, different

strategies were then proposed from renewables. On one hand, research is focused on adapting the existing thermocatalytic routes for the conversion of gas, liquid and solid fossil raw materials. For instance, efforts are put on the validation of biomass gasification, pyrolysis and on the steam reforming of various biomass derived biofuels, *in primis* bioethanol. All these routes can be seen as a way to exploit the solar energy stored in biomass in form of hydrogen, to be used as intrinsically green fuel. On the other hand, the direct exploitation of solar energy would be appreciable and for this reason photocatalytic routes are being developed for hydrogen production.

The most direct reaction would be water splitting



which, however, is highly endothermic and endoergic ($\Delta G^0 = 237$ kJ/mol). Various attempts to split water photocatalytically have been reported, starting from the first pioneering studies by Fujishima and Honda (Fujishima and Honda, 1972). However, the productivity achieved for direct water photosplitting is largely insufficient for practical exploitation (Chiarello and Selli, 2014). This is

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mainly attributed to the water oxidation half reaction, which is a slow 4-electrons process. The use of organic electron donors was the key to improve productivity. Starting from methanol, the simplest molecule, up to carbohydrates and other biomass derived compounds, many examples have been reported for the use of oxygenate organic compounds as hole scavengers in a process that is conventionally defined photoreforming (Christoforidis and Fornasiero, 2017; Iervolino et al., 2017; Li et al., 2015; Rossetti, 2012; Serra et al., 2016; Vaiano et al., 2015).

Indeed, a separated electron-hole couple is photogenerated upon absorption of solar radiation by the semiconductor used as photocatalyst. The electron promotes the reduction of a proton to hydrogen (or of any other reducible substrate), while the organic molecule consumes the holes being progressively oxidised to CO₂.

Many recent reports deal with materials synthesis and activity testing, but few papers propose photoreactors design or the conceptual design and sizing of the plant. Most importantly, besides defining specific productivity, no conceptual assessment of process feasibility is usually proposed. Therefore, the aim of this paper is to check the feasibility of a photoreforming plant to produce hydrogen from different organic substrates, based either on original activity testing results and state of the art literature data.

Furthermore, the photoreduction of CO₂ is investigated as a mean to store solar energy in form of regenerated organic fuels, to be subsequently used as chemicals, fuels or even reactants for photoreforming.

To date, no conclusion on the feasibility of an integrated plant, not on photoreactor sizing is available for this application. Hence, the purpose of this work is to assess quantitatively the potential if the processes of (i) photoreforming of organic substrates and (ii) the photoreduction of CO₂. Both are intended as energy storage strategies. The investigation takes into account different geographic locations and both literature and experimental data on productivity for these reactions. The comparison and suggestion on feasibility is based on quantitative parameters appropriately set.

2. Experimental

2.1. Photocatalysts

Details on catalysts preparation and characterisation are reported elsewhere (Galli et al., 2017; Rossetti et al., 2015, 2014a). Briefly, different commercial samples of TiO₂, constituted by pure anatase (A) (from Aldrich), pure rutile (R) (from Aldrich) or a mixture of them (Evonik P25) were used as photocatalysts. Au was added with 0.1 wt% amount through a deposition precipitation technique and used for photoreforming of methanol, whereas pure P25 TiO₂ was used for the photoreduction of CO₂.

For the preparation of Au/TiO₂, 2 g of TiO₂ were suspended in 200 mL water and added with 0.2 mL Au from NaAuCl₄ and 5 g urea and left under stirring for 4 h at 80 °C. The catalyst was filtered and washed several times with water. The material was then suspended in distilled water and a solution of NaBH₄ (0.1 M) was added (NaBH₄/Au = 4 mol mol⁻¹) under stirring at room temperature. The sample was filtered, washed and dried at 100 °C for 4 h. Au content (0.1%) was confirmed by Atomic Absorption Spectroscopy (AAS) analysis of the filtrate, on a Perkin Elmer 3100 instrument.

2.2. Photoreactor for photoreforming

A cylindrical 500 mL glass photoreactor was used, surrounded with a cooling jacket fed with water. Two different lamps were placed on the top of the reactor, irradiating the suspension through a quartz window. A Jelosil 250 W lamp was used, with maximum of emission at 365 nm and mean measured irradiance 113 W/m². A different lamp, with measured irradiance at the same wavelength of 0.5 W/m² was also used for comparison.

200 mL of solution with methanol concentration ranging from 1 to

15 wt% was added with 0.2 g of photocatalyst and magnetically stirred. Before switching on the lamp, the solution was outgassed by flushing with 200 NL/h of N₂ for 10 min.

The liquid phase was analysed either by means of an Agilent 6890 gaschromatograph, with a FID detector or by using a HPLC (Agilent 1220 Infinity) using a suitable column (Alltech OA-10308, 300 mm 7.8 mm) with UV and refractive index (Agilent 1260 Infinity) detectors. Aqueous H₃PO₄ solution (0.1 wt%) was used as the eluent. The gas phase was analysed with an Agilent 7890 gaschromatograph, furnished with a TCD detector and calibrated to quantify H₂, CO and CO₂.

Sampling of the liquid phase was periodically done (every 30 min at the beginning of the reaction, every 1–2 h later). Sampling of the gas phase was carried out every 2–3 h by collecting 10 mL of gas to avoid excessive dilution of the sample.

2.3. Photoreactor for CO₂ photoreduction

The photoreduction of CO₂ was carried out in a high pressure photoreactor as described in (Galli et al., 2017; Rossetti et al., 2015, 2014a). The operation up to 20 bar allowed to overcome one of the main limitations of the reaction, *i.e.* the poor CO₂ solubility in water, which limits the availability of the reactant on photocatalyst surface.

Specifically, the results here reported were collected at 7 bar CO₂ pressure and 80 °C. The reactor skeleton is made of AISI 316 stainless steel (volume = 1.7 L). A 125 W medium-pressure Hg vapour axial immersion lamp was used, emitting in the 254–364 nm range. The emitted power was experimentally measured as 104.2 W/m². The photoreactor was filled with 1.2 L of solution and the catalyst was suspended in it with 0.5 g/L concentration. Outgassing was performed before each test under a constant CO₂ flow of 15 mL/min at 13 bar. Then, CO₂ saturation was completed overnight by applying a static 7 bar pressure of CO₂ (Rossetti et al., 2014).

An inorganic hole scavenger, sodium sulphite (2.0 g) was added. Whenever the sulphite was still present in the reaction medium it led to the accumulation of organic products in the solution. After its consumption organics were used as hole scavengers, with formation of hydrogen (consecutive photoreforming (Galli et al., 2017).

3. Results and discussion

3.1. Photoreforming of methanol: Effect of irradiance and of catalyst composition

The reaction was first tested by using the lowest power lamp, with measured irradiance 0.5 W/m². The photocatalyst was 0.1 wt% Au supported on TiO₂ P25, dispersed in a 1 wt% methanol solution.

TiO₂ was selected as semiconductor, due to presently unrivalled commercial availability at moderate cost, stability and appropriate band potentials for the proposed reaction. One major drawback is that all its polymorphs (anatase, rutile or brookite) have quite big band gap (3.0–3.2 eV) and thus it can absorb only the UV portion of the spectrum. This limits the possibility to exploit efficiently solar light. To account for this, UVA lamps were used during testing and the useful fraction of solar spectrum, only, was considered during computation of solar energy storage efficiency and productive potential.

Metals addition on titania surface improved its absorption potential in the visible range (Aramendia et al., 2008; 2007; Ilie et al., 2011; Pichat et al., 1984; Rossetti et al., 2014). Furthermore, the metal can entrap the photogenerated electrons by forming a Schottky barrier, so preventing its recombination with the valence band holes (Linsebigler et al., 1995). In addition, metals decrease the overpotential for H₂ occurring with bare TiO₂ (Lee and Mills, 2003). The amount of metal is typically below 1 wt%, because too high loading can act as a recombination centre for electrons and holes (Colmenares et al., 2011; Pichat et al., 1984) and shield the semiconductor surface limiting light

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