Photoreactors design for fuels production

Gianguido Ramis[1], Elnaz Bahadori[1], Antonio Tripodi[2], Ilenia Rossetti[2]

1 Dip. di Ingegneria Civile, Chimica e Ambientale, Università degli Studi di Genova and INSTM Unit Genova, Via all'Opera Pia 15A, 16100, Genova, Italy

2 Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, INSTM Unit Milano-Università and CNR-ISTM, via C. Golgi, 19, I-20133 Milano, Italy

**Corresponding author: gianguidoramis@unige.it*

Highlights

- High pressure and high temperature photocatalysis explored
- Productivity boosted by unconventional reaction conditions
- Tunable selectivity to different fuels from renewable or waste materials

1. Introduction

Photocatalysis can be seen as a route for the storage of solar energy by producing "solar fuels", i.e. with artificial photosynthesis. In this work, we dealt with two challenging applications: i) the production of hydrogen through photoreforming of aqueous solutions of organic compounds and ii) the photoreduction of CO_2.

Different carbohydrates (glucose, xylose and arabinose, as well as levulinic and formic acid) were used as renewable substrates for photoreforming, since they may be rather easily obtained from the hydrolysis of biomass. On the other hand, the transformation of CO_2 into regenerated organic compounds, to be used as fuels or chemicals (CH_4, HCOOH, HCHO, CH_3OH) was also studied. Our attention was predominantly focused on the development of innovative photoreactors, operating under unconventional conditions, with the fine tuning of the operation parameters. In particular, we have set up and optimized a new photoreactor operating at pressure up to 20 bar and relatively high temperature (up to 90°C) which allowed to overcome one of the main limitations for the photoreduction of CO_2 in liquid phase, *i.e.* the low CO_2 solubility. The possibility to increase the operating pressure also allowed to explore unconventional reaction conditions, evidencing an unexpected boost of hydrogen productivity when increasing temperature in the case of the photoreforming of carbohydrates.

2. Methods

The selected photocatalysts were based on TiO_2, since the main focus was reactor optimization. The materials were prepared by flame spray pyrolysis as dense nanoparticles, or in mesoporous form through a soft template synthesis, and compared with commercial samples of nanostructured TiO_2 P25 by Evonik. Different metals, such as Cu and Au, Pt, Pd, Ag, Ni, with loading ranging from 0.1 to 1 mol% were added as co-catalysts (mono or bimetallic formulations). The role of the metals was that of electron sinks, to inhibit the electron-hole recombination and they were also selected due to the formation of a plasmon resonance band which improves visible light absorption. The photocatalytic activity tests have been carried out in batch mode using a high pressure photoreactor (up to 20 bar, 95°C), using a UVA immersion lamp, coaxial with the photoreactor (λ_{max} = 365 nm, ca. 77 W/m^2).

3. Results and discussion

As for the photoproduction of H_2 we have investigated extensively the effect of pressure, temperature, carbohydrate and catalyst concentration, selecting 80°C, 4 bar, 5 g/L of carbohydrate, 0.5 g/L of catalyst and neutral pH as the best operating conditions. The highest productivity was achieved with 0.1 mol%Pt/TiO_2 or 1 mol% Au_6Pt_2/TiO_2, leading to ca. 14 mol/h kg_{cat} of hydrogen.

As for the photoreduction of CO_2, operation at high pressure allowed to boost the conversion to partially reduced compounds (HCOOH, HCHO and CH_3OH), with much more limited conversion to CO and CH_4. The present high pressure photoreactor also showed extremely versatile to drive the reaction towards the desired product among those listed by tuning pressure, temperature, reaction time and pH. The highest productivities reached up to now were obtained with 0.2% Au/TiO_2: 40 mol/h kg_{cat} of HCOOH (7 bar, 80°C, pH=14, 24 h reaction time), 17 mol/h kg_{cat} of HCHO (7 bar, 80°C, pH=14, 6 h reaction time) and 1.7 mol/h kg_{cat} of CH_3OH (7 bar, 80°C, pH=7, 24 h reaction time, 0.2% CuO/TiO_2 as catalyst).

The increase of pressure from 7 to 19 bar almost doubled the amount of HCOOH obtained and, also in this case, the increase of temperature allowed to increase the productivity. This was unexpected, since the increase of temperature is often discussed as negative for photocatalysis due to an increased recombination rate of the photogenerated charges.

The apparent quantum yield (AQY) has been here calculated as follows:

$$AQY\ (\%) = \frac{\text{moles of product(i)}\ per\ second\ \times\ \nu(i)}{Incident\ photons\ per\ second}$$

where ν(i) is the number of electrons consumed to reduce CO_2 to the desired product and is directly calculated from the productivity data here reported. The incident photons flow has been calculated based on the measured intensity of radiation. Considering the productivities here reported we have calculated an AQY much higher than 10% in the best cases.

4. Conclusions

In this work we have investigated the effect of unconventional reaction conditions, i.e high pressure and relatively high temperature, on two of the most challenging photocatalytic processes, such as the photoreduction of CO_2 and the production of H_2 from carbohydrates. The increase of temperature to 80-90°C revealed beneficial for both reactions. The increase of pressure boosted the productivity for CO_2 photoreduction to results presently unrivalled in the literature. For this latter application, the use of this photoreactor also allowed to tune the selectivity towards different compounds by simply changing the reaction conditions.

The main achievement, besides the interesting products yields, is the development of a new concept of photoreactor, which can open new unexplored routes in photocatalysis.