

H₂ production through photoreforming of carbohydrates

Gianguido Ramis*¹, Elnaz Bahadori¹, Antonio Tripodi², Ilenia Rossetti²

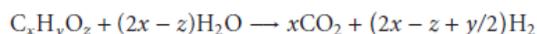
¹ DICCA, Università degli Studi di Genova and INSTM Unit-Genova, Genoa (Italy) * gianguidoramis@unige.it

² Dip. di Chimica, Università degli Studi di Milano, CNR-ISTM and INSTM Unit-Milano università, Milan (Italy)

INTRODUCTION

In this work, we dealt with the production of hydrogen through photoreforming of aqueous solutions of organic compounds.

The photocatalytic reforming occurs through the following general reaction:



which is promoted by a photocatalyst. Different carbohydrates (glucose, xylose and arabinose, as well as levulinic and formic acid) were used as renewable substrates, since they may be rather easily obtained from the hydrolysis of biomass. 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 boost the productivity of H₂. The possibility to increase the operating pressure allowed to explore unconventional reaction conditions, evidencing an unexpected improvement of hydrogen productivity when increasing temperature in the case of the photoreforming of carbohydrates.

EXPERIMENTAL/THEORETICAL STUDY

The selected photocatalysts were based on TiO₂. 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 TiO₂ 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 samples were characterized by N₂ adsorption-desorption, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and temperature programmed reduction/oxidation (TPR/TPO).

The photocatalytic activity tests have been carried out in batch mode using a high pressure photoreactor described elsewhere [1,2], using a UVA immersion lamp, coaxial with the photoreactor ($\lambda_{max} = 365$ nm, ca. 77 W/m²).

RESULTS AND DISCUSSION

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/TiO₂ or 1 mol% Au₆Pt₂/TiO₂, leading to ca. 14 mol/h kg_{cat} of hydrogen.

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

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

where $\nu(i)$ is the number of electrons consumed to reduce H⁺ to 0.5 H₂ 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.

CONCLUSION

In this work we have investigated the effect of unconventional reaction conditions, i.e high pressure and relatively high temperature, on one of the most challenging photocatalytic processes, such as the production of H₂ from carbohydrates. The increase of temperature to 80-90°C revealed beneficial and relatively high productivity has been achieved.

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.

REFERENCES

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