Innovative high pressure photoreactors for the photoreduction of CO_2

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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 one of the most challenging applications: the photoreduction of CO_2. The transformation of CO_2 into regenerated organic compounds, to be used as fuels or chemicals (CH_4, HCOOH, HCHO, CH_3OH) was 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 productivity with respect to literature results.

EXPERIMENTAL/THEORETICAL STUDY

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 samples were characterized by N_2 adsorption-desorption, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and temperature programmed reduction/oxidation (TPR/TPO).

The photocatalytica 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 (λ_{max} = 365 nm, ca. 77 W/m^2).

RESULTS AND DISCUSSION

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.

CONCLUSION

In this work we have investigated the effect of unconventional reaction conditions, i.e high pressure and relatively high temperature, on the photoreduction of CO_2. The increase of temperature to 80-90°C revealed beneficial and 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.

REFERENCES

1. F. Galli, M. Compagnoni, D. Vitali, C. Pirola, C. Bianchi, A. Villa, L. Prati, I. Rossetti, Appl. Catal. B: Environmental 200, 386 (2017).
2. E. Bahdori, A. Tripodi, A. Villa, C. Pirola, L. Prati, G. Ramis, I. Rossetti, Catalysts 8, 430 (2018)

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