Photoreactors Design for Hydrogen Production

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ABSTRACT

The production of hydrogen through photoreforming of aqueous solutions of organic compounds is considered as a way to exploit solar energy storage in the form of hydrogen. The photocatalytic reforming occurs through the following general reaction:

$$C_xH_yO_z + (2x - z)H_2O \longrightarrow xCO_2 + (2x - z + y/2)H_2$$

which is promoted by a photocatalyst. In this work, we dealt with the use of different sugars, namely glucose, xylose and arabinose, as well as levulinic and formic acids as substrates derived from the hydrolysis of biomass. Examples of real hydrolysed solutions (from cellulose residua or lignocellulosic biomass) have been also tested. Our attention was predominantly focused on the development of innovative reactors, possibly operating under unconventional conditions, with fine tuning of the operation parameters.

The selected photocatalysts were based on TiO_2. The materials were prepared by flame spray pyrolysis and compared with commercial samples of nanostructured TiO_2 P25 by Evonik or with titania obtained by precipitation. Different metals, such as Cu and Au, with loading ranging from 0.1 to 0.5 wt% were added as co-catalysts. 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 photoreforming reaction was carried out in different prototypes of photoreactors specifically developed in our lab.

In one reactor configuration, an external 200 W lamp was used, with emission wavelengths centred around 365 nm. A first photoreactor was developed with internal capacity ca. 0.3 L, with big head space for gas collection and very efficient mixing of the suspension thanks to an optimized length/diameter ratio (L/D) ca. 2. A drawback was the poor irradiation efficiency of the suspension, which limited the overall productivity, irrespectively or the substrate. The same UVA radiation was tested also in a home designed photoreactor with an immersion lamp (75 or 150 W, coaxial with the reactor). Two reactor sizes were tested, ca. 200 ml or 1.5 L. A significant amount of H_2 was obtained with very simple catalyst formulations, e.g. 20 mol kg_{cat}^{-1} h^{-1} were obtained at 4 bar, 80 °C over commercial TiO_2 samples and using glucose as substrate. This result is very remarkable with respect to similar research in conventional photoreactors.

Reactor modelling is in progress for both applications, including the optimization of radiation distribution in the photoreactor.

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