

Solar Photoreforming of biomass and plastic-derived materials using carbon-based photocatalysts

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Significance and Relevance

Energy from renewables is central for the sustainability. Sunlight-driven fuels production is a sustainable and economical approach to generate energy vectors, such as hydrogen, through solar photoreforming. In addition, a today relevant challenge is the management of the countless natural wastes, such as lignocellulose with $120*10^9$ T/y produced from agricultural, grass and wood¹. Furthermore, the contextual presence of synthetic waste such as plastic materials like PS, PP or PE (production of $800*10^9$ T/y)¹ amplifies this environmental issue. Therefore, the novelty of this work is the use of non-critical photocatalysts, in the solar photoreforming of biomass and plastic-derived materials.

Preferred and 2nd choice for the topic: (1) H₂ storage and transportation, green H₂ production, hydrogen vectors; (2) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization *Preferred presentation*: Oral preferred or Short Oral

Introduction and Motivations

Photocatalytic hydrogen production is amongst the top ten emerging technologies in chemistry. In particular, the photoreforming (PR) of organic substrates is an attractive way to obtain green H_2 together with the valorization of waste or biomass. This process combines water reduction with the oxidation of a sacrificial agent using a semiconductor. The choice of the organic substrate is fundamental to promote the H_2 production. In this work, we originally proposed waste-derived materials (biomass and plastics) as organic scavengers in order to produce H₂ with the simultaneous waste disposal. However, one of the necessary steps for the waste photoreforming reaction is the efficient solubilization of these organic substrates through various pre-treatments as the alkaline hydrolysis, using at the same time a photocatalytic system resistant at these extreme conditions. In recent years the scientific community focused on the study of carbon-based materials for their remarkable electrical, thermal and mechanical properties. The focus of this work was to investigate the performance of metal carbides MC (SiC, MoC, TiC) combined with the graphitic carbon nitride (g- C_3N_4) in different amounts. The carbon nitride possesses the advantages of low cost, non-toxic, thermodynamic stability, and remarkable optical properties². The metal carbides show promising applications, with excellent physicochemical properties, such as high adsorption capacity, high melting point, good electrical conductivity, high thermal stability, and hardness³.

Materials and Methods

For the preparation of bulk g-C₃N₄ a thermal polymerization has been used as reported in ref². The MC systems were prepared with a hydrothermal synthesis⁴. The two materials were joined through a physical treatment by sonication followed by a calcination in an oven. The photocatalytic tests were performed with 50 mg of the photocatalyst, homogeneously suspended in an aqueous solution containing the sacrificial agent (40 mL of deionized water and 10 mL of biomass (cellulose) and plastics (PS, PE)-derived materials, previously pre-treated) inside the reactor. Then, the reactor was irradiated for 5 h using a solar lamp ⁵. On the most promising photocatalysts, in order to increase the production of H₂, Pt (1 wt%) has been added as co-catalyst, using the wetness impregnation method.



Results and Discussion

The focus of this work is the study of the performance of carbon-based catalysts as $g-C_3N_4$ and MoC introducing Pt as co-catalysts to further improve the H_2 formation.

A good production of H₂ was verified with all the investigated sacrificial agents (Fig.1)- Interestingly an increase of H₂ production was found in the presence of carbon nitride and a further increase with the addition of Pt. The PS photoreforming led to the lowest H₂ production. This can be due to the fact that synthetic waste, such as plastic, has C-C bonds that are extremely difficult to break, especially in the presence of an aromatic ring as the PS case. Furthermore, in the case of cellulose, the basic pH pretreatment allows to improve the electrostatic interaction between the organic substrate and the catalyst. The performance of the MoC-g-C₃N₄ composites, prepared with an easy procedure, was promising to propose a new class of unconventional photocatalysts, instead of the most used metal oxides-based systems. The performance will be compared to similar systems as SiC-g-C₃N₄ and TiC-g-C₃N₄ composites. The results obtained in this work can pave the way for future perspectives in which the wastes or the pollutants can be considered new raw materials to obtain H₂, preserving, at the same time, the environment by the emerging contaminants.



Figure 1 Comparison among different investigated systems

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