Photothermal CO_2 hydrogenation over molybdenum oxysulfide-based heterojunctions

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Highlights

- Photocatalytic MoS_2/CeO_2 heterojunctions are obtained by high-energy ball miling
- Metallic clusters are deposited by photo-assisted deposition
- CO_2 hydrogenation can be achieved from UV to IR wavelengths

1. Introduction

The use of solar energy has been explored as a using diverse catalytic procedures and reactor configurations to produce the so-called solar fuels as a way to achieve a net-zero carbon economy by converting atmospheric CO_2, together with H_2 from renewable sources [1]. For this applications, molybdenum sulfide (MoS_2) shows remarkable properties for photocatalytic applications, provided the high concentration of active sites suitable for reactant adsorption, charge separation and migration, and photoreduction [2]. Surface defects and deposition of metal clusters in the basal plane enhance the photocatalytic activity for gas-phase CO_2 hydrogenation. However, MoS_2 tends to the deactivation through hole oxidation that can be avoided in amorphous oxysulfides (MoO_xS_y) to provide mixed oxidation states for Mo, along with vacancies in the sulfur sublattice [3].

However, these MoO_xS_y-based materials undergo deactivation under reaction conditions, which can be solved by adequately tuning the semiconductor bandgap with another photoactive substrate. Therefore, with the aim of expanding the photocatalytic activity of MoO_xS_y towards the visible and infrared spectrum and increase CO_2 conversion, heterojunctions of nanoparticulate MoO_xS_y and CeO_2 were synthesized. The use of these heterostructures notably improves the separation of photogenerated charge carriers, which favor redox processes during the gas phase reaction.

2. Methods

Amorphous MoO_xS_y and CeO_2 semiconducting heterojunctions, using a combination of mild hydrothermal and high-energy ball milling techniques. Briefly, to synthesize low-crystallinity nanostructured MoO_xS_y, ammonium molybdate and thiourea were dissolved in deionized water and placed in a Teflon-lined stainless steel autoclave at 150 ºC for 12 h. Finally, the black solid obtained was dried at 80 °C overnight and pulverized with an agate mortar for 10 min. Ball milling mixtures were performed in a Retsch PM100 planetary mill with a 100-ml volume agate jar and ten 1-cm agate balls. A mass of 500 mg of CeO_2 and 50 mg of MoO_xS_y were used for the synthesis. Rotation speed was set at 300 rpm for a period of 6 h. Materials were analyzed using XRD, STEM and XPS techniques.

For the photocatalytic tests, the fixed-bed reactor was filled with a 1:4 CO_2:H_2 mixture at 15 sccm to achieve an absolute pressure of 1.2 bar. The fixed bed was irradiated under 9-W LED light of variable wavelengths, as bed temperature was adjusted to 573 K. Reaction productivity and CO_2 conversion was analyzed using gas chromatography in a Shimadzu GC2030.

3. Results and discussion

Heterojunctions exhibit a complex surface structure with Mo^{4+}, Mo^{5+} and Mo^{6+} cations and defects in the sulfide sublattice, as well as metal clusters interacting with the CeO_2 support. Photocatalytic CO_2

hydrogenation tests show up to 8% of CO_2 conversion rate and continuous production of CO and CH_4 in an under UV light at 365 nm (Figure 1). The electronic and chemical environments of MoO_xS_y/CeO_2 catalysts influence the gas adsorption and CO_2 hydrogenation, while keeping the amorphous nature of oxysulfides seems to be key for enhancing the photocatalytic performance.

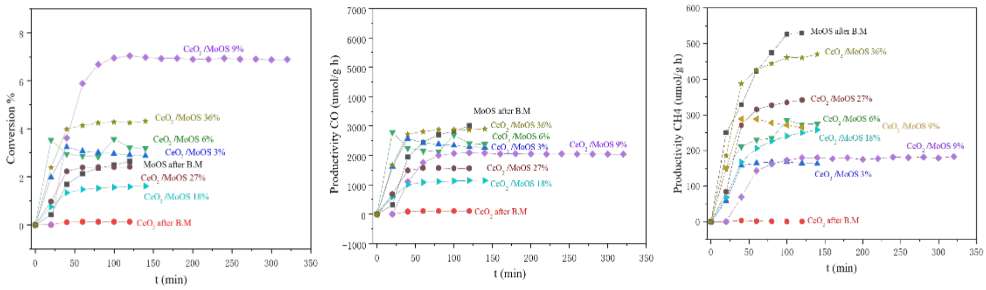

Figure 1. CO_2 conversion (a), CO productivity (b) and CH_4 productivity for CO_2 hydrogenation over MoO_xS_y/CeO_2 photocatalytic heterojunctions under 365-nm LED irradiation at 573 K (CO_2:H_2 1:4, 15 ml/min, 1.2 bar)

The electronic and chemical environments of MoS_2/CeO_2 catalysts influence the gas adsorption and CO_2 hydrogenation, while keeping the amorphous nature of MoS_2 layers is key for enhancing the photocatalytic performance. In addition, in situ DRIFTS tests of CO_2 hydrogenation over MoO_xS_y/CeO_2 at 523 K shows monodentate and polydentate HCO_3^- units formed on the surface. In addition, in situ DRIFTS analysis of CO_2 hydrogenation over MoO_xS_y-based catalysts at 523 K shows monodentate and polydentate HCO_3^- units formed on the surface (Figure 5).

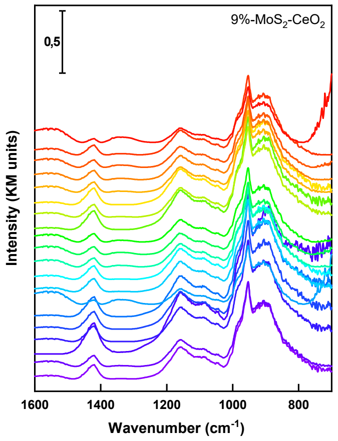

Figure 2. *In situ* DRIFTS analysis of the CO_2 hydrogenation over MoO_xS_y/CeO_2 photocatalytic heterojunctions at 523 K (CO_2:H_2 1:4, 15 ml/min, 1.2 bar)

4. Conclusions

Photothermal CO_2 hydrogenation could be carried out over nanostructured MoS_2/TiO_2 catalysts with enhanced CO and CH_4 production in the millimolar range. The introduction of metal clusters led to efficient photocatalytic heterojunctions able to perform CO_2 hydrogenation under a range of wavelengths, from UV up to infrared. This feature could be of interest for the development of photocatalytic devices with applications in the carbon capture and utilization technologies.

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References

[1] T. Auger, J. Trüby, P. Balcombe, and I. Staffell, Joule, 5 (2021) 1462–1484.
[2] Y. Liu *et al.* Chem Catal, 1 (2021) 44–68.
[3] A. Sanz-Marco *et al.* Carbon Energy, (2025) e685.

Keywords
MoS_2; CeO_2; CO_2 hydrogenation; Photocatalysis