Modified Montmorillonite-based catalysts for the photothermo-catalytic reduction of CO_2 into solar fuels

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Significance and Relevance

The structural modification of Montmorillonite K30 with the intercalation of Ni and Ce ions and the subsequent coating with mixed Mn and Cu metal oxides allowed to obtain a performing and green catalyst used for the photothermo-catalytic CO_2 conversion into solar fuels (CO and CH_4).

Preferred and 2nd choice for the topic: (1) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization /(2) CO_2 utilization and recycling.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

The CCU (carbon capture and utilization) permits to mitigate the impact of carbon dioxide, the main greenhouse gas, and to overcome the use of fossil fuels thanks to its valorization towards the conversion into solar fuels[1]. In this work the reduction of CO_2 led to CO and CH_4 using a hybrid catalytic approach as the photothermo-catalysis[2], and unconventional and not critical photocatalysts, as the composites formed between montmorillonite K30 and Mn-Cu mixed oxides.

Materials and Methods

The modification of K30 with Ni and Ce was made at first, activating the Montmorillonite with acetone and after adding the corresponding Ni and Ce nitrate precursors. The obtained slurry was then treated with a hydrothermal method. The coatings with Mn and Cu oxides were done on the as-obtained K30-Ni/Ce with precipitation method using KOH 1M. The catalytic tests were conducted at 120°C in a cylindrical batch reactor using a solar lamp and irradiating for 5h. The analysis of the reaction products was carried out by GC-TCD/FID. The structure and the morphology of the as-synthesized catalysts was investigated by SEM and FT-IR, while the optical band gap was evaluated by UV-DRS. The catalysts were also characterized by Raman, H_2-TPR, CO_2-TPD and N_2- physisorption measurements.

Results and Discussion

The best performance was obtained by K30-Ni/Ce@MnCuO$_x$ with a 77% of CO_2 conversion and 13.9 and 4.9 mmol/gcat•h (figure 1) of formed CO and CH_4, respectively. For this sample stability tests were also conducted using a H_2 flow for the reduction of the fresh sample and for its re-activation (figure 2). Indeed, after a deactivation of 10% in the third run (each run is a photothermal test of 5h), in the subsequent run the sample was reactivated by the H_2 flow, reaching the same photothermo-catalytic activity of the first run after additional 10 h of solar photothermal conditions (figure 2). These results show that the coating using non-critical mixed metal oxides improves the performance of the K30 modified with Ni and Ce. The photothermo-catalysis also represents a greener strategy to mitigate and to valorize the CO_2 impact. Finally, the performance of this modified clay was compared with the new class of "artificial clays" as MXenes prepared using as precursor a MAX phase of Ti_3AlC_2. The MXenes were also modified with Silica, Titania and Ceria to improve photocatalytic and thermocatalytic activity.

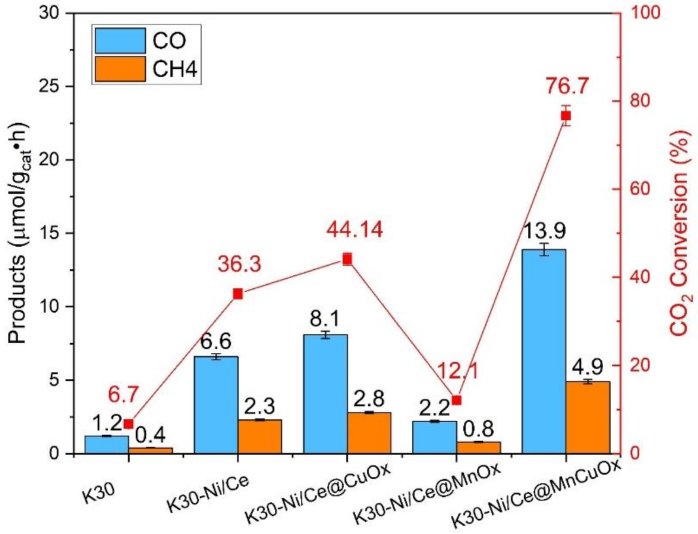

Figure 1 Solar photothermo-catalytic CO_2 reduction at T = 120 ◦C after 5 h of simulated solar irradiation.

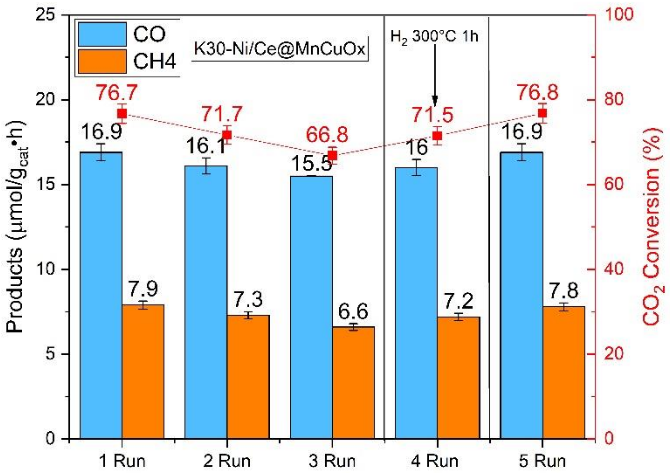

Figure 2 Stability test for the K30-Ni/Ce@$MnCuO_x$ in the solar photothermo-catalytic CO_2 reduction at T=120◦C.

References

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2. R. Ma, J. Sun, D.H. Li, J.J. Wei, *International Journal of Hydrogen Energy* **2020**, *45*, 30288-30324

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