Intensified solar thermochemical carbon dioxide splitting over iron-based perovskite

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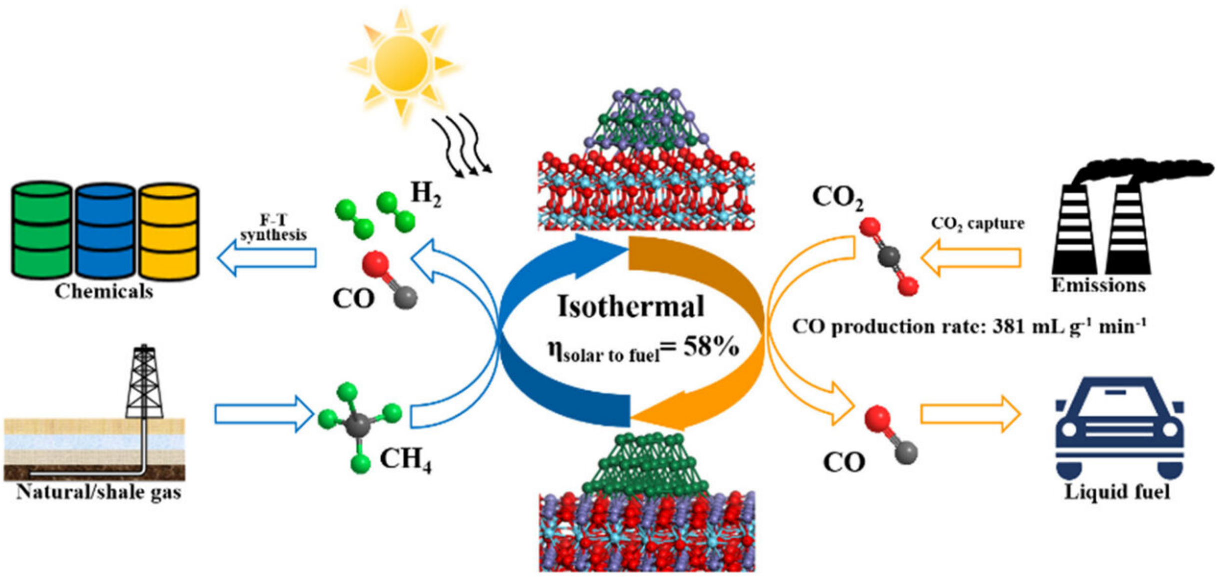

Practical solar fuel production via two-step solar thermochemical CO_2 splitting (STCS), a promising method. We demonstrate that FeNi alloy embedded in perovskite substrate enables near complete CO_2 splitting and record CO production rate of 381 mL mL g^{-1} min^{-1} (STP). This unprecedented performance is ascribed to stabilization of oxidized Fe cations by in-situ involving into robust perovskite matrix. The thermodynamic analysis predicts a solar-to-fuel efficiency as high as 58% even without any sensitive heat recovery. Credit: Chinese Journal of Catalysis

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Anthropogenic CO_2 is the main cause of climate change. There is a pressing need to develop efficient technologies for chemical/fuel production from CO_2, ultimately realizing carbon circularity. Among all the various renewable energy solutions, the two-step solar thermochemical CO_2-splitting (STCS), exploiting concentrated solar energy of entire solar spectrum to drive redox reactions, shows great promise given its ultra-high theoretical solar-to-fuel efficiency.

Isothermal chemical cycles have been widely explored by exquisite design of redox oxides and varying operating conditions. It was found that the introduction of reducing agents (e.g. hydrogen, methane and biomass) would significantly lower the reduction temperatures of metal oxides to match that of the CO_2 splitting process. In particular, when the reducing agent is methane, the main component of the globally abundant natural gas and shale gas, syngas (mixture of H_2 and CO) can be produced as a form of solar fuel. When coupled with CO_2 splitting, such two-step redox scheme has the potential to provide versatile and high quality feedstock for methanol synthesis, acetic acid synthesis and Fischer-Tropsch (F-T) synthesis, all of which play critical roles in a sustainable energy future.

The redox materials, serving as both oxygen carrier and catalyst during the thermochemical cycles, are the key to high performance STCS process. The earth abundant and environmentally benign iron-based oxides have attracted increasing attention due to their low reduction temperature and high oxygen storage capacity. Thus, the development of a new efficient iron-based oxygen carrier for the two-step STCS process is important and urgent.

Recently, a research team led by Prof. Xiaodong Wang from Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS) reported a novel material consisting of iron-nickel alloy embedded in perovskite substrate for intensified CO production *via* the two-step STCS process. The novel material achieves an unprecedented CO production rate of 381 mL g^{-1} min^{-1} (STP) with 99% CO_2 conversion at 850 ºC, outperforming the state-of-the-art materials. In-situ structural analyses and DFT calculations show that the alloy/substrate interface are the main active sites for CO_2 splitting. The preferential oxidation of FeNi alloy at the interface (as opposed to forming a FeO_x passivation shell encapsulating bare metallic iron) and the rapid stabilization of the iron oxide species by the robust perovskite matrix, significantly promotes the conversion of CO_2 to CO. The facile regeneration of the alloy/perovskite interfaces is realized by isothermal methane reduction with simultaneous production of syngas (H_2/CO = 2, syngas yield > 96%). Overall, the novel perovskite-mediated dealloying-exsolution redox system facilitates highly efficient solar fuel production with a theoretical solar-to-fuel efficiency of up to 58% in the absence of any heat integration. The results were published in *Chinese Journal of Catalysis*.

More information: Yue Hu et al, Intensified solar thermochemical CO2 splitting over iron-based redox materials via perovskite-mediated dealloying-exsolution cycles, *Chinese Journal of Catalysis* (2021). DOI: 10.1016/S1872-2067(21)63857-3

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