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Original
Solar fuels: Advancements in photothermal CO2 conversion to light olefins / Tauro, A., Salomone, F.. - In: CHEM CATALYSIS. - ISSN 2667-1093. - ELETTRONICO. - 4:4(2024), pp. 1-3. [10.1016/j.checat.2024.100979]

Availability:
This version is available at: 11583/2987938 since: 2024-04-24T10:18:55Z

Publisher:
Elsevier

Published
DOI:10.1016/j.checat.2024.100979

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14 October 2026

Solar fuels: Advancements in photothermal CO_2 conversion to light olefins

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Summary

Solar-driven catalysis has recently gained importance as a sustainable alternative to traditional energy-intensive processes. In this issue of Chem Catalysis, Song et al. have thoroughly examined the mechanisms of photothermal CO_2 hydrogenation to olefins. Our preview provides concise insights into their comprehensive study, highlighting perspectives and developments in CO_2 utilization.

Main Text

Carbon dioxide (CO_2) hydrogenation has emerged as a pivotal process in combatting greenhouse gas emissions while concurrently generating essential synthetic fuels and chemicals. Among the plethora of resultant products, synthetic fuels such as methane, methanol, hydrocarbons, as well as chemicals like methanol stand out prominently. Light olefins such as ethylene and propylene are essential molecules in the petrochemical industry for the manufacture of plastics and several chemicals[1]. The global market value of light olefins and their derivatives is expected to grow progressively in the next decade. Currently, light olefins are produced from non-renewable fossil resources, but their substitution with carbon capture and utilization (CCU) processes seems to be an alternative to build a more sustainable society model. One of the most explored thermocatalytic

processes is the methanol-to-olefins (MTO) route[1]; however, the Fischer-Tropsch synthesis (FTS) process, renowned for its historical significance in producing synthetic fuels, has witnessed a resurgence of interest in recent times owing to its capability to directly convert CO_2[2]. Originating during World War II as an alternative source of liquid fuel from syngas feedstock, FTS has gained renewed attention amidst the climate change crisis due to its potential to utilize CO_2. Notably, the high-temperature FTS route, utilizing iron-based catalysts, offers a pathway primarily to olefins, which can subsequently undergo processes like oligomerization, aromatization, and isomerization to yield gasoline or polymers[3]. The process of CO_2 hydrogenation unfolds in two distinct stages: first, the Reverse Water Gas Shift (RWGS) reaction, wherein CO_2 is converted to CO, usually occurring on iron oxide phases; and then FTS process, which transforms CO into hydrocarbons[3,4]. Moreover, alongside traditional thermal catalytic conversion of CO_2, significant strides have been made in developing photocatalytic processes. These processes, operating under mild conditions, hold promise for circumventing the need for costly operational parameters like high pressure and temperature. Furthermore, the concept of photothermal processes has recently emerged, wherein natural light energy is harnessed to produce heat, driving chemical reactions efficiently. This integration of photothermal processes could potentially combine the advantages and performance attributes of both thermocatalysis and photocatalysis, further enhancing the efficacy and sustainability of CO_2 hydrogenation processes. At the current state-of-the-art, thermocatalytic CO_2-modified FTS reaches a technological readiness level (TRL) of about 6–7[4]; whereas the photothermal process is still at a laboratory stage level, achieving a TRL of about 3–4.

Among the photothermal processes, the authors of the previewed article have focused on the photo-assisted thermocatalytic CO_2 hydrogenation to light olefins, showing its potentialities and deepening the knowledge in the reaction mechanisms. Song et al. (2024)[5] have deepened the knowledge on the CO_2 hydrogenation to light olefins under photothermal reaction condition by using a K-promoted Ru/Fe_3O_4 catalyst. The performance that has been achieved are 0.63 mmol g^{-1} h^{-1} with an olefin/paraffin molar ratio of 10.2. They have demonstrated that the combination of the promoter and the photocatalytic activity of the $Ru\text{-}Fe_3O_4$ interface favours the desorption of olefins inhibiting their consecutive hydrogenation into paraffin. These valuable insights have been carried out studying the CO_2 hydrogenation reaction on K-promoted Ru/Fe_3O_4 and unpromoted Ru/Fe_3O_4 coupled with *in situ* time-resolved diffuse reflectance infrared spectroscopy (DRIFTS) and synchronous

illumination X-ray photoelectron spectroscopy (SI-XPS). Moreover, the hydrogenation of a probe molecule (i.e., ethylene) was analysed by means of chopped-light measurements. At the same time, density functional theory (DFT) calculations have been performed to model the catalytic system on the surface of the catalyst. This methodology allows the authors to reveal the photothermal catalytic CO_2 hydrogenation mechanism on the surface of the catalyst and confirm it with the experimental observations. On the one hand, intermittent light measurements carried out on the unpromoted Ru/Fe_3O_4 sample revealed that ethylene is easily hydrogenated under illumination, whilst the addition of K into the catalyst significantly inhibits this reaction. On the other hand, *in situ* DRIFT measurements performed on the K-promoted Ru/Fe_3O_4 showed completely different signals under dark and irradiation conditions. Two signals at 1658 cm^{-1} and 3084 cm^{-1} were indeed detected under irradiation conditions that were ascribed to stretching vibrations of C=C and =C–H bonds, respectively, indicating that FTS to olefins occurs only under irradiation and not under dark conditions. In addition, catalytic tests have revealed that olefins are stable products only when the Ru-impregnated catalyst (or support) also contains K as additive, otherwise alkanes and methane are the detected products. This feature suggests that K inhibits the olefins hydrogenation process near the Ru interface as depicted in Figure 1.

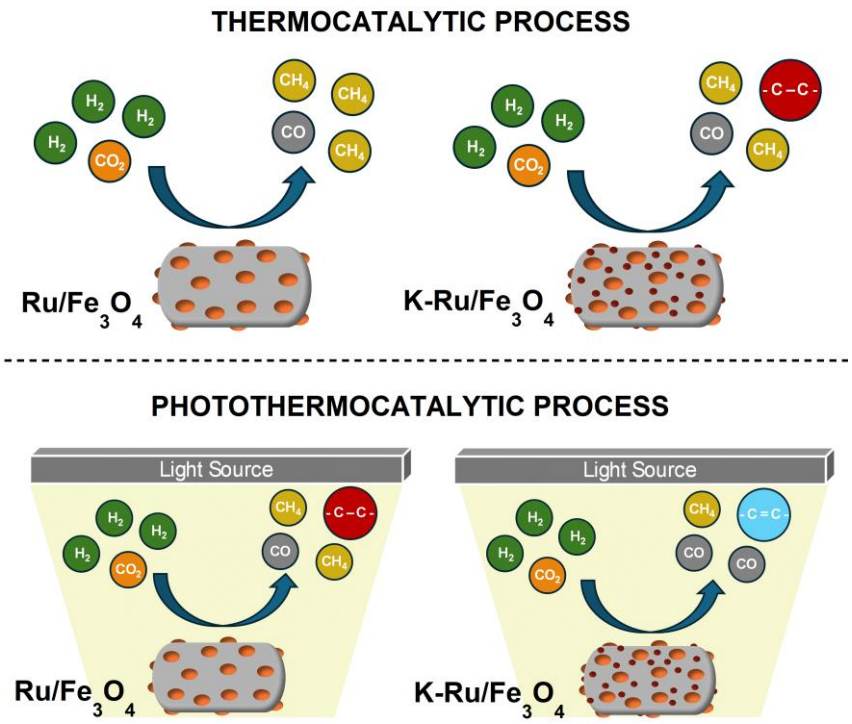

Fig. 1 Schematic results of thermal and photothermal catalytic CO_2 hydrogenation on both unpromoted and K-promoted Ru/Fe_3O_4 catalysts.

To investigate the electronic interactions between K, Ru and Fe_3O_4, X-ray absorption spectroscopy (XAS) measurements were carried out at the synchrotron. Extended X-ray absorption fine structure (EXAFS) spectra showed that increasing the Ru content in the samples, the coordination number of Ru-Fe increased from 0.5 to 1.4 by adding K; moreover, it decreased by rising the Ru content above 3 %wt. The increase of the coordination number of Ru-Fe suggests the formation of a Ru-FeO_x interface, that was corroborated by XPS and transmission electron microscopy (TEM). Moreover, X-ray absorption near edge structure (XANES) spectra revealed a partial oxidation of Ru and confirmed that the addition of K as an electron donator to Ru further promotes the formation of interfacial sites between Ru and Fe_3O_4. These results are in accordance with the literature, in fact, Mateo et al. (2019)[6] have demonstrated that the photothermal CO_2 reduction occurs preferentially on non-stoichiometric RuO_x active sites thanks to the reversibility of the oxidation-reduction cycles of the Ru nanoparticles[6,7]. Among the possible design strategies[7,8], in the previewed article, Song et al. (2024)[5] have exploited two features of a plasmonic metal such as Ru: (i) the concentration of active sites was increased by widening the metal-metal oxide interface and (ii) the light absorption was enhanced thanks to the localized surface plasmon resonance (LSRP) effect of Ru nanoparticles. The CO hydrogenation into CHO is indeed characterized by a high energy barrier[7]; however, in the literature has been reported that hot electrons generated on plasmonic metal nanoparticles upon light absorption enhance the CO_2 activation and its conversion into CO, while alloy structures seem to promote C–C coupling[7]. For instance, p-n heterojunctions in Cu-Fe catalysts or Co-Fe alloy structures may boost the performance in CO_2 reduction[7,9]. However, Song et al. (2024)[5] have stated that the Ru-Fe binary oxide interface seems to be the most performing active sites in photothermal catalysts for CO_2 conversion to olefins compared to the other combinations.

Catalyst stability remains a crucial aspect that researchers must cope with. Song et al. (2024)[5] showed that in cyclic batch photothermal tests the CO_2 conversion was slightly affected by deactivation, while the C_{2+} yield decreased from 10 % to 3 % during 10 cycles. The change in selectivity was ascribed to coking and masking phenomena caused by heavier hydrocarbons. This feature is of significant interest in thermocatalytic CO_2 hydrogenation via FTS to liquid fuels, given that Fe-based catalysts undergo a multifaceted evolution during the FTS reaction[3,10]: (i) reduction of iron oxides into metallic iron, (ii) carburization of the iron species under CO exposure, (iii) formation of an amorphous FeO_x phase that accelerate the RWGS reaction, reaching a

steady-state reaction condition. Hence, in-depth *in situ* and *in operando* characterizations of the photothermal Fe-based catalysts should be carried out to elucidate the mechanisms of the catalyst evolution under reaction conditions and unveil novel insights into this complex reaction system. In addition, Song et al. (2024)[5] have demonstrated the viability of the photothermal process with experiments using natural sunlight despite the low product yields.

It is worth analysing the practical aspects of photothermal catalysis to identify research opportunities and possible improvements. This will help harness the potential of solar-driven CO_2 conversion into value-added synthetic products on a larger technological scale[7]. As aforementioned, stable performance of photothermal catalysts is of vital importance to design a process and demonstrate its feasibility on larger scale. Thus, deactivation phenomena should be investigated and prevented to stabilize the catalytic performance. Secondly, the design of photothermal catalytic reactor cells should be optimized to improve the light absorption and maximize gas-solid contact while preventing stagnant regions or bypass phenomena. The reaction conditions may have to be carefully analysed to unveil trends of the performance by varying different parameters (e.g., temperature, pressure, residence time, H_2/CO_2 molar ratio, photon flux). Several factors make photocatalytic systems appear daunting, including restricted light utilisation leading to low process yields, dependency on the light source like all other solar technologies, present inefficiencies, and high specific costs of the technology. Nonetheless, photothermal catalytic systems may have the potential to overcome these weaknesses providing enhanced energy efficiency under milder reaction conditions. In addition, properties of photothermal catalysts may be tailored to optimise performance of specific reactions and control the productivity selectivity. In conclusion, our preview offers a glance at the outstanding study of Song et al. that has been published in this issue of Chem Catalysis, pointing out key discoveries and new ideas on the advancements made in photothermal CO_2 utilization.

Acknowledgments

The authors acknowledge the Italian Ministry of University and Research (MUR), program FSE REACT-EU PON Ricerca e Innovazione 2014-2020 (D.M. 1062/2021), and PNRR program (DM 352/22) funded by the

“Next Generation EU” program of the EU. This manuscript reflects only the authors’ views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

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