

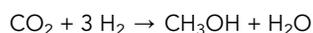
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Light and Heat Joining Forces: Methanol from Photothermal CO₂ Hydrogenation

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In a study recently reported in *Joule*, Ozin and co-workers used In₂O_{3-x}(OH)_y as a highly selective photothermal catalyst for the production of methanol by CO₂ hydrogenation at atmospheric pressure. This work constitutes a significant step toward the incorporation of solar energy in the production of chemicals.

Methanol is an important building-block molecule that can be transformed into a great variety of chemicals, including fuels as diverse as gasoline or dimethylether. Interestingly, being a liquid, methanol has a higher energy density than other energy-relevant light molecules, such as methane, and this fact facilitates its storage and transportation. These, among other characteristics, led Prof. George A. Olah to advocate the development of a methanol economy based on the use of this alcohol as an energy vector.¹ Although traditionally this chemical has been produced at industrial scale from syngas, and accordingly from fossil resources, in the last few years a significant effort has been devoted to the hydrogenation of CO₂ according to the following reaction:



The use of this archetypical greenhouse gas as feedstock provides an attractive way to recycle this molecule. CO₂ is present in significant concentrations in the outlet stream of many industrial processes, but it cannot be easily converted into products of interest. Catalytic hydrogenation over Cu-ZnO catalysts can be achieved at moderate temperatures (ca. 300°C), but it is necessary to operate at high pressure as a result of the thermodynamic constraints of the process. In addition,

competition with the reverse water-gas shift reaction (CO₂ + H₂ → CO + H₂O) generates an important proportion of CO, which reduces the overall yield of methanol. Strategies for overcoming this limited selectivity by increasing the hydrogenation activity of the catalyst have been effective in enhancing methanol production, but they rely on the utilization of catalysts containing expensive noble metals, such as Pd.²

Recently, a team led by Profs L. He and X. Zhang from Soochow University in China and the research group of Prof. G.A. Ozin from Toronto University in Canada established a fruitful collaboration to explore a radically new CO₂ hydrogenation approach that combines heat and light for more efficient activation of the reaction. In a study just reported in *Joule*, these researchers used In₂O_{3-x}(OH)_y as a photothermal catalyst; although it was already active at 200°C–300°C for methanol production, this catalyst showed a remarkably enhanced methanol yield under simultaneous illumination with a Xe lamp.³ Notably, this process took place at atmospheric pressure and, accordingly, at operation conditions much softer than those applied in conventional thermal hydrogenation. Production rates were rather high (0.06 mmol g⁻¹h⁻¹) but appreciably lower than those obtained in the conventional process

with thermally activated catalysts at 4.5 MPa and at a similar temperature range (the latter rates are typically about two orders of magnitude larger).² Interestingly, selectivity was comparable to but slightly lower than that obtained over Cu-ZnO catalyst in purely thermal conditions. The quantum efficiency of the best catalyst was about 0.19% at 250°C, and this low value indicates that there is still considerable room for improving the photoactivated process. Even so, it is worth emphasizing that this photothermal process allows CO₂ conversion rates that are at least 10-fold higher than those obtained in the more challenging, purely photocatalytic process using H₂O as an electron donor.⁴ On the other hand, although an initial ~40% drop in the methanol formation rate was observed in the first hour, subsequently the catalytic activity remained stable after 20 hr on stream. However, the presence of a small amount of metallic In in the used catalysts suggests that in the long term, progressive deactivation is possible.

Previous studies have also explored the photothermal activation of CO₂ hydrogenation by using a variety of catalysts, including, among others, Ru/Al₂O₃,⁵ Pd/Nb₂O₅,⁶ and Ni/SiO₂·Al₂O₃.⁷ These experiments showed remarkably high activity that was at least two orders of magnitude higher than for the pure photocatalytic process; however, for those assays, the main product was either methane or CO. This singles out the potential of the In₂O_{3-x}(OH)_y catalysts, whose notable methanol yield under illumination is partly attributed to the increased lifetime of photoinduced

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charge carriers and is positively correlated with the high aspect ratio of the rod-like microstructures used in the *Joule* study. Furthermore, previous investigations have revealed the importance of surface frustrated Lewis pairs (SFLPs) in promoting the selectivity of the photocatalytic hydrogenation of CO₂.⁸ These defects, formed by a surface In-OH moiety in the vicinity of an oxygen vacancy, promote the heterolytic splitting of the H₂ molecule. Accordingly, hydrogen dissociation creates an indium hydride and a hydroxide group with acidic character. As a consequence, the presence of SFLP centers boosts the selectivity to CO generation for CO₂ hydrogenation under purely photocatalytic conditions. In the case of the photothermal reaction, density functional theory calculation provides a feasible route that underlines the crucial role of SFLPs in the production of methanol. Nevertheless, experimental confirmation of this mechanism is needed, particularly for better ascertaining the interplay between light and heat activation on In₂O_{3-x}(OH)_y.

Indubitably, the present work by Ozin and co-workers³ provides new momentum for research on the photothermal hydrogenation of CO₂ and opens up a promising route for achieving a more sustainable process for methanol production. As the authors of this *Joule* article recognize, utilization of these catalysts with solar radiation can potentially increase the still modest quantum efficiency currently reached, but this will require a considerable

effort in designing efficient solar photoreactors for simultaneous heat and light activation. That endeavor cannot be separated from material engineering because the adequate arrangement of the catalysts inside the photoreactor will be crucial for fully exploiting its full potential. In this respect, it will be necessary to work at different scales, from the architecture of nanocrystal superstructures to the macroscopic shaping of the catalyst. In this way, it could be of interest to try and align the catalyst rods in an array parallel to the light, as suggested by Prof. Nathan Lewis for maximizing the efficiency of electrochemical devices.⁹ On the other hand, the significant success of In₂O_{3-x}(OH)_y in achieving competitive methanol production does not preclude the existence of certain weaknesses. Long-term stability of this catalyst could be a relevant issue for practical applications, particularly considering the significant cost of In, which could be affordable only for long-lived systems. In addition, developing catalysts with an even better overall performance, possibly by enhancing the photoactivated contribution, should be a goal of future investigations.

In summary, this new work is an important stepping stone toward the great challenge of CO₂ valorization using renewables resources. Although photothermal hydrogenation relies on a sustainable supply of hydrogen for curtailing the overall carbon footprint, this process provides an attractive and viable route for introducing solar

energy into chemical production, which has a huge potential for development.

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