Light-assisted thermal catalysis for hydrogen storage in a "methanol economy"

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Abstract

As proposed by Nobel laureate G.A. Olah, methanol is a highly versatile hydrogen carrier and platform chemical that might form the foundation of a sustainable economy [1]. The heterogeneously catalyzed methanol synthesis is an established industrial process, known already for over a century. It requires elevated pressures, and the used high-pressure synthesis gas is commonly obtained from fossil resources. Within the scope of a sustainable economy, it is desirable to convert low-pressure CO_2-rich gases, for example derived from flue gases, with hydrogen from water electrolysis. Previous works have demonstrated that an additional irradiation of a reacting thermal heterogeneous catalyst at 20 bar increased methanol yield already at lower temperature [2].

Here, we studied systematically the influence of the reaction conditions on light-assisted methanol synthesis and methanol reforming at ambient pressure on a series of doped Cu/ZnO-based catalysts. Different from the observations at 20 bars, it was hardly possible to increase the yields of methanol with light, regardless of whether only visible, only UV, or both UV and visible light was used. Slightly increased methanol yields are only achievable under very limited sets of temperature, irradiation conditions, and synthesis gas compositions.

However, two reactions were significantly enhanced by light: Firstly, when irradiating the reacting catalysts with visible light in CO_2:H_2 atmosphere, the reverse water gas shift reaction (RWGS) was dramatically enhanced compared to the steady state in the dark, such that the CO formation rate in some cases was improved by a factor of 10. Secondly, some Cu/ZnO-based catalysts proved to be exceptionally active in methanol decomposition, achieving ~90% conversion at relatively mild conditions.

In conclusion, the results highlight two potential applications of light-assisted thermal catalysis: (i) for a first-stage conversion of CO_2 to CO for follow-up processes such as methanol synthesis or the Fischer-Tropsch process, and (ii) for rapid methanol decomposition or steam reforming under mild conditions, when methanol is used a hydrogen storage molecule.

[1] G.A. Olah, A. Goeppert, G.K.S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, 3. Edition, Wiley-VCH, Weinheim, 2018.

[2] B. Xie, R.J. Wong, T.H. Tian, M. Higham, E.K. Gibson, D. Decarolis, J. Callison, K.-F. Aguey-Zinsou, M. Bowker, R.A. Catlow, J. Scott, R. Amal, *Nature Commun.* **11** (2020) 1615.