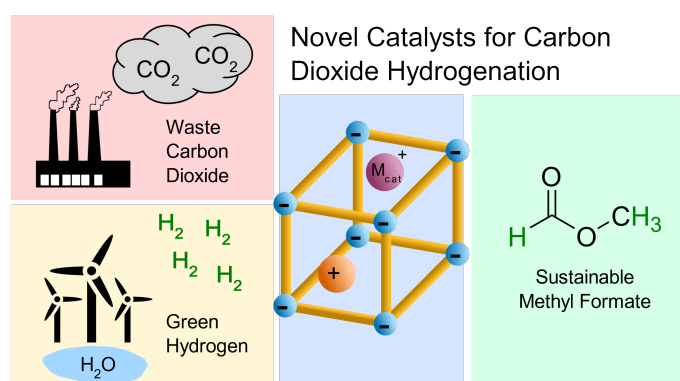


CO₂ Hydrogenation to Methyl Formate using CO₂ as the Sole Carbon SourceR. C. Turnell-Ritson¹, P. J. Dyson^{1*}¹École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

The atmospheric concentration of CO₂ is still increasing, despite international efforts to curb emissions. The removal of CO₂ from the atmosphere is a high-cost endeavour, necessitating economic incentives for carbon capture. More importantly, the use of the near-unlimited C₁ resource of atmospheric CO₂ as a building block for process chemicals is essential to a sustainable future.¹ We have developed efficient catalysts for the hydrogenation of CO₂ to formic acid (FA) and methanol. Additionally, we have combined these C₁ building blocks into methyl formate (MF) in one system. Our catalysts are based on the encapsulation of noble metal complexes and sub-nanoparticles in the pores of zeolites, leveraging the acidity of the support and the principle of nanoconfinement to accelerate these multi-step reactions.



A Ru-based catalyst was developed for the hydrogenation of CO₂ to FA, and simultaneously facilitates fast esterification to MF (TOF > 100 h⁻¹), comparable to similar catalysts which operate at higher temperatures and pressures.^{2,3} A second series of catalysts, both from the literature and developed in our lab, are capable of CO₂ and FA hydrogenation to MeOH under the applied conditions. Combining two appropriate catalysts, MF in which both C atoms derive from CO₂ is formed. In the presence of a methoxide additive, the MF can be decarbonylated to give high CO concentrations (>20%) at a much lower temperature than traditional reverse water gas shift reactions.⁴ The structures of these catalysts will be discussed, and the reaction mechanisms will be explored to understand the key catalyst features which enable their reactivity. The present work allows the formation of three major C₁ synthons widely used in industry using CO₂ under relatively mild conditions. An outlook on coupling CO₂ hydrogenation with C-C bond-forming reactions will be described, as we progress towards the sustainable and selective synthesis of C₂₊ products from atmospheric carbon.

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