

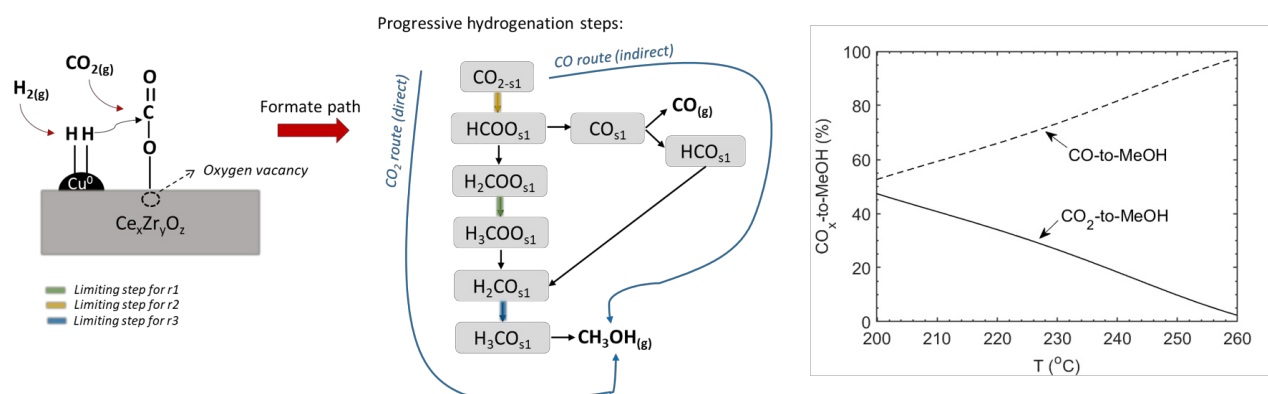
Kinetic modeling of the methanol synthesis from CO₂ and H₂ over a CuO/CeO₂/ZrO₂ catalyst: the role of CO₂ and CO hydrogenation

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The conversion of CO₂ into valuable chemicals has recently received considerable attention in the scientific community, as it is a key step to tackle the climate change issue. In this context, the CO₂ conversion to methanol is particularly appealing due to the high methanol demand worldwide, mainly as chemical intermediate. However, due to the thermodynamic stability of the CO₂ molecule, efforts are required to develop suitable catalysts for increasing its reactivity. The latest advancement in this area revealed that reducible mixed solid oxides with the ability to create oxygen vacancies, such as CeO₂/ZrO₂ solutions, favor the CO₂ adsorption and activation. As a matter of fact, different researchers have recently reported the promising performance of the Cu-Ce-Zr mixed oxides catalyst for the CO₂ hydrogenation to methanol [1][2].

In this study we investigate the kinetics of this system, with the intent to elucidate the reaction pathways and to gain a deeper understanding into the relative roles of Cu-sites and oxygen vacancies. We propose a detailed analysis for single-site, dual-sites and three adsorption sites kinetic models, based on hypothesis retrieved from literature. The kinetic parameters are determined via optimization algorithm based on the minimization of the RMSE (root mean square errors). We use statistic indicators and physicochemical constraints as tool for model discrimination. The mechanism resulting from the best performing model matches with the most recent findings: the formation of the HCOO_{s1} intermediate is the key and lowest step. Furthermore, we quantify the relative contribution of CO₂ (direct pathway) and CO (indirect pathway) to the methanol synthesis, as a function of the reaction conditions (i.e., temperature, pressure and H₂ concentration). Surprisingly, when CO₂ is the sole - or primary - carbon source, methanol is mostly formed via the indirect path: CO₂ first converts to CO which is further hydrogenated to methanol.



Schematic representation of the reaction mechanism (left) and relative contribution of the CO₂ and CO hydrogenation to the methanol synthesis as a function of the reaction temperature (right)

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- [2] Weiwei Wang, Zhenping Qu, Lixin Song, Qiang Fu. (2020). *Journal of Catalysis*, 129. DOI: [10.1016/j.jcat.2019.12.022](https://doi.org/10.1016/j.jcat.2019.12.022)