C2FUEL

European Union's Horizon 2020

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Kinetic modelling of the methanol synthesis from CO_2 and H_2 over a $CuO/CeO_2/ZrO_2$ catalyst: the role of CO_2 and CO hydrogenation

Serena Poto, Damian Vico van Berkel, Fausto Gallucci, M. Fernanda Neira d'Angelo

Sustainable Process Engineering, Chemical Engineering and Chemistry, Eindhoven University of Technology

INTRODUCTION

The CO_2 valorization to **methanol** (Eq.1-3) is a particularly attractive solution to mitigate **global warming** as well as to build a **circular carbon economy**.

(1) $CO_2 + 3H_2 \rightleftharpoons \mathbf{CH_3OH} + H_2O$ $\quad \Delta H_0$ = -49.5 kJ/mol

(2) $CO_2 + H_2 \rightleftharpoons CO + H_2O$ $\quad \Delta H_0$ = +41.2 kJ/mol

(3) $CO + 2H_2 \rightleftharpoons \mathbf{CH_3OH}$ $\quad \Delta H_0$ = -90.5 kJ/mol

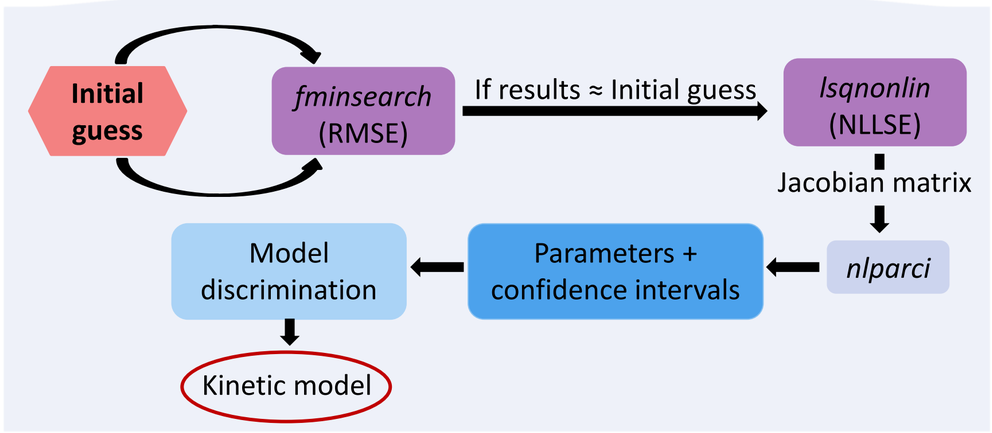
Recently, the **$Cu/CeO_2/ZrO_2$** catalyst has been identified as a promising formulation due to improved **thermal stability**, high **redox ability**, high **oxygen storage capacity**. In this study we explore the kinetic of this system.

Main objectives:

- Understand the **reaction mechanism** (number, type and role of active sites)
- Assess the main **Carbon Source** for methanol synthesis
- Provide **tool** for reactor design and optimization

METHODOLOGY

1. Catalyst synthesis, characterization and testing
2. Fitting routine
3. Results analysis: Modeling vs Experimental

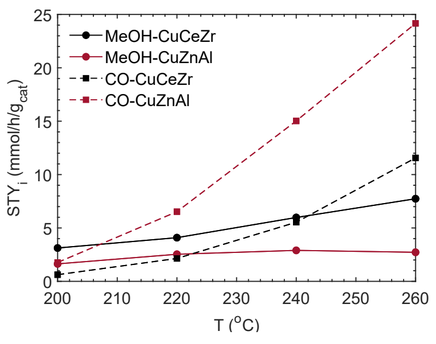


Best performing model: Dual-site LHHW kinetic model[1], based on two adsorption sites which considers both CO_2 and CO hydrogenation to methanol.

1. **Cu^0** sites for dissociative H_2 adsorption
2. **Oxygen vacancies** of CeZr interface for CO_2 activation via oxygen atom

RESULTS

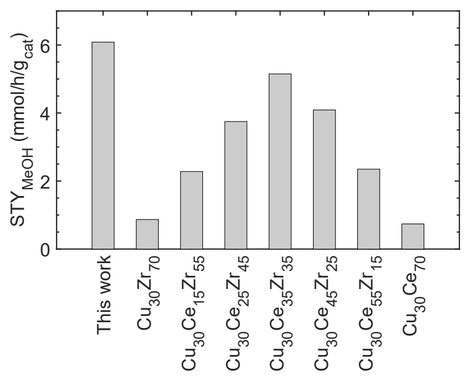
The synthesized $Cu/CeO_2/ZrO_2$ catalyst outperforms the benchmark formulation ($Cu/ZnO/Al_2O_3$) and shows improvement with respect to the state-of-the art of catalyst based on the same oxides.

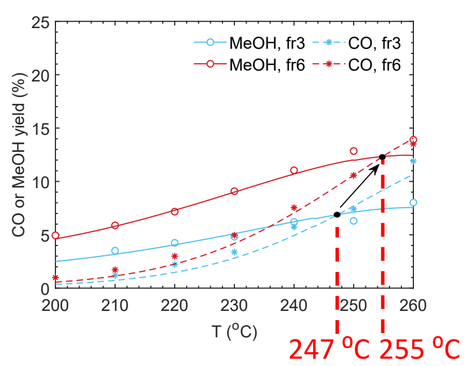


Definition of the **crossover temperature point**:

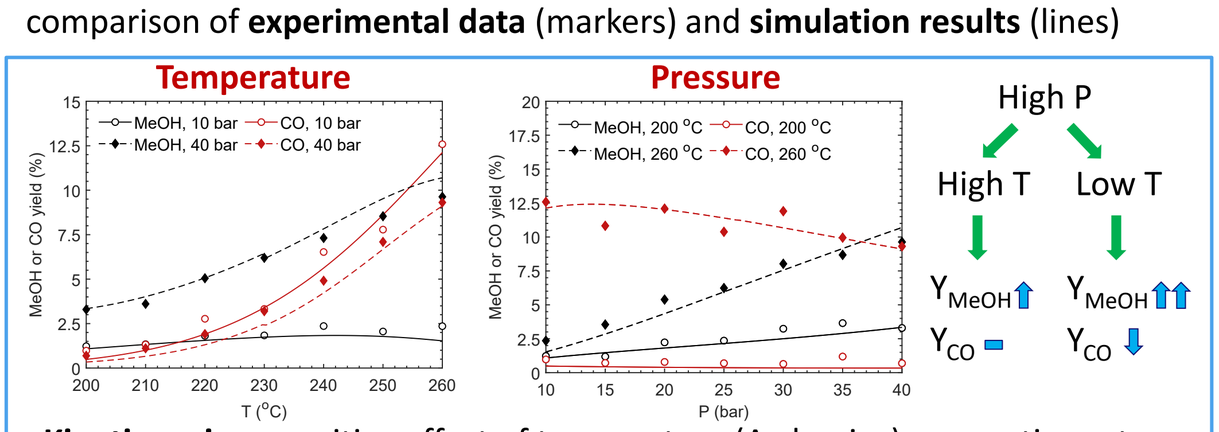
$$T \geq T_{cross}, Y_{CO} > Y_{MeOH}$$

- T_{cross} is c.a. 240 °C for the novel catalyst, while the benchmark displays higher Y_{CO} for the entire temperature region.
- T_{cross} is a function of the H_2:CO_2 ratio



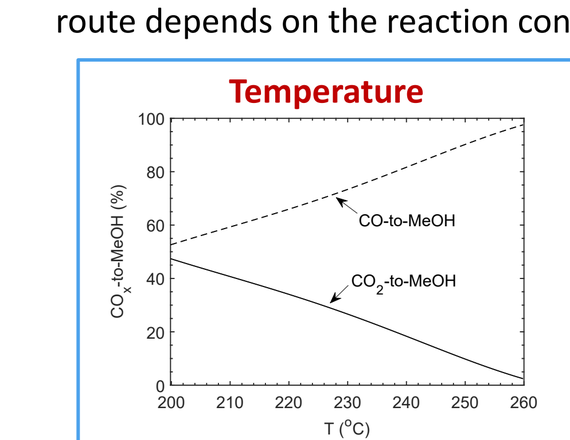


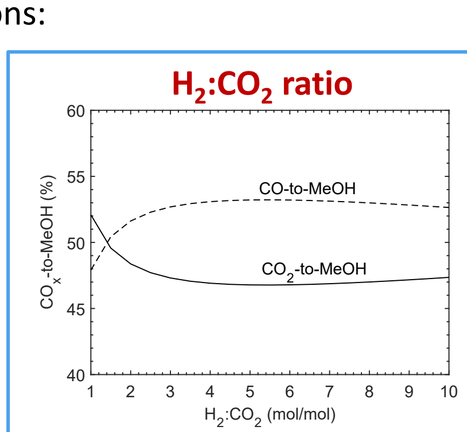
Catalyst performance:
comparison of **experimental data** (markers) and **simulation results** (lines)

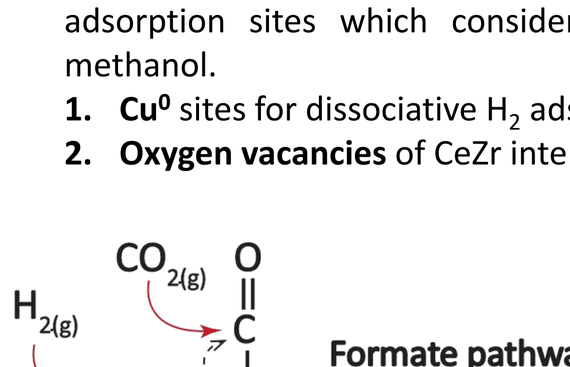


Kinetic regime: positive effect of temperature (Arrhenius) on reaction rates
Temperature **positive effect** on **MeOH yield** increases at **higher pressure**

The extent of **methanol formation** via the **CO_2 (direct)** and **CO (indirect)** route depends on the reaction conditions:







CONCLUSIONS

- The CO_2 adsorption via the oxygen atom favors the formate pathway (series of hydrogenation steps)
- Both CO and CO_2 contribute to methanol synthesis. However, the extent of CO-to-MeOH and CO_2-to-MeOH is a function of the reaction conditions (i.e., temperature, pressure and H2 concentration)
- The $Cu/CeO_2/ZrO_2$ catalyst outperforms the benchmark formulation

ACKNOWLEDGEMENT

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 838014 (*C2Fuel* project).

1. Graaf, G. H., E. J. Stamhuis, and A. A. C. M. Beenackers. "Kinetics of low-pressure methanol synthesis." *Chemical Engineering Science* 43.12 (1988): 3185-3195.