Experimental and modeling of Sorption-Enhancement Reaction Process with in-situ water removal for a methanol production from CO_2

Enrico ANTONUCCIO, David EDOUARD, Frédéric BORNETTE, Guillaume AUBERT, Pascal FONGARLAND*
[1]*CP2M, University of Lyon1, CPE - CNRS, 3 Rue Victor Grignard 69100 Villeurbanne, France.*
*pascal.fongarland@univ-lyon1.fr

Significance and Relevance

Sorption enhancement applied to methanol synthesis is a recent concept to improve methanol productivity for CO_2 hydrogenation. While different studies have shown its virtual advantages using simulation approaches, there is still very few experimental studies related to SERP concept for methanol synthesis and different issues that are addressed: reliability of existing kinetic and sorption models for zeolite-type sorbents, methanol co-adsorption often neglected, materials stability during cycles and operating parameters optimization.

Preferred/2nd choice: Sustainable and clean energy / CO2 utilization and recycling

Preferred presentation: Oral

Introduction and Motivations

The necessity to find an alternative route from fossil carbon for the synthesis of valuable fuels imposes the use of CO_2-rich syngas. Methanol is an excellent candidate for this: being liquid at ambient temperature and pressure, it shows a better exergy than hydrogen or hydrocarbons of similar molecular weight. Furthermore, it is a versatile building block in chemical industry: it can be either oxidized to formaldehyde or dehydrated to di-methyl-ether. Anyhow, the yield of the conventional methanol synthesis process is threatened on the one hand by the thermodynamic equilibrium of the exothermic reaction, and on the other by a parallel reaction, rWGS. High temperature is required for the breakage of the stable CO_2 bonds, but the latter would boost the parallel CO production, thus decreasing selectivity.

$$CO_2 + 3H_2 \underset{-Q}{\Leftrightarrow} CH_4O + H_2O$$
$$CO_2 + H_2 \underset{+Q}{\Leftrightarrow} CO + H_2O$$

To improve the yield of methanol, one strategy lies in the use of a sorbent (zeolites or MOF) that can adsorb water and/or methanol in situ. The solution consists in exploiting Le Chatelier's principle to favorably displace the chemical equilibrium of the key reaction rightward. This is made possible by temperature induced reaction and regeneration cycles, thus approaching the 'SERP' (Sorption Enhanced Reaction Process) technology.[1] The aim of our project is from one hand to acquire a better understanding of the interaction between the various contributions (material transfer, heat, catalytic reaction and sorption) via experimental and modeling/simulation to carry out the process in lab scale to efficiently design it (duration and nature of cycles, integration of operations, scale-up…).

Materials and Methods

For experimental part, a lab-scale fixed-bed reactor was filled with a commercial catalyst (Cu/ZnO/Al2O3) while different adsorbents were tested (3A, 4A, 5A, 13X zeolites (molecular sieves)). To continuously analyze the downstream products (CO, CO2, H2, CH3OH, H2O) the exiting gas was sampled and sent to a GC and 2 TCD while inlet gas was supplied via mass flow controllers. Temperature and pressure are kept constant inside the insulated oven that hosts the reactor via a backpressure regulator and an electrical resistance.

Experimental data have been modeled by a dynamic, heterogeneous, non-ideal plug flow reactor model. Mass and energy balance equations are discretized in space by a finite element approximation, using Matlab software for time integration. The resulting set of ordinary and algebraic differential equations was integrated with respect to time using Matlab's ode15s function, specifically capable of solving stiff differential equation systems.

Results and Discussion

Firstly, we have measured water and methanol uptake capacity for each sorbent using breakthrough curve injected via step impulsion to the reactor. Zeolite 4A had the best (isovolume) performances in terms of max working load: 10.8 w/w% uptake at 250°C. Then the coupling reaction/sorption was investigated. Figure 1 presents an example of results of the sorption enhanced CO_2 conversion at 235 °C and 15 bar, under stoichiometric conditions. For this, the commercial catalyst was homogeneously mixed with the selected adsorbent with a 1:3 mass ratio. The effects of the intensifications are appreciable in the overshoot in the produced CO concentration, that flattens at the equilibrium only when the breakthrough of water and methanol occurs, indicating that the adsorbent is saturated and can no longer boosts the equilibrium. Two cycles are presented, each spaced out by a temperature induced purge under pure nitrogen (at 250°C). The previously adsorbed methanol can be recovered in the purge phase or condensed to augment its purity.

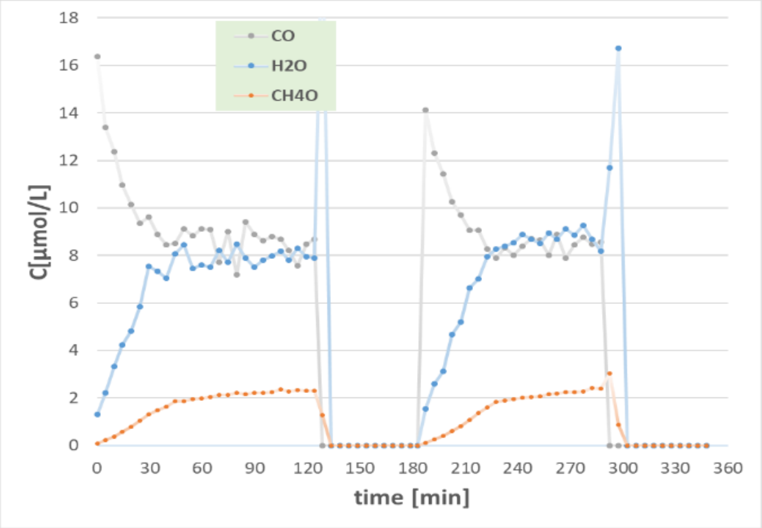

Figure 1. Concentration vs. time at the reactor outlet for the products: water (blue), CO (gray), methanol (orange). Feed flowrate = 60 STPccm/min, 1g of $Cu/ZnO/Al_2O_3$ catalyst.

As shown by the previous results, the SERP can temporary take over the thermodynamic boundaries. In order to maximize this lapse of time, the best way is to choose the most suitable adsorbent that must be selective, performing at high temperature, robust and easily to regenerate. Then, it is possible to wisely design the duration of each phase of the process (reaction and purge) and choose the regeneration strategy (by temperature or pressure swing). Modeling of our SERP experiments have shown that literature model for water and methanol adsorption were not always adequate confirming the necessity to perform experimental validations.

1. References

[1] Guffanti, S.; Visconti, C. G.; Groppi, G.. Ind. Eng. Chem. Res. 2021, 60 (18), 6767–6783

Acknowledgements

French ANR