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## Membrane reactors for methanol synthesis: from material science to process simulation

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### Introduction

The catalytic hydrogenation of CO<sub>2</sub> to methanol and DME with hydrogen (synthesized from low-carbon energy) aims to provide a sustainable alternative to fossil hydrocarbons. However, large quantities of water, generated during the reaction, limit production yields and prematurely deactivate the catalyst.<sup>1</sup> To address this problem, the use of membranes able to selectively separate water within the catalytic reactor has shown to be effective in the literature.<sup>2</sup>

To highlight the advantages of membrane reactors (MR) compared to conventional fixed bed reactors (CR) at the process scale, reliable and extensive models are needed to predict the separation performances of membranes as well as the activity and stability of catalysts under reaction conditions (200-300°C; 35-50 bar). This research aims to conduct extensive experiments on materials (membranes and catalysts) synthesized in-house in order to develop accurate models of membrane reactors for process simulation.

### Materials and Methods

Zeolite microporous membranes, deposited on tubular alumina supports (the support provides mechanical strength to the membrane), are obtained by hydrothermal synthesis. LTA and SOD zeolites were selected for membrane preparation because of their high selectivity for water (hydrophilicity) (Figure 1). For LTA membranes, two synthesis routes have been explored: (1) primary growth, carried out in one-step on supports functionalized with 3-aminopropyltriethoxysilane (APTES), and (2) secondary growth, carried out in two steps corresponding to the deposition of LTA seeds by dip-coating followed by a hydrothermal synthesis. SOD membranes were prepared *via* two successive hydrothermal syntheses on bare supports.

CRs and MRs are modeled with 1D plug-flow models in Python language and implemented for process simulations in ProSimPlus3 through a VBS script. Reaction kinetics and membrane performance data have been extracted from the literature while awaiting for in-house trials.<sup>3,4</sup>

### Results and Discussion

In one part, secondary growth method for LTA zeolite membrane preparation is more complex to implement. However, this method is more reliable and membranes display less macroscopic defects. In fact, this approach enables finer control of crystal growth by decoupling the nucleation stage from the growth stage. On the other part, SOD membrane

synthesis trials have demonstrated the difficulty of creating a homogeneous membrane in a single hydrothermal synthesis. The density of the zeolite deposit was increased through the implementation of protocol with two successive hydrothermal syntheses.



Figure 1. SEM micrographs of LTA and SOD zeolite membranes deposited on the inside of tubular alumina supports.

Process simulations showed that MRs, by improving the CO<sub>2</sub> conversion through the separation of water in the reaction zone, requires lower recycle ratios than CRs. This caused a beneficial cascading effect with a reduction of 19% of the overall energy consumption for the MR process (Figure 2) as well as lowering by 10% the amount of catalyst required to operate at the same space velocity.

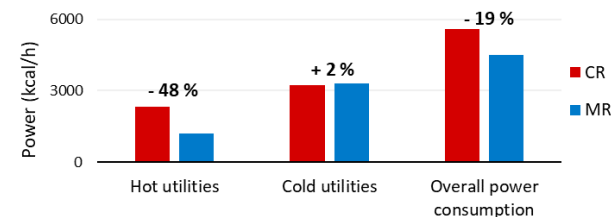


Figure 2. Overall power consumption and power consumption of hot and cold utilities for the CR process and MR process. Hot and cold utilities and power consumption of compressors are included in the overall power consumption.

### Significance

This multidisciplinary research aims to rigorously evaluate the relevance of membrane reactors at the process scale by bridging the gap between materials science and process simulation. The goal is to synthesize, experiment and model all the required materials to improve the accuracy of membrane reactor models and to identify the bottlenecks hindering the scale-up of membrane reactor processes within each fields.

### References

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