Intensification of Water-Gas Shift Reaction in a MOF-Membrane Microreactor

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Highlights

- Water Gas Shift reaction is modeled in a membrane microchannel reactor.
- $Pt-CeO_2$ and ZIF-7 are used as the catalyst and the membrane, respectively.
- Using steam as the sweep gas boosts membrane reactor performance.
- The membrane reactor is more efficient than the conventional two-reactor operation.

1. Introduction

Water Gas Shift (WGS: $CO+H_2O=CO_2+H_2$) plays key roles in the H_2 purification step of conventional steam reforming and ammonia synthesis processes. The exothermic reaction is thermodynamically limited at high temperatures, so practical implementation of WGS necessitates two consecutive reactors. The high-temperature WGS reactor operates at 573-673 K and comprises Fe-Cr based catalysts. This unit is followed by the low-temperature (473-573 K) WGS reactor packed with Cu-based catalysts [1]. While Cu is very active at low temperatures, its operation is limited by ~600 K above which the risk of hydrothermal sintering becomes critical. Along these lines, Pt-based catalysts (e.g. $Pt-CeO_2$) allows operability in a broader temperature range (473-673 K) [1] and can rule out the need of using two reactors. Nevertheless, the advantage of using $Pt-CeO_2$ diminishes at ~620 K above which the reaction becomes limited by thermodynamics. *In-situ* withdrawal of H_2 by a H_2-permselective membrane to promote CO conversion is a strategy to overcome thermodynamic limitations. Due to its infinite selectivity towards to H_2, Pd is the common material for such purposes. Alternatively, silica gels and MOF membranes are considered due to the relatively high cost, low H_2 permeance and sulfur poisoning of the Pd-based counterparts [2]. Among MOF-based membranes, Zeolite Imidazolate Frameworks (ZIF) are suitable due to their high H_2 permeability and thermal stability [3]. The present work aims to develop a mathematical model of a membrane microreactor comprising $Pt-CeO_2$ catalyst and ZIF-7 membrane. Upon validation by using literature-based experimental data [3,4], the model is used to investigate the effects of temperature, pressure, type and flow rate of the permeate stream. Moreover, the performance of the membrane reactor is benchmarked with that of the two-reactor configuration.

2. Methods

Calculations are performed by considering a membrane microreactor geometry presented in [5]. Catalyst $Pt-CeO_2$ is assumed to be coated on the retentate side wall of the rectangular channel as a thin layer and ZIF-7 membrane separates the reactor into permeate and retentate sides. Initial analysis of the results show that isothermal conditions can be provided by sending the sweep flow approximately 5°C lower than retentate flow. Thus, simulations are performed by using as an isothermal 1D steady state model in co-current arrangement. The model involves component mass and energy balances for permeate and retentate sides. Component balances include the terms for the reaction kinetics and permeation through the membrane. Related permeability data are taken from [3] and kinetic data is adopted from [6]. Permeation fluxes are calculated using the Sievert's Law.

3. Results and discussion

Figure 1 shows the CO conversion results of using either steam or Ar as permeate gas at 1 bar pressure in each channel with co-current flow arrangement. The slight improvement in CO conversion in Ar sweep arrangement compared to no-membrane case is due to the transfer of H_2 through the membrane. H_2 has the highest permeance through the membrane and has the highest fraction at the inlet. Thus, its transfer through the membrane drives the forward reaction. In addition to H_2, permeation of H_2O, CO and CO_2 (in descending order) is allowed by the ZIF-7 membrane [3]. Therefore, using steam instead of Ar as the sweep gas increases CO conversion further since transfer of steam from permeate to retentate increases partial pressure of steam in retentate and boosts the forward reaction. In addition, setting sweep molar flow rate to 10 times of that of the RIMF is found to be sufficient to ensure that partial pressures on the permeate side do not increase much to hinder further transfer through the membrane (Figure 1).

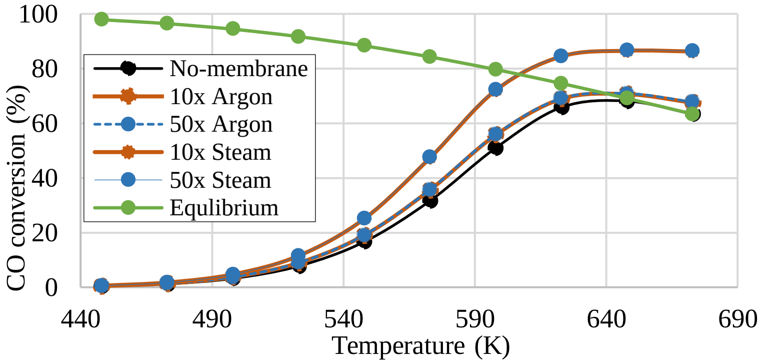

Figure 1. Effect of Sweep Type and Molar Flow Rate (Residence time: 2.37 g_{cat}.h/mol, Retentate Inlet Molar Flow Rate (RIMF): 9.1x10^{-3} mol/h, 10-50x: 10-50 times of RIMF)

To compare the results with conventional method, upstream is assumed to enter the adiabatic Fe/Cr catalyzed high temperature WGS at 623 K and 10 bar. Through various parameter analysis, optimum result is found as 52% CO conversion at residence time of 19.0 g_{cat}.h/mol and outlet temperature is found to be 718 K. Following that, the optimum result at the end of the low temperature WGS is found to be 89% CO conversion at 1.20 g_{cat}.h/mol and 473 and 541 K at the inlet and outlet, respectively. Since ZIF-7 membrane allows the transfer of each gas on some degree, optimum results might change considering CO conversion, permeate mole fractions, total mol fractions and H_2 recovery. However, 94% CO conversion at 673 K inlet with 11.8 g_{cat}.h/mol residence time can be acquired. Also, assuming both channel contents are mixed after the outlet, dry CO fraction is 0.4% lower than conventional method, which is important since CO fraction must be around several ppm level for both fuel cells and NH_3 synthesis. Additionally, dry CO_2 fraction also decreases from 21% to 8%. Lastly, conventional method requires cooling from 718 to 473 k between the two reactors, whereas membrane case requires only 50 K heating before the reactor inlet.

4. Conclusions

A microchannel membrane WGS reactor comprising Pt-CeO_2 catalyst and ZIF-7 membrane is modeled. Specific to the steam permeability of ZIF-7, the sweep gas type leads to significant benefits in reactor performance. H_2 transfer through the membrane is not enough to drive the reaction forward when Ar is used as the sweep gas. Nevertheless, the use of steam as the sweep gas allows up to ~10% increase in CO conversion. Additionally, performance of the microchannel reactor is compared with the conventional two reactor system. Significant improvement on CO conversion, outlet CO and CO_2 fractions and energy requirement are observed. Further optimization studies are ongoing.

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Keywords

Membrane, Microchannel, Process intensification, Water Gas Shift