Effect of membrane selectivities on WGS reaction in a nonisothermal membrane reactor

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In this work, the water gas shift (WGS) reaction was theoretically investigated by means of a 1-D nonisothermal model in a catalytic membrane reactor (MR) considering a self-supported Pd-Ag and a SiO_2 supported membranes. In particular, CO conversion, H_2 recovery and its purity were analysed and compared for the two membranes. The feed pressure effect as a driving force promoting permeation instead of the sweep gas was also studied. Furthermore, MR performance was analyzed in terms of the Damköler number (Da) as a global parameter taking into account characteristic times of the reaction and flow rate. The advantage of MR use with respect to the traditional reactor (TR) was also discussed.

Introduction

In the last few decades many scientific studies on the use of catalytic MRs in integrated plants for H_2 production have been developed. Particular attention has also been focused on the upgrading step, generally consisting in the WGS reaction that reduces CO content at the same time producing more H_2.
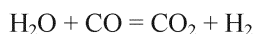
$$H_2O + CO = CO_2 + H_2 \qquad\qquad \Delta H^0{}_{298} = -41 \text{ kJ/mol}$$

CO concentration allowed in the final stream depends on the final use of the gas. New technologies such as PEMFCs, requiring CO-free (<10 ppm) hydrogen, are also promoting innovative WGS processes. Innovative systems and technologies, such as MRs, allow a greater CO conversion than TR ones (Barbieri et al. 2005), improving the process efficiency in accordance with the Process Intensification Strategy (Stankiewicz and Moulijn, 2000). The performance of an MR strictly depends on the membrane type. In fact, a Pd-alloy membrane, showing an infinite H_2 selectivity, allows a pure H_2 permeate stream to be obtained, but lower permeating fluxes can be reached in the temperature range investigated (220-320°C). On the contrary, even though a silica-based membrane exhibits higher permeating flux, it produces an impure H_2 permeate stream, whose composition depends on the membrane selectivities.

Mathematical tools

The MR considered was made of two concentric tubes: the outer tube (the shell) and the inner tube (the membrane). The hypotheses of the model are the following:

- Plug flow in retentate and permeate streams.
- Constant pressure on the permeate side.
- Co-current flow configuration.
- Pressure drops along the catalytic bed following Ergun's equation.

The balance equations are written in dimensionless variables and the Damköler (Da) number was identified as the process-characterizing dimensionless group. It represents the ratio between the axial flow and reaction characteristic times evaluated for the reference species (CO in this case) at the inlet conditions. Eq.(1) defines Da as the ratio of CO reaction rate calculated at the inlet for the whole reaction volume and CO feed flow rate. A $Da=1$ represents the best operating conditions, since all the catalyst amount is exploited for the reaction.

$$Da = \frac{r_{CO}\big|_{z=0} \cdot V_{\text{Reaction}}}{F_{CO}^{\text{Feed}}} = \frac{\text{Characteristic space time}}{\text{Characteristic reaction time}} \tag{1}$$

$$\text{Reaction side: } \frac{d\sum_{i=1}^{n}\overline{F}_i^{\text{Reaction}}}{d\overline{z}} = \overline{r}_{CO}\,Da - \frac{\sum_{i=1}^{n}J_i A^{\text{Membrane}}}{F_{CO}^{\text{Feed}}} \tag{2}$$

$$\text{Permeation side: } \frac{d\sum_{i=1}^{n}\overline{F}_i^{\text{Permeation}}}{d\overline{z}} = \frac{\sum_{i=1}^{n}J_i A^{\text{Membrane}}}{F_{CO}^{\text{Feed}}} \tag{3}$$

Energy balance:

Reaction side:

$$\sum_{i=1}^{n}\frac{d\left(\overline{F}_i^{\text{Reaction}}\,\overline{\Delta H}_i^{\text{Reaction}}\right)}{d\overline{z}} = \frac{U^{\text{Shell}}A^{\text{Shell}}T^{\text{Furnace}}}{F_{CO}^{\text{Feed}}\Delta H_{CO}^{\text{Feed}}}\left(1 - \overline{T}^{\text{Reaction}}\right)+$$

$$-\frac{U^{\text{Membrane}}A^{\text{Membrane}}T^{\text{Furnace}}}{F_{CO}^{\text{Feed}}\Delta H_{CO}^{\text{Feed}}}\left(\overline{T}^{\text{Reaction}} - \overline{T}^{\text{Permeation}}\right)-\frac{A^{\text{Membrane}}}{F_{CO}^{\text{Feed}}\Delta H_{CO}^{\text{Feed}}}\sum_{i=1}^{n}J_i\Delta H_i\Bigg|^{Reaction} \tag{4}$$

Permeation side:

$$\sum_{i=1}^{n}\frac{d\left(\overline{F}_i^{\text{Permeation}}\,\overline{\Delta H}_i^{\text{Permeation}}\right)}{d\overline{z}} = \frac{U^{\text{Membrane}}A^{\text{Membrane}}T^{\text{Furnace}}}{F_{CO}^{\text{Feed}}\Delta H_{CO}^{\text{Feed}}}\left(\overline{T}^{\text{Reaction}} - \overline{T}^{\text{Permeation}}\right)+$$

$$+\frac{A^{\text{Membrane}}}{F_{CO}^{\text{Feed}}\Delta H_{CO}^{\text{Feed}}}\sum_{i=1}^{n}J_i\Delta H_i\Bigg|^{Permeation} \tag{5}$$

The Hydrogen permeated through the membrane was evaluated in terms of the lamped parameter Recovery Index (RI), estimated from the reactor outlet streams representing the overall hydrogen fraction permeated through the membrane.

$$\text{Recovery Index} = RI_{H_2} = \frac{(F\ y)_{H_2}^{\text{Permeate}}}{(F\ y)_{H_2}^{\text{Permeate}} + (F\ y)_{H_2}^{\text{Retentate}}} \tag{6}$$

Table 1 reports the characteristics of both the membrane considered in the simulations.

Table 1 –Characteristics of the membrane used in the simulations

Membrane type	self-supported Pd-Ag (Scura et al. 2005)	stainless steel supported silica (Brunetti et al. 2007)
Thickness	60 µm	6 µm (SiO_2) 1.5 mm (support)
H_2 permeance	1.3 mmol/m^2 s $Pa^{0.5}$	6.2 mmol/m^2 s Pa
H_2 selectivity, -		
H_2/CO		30
H_2/CO_2	∞	25
H_2/H_2O		20

Results and Discussions

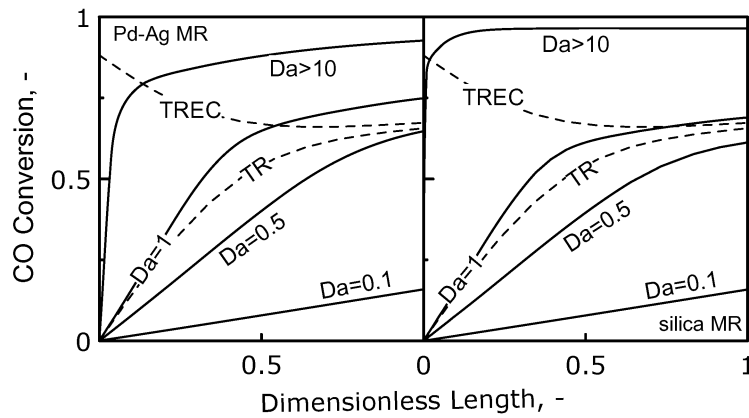CO conversion achieved increases along MR abscissa up to a plateau, reached faster at a higher Da (Figure 1).

Figure 1 – CO conversion as a function of dimensionless length for different Da values. T^{Furnace}=280°C; P^{Feed} = 1,000 kPa

This trend is shown both in the cases of a Pd-Ag or silica MRs. At a set furnace temperature, a high Da implies a higher space time, thus CO conversion is improved.

On the contrary, a low Da means a reaction time much higher than the space time; therefore, the contact time among reactants and catalyst is low and the conversion is depleted. No more improvements in terms of CO conversion can be obtained for both MRs considered for $Da>10$. The Pd-Ag MR allows only H_2 to be removed from the reaction zone, shifting the reaction towards conversion improvements. Also, the other gases permeate through the membrane in the silica MR which means on one side CO conversion improvement by product removal and in the meantime CO and H_2O permeation deplete the conversion. Therefore, a higher CO conversion can be reached using the Pd-Ag MR for the same Da. Furthermore, in both the cases, MR CO conversion is always higher than TR one and exceeds TREC (Traditional Reactor Equilibrium Conversion) for $Da \geq 1$.

As CO conversion, RI increases along MR up to a plateau, which value is reached faster for a higher Da. This owing to the favoured conversion at a high Da implying higher hydrogen removal. However, RI achieved in the Pd-Ag MR is lower than the other one (Figure 2). This is due to the higher permeance value of the silica MR that allows a higher H_2 amount to be recovered, though it is not pure. On the contrary, the Pd-Ag MR shows lower H_2 permeance, but ensures 100% purity of the recovered H_2.
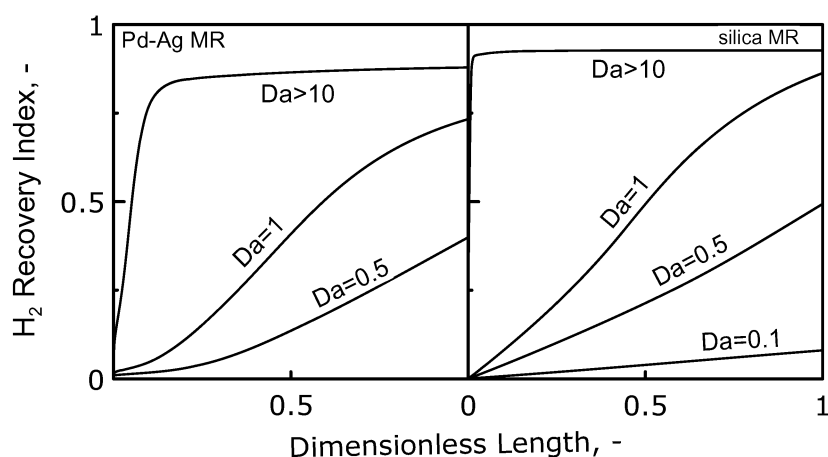

Figure 2 – Recovery Index as a function of dimensionless length for different Da values. $T^{Furnace}=280°C$; $P^{Feed} = 1,000$ kPa

The feed pressure has the effect of increasing the hydrogen production and the permeation driving force. As the reaction stoichiometry, the process is not influenced by the pressure in a TR, but in an MR its effect is important. In particular, this effect is always positive (in terms of conversion and RI) for a Pd-alloy MR, in which only H_2 is removed from reaction volume, whereas for a silica MR it strictly depends on the component selectivities. In the operating conditions considered here, the conversion and RI are increased by a higher feed pressure also in the silica MR, where nevertheless a higher feed pressure implies higher amounts of the other gases in the permeate stream with consequent lower H_2 purity (Figure 3).
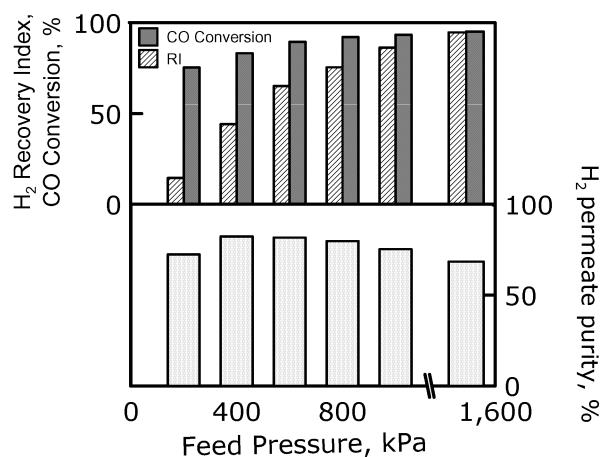
Figure 3 – SiO$_2$ supported MR. H$_2$ recovery index, CO conversion and H$_2$ permeate purity as a function of feed pressure. T^{Furnace}=280°C. Da=1

The advantage in MRs with respect to the conventional reactors is summarized in Figure 4 in terms of reactor size reduction, moving in the logic of the Process Intensification Strategy. MR volume is about 1/3 of TR volume required at the same operating conditions (1000 kPa, 280°C) using a Pd-Ag membrane (Brunetti et al. 2005). Whereas, it is about one half of TR volume when a silica membrane with H$_2$/CO selectivity equal to 30 is considered. This reduction volume also affects the required catalyst amount and implies significant advantages in terms of reduced equipment costs.
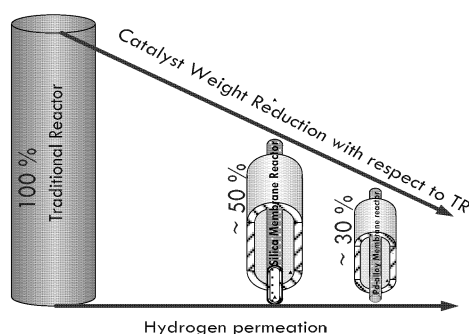

Figure 4 - Reduction of MR volumes with respect to a TR. The same CO conversion of 95% of TREC is imposed as target for all reactors.

Conclusions

The WGS reaction was investigated by means of a 1-D nonisothermal model in an MR considering a self-supported Pd-Ag and a silica supported membranes.

The permeation of only H_2 (Pd-Ag MR) allows a pure H_2 stream on the permeate side and a CO conversion higher than that calculated for the silica MR characterized by the permeation of all the species involved. However, a higher H_2 recovery index is achievable with the silica MR showing higher H_2 permeance.

The same CO conversion of a TR can be reached by an MR in a lower reaction volume. In particular MR volume is about 1/3 and a half for Pd-Ag and silica MR, respectively, of TR one for reaching 95% of TR equilibrium conversion. Clear gains in terms of reactor size and better reactant exploitation are assured by MRs.

Acknowledgments

References

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