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Modeling of autothermal reforming of methane in a fluidized bed reactor with perovskite membranes

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ABSTRACT

The performance of perovskite membrane-assisted fluidized bed reactors for ultra-high purity hydrogen production through autothermal reforming of methane has been investigated using numerical simulations. Two different three-phase phenomenological models have been developed differing in their description of the mass transfer between the membranes and the emulsion, cloud and bubble phases, where the parameters in the oxygen permeation flux expression were determined from new experimental data. The calculation of the required oxygen-to-carbon ratio is based on overall enthalpy balance. The reactor performance without and with O\textsubscript{2} permeation was investigated and compared. The two models of perovskite membrane-assisted fluidized bed reactors produce basically the same results, indicating that the external mass transfer from the membranes to the bulk of the fluidized bed is not rate limiting, but clearly show that the fluidized bed membrane reactor can largely outperform ordinary fluidized bed reactors for the autothermal reforming of methane. It has been demonstrated that with perovskite membrane-assisted fluidized bed reactors autothermal operation with a high CH\textsubscript{4} conversion and H\textsubscript{2} yield can be achieved with a relatively small catalyst inventory.

1. Introduction

Sustainable production of hydrogen, as a clean energy carrier and an important reactant in numerous chemical and metallurgical processes, could alleviate growing concerns about the world's energy supply, security, air pollution and greenhouse gas emissions [1–3]. In most industries, hydrogen is being generated through steam reforming or partial oxidation of natural gas in classical carbon-inefficient parallel fixed bed reactors with downstream purification by pressure swing adsorption (PSA). With fluidized bed membrane reactors (FBMRs), a better performance for the production of pure hydrogen can be achieved, and have thus been attracting increasing attention over the past decade [4].

Many novel concepts of fluidized bed membrane reactors for hydrogen production through autothermal reforming of hydrocarbons have been developed, in most cases employing palladium-based membranes for hydrogen extraction and feeding pure oxygen directly [4]. Perovskite membrane-assisted fluidized bed reactors (PMAFBRs) combine the advantages of both fluidized bed operation and O\textsubscript{2} separation via perm-selective membranes, i.e. better mass and heat transfer characteristics and selective feeding of O\textsubscript{2} for autothermal reforming, avoiding a separate costly cryogenic air separation unit. Some experimental tests with perovskite membrane-assisted packed bed reactors have been reported for the partial oxidation of methane [5–7], but few studies report experimental tests for autothermal reforming of hydrocarbons in PMAFBRs because of current technical limitations of membrane technologies, in particular issues related to membrane and sealing stability [3,8,9]. In particular, mechanical stability of the membrane could be reduced by the attrition of the particles moving in the fluidized bed. This should be better studied in a long term experimental work. However, the potential benefits of the PMAFBR system can be explored and quantified through reactor modeling, beyond the range of parameters that can currently be studied experimentally in view of the mentioned technological, economic and safety limitations, which is the objective of this paper.

Methane steam reforming is endothermic, whereas water-gas-shift is...
### Nomenclature

#### Notations

**A**  
Cross sectional area of reactor, [m²]

**A_m**  
Membrane cross sectional area, [m²]

**A_m,p**  
Membrane total permeation area, [m²]

**Ar**  
Archimedes number, –

**A_j**  
Arrhenius pre-exponential factor for j-th reaction, [units depend on the reaction, Table 4]

**A_{CH_4}^{OX}, A_{O_2}^{OX}**  
Pre-exponential factors for CH₄ and O₂ respectively, to calculate adsorption coefficients [bar⁻¹]

**c_{1}, c_{2}**  
Constants for calculation of incipiently fluidized bed height, –

**c_{i,0}**(b,c,e)  
Initial concentration of ith component in bubble, cloud, and emulsion phase, [mol·m⁻³]

**c_{i,d}**  
Initial total molar concentration of ith component, [mol·m⁻³]

**c_{i,d}**  
Final total molar concentration of ith component, [mol·m⁻³]

**C_{O_2,m}**  
O₂ concentration in membrane tube, [mol·m⁻³]

**C_{pm}**  
Average molar heat capacity of gas mixture, [J·mol⁻¹·K⁻¹]

**d_b**  
Bubble size at position h, [m]

**d_b,0**  
Initial bubble size, [m]

**d_b,avg**  
Average bubble size, [m]

**d_b,max**  
Maximum bubble size, [m]

**d_i**  
Inner diameter of perovskite membrane tube, [m]

**d_o**  
Average diameter of perovskite membrane tube, [m]

**d_o**  
Outer diameter of perovskite membrane tube, [m]

**D**  
Diameter of reactor, [m]

**D_j**  
Diffusion coefficient of ith component, [m²·s⁻¹]

**D_o**  
Diffusion coefficient of O₂ vacancy in Eq. (1), [m²·s⁻¹]

**ε_{(b,c,e)}**  
Volume fraction of bubble phase, cloud phase, or emulsion phase, –

**ε_{mass}**  
Total mass balance error, g·s⁻¹

**E_{act,j}**  
Activation energy for j-th reaction, [kJ·mol⁻¹]

**F_{CH_4,feed}**  
CH₄ flow rate at inlet, [mol·h⁻¹]

**F_{CH_4,b(c,e)}**  
CH₄ flow rate at the height h in k-th phase, [mol·h⁻¹]

**F_{O_2,D,alk}**  
CO flow rate at the height h in k-th phase, [mol·h⁻¹]

**F_{H_2e}**  
Flow rate of sweep gas He, [SL·min⁻¹]

**F_{H_2,t}**  
Total molar flow rate at inlet, [mol·h⁻¹]

**g**  
Gravity acceleration rate, [m·s⁻²]

**h**  
Distance in axial direction of the reactor bed, [m]

**H_{f}**  
Enthalpy of ith component at temperature T, [J·mol⁻¹]

**H_{f,c}**  
Fluidized bed height including free board, [m]

**H_{inf}**  
Incipiently fluidized bed height, [m]

**I_{O_2,exp}**  
Actual O₂ permeation flux through a perovskite membrane, [Sml·cm⁻²·min⁻¹]

**J_{O_2,mod}**  
Theoretical O₂ permeation flux through a perovskite membrane, [Sml·cm⁻²·min⁻¹]

**J_{O_2,b(c,e)}**  
O₂ permeation flux in bubble, cloud, or emulsion phase, [mol·m⁻²·s⁻¹]

**k_{f}, k_{e}**  
Constants of surface reaction rates at both sides of membrane

**k_{j,bh}**  
Reaction rate constant for j-th reversible reaction, –

**K_{bc}**  
Mass transfer coefficient between bubble phase and cloud phase, [s⁻¹]

**K_{ce}**  
Mass transfer coefficient between cloud phase and emulsion phase, [s⁻¹]

**K_{cat}**  
Catalyst dilution factor, –

**K_{CH_4}^{aq}, K_{O_2}^{OX}**  
Equilibrium constant for j-th reaction, –

**K_{CH_4}^{OX}, K_{O_2}^{OX}**  
Adsorption coefficients for CH₄ and O₂, respectively, in combustion kinetics, [bar⁻¹]

**l**  
Distance along the perovskite membrane tube, [m]

**L_{m}**  
Length of perovskite membrane tube, [m]

**m_{cat}**  
Total catalyst loading, [g]

**m_{cat,k}**  
Catalyst loading in each phase, calculated by solid fraction, k = b,c,e, [g]

**M_{i}**  
Molecular weight for ith component, [g·mol⁻¹]

**M_r**  
Average molecular weight of gas mixture, [g·mol⁻¹]

**M_{in,CH_4(O)}**  
Mass flow rate of C, H, O atoms in reactor inlet, [g·s⁻¹]

**M_{in,CH_4(O)}**  
Mass flow rate of O atoms in membrane inlet and outlet, [g·s⁻¹]

**M_{out,CH_4(O)}**  
Mass flow rate of C, H, O atoms in reactor outlet, [g·s⁻¹]

**n**  
Number of component, –

**N**  
Number of perovskite membranes, –

**P_{i}**  
Partial pressure of ith component, [bar]

**P**  
Reactor pressure, [bar]

**P_{m}**  
Pressure in membrane tube, [bar]

**P_{e}**  
Pebble number, –

**P_{O_2,H_2}**  
Partial pressure of O₂ in the retentate side, [Pa]

**P_{O_2,flow}**  
Partial pressure of O₂ in the permeate side, [Pa]

**r_{j}**  
Reaction rate for j-th reaction in Table 3, [mol·s⁻¹·m⁻³]

**r_{j,b(c,e)}**  
Reaction rate of j-th reaction in bubble, cloud, or emulsion phase, [mol·s⁻¹·m⁻³]

**r_{v,ex}**  
Steam to carbon ratio, oxygen to carbon ratio, –

**R**  
Gas constant, [J·mol⁻¹·K⁻¹]

**R_{b,c,e}**  
Average reaction rate of j-th reaction in bubble, cloud, or emulsion phase, [mol·s⁻¹]

**S_{CO,H}**  
CO selectivity at the height h along the reactor, –

**T**  
Reactor temperature, [K]

**T_{feed}**  
Feed temperature, [K]

**T_{m}**  
Membrane temperature, [K]

**t_m**  
Perovskite membrane thickness, [m]

**u_{b,0}**  
Initial bubble velocity, [m·s⁻¹]

**u_{avg}**  
Average rise velocity of a swarm of bubbles, [m·s⁻¹]

**u_{in}**  
Average velocity in perovskite membrane tube, [m·s⁻¹]

**u_{mf}**  
Minimum fluidization velocity, [m·s⁻¹]

**uratio**  
Ratio u_{in} to u_{mf} ratio

**υ_{j}**  
Stoichiometric coefficient of ith component for j-th reaction, –

**V_{b(c,e)}**  
Volume of bubble phase, cloud phase, or emulsion phase, [m³]

**V_{m}**  
Volume of membrane tubes, [m³]

**x_i**  
Molar fraction of each component, –

**x_{O_2,m,O_2}**  
Initial O₂ molar fraction in membrane tube, –

**X_{CH_4,b}**  
CH₄ conversion at the height h along the reactor, %

**Y_{CH_4,h}**  
H₂ yield at the height h along the reactor, %

### Greek letters

**ΔH_{OX}^{CH_4}**  
Adsorption heat of ith component, [J·mol⁻¹]

**ΔH_{F}**  
Enthalpy change of j-th reaction, [kJ·mol⁻¹]

**ΔG_{j}**  
Gibbs free energy for j-th reaction, [mol·s⁻¹·m⁻³]

**ε_{bed}**  
Porosity of bed, –

**ε_{mf}**  
Voidage in minimal fluidization condition, –

**θ_{b(c,e)}**  
Solid fraction in bubble phase, cloud phase, or emulsion phase, –

**µ**  
Viscosity of gas mixture, [Pa·s]

**µ_{b(c,e)}**  
Viscosity of ith component, [Pa·s]

**ρ**  
Fluid density, [kg·m⁻³]

**ρ_{c}**  
Catalyst mass per unit phase volume, [kg·cat·m⁻³·(phase volume)]

**ρ_{g}**  
Density of gas mixture, [kg·m⁻³]
a mildly exothermic reaction. When O₂ is introduced, the heat needed for the reforming reaction is supplied through partial oxidation of methane, realizing overall autothermal reforming of methane, which allows efficient energy integration. There are two ways to introduce O₂, using a direct feed of air or feeding via O₂ permeable membranes. The former way has two drawbacks: (i) the exhaust gas mainly consists of N₂ and CO₂, thus the separation is difficult and costly if CO₂ capture is required. (ii) in the case with H₂ permeable membranes, the N₂ dilution decreases the concentration of H₂ in the reactor, reducing the driving force for H₂ permeation through the membranes and resulting in a larger membrane area needed. Feeding pure O₂ to realize autothermal reforming requires a costly air separation unit [10]. According to the reasons above, O₂ permeable membranes have been widely researched in the past decades, mainly including mixed ionic electronic conducting (MIEC) membranes, ion transport membranes, and O₂ transport membranes. MIEC perovskite-type membranes have been attracting increasing attention because of their flexible elemental compositions. Many perovskite membranes have been developed, and some of them exhibited high O₂ permeation fluxes [11–17]. However, tubular perovskite membranes with high stability and durable sealing technology still remain to be developed for industrial applications [18].

In a few publications the CH₄ conversion and H₂ yield without and with perovskite membranes have been compared using reactor modeling, showing that the perovskite membrane reactors can achieve much higher H₂ yields [19–21]. Chen and Elnashaie [22] simulated two configurations of circulating PMAFBRs for autothermal reforming of heavy hydrocarbons, and explored the effect of the number of perovskite membranes on the reactor performance. Patil et al. [9] designed a membrane fluidized bed reactor with a power output of 100–200 W using two zones and two types of membranes. Dense perovskite membranes are inserted in the partial oxidation bottom section (900–1000 °C), and palladium-based membranes are located in the steam reforming top section (500–600 °C). A reactor model was developed and the effect of hydrogen removal was investigated, assuming that all reactions take place in the emulsion phase. Abashar and Elnashaie [23] have used a model to systematically investigate the influence of O₂ distribution by employing discrete injection points along the height of the reformer. Their simulation results showed that the staged distributive feeding of O₂ promotes the shift of the thermodynamic equilibrium and improves the H₂ yield.

In this work, two three-phase models are developed for PMAFBRs according to a different description of the mass transfer between the perovskite membranes and the three phases, where reactions can occur in all three phases, assuming that the cloud and emulsion phases are at minimum fluidization conditions. The modeling of the O₂ flux through the O₂ perm-selective membranes is based on experimental data obtained for a BaCo₀.₄Fe₀.₄Zr₀.₂O₃₋₅ (BCFZ) perovskite capillary membrane supported on an Al₂O₃ tube. The results for the autothermal reforming of methane with the two reactor models are compared for a fluidized bed reactor with and without perovskite membranes. Furthermore, the impact of the operating conditions, viz. operating temperature, fluidization velocity and operating pressure, on the reactor performance are investigated.

2. Model development

2.1. Membrane modeling

The O₂ permeation flux through a perovskite membrane tube was fitted to experimental data using a 1D model developed in Matlab, considering a membrane tube as illustrated in Fig. 1 and using the following assumptions:

1. The membrane module operates at steady state under isothermal conditions.
2. Axial diffusion is negligible (Pe number > 1).
3. Ideal gas law is applicable.
4. Reactions take place on the membrane surface.
5. The flux expression by Xu and Thomson [24], see Eq. (1), is used to describe the O₂ permeation through the membrane:

\[ J_{O_2} = \frac{k_i D_i (P_{I/O_2}^i - P_{O_2}^i)}{k_r (d_o - d_i) P_{O_2}^i + D_r (P_{O_2}^i + P_{O_2}^o)} \]

where \( k_i \) and \( k_r \) are constants for the surface reaction rates at both sides of the membrane, \( D_i \) is the diffusion coefficient of O₂ vacancies, \( n \) is the pressure order, which depends on the membrane thickness and \( d_o, d_i \) are the outer and inner diameter of the membrane tube, respectively.

A BaCo₀.₄Fe₀.₄Zr₀.₂O₃₋₅ (BCFZ) perovskite capillary membrane was tested under different temperatures, which was manufactured by a spinning and phase inversion method [25,26], with a thickness of 0.37 mm and an outer diameter of 3.8 mm. The membrane tube is fitted to experimental data using a 1D model developed in Matlab.
Table 1
O₂ permeation flux for the BCFZ perovskite capillary membrane module.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>J_{O2,exp} [Sml min⁻¹ cm⁻²]</th>
<th>J_{O2,model} [Sml min⁻¹ cm⁻²]</th>
<th>J_{O2,exp} [Sml min⁻¹ cm⁻²]</th>
<th>J_{O2,model} [Sml min⁻¹ cm⁻²]</th>
<th>J_{O2,exp} [Sml min⁻¹ cm⁻²]</th>
<th>J_{O2,model} [Sml min⁻¹ cm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>850 °C</td>
<td>0.075</td>
<td>0.670</td>
<td>0.891</td>
<td>0.900</td>
<td>1.321</td>
<td>1.169</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.763</td>
<td>1.140</td>
<td>1.100</td>
<td>1.535</td>
<td>1.477</td>
</tr>
<tr>
<td></td>
<td>0.225</td>
<td>0.812</td>
<td>1.237</td>
<td>1.210</td>
<td>1.653</td>
<td>1.652</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>0.862</td>
<td>1.315</td>
<td>1.283</td>
<td>1.756</td>
<td>1.771</td>
</tr>
<tr>
<td></td>
<td>0.375</td>
<td>0.889</td>
<td>1.383</td>
<td>1.338</td>
<td>1.833</td>
<td>1.860</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.931</td>
<td>1.441</td>
<td>1.404</td>
<td>1.894</td>
<td>1.968</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.964</td>
<td>1.500</td>
<td>1.443</td>
<td>1.957</td>
<td>2.034</td>
</tr>
</tbody>
</table>

Table 2
Comparison of $D_v$, $k_r$, and $k_f$ in terms of pre-exponential coefficient and activation energy.

<table>
<thead>
<tr>
<th></th>
<th>$D_v$ pre-exponential [m² s⁻¹]</th>
<th>activation energy [kJ mol⁻¹]</th>
<th>$k_r$ pre-exponential [mol m⁻² s⁻¹]</th>
<th>activation energy [kJ mol⁻¹]</th>
<th>$k_f$ pre-exponential [m Pa⁻⁰·⁵ s⁻¹]</th>
<th>activation energy [kJ mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our model</td>
<td>(10 ± 0.1) × 10⁻¹</td>
<td>75.6 ± 0.1</td>
<td>(1.1 ± 0.01) × 10⁴</td>
<td>83.28 ± 0.2</td>
<td>(2.9 ± 0.01) × 10⁷</td>
<td>268 ± 0.4</td>
</tr>
<tr>
<td>Xu and Thomson [24]</td>
<td>(1.58 ± 0.01) × 10⁻⁶</td>
<td>73.6 ± 0.2</td>
<td>(2.07 ± 0.02) × 10⁸</td>
<td>241.3 ± 0.1</td>
<td>(5.9 ± 0.08) × 10⁴</td>
<td>226.9 ± 0.2</td>
</tr>
<tr>
<td>Hong et al. [27]</td>
<td>(1.01 ± 0.05) × 10⁻⁶</td>
<td>75.6 ± 0.5</td>
<td>(1.75 ± 0.087) × 10¹⁵</td>
<td>377 ± 0.4</td>
<td>(9.21 ± 0.44) × 10⁶</td>
<td>268 ± 0.5</td>
</tr>
</tbody>
</table>

Table 3
Kinetic equations for reforming and combustion of methane.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction rate equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane steam reforming on a Ni/Al₂O₃ catalyst [28]</td>
<td>$r_1 = \frac{k_1(p_{H_2O}p_{H_2} - p_{H_2}p_{H_2O}/K_{eq,MSR})}{P_{H_2O}^{1.596}}$ (2)</td>
</tr>
<tr>
<td>Water-gas shift on a Ni/Al₂O₃ catalyst [28]</td>
<td>$r_2 = \frac{k_2(p_{H_2O}p_{H_2} - p_{H_2}p_{H_2O}/K_{eq,WGS})}{P_{H_2O}}$ (3)</td>
</tr>
<tr>
<td>Methane combustion on a Pt/Al₂O₃ catalyst [29]</td>
<td>$r_3 = \frac{k_3b(p_{CH_4}p_{O_2} - p_{CH_4}p_{O_2}/K_{eq,OX})}{(1 + K_{eq,OX}p_{CH_4} + K_{eq,OX}p_{O_2})} + \frac{k_3b(p_{CH_4}p_{O_2} - p_{CH_4}p_{O_2}/K_{eq,OX})}{(1 + K_{eq,OX}p_{CH_4} + K_{eq,OX}p_{O_2})}$ (4)</td>
</tr>
</tbody>
</table>

Where $\rho_i$ is catalyst mass per unit phase volume. $p_i$ is partial pressure of $i$ component. $r_1, r_2, r_3$ have the unit of mol s⁻¹ m⁻³. $k_i = A_i exp(-E_{act,i}/RT)$, $K_{eq,OX} = A_{OX} exp(-\Delta H_{OX}/RT)$, $K_{eq,OX} = exp(-\Delta G_{OX}/RT)$.

Table 4
Parameters for the reaction rate equations.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
<th>Unit</th>
<th>Constant</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>2.62 × 10⁵</td>
<td>mol bar⁻⁰·⁴ kgcat⁻¹ s⁻¹</td>
<td>$E_{act,1}$</td>
<td>106.9</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>$A_2$</td>
<td>2.45 × 10⁵</td>
<td>mol bar⁻¹ kgcat⁻¹ s⁻¹</td>
<td>$E_{act,2}$</td>
<td>54.5</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>$A_3a$</td>
<td>8.11 × 10⁵</td>
<td>mol bar⁻¹ kgcat⁻¹ s⁻¹</td>
<td>$E_{act,3a}$</td>
<td>86</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>$A_3b$</td>
<td>6.82 × 10⁵</td>
<td>mol bar⁻¹ kgcat⁻¹ s⁻¹</td>
<td>$E_{act,3b}$</td>
<td>86</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>$A_{CH_4}$</td>
<td>1.26 × 10⁻¹</td>
<td>bar⁻¹</td>
<td>$\Delta H_{CH_4}^{OX}$</td>
<td>7.87 × 10⁻⁷</td>
<td>bar⁻¹</td>
</tr>
<tr>
<td>$A_{O_2}$</td>
<td>7.87 × 10⁻⁷</td>
<td>bar⁻¹</td>
<td>$\Delta H_{O_2}^{OX}$</td>
<td>-92.8</td>
<td>kJ mol⁻¹</td>
</tr>
</tbody>
</table>

3a Subscript of the parameter $k$ in Equation (4) for the reaction rate of methane combustion.
3b Subscript of the parameter $k$ in Equation (4) for the reverse reaction rate of methane combustion.
supported by an alumina tube, sealed by gold paste (MaTecK 902904, 85–90% Au) and glass powder (Schott 8252 dissolved in pure ethanol). As sweep gas, helium (99.995%) was fed into the membrane tube with a flow rate in the range $F_{\text{He}} = 0.075 – 0.6\ \text{SL min}^{-1}$. The membrane module was kept under ambient pressure, so that the absolute partial pressure of O$_2$ at the retentate side $P_{O_2,\text{H}_2} = 0.21\ \text{bar}$. The permeate side was connected with a Micro-GC (Varian CP-4900). The N$_2$ content in the permeate stream was always less than 0.71% for all operating conditions, thus the selectivity was high and the sealing performed well. The membrane flux model is verified with a parity plot comparing the theoretical O$_2$ permeation flux $J_{O_2,\text{model}}$ with experimental data $J_{O_2,\text{exp}}$ shown in Fig. 2. The developed flux expression with the parameters listed in Table 2 can well describe the experimental data with an average error of 2.8%, as shown in Table 1.

In Eq. (1), the pressure order $n$ was set to a value of 0.5, because the membrane is sufficiently thick. The constants $k_i$, $k_r$, and $D_i$ have been compared with other simulation results published by others, listed in Table 2. Under the same operating conditions, the calculated oxygen permeation fluxes with our model are somewhat higher than those using the parameters calculated by Hong et al. [27] and Xu and Thomson [24], which can be related to differences in the membrane materials, shapes, thicknesses, and model assumptions. Xu and Thomson used La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ membranes, and Hong et al. modified the oxygen permeation model considering local flow variations.

2.2. Reaction kinetics

Different kinetic models of catalytic reforming reactions are available in the literature, mainly including methane steam reforming (MSR), dry reforming of methane, oxidation of methane, and water-gas-shift (WGS). Xu and Froment developed the intrinsic kinetics of MSR using a Ni/MgO-Al$_2$O$_3$ catalyst [2]. Numaguchi and Kikuchi proposed kinetic models for MSR and WGS over a Ni/Al$_2$O$_3$ catalyst in an integral flow reactor accounting for mass and heat balances [28]. Trimm and Lam developed a model for methane combustion reactions based on measurement over a Pt/Al$_2$O$_3$ catalyst supported on porous and non-porous alumina fibres [29]. In this work, an autothermal reforming (ATR) kinetic model is built, including the following three reactions:

Methane steam reforming

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2, \Delta H_{298}^0 = 206\ \text{kJ mol}^{-1}. \]  

(R1)

Water-gas shift

\[ \text{CO} + \text{H}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2, \Delta H_{298}^0 = -41\ \text{kJ mol}^{-1}. \]  

(R2)

Methane combustion:

\[ \text{CH}_4 + 2\text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + \text{CO}_2, \Delta H_{298}^0 = -802\ \text{kJ mol}^{-1}. \]  

(R3)

The kinetics used in this work have been listed in Table 3. The Arrhenius parameters, adsorption coefficients for CH$_4$ and O$_2$, equilibrium constants for MSR and WGS, and the van’t Hoff pre-exponential factors are listed in Table 4.

2.3. Reactor modeling

2.3.1. Main model assumptions

A perovskite membrane-assisted fluidized bed reactor (PMAFBR) for hydrogen production through autothermal reforming of methane is shown schematically in Fig. 3. Preheated CH$_4$ and H$_2$O are mixed and fed into the reactor via a porous bottom distributor. $H_{\text{mf}}$ is the fluidized bed height when the inlet velocity is the minimum fluidization velocity $u_{\text{mf}}$, and $H_i$ is the bed height at a higher fluidization velocity $u_i$. A bundle of perovskite membrane tubes is inserted, assuming that all the membranes in the membrane module have the same permeation performance as the tested BCFZ membrane above and have the same length as the fluidized bed height, i.e. the membranes are submerged such that the top of the membranes is at the surface of the fluidized suspension. Pressurized and preheated air is fed into the membrane tubes with a velocity of $u_{\text{in}}$. The fluidized bed contains a Ni-based catalyst with a density of 2000 kg m$^{-3}$ and an equivalent diameter of

![Fig. 3. Schematic of a perovskite membrane-assisted fluidized bed reactor at (a) minimum fluidization conditions and (b) in the freely-bubbling fluidization regime.](image-url)
Table 5
An overview of the hydrodynamic parameters for the FBR and PMAFBRTable 5 (continued).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average density of gases</td>
<td>( \rho_g = \frac{3T}{(1000RT)} )</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>Viscosity for single gas [39]</td>
<td>( \mu_i = 2.669 \times 10^{-5} \sqrt{MT/(\pi^2\eta_i)} )</td>
<td>Pa s</td>
</tr>
<tr>
<td>Viscosity for mixture gas [40]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Archimedes number [41]</td>
<td>( Ar = g(\rho_p - \rho_g)g\delta_p/\mu^2 )</td>
<td></td>
</tr>
<tr>
<td>Minimum fluidization velocity [35]</td>
<td>( u_{mf} = \mu(\sqrt{2.72^2 + 0.0408Ar - 27.2}/\rho_d )</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>Superficial velocity at inlet</td>
<td></td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>Initial bubble size for porous distributor [38]</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>Maximum bubble size [38]</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>Bubble diameter at position ( h ) [38]</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>Average diameter of bubbles [9]</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>Bubble initial velocity</td>
<td></td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>Average rising velocity of swarm of bubbles</td>
<td></td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>Height of incipiently fluidized bed</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>Constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bed height including freeboard</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>Porosity of bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase volume fraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase volume</td>
<td></td>
<td>m(^3)</td>
</tr>
<tr>
<td>Average reaction rate</td>
<td></td>
<td>mol s(^{-1})</td>
</tr>
<tr>
<td>Phase solid fraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst mass in each phase</td>
<td></td>
<td>g</td>
</tr>
<tr>
<td>Mass exchange coefficient</td>
<td></td>
<td>s(^{-1})</td>
</tr>
<tr>
<td>Gas velocity in bubble phase</td>
<td></td>
<td>m s(^{-1})</td>
</tr>
</tbody>
</table>

200 \( \mu \)m, thus the catalyst particle can be classified as Geldart B and intraparticle mass transfer limitations can be avoided [30]. Two models have been developed according to differences in the description of the mass transfer between the membranes and the three phases, viz. the emulsion, cloud, and bubble phases, as illustrated in the partially enlarged detail in Fig. 3 (b).

To simplify the model, the following assumptions are made:

1) The fluidized bed contains three phases, the bubble, cloud and emulsion phase, where the mass transfer between bubble and cloud, and cloud and emulsion are given by \( K_{bc} \) and \( K_{ce} \) respectively.
2) The system is isothermal and the temperatures are uniform along
For model 1, it is assumed that the mass transfer between the membrane and the fluidized bed only occurs via the emulsion phase, whereas for model 2, O₂ can permeate into all three phases, and the effective membrane area for the exchange between the membranes and each phase is proportional to their volume fraction. Using and comparing the results of the two models a better understanding of the effect of bubbles close to the membranes on the membrane flux and on the product selectivity can be obtained.

2.3.2. Hydrodynamics and mass transfer

Many three-phase models have been developed with slightly different assumptions and different definitions of the cloud phase [31–35]. Deshmukh et al. [36,37] developed a model for a membrane-assisted fluidized bed reactor, which divides the fluidized bed into a series of stirred tank reactors (CSTRs). In this simplified model, the cloud phase and emulsion phase in each CSTR are assumed at minimum performance of a fluidized bed reactor, since it directly affects the mass transfer rate. In this work, a porous plate distributor is employed, and the bubble diameter is calculated using the method by Mori and Wen [38]. The used hydrodynamic and mass transfer closures have been listed in Table 5 (where the influence of the membrane bundle on the hydrodynamics and mass transfer has been ignored) and the mass and enthalpy balances have been summarized in Table 6.

3. Simulation results

To quantify the benefits of integrating perovskite membranes in a fluidized bed reactor and investigate the reactor performance, simulations with and without perovskite membranes are compared under the same operating conditions, the same oxygen-to-carbon and steam-to-carbon ratios. In a fluidized bed reactor without membranes, air is fed directly into the reactor from the bottom, preheated and premixed with CH₄ and H₂O. The reactor performance is quantified in terms of CH₄ conversion, H₂ yield, and H₂ molar fraction in the exhaust stream. For a point at height h along the reactor, the CH₄ conversion (X_{CH₄,h}), yield of H₂ (Y_{H₂,h}), and CO selectivity (S_{CO,h}) are defined as:

### Table 6

Mass balances and enthalpy balance.

<table>
<thead>
<tr>
<th>Item</th>
<th>Equation</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component i</td>
<td>bubble</td>
<td>$\frac{dc_i^{b,m,\text{gas}}}{dV_i^b} = \sum_{j=1}^{3} \nu_{ij} f_{ij,b} + \frac{\beta_{b,m,p} \Delta H_{ij,b}}{V_i}$</td>
</tr>
<tr>
<td></td>
<td>cloud</td>
<td>$\frac{dc_i^{c,m,\text{gas}}}{dV_i^c} = \sum_{j=1}^{3} \nu_{ij} f_{ij,c} + \frac{\beta_{c,m,p} \Delta H_{ij,c}}{V_i}$</td>
</tr>
<tr>
<td></td>
<td>emulsion</td>
<td>$\frac{dc_i^{e,m,\text{gas}}}{dV_i^e} = \sum_{j=1}^{3} \nu_{ij} f_{ij,e} + \frac{\beta_{e,m,p} \Delta H_{ij,e}}{V_i}$</td>
</tr>
<tr>
<td></td>
<td>membrane</td>
<td>$\frac{dc_i^{m,\text{mem}}}{dV_m} = -(\varepsilon_a \beta_{a,m,p} \Delta H_{ij,b} + \varepsilon_a \beta_{a,m,p} \Delta H_{ij,e})$</td>
</tr>
<tr>
<td>Error</td>
<td></td>
<td>$\epsilon = \frac{\sum_{k=0 \to \infty} (M_{m,C} + M_{m,H} + M_{m,O}) - \left( \sum_{k=0 \to \infty} (M_{m,C} + M_{m,H} + M_{m,O}) \right)}{M_{m,\text{init,O}}}$</td>
</tr>
<tr>
<td>Enthalpy balance</td>
<td></td>
<td>$\left( \sum_{i=1}^{N} c_i \Delta H_i^m \right)<em>{in} - \left( \sum</em>{i=1}^{N} c_i \Delta H_i^m \right)_{out} = 0$</td>
</tr>
</tbody>
</table>

### Table 7

An overview of the operation parameters in the base cases for FBR and PMAFBR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor diameter</td>
<td>D = 0.5</td>
<td>m</td>
</tr>
<tr>
<td>Fluidized bed (initial packed bed)</td>
<td>H = 1</td>
<td>m</td>
</tr>
<tr>
<td>Cross sectional area</td>
<td>$A = \pi D^2 / 4$ (FBR)</td>
<td>m²</td>
</tr>
<tr>
<td></td>
<td>$A = \pi D^2 / 4$ (PMAFBR)</td>
<td>m²</td>
</tr>
<tr>
<td>Feed temperature</td>
<td>$T_{\text{feed}} = 810$</td>
<td>ºC</td>
</tr>
<tr>
<td>Reactor temperature</td>
<td>$T = 900$</td>
<td>ºC</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>$P = 1$</td>
<td>bar</td>
</tr>
<tr>
<td>Catalyst diameter (Ni-based)</td>
<td>$d_p = 2 \times 10^{-4}$</td>
<td>m</td>
</tr>
<tr>
<td>Catalyst density</td>
<td>$\rho_p = 2000$</td>
<td>kg m⁻³</td>
</tr>
<tr>
<td>Solid fraction in bubble phase</td>
<td>$\eta_p = 0.001$</td>
<td></td>
</tr>
<tr>
<td>Membrane diameter</td>
<td>$d_{m} = 3.8$</td>
<td>mm</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>$t_m = 0.37$</td>
<td>mm</td>
</tr>
<tr>
<td>Membrane cross sectional area</td>
<td>$A_m = N_{m} d_{m}^2 / 4$</td>
<td>m²</td>
</tr>
<tr>
<td>Total membrane permeation area</td>
<td>$A_{m,p} = N_{m} \pi d_{m,\text{mem}}$</td>
<td>m²</td>
</tr>
<tr>
<td>Temperature in membrane tube</td>
<td>$T_m = 900$</td>
<td>ºC</td>
</tr>
<tr>
<td>Pressure in membrane tube</td>
<td>$P_m = 1$</td>
<td>bar</td>
</tr>
<tr>
<td>Initial O₂ molar fraction in membrane tube</td>
<td>$X_{m,0,\text{O}_2} = 0.21$</td>
<td></td>
</tr>
<tr>
<td>Velocity in membrane tube</td>
<td>$u_m = 1.5$</td>
<td>m s⁻¹</td>
</tr>
</tbody>
</table>
When $h = H_f$, the overall CH$_4$ conversion, H$_2$ yield, and CO selectivity are obtained.

### 3.1. Effect of temperature

The oxygen-to-carbon ratio $r_{oc}$ needed to realize autothermal operation is calculated for the base case settings listed in Table 7 using the overall enthalpy balance over the reactor inlet and outlet and is given for different operating temperatures in Fig. 4 (a). The effects of the temperature on the CH$_4$ conversion, H$_2$ yield, and CO selectivity are shown in Fig. 4 (b)–(d), respectively. For all the operating conditions investigated the PMAFBR accomplishes a much higher CH$_4$ conversion (especially at lower temperatures), a higher CO selectivity, a much higher H$_2$ yield and a much higher H$_2$ outlet fraction than the FBR, thanks to the avoidance of N$_2$ dilution. To achieve higher fluidized bed temperatures, a higher $r_{oc}$ is required and the CH$_4$ conversion approaches 100% for both the FBR and the PMAFBR. The H$_2$ yield increases with increasing temperature, reaches a maximum value and then decreases when further increasing the temperature and the CO selectivity increases with increasing temperature, corresponding to the trade-off of increased H$_2$ production rate at higher temperatures, but also increased CH$_4$ combustion to reach the higher temperatures. The required membrane area decreases for operation at higher temperatures due to the increased O$_2$ permeation rates, as shown in Fig. 4 (a).

The performances of the ordinary fluidized bed reactor and the perovskite membrane-assisted fluidized bed reactor have been
compared for a selected base case with the operation conditions and parameters listed in Table 7. Here the catalyst inventory, oxygen-to-carbon ratio, and steam-to-carbon ratio, etc. have been kept the same, and the influences of the distributive O2 addition via the membranes on the reactor performance have been investigated with the two models with a different description of the mass transfer between the membranes and the fluidized bed. When $r_{oc}$ equals 0.514, an autothermal system with a feed temperature of 810 °C and an outlet temperature of 900 °C can be attained, and the simulation results are listed in Table 8. The maximum mass balance error for the three cases is $8.88 \times 10^{-10} \text{ gs}^{-1}$. As can be deduced from the results shown in Table 8, Model 1 and Model 2 give basically the same results, indicating that the mass transfer rate between the bubble and the cloud ($K_{bc}$), and the cloud and the emulsion ($K_{ce}$) are not rate limiting and are relatively fast in comparison to the reaction rates. In the following sections only the results of Model 2 for the PMAFBR will be shown.

Reactors with and without perovskite membranes have been designed and compared for a fixed H2 production rate of 330 mol h$^{-1}$, where the reactor temperature, pressure, and feed ratios have all been kept the same. The FBR needs a somewhat larger reactor size and a much higher CH4 feed rate (almost 20%) to realize the same H2 production rate.

### Table 8
Simulation results of the base cases for FBR and PMAFBR

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FBR</th>
<th>PMAFBR (Model 1)</th>
<th>PMAFBR (Model 2)</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4 feed flow rate (mol h$^{-1}$)</td>
<td>373.4</td>
<td>373.4</td>
<td>373.4</td>
<td>mol h$^{-1}$</td>
</tr>
<tr>
<td>H2O/CH4 (molar ratio)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>O2/CH4 (molar ratio)</td>
<td>0.514</td>
<td>0.513</td>
<td>0.513</td>
<td></td>
</tr>
<tr>
<td>$m_{cat}$</td>
<td>0.592</td>
<td>0.592</td>
<td>0.592</td>
<td>kg</td>
</tr>
<tr>
<td>$u_{ml}$</td>
<td>0.4438</td>
<td>0.4417</td>
<td>0.4417</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>$u_{at}$</td>
<td>0.014</td>
<td>0.0157</td>
<td>0.0157</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>Membrane area</td>
<td>– 0.72</td>
<td>0.72</td>
<td>0.72</td>
<td>m$^{2}$</td>
</tr>
<tr>
<td>Average MSR rate in emulsion phase $R_{3,em}$</td>
<td>23.6</td>
<td>28.7</td>
<td>28.8</td>
<td>mmol s$^{-1}$</td>
</tr>
<tr>
<td>Average WGS rate in emulsion phase $R_{2,em}$</td>
<td>4.3</td>
<td>5.2</td>
<td>5.3</td>
<td>mmol s$^{-1}$</td>
</tr>
<tr>
<td>Average combustion rate in emulsion phase $R_{1,em}$</td>
<td>6.8</td>
<td>1.4</td>
<td>1.2</td>
<td>mmol s$^{-1}$</td>
</tr>
<tr>
<td>Outlet H2 molar fraction (%)</td>
<td>60.11</td>
<td>60.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outlet H2O molar fraction (%)</td>
<td>19.38</td>
<td>19.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final $X_{CH4}$ (%)</td>
<td>95.74</td>
<td>99.93</td>
<td>99.92</td>
<td></td>
</tr>
<tr>
<td>Final $S_{CO}$ (%)</td>
<td>64.85</td>
<td>79.38</td>
<td>79.51</td>
<td></td>
</tr>
<tr>
<td>Final $Y_{H2}$ (%)</td>
<td>75.41</td>
<td>88.2</td>
<td>88.37</td>
<td></td>
</tr>
<tr>
<td>H2 production rate (mol h$^{-1}$)</td>
<td>281.59</td>
<td>329.37</td>
<td>329.99</td>
<td></td>
</tr>
</tbody>
</table>

### Table 9
Operating and design parameters for a FBR and PMAFBR with a H2 production rate of 330 mol h$^{-1}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FBR</th>
<th>PMAFBR (model 2)</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor diameter</td>
<td>0.55</td>
<td>0.5</td>
<td>m</td>
</tr>
<tr>
<td>Reactor height including freeboard</td>
<td>1.286</td>
<td>1.183</td>
<td>m</td>
</tr>
<tr>
<td>CH4 feed flow rate (mol h$^{-1}$)</td>
<td>440.53</td>
<td>373.44</td>
<td></td>
</tr>
<tr>
<td>Catalyst inventory ($m_{cat}$)</td>
<td>0.614</td>
<td>0.592</td>
<td>kg</td>
</tr>
<tr>
<td>Membrane area</td>
<td>– 0.72</td>
<td>– 0.72</td>
<td>m$^{2}$</td>
</tr>
<tr>
<td>Number of membrane tube</td>
<td>– 51</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Total cross-sectional area of membrane</td>
<td>– 0.00058</td>
<td>–</td>
<td>m$^{2}$</td>
</tr>
</tbody>
</table>

Fig. 5. Effects of velocity on (a) CH4 conversion, (b) H2 production rate, (c) H2 yield and H2 molar fraction at the outlet, and (d) H2O molar fraction at outlet, for the FBR and PMAFBR (other operating conditions are listed in Table 7).
production rate, as listed in Table 9. The effects of changes in superficial velocity and operating pressure on reactor performances are investigated in the next sections, to further optimize the reactor design.

3.2. Effect of superficial velocity

The superficial velocity is an important parameter, which influences the reactor performance to a large extent. With increasing fluidization velocities, the required membrane area increases from 0.48 m² to 1 m². The influences of the superficial velocity on the CH₄ conversion, H₂ production rate, H₂ yield, and H₂O outlet mole fractions are shown in Fig. 5. As can be seen, the H₂ production can be increased by increasing the gas velocity, but at the expense of increasing CH₄ losses. Note that the reactor size was adjusted to realize the same velocity and the same CH₄ feed flow rate for the FBR and PMAFBR. For example, in the PMAFBR with a diameter of 0.5 m, when the velocity is 1.3 m s⁻¹, 315.5 mol h⁻¹ CH₄ is fed. To keep the same velocity and the same feed flow rate, a diameter of 0.673 m is needed for the FBR. The PMAFBR has a prominently higher H₂ production rate and corresponding H₂ outlet fraction compared to the FBR, corresponding to higher steam reforming and WGS reaction rates.

3.3. Effect of pressure

Finally, the influence of the operating pressure is investigated, still using the membrane permeation parameters listed in Table 2. The pressure in the membrane tubes has been kept equal to the pressure in the reactor. Under higher pressures, the oxygen-to-carbon ratio needed to realize autothermal condition decreases, as shown in Fig. 6 (a). As expected, the H₂ production rate increases with increasing pressures for both the FBR and the PMAFBR, and the PMAFBR still achieves a much higher H₂ production rate than the FBR with the same superficial velocity. The H₂ yield increases with increasing pressures, while it levels off at about 3 bar for the PMAFBR, and at about 2 bar for the FBR. All three reaction rates in the three phases increase, corresponding to higher component concentrations at higher operating pressures, e.g. the average methane steam reforming rate in the emulsion phase increases from 22.3 mmol s⁻¹ at 1 bar to 63.9 mmol s⁻¹ at 3 bar for the FBR, and increases from 28.8 mmol s⁻¹ at 1 bar to 78.4 mmol s⁻¹ at 3 bar for the PMAFBR.

4. Conclusions

The autothermal reforming in fluidized bed reactors with and without integrated O₂ perm-selective membranes has been investigated via modeling. Two three-phase reactor models for perovskite membrane-assisted fluidized bed reactors have been evaluated, having a different description of the O₂ mass transfer between the membranes and the three phases. It has been shown that both models give basically the same results, indicating that for the considered reaction system and membrane permeability the external mass transfer rate from the membranes to the bulk of the fluidized bed is not rate limiting. An overall enthalpy balance is used to calculate the required oxygen-to-
carbon ratio to achieve autothermal operation, assuming a uniform temperature throughout the fluidized bed. The required oxygen-to-carbon ratio increases with increasing system temperatures, whereas it decreases with increasing operating pressure. The reactor performance with and without integrated perovskite membranes have been compared at identical operating conditions. It has been demonstrated that perovskite membrane-assisted reactors provide clear advantages over fluidized bed reactors without membranes, yielding a higher CH$_4$ conversion, higher H$_2$ production rate, higher H$_2$ yield and H$_2$ outlet molar fraction. A design has been made for a perovskite membrane-assisted fluidized bed reactor with a H$_2$ production rate in the range of 220–870 mol h$^{-1}$. The influences of operating conditions, viz. temperature, superficial velocity and pressure, on the reactor performance have been investigated. Operation at higher temperatures increases the CH$_4$ conversion, whereas the CH$_4$ conversion tends to flatten when the temperature is above 900 °C for the perovskite membrane reactors. The H$_2$ production rate and H$_2$ yield both increase with increasing pressures, while the H$_2$ yield levels off at about 3 bar. With an increase in the fluidization velocity, the H$_2$ production rate increases at the expense of a lower CH$_4$ conversion. Thus, a trade-off should be made when selecting the optimal fluidization velocity.

Acknowledgements

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References

[4] H.H. Wang, Y. Cong, W.S. Yang, Investigation on the partial oxidation of methane to syngas in a tubular Ba$_2$Sr$_{0.5}$Co$_{0.5}$Fe$_{1.5}$O$_{4.5}$ membrane reactor, Catal. Today 82 (2003) 157–166.