Simultaneous overcome of the equilibrium-limitations in BSCF oxygen-permeable membrane reactors: water splitting and methane coupling

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Abstract

The equilibrium-limitations of water splitting and the coupling of methane to C₂ hydrocarbons (ethane + ethylene) were simultaneously overcome by using a perovskite Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋₆ (BSCF) oxygen-permeable membrane reactor. Oxygen produced from thermal water splitting was transported through the BSCF membrane and consumed in the coupling of methane. The BSCF membrane consists of an about 70 µm thick dense BSCF layer on an about 0.8 mm thick porous BSCF layer as support. By applying the membrane reactor concept instead of a fixed bed reactor without oxygen supply, the methane conversion was increased from 3.7 % to 26 % while the C₂ yield increased from 3.1 % to 6.5 %. In both experiments, the supported 2 wt. % Mn - 5 wt. % Na₂WO₄ catalyst was used at 950 °C. Simultaneously, about 9 % of the H₂O injected was converted to hydrogen with a production rate of about 3.3 cm³ min⁻¹ cm⁻² at 950 °C which is higher than 1 m³ (STP) H₂ m⁻² h⁻¹.

Keywords: water splitting, methane coupling, equilibrium limitation, oxygen permeable membrane, perovskite
1. Introduction

Increasing R&D activities can be observed to convert methane into useful chemicals [1-5]. The direct coupling of methane to C₂ hydrocarbons (ethane + ethylene) is considered as a promising process for the reasonable utilization of natural gas resources because no intermediate step is required [6-8]. However, the production of C₂ through the non-oxidative coupling of methane (reaction 1) is suffering from the relatively low methane conversion as well as C₂ yield [9-11].

\[ 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2 \quad (1) \]

The low equilibrium constant of reaction (1) is due to the positive Gibbs Enthalpy (\(\Delta_R G\) (1000 K) = + 71 kJ⋅mol\(^{-1}\)) [12]. However, the C₂ production can be improved when the produced hydrogen is selectively combusted to water. In the so-called oxidative coupling of methane (2), the equilibrium is completely on the side of the products (\(\Delta_R G\) (1000 K) = - 159.7 kJ⋅mol\(^{-1}\)). Oxidative coupling of methane to C₂ in oxygen transporting membrane reactors has found, therefore, also industrial interest [13].

\[ 2\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O} \quad (2) \]

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2 \quad (3) \]

On the other hand, water splitting (3) at high temperatures is also a thermodynamically controlled reaction. Only small amounts of hydrogen can be generated at equilibrium due to the very low equilibrium constant of \(K \approx 2 \times 10^{-8}\) even at 950 °C [14]. One technique to enhance the hydrogen production rate from the equilibrium-limited water splitting is
the in situ removal of the simultaneously produced oxygen using a mixed oxygen ion and electron conducting membrane [15-17], which has been thoroughly studied for oxygen separation from air [18], methane conversion [19] and oxidative dehydrogenation of hydrocarbons [20].

Recently, we have reported several successful couplings of oxygen-producing with oxygen-consuming reactions in membrane reactors [21, 22] using oxygen transporting perovskite membranes. Jiang et al. [23] reported the simultaneous production of synthesis gas and hydrogen by coupling the partial oxidation of methane with water splitting, which was also reported by Evdou et al. [24]. Further, the effective decomposition of NO [25] and N₂O [26] was achieved by coupling with the partial oxidation of methane to synthesis gas. In this paper, the combination of thermal water splitting with the oxidative coupling of methane (OCM) to ethane and ethylene is for the first time reported. A novel asymmetric BSCF disc membrane [27, 28] with high oxygen permeation flux ($J_{o_2}$) is used in our membrane reactor.
2. Experimental Section

2.1. Preparation and characterization of membrane

The asymmetric $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) perovskite oxygen transporting membranes consist of a dense oxygen separation layer and a porous support layer. Both layers were manufactured by tape casting using a commercial BSCF powder (Treibacher Industrie AG, Austria), which provides perfect chemical compatibility and the same thermal expansion of the two layers. Two different slurries were prepared for the membrane layer and support layer. The slurry for the support layer contained 20 wt. % corn starch (Cargill, Germany) in relation to the total solid content, whereas the slurry used for the membrane layer did not contain any corn starch as pore former. After sintering of the disc membrane at 1100 °C for 3 hours in air, it consists of a dense top layer of about 70 $\mu$m and an 830 $\mu$m thick porous support layer with 34 % open porosity [29], as shown in Fig. 2.

The crystallinity of the BSCF perovskite membrane before (unused) and after (used) reactions was characterized by X-ray diffraction using a Bruker D8 instrument with Cu $K_\alpha$ radiation. A JEOL JSM-6700F field-emission scanning electron microscope was used to the surface morphology study of the BSCF membranes.

2.2. Preparation of the catalyst

The perovskite BSCF membrane itself works also as a catalyst for water splitting. The catalyst applied for OCM consists of 2 wt. % Mn and 5 wt. % $\text{Na}_2\text{WO}_4$ supported on $\text{SiO}_2$ [30, 31]. For catalyst preparation, $\text{SiO}_2$ (Davisil, Grade 636, Sigma-Aldrich) was
impregnated with aqueous Mn(NO₃)₂·4H₂O (Sigma-Aldrich) solution and the mixture was dried at 110 °C for 4 h. This sample was then impregnated with an aqueous solution of Na₂WO₄·2H₂O (Sigma-Aldrich) to get a catalyst containing 2 wt. % Mn and 5 wt. % Na₂WO₄ (grain size area 0.07 µm²). Finally, the impregnated sample was heated at 800 °C for 8 h. Further information can be found in [12].

2.3. Disc membrane reactor and permeator

For membrane evaluation, the oxygen permeation of the BSCF membrane was studied in a self-made high-temperature oxygen permeator (see Fig. 1) as described previously [32]. The disc membrane was sealed by using Heraeus gold paste onto the alumina tube at 950 °C for 5 h. The oxygen permeation was first studied under the air/He oxygen partial pressure gradient. Air was fed at a rate of 100 cm³ min⁻¹ to the feed side; a mixture of He (49 cm³ min⁻¹) and Ne (1 cm³ min⁻¹) as the internal standard gas was fed to the sweep side. The porous side of the BSCF membrane was exposed to the air, the dense one to the methane side.

In addition, the same permeator has been used as membrane reactor for the combination of water splitting and coupling of methane, with an OCM catalyst on the methane side (see Fig. 1). A mixture of steam and He was fed to the water splitting side and a mixture of CH₄ and He with traces of Ne as internal standard was fed to the methane coupling side. The porous side of the BSCF membrane was exposed to the water splitting side; the catalyst containing 2 wt. % Mn and 5 wt. % Na₂WO₄ was packed on top of the dense side of the BSCF membrane, i.e. on the methane coupling side. The study of the methane coupling without membrane support was performed in a fixed-bed reactor which consists
of a dense alumina tube with an inside diameter of 4 mm containing 0.5 g 2 wt. % Mn and 5 wt. % Na2WO4 catalyst.

All gas flows (CH₄, Ne, He) were controlled by gas mass-flow controllers (Bronkhorst). The concentrations of the outlet gases were measured online by a gas chromatograph (Agilent 6890). The relative leakage of O₂ was found to be less than 5% of the total amount of O₂ detected. The H₂O flow was controlled by liquid mass-flow controllers (Bronkhorst), all pipes connecting reactor and gas chromatograph were heated to 180 °C.

Hydrogen production rate on the water splitting side was calculated from the total outlet flow rate Fws (water splitting, cm³ min⁻¹), hydrogen concentration c (H₂), and membrane area S (cm²) by using the equation below:

\[ j(H₂) = \frac{F_{ws} \times c(H₂)}{S} \]

The ethane and ethylene production rates were calculated from the total flow rate on the methane side Fout(cm³ min⁻¹), the ethane or ethylene concentration, c(C₂H₆) or c(C₂H₄). The CH₄ conversion X(CH₄), the C₂ hydrocarbons selectivity, also S(C₂H₄) + S(C₂H₆), S(C₂) and the C₂ yield Y(C₂) were calculated as:

\[ X(CH₄) = \left[ \frac{F(out, C₂) \times 2 + F(out, CO) + F(out, CO₂)}{F(out, C₂) \times 2 + F(out, CO) + F(out, CO₂) + F(out, CH₄)} \right] \times 100\% \]

\[ S(C₂) = \left[ \frac{F(out, C₂) \times 2}{F(out, C₂) \times 2 + F(out, CO) + F(out, CO₂)} \right] \times 100\% \]

\[ Y(C₂) = X(CH₄) \times S(C₂) \]

where F(i) is the flow rate of species i on the methane coupling side of the disc membrane. By using gas chromatography, if Ne is present in the water splitting side, the
leakage can be detected. Both the leakage detection and the catalytic measurements could be conducted at the same time.

3. **Results and discussion**

3.1. **Asymmetric BSCF membrane**

The BSCF disc membrane (Fig. 2) consists of a 70 µm dense layer and an 830 µm porous support layer. Fig. 2b indicates that the two layers are well attached to each other and no interface delamination or crack formation were observed. Some small closed pores can be seen in the membrane layer, whose density is about 97 % (Fig. 2b) [29] assuring sufficient gas-tightness. SEM (Fig. 2c) of the BSCF membrane shows that the dense BSCF layer is well sintered and no cracks could be detected. The support (Fig. 2d) is a fine-grained porous layer with about 34 % open porosity enabling gas transport through the support. Further details can be found in [29] and references therein.

3.2. **Oxygen permeation**

The oxygen permeation under an air/He oxygen concentration gradient was studied between 850 °C and 950 °C. Fig. 3 depicts the effect of temperature on the oxygen permeation flux of the BSCF disc membrane. Noticeable high fluxes were obtained, and the permeation fluxes increased with increasing temperature. A previous study [33] pointed out that both bulk diffusion of oxygen ions and the surface exchange processes are key factors which determine the permeation flux. Due to the thin dense BSCF layer of 70 µm, the contribution of the bulk oxygen ions diffusion to the overall oxygen transport resistance is relative low. Also the surface reaction is enhanced, since more sites for the dissociation of molecular oxygen to oxygen ions are provided by the porous support layer. Therefore, a relative high oxygen flux of 3.3 cm³ min⁻¹ cm⁻² was obtained at 950
°C when using He as sweep gases, which is higher than the oxygen permeation flux reported in previous work [32]. On the other hand, concentration polarization effects for oxygen can occur in the porous support and as a consequence, the estimated permeation flux is lower than expected from Wagner theory [29].

Fig. 4 demonstrates the influence of the sweep gas flow rate on the oxygen permeation. An almost doubling of the oxygen permeation rate can be observed when the sweep gas rate is raised from 10 to 50 cm³ min⁻¹. A further increase of the sweep gas flow rate only slightly improves the oxygen permeation flux and \( J_{O_2} \) reaches 3.7 cm³ min⁻¹ cm⁻² at a sweep rate of 150 cm³ min⁻¹. Due to the well-known Wagner theory, the driving force for the oxygen permeation is the oxygen partial pressure gradient between the two sides of the membrane [34]. \( J_{O_2} \) can be enhanced by increasing the oxygen partial pressure gradient via increasing the sweep gas flow rate.

3.3. Coupling of methane: oxidative and non-oxidative

The coupling of methane to C₂ was studied using 2 wt. % Mn and 5 wt. % Na₂WO₄ on SiO₂ as catalyst at 950 °C (Fig. 5) in both (i) fixed bed reactor and (ii) membrane reactor. Compared to the fixed bed reactor, where only 3.7 % methane conversion can be realized according to reaction (1), a remarkably higher methane conversion of 26 % is obtained in the membrane reactor according to reaction (2). Correspondingly, the C₂ yield also raises from 3.1 % to 6.5 % in the membrane reactor mode. This experimental finding can be explained as follows. With increasing temperature, the equilibrium constant of the thermal water splitting increases, and higher oxygen partial pressures are found on the water side. Rising temperature also increases the oxygen transport performance of the BSCF membrane. On the methane coupling side, with increasing temperature more -CH₃
radicals are formed over the catalyst which recombine in a homogeneous gas phase reaction to C\textsubscript{2}H\textsubscript{6}, which can undergo a subsequent dehydrogenation to C\textsubscript{2}H\textsubscript{4}. Since the oxygen permeated through the membrane is consumed quickly by the hydrogen combustion, the oxygen partial pressure on the methane coupling side is very low and a continuous flow of oxygen from the water side to the methane side starts. Compatibility of the two reactions means that the amount of oxygen transported through the BSCF membrane is the stoichiometric amount of oxygen for the selective hydrogen combustion. As a result, the methane conversion increases be the factor 6 when the catalytic membrane reactor concept is applied.

Fig. 6 shows the temperature dependence of the conversion of methane, the selectivity and yield of C\textsubscript{2} formation when feeding 20 cm\textsuperscript{3} min\textsuperscript{-1} CH\textsubscript{4}. The methane conversion as well as the C\textsubscript{2} yield increase with increasing temperature. It is noteworthy that the C\textsubscript{2} selectivity increases with increasing temperature in the temperature range < 925 °C and decreases for temperatures > 925 °C. Obviously, best compatibility between the two reactions was achieved under our experimental conditions at 925 °C.

3.4. Hydrogen production from water splitting

In a previous paper we reported that if only helium is used as sweep gas to remove the oxygen generated from water splitting in the case of a hollow fiber membrane, the hydrogen production rate is very low even at 950 °C [23]. Higher oxygen partial pressure gradients, and thus higher driving forces, can be reached if the oxygen partial pressure on the permeate side is decreased by consuming the oxygen in a chemical reaction, here in the selective hydrogen combustion. Fig. 7 presents the hydrogen production rate on the water dissociation side at various temperatures with methane coupling on the opposite
side of the membrane. By feeding 100 cm$^3$ min$^{-1}$ of a He/CH$_4$ mixture with 20 % CH$_4$, the hydrogen production rate increases from 0.4 to 3.3 cm$^3$ min$^{-1}$ cm$^{-2}$ when rising the temperature from 850 to 950 °C. Thus, a hydrogen production rate of over 1 m$^3$ (STP) H$_2$ m$^{-2}$ h$^{-1}$ can be achieved at 950 °C. Since no oxygen was detected on the steam side, oxygen produced from water splitting was transported to the methane side, and has been consumed there by OCM. The oxygen production rate is around 1.65 cm$^3$ min$^{-1}$ cm$^{-2}$ (50% of the hydrogen production rate), which is lower than that in the case of oxygen permeation under an air/He oxygen partial pressure gradient. Several factors are responsible for this experimental finding: a) the equilibrium constant of the endothermic water splitting is increased leading to higher oxygen-equilibrium concentrations at high temperatures, b) the oxygen transport through the BSCF membrane is enhanced with increasing temperature according to Wagner Theory [35], and c) oxygen is consumed faster in the OCM at higher temperatures.

Fig. 8 presents the room temperature X-ray diffraction patterns of the unused and used BSCF disc membranes. The starting BSCF membrane is mainly composed of cubic BSCF perovskite, but also small amounts of a foreign phase identified as hexagonal perovskite can be found [36]. After 20 h use in the OCM reaction, a decrease of the perovskite reflections is observed while the reflections of different cobalt-containing phases increased. In previous works, the extraction of cobalt species from perovskite in high-temperature reactions was reported [37, 38]. Obviously, cobalt escapes from the BSCF bulk phase and form different cobalt oxides of low oxidation state and even metallic cobalt, when BSCF is operated in reducing atmospheres. We have to state, therefore, that the cobalt-containing perovskite BSCF is not long-time stable under the
reaction conditions of OCM. Thus, further search for perovskite materials that are more stable under reducing atmospheres is required.
4. Conclusion

Methane coupling and water dissociation were for the first time successfully combined in a catalytic membrane reactor. The achievable conversions of the two equilibrium-limited reactions under study, the water splitting and the methane coupling were significant improved. The methane conversion was enlarged from 3.7 % to 26 % while the \( \text{C}_2 \) yield increased from 3.1% to 6.5 % using a 2 wt. % Mn - 5 wt. % \( \text{Na}_2\text{WO}_4 \) on \( \text{SiO}_2 \) as catalyst at 950 °C. On the other hand, although the equilibrium constant of water splitting is only about \( 2 \times 10^{-8} \) at this temperature, about 9 % \( \text{H}_2\text{O} \) were converted because of the \textit{in situ} removal of oxygen through the BSCF membrane. As a result, a hydrogen production rate of \( 3.3 \text{ cm}^3 \text{ min}^{-1} \text{ cm}^{-2} \) is achieved on the water splitting side of the membrane. The catalytic membrane reactor provides not only a possibility to overcome equilibrium limitations; it also separates the different products inherently. However, the BSCF membrane turned out to be not long-time stable in the reducing atmosphere of the methane coupling.

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Fig. 1. Schematic diagram of performing oxidative methane coupling and water splitting in an oxygen-transporting perovskite disc membrane reactor.
Fig. 2. SEM micrographs of the unused BSCF membrane: a) overview of the membrane, b) cross section of the dense BSCF part, c) surface of the dense BSCF side, d) cross section of the porous BSCF part which acts as support for the dense part.
Fig. 3. Oxygen-permeation flux as a function of temperature through a BSCF membrane.

Feed side: $F_{\text{Air}} = 100 \text{ cm}^3 \text{ min}^{-1}$; Sweep side: $F_{\text{He}} = 49 \text{ cm}^3 \text{ min}^{-1}$ and $F_{\text{Ne}} = 1 \text{ cm}^3 \text{ min}^{-1}$. 
Fig. 4. Oxygen-permeation flux through a BSCF membrane at 950 °C as a function of the sweep gas flow rate. Feed side: $F_{\text{Air}} = 100 \text{ cm}^3 \text{ min}^{-1}$; Sweep side: $F_{\text{Ne}} = 1 \text{ cm}^3 \text{ min}^{-1}$ and $F_{\text{He}} = F_{\text{sum}} - F_{\text{Ne}}$. 
Fig. 5. Methane conversion (left) and C₂ yield (right) with and without membrane as a function of temperature with diluted methane as feed. The flow rates for the membrane reactor are on the water splitting side: $F_{H_2O} = 30 \text{ cm}^3 \text{ min}^{-1}$ and $F_{He} = 10 \text{ cm}^3 \text{ min}^{-1}$, on the methane coupling side: $F_{Ne} = 1 \text{ cm}^3 \text{ min}^{-1}$, $F_{CH_4} = 20 \text{ cm}^3 \text{ min}^{-1}$ and $F_{He} = 79 \text{ cm}^3 \text{ min}^{-1}$. Without membrane: $F_{Ne} = 1 \text{ cm}^3 \text{ min}^{-1}$, $F_{CH_4} = 20 \text{ cm}^3 \text{ min}^{-1}$ and $F_{He} = 79 \text{ cm}^3 \text{ min}^{-1}$. 0.5 g catalyst.
Fig. 6. Methane conversion $X(\text{CH}_4)$, ethane + ethylene selectivity $S(\text{C}_2)$ and yield $Y(\text{C}_2)$ as a function of temperature. Water splitting side: $F_{\text{H}_2\text{O}} = 30 \text{ cm}^3 \text{ min}^{-1}$ and $F_{\text{He}} = 10 \text{ cm}^3 \text{ min}^{-1}$, methane coupling side: $F_{\text{Ne}} = 1 \text{ cm}^3 \text{ min}^{-1}$, $F_{\text{CH}_4} = 20 \text{ cm}^3 \text{ min}^{-1}$ and $F_{\text{He}} = 79 \text{ cm}^3 \text{ min}^{-1}$. 0.5 g catalyst.
Fig. 7. H$_2$ production rates as a function of temperature for the BSCF membrane reactor.

Water splitting side: F$_{\text{H}_2}\text{O}$ = 30 cm$^3$ min$^{-1}$ and F$_{\text{He}}$ = 10 cm$^3$ min$^{-1}$, methane coupling side: F$_{\text{Ne}}$ = 1 cm$^3$ min$^{-1}$, F$_{\text{CH}_4}$ = 20 cm$^3$ min$^{-1}$ and F$_{\text{He}}$ = 79 cm$^3$ min$^{-1}$, 0.5 g of catalyst.
Fig. 8. XRD patterns of unused and used (after 20 h in the membrane reactor, applying for OCM/water splitting at the temperature range between 850 and 950 °C) BSCF membranes. Shown is the dense BSCF layer exposed to the methane coupling side.
Reference