

Article

Performance Evaluation of Different Reactor Concepts for the Oxidative Coupling of Methane on Miniplant Scale

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Abstract

In this study, three different reactor concepts for the oxidative coupling of methane (OCM) reaction are examined at the miniplant scale. Their performance and response to variations in key process parameters, such as temperature and gas hourly space velocity (GHSV), are evaluated over a wide range. In addition to the conventional Packed Bed Reactor (PBR), Packed Bed Membrane Reactor (PBMR), and Chemical Looping Reactor (CLR) approaches were tested. The PBMR was realized with a porous ceramic α -Alumina membrane as air/O₂ distributor. The CLR was operated in a poly-cyclic operation. Similarities of the different reactor concepts as well as layout-immanent differences with regard to changes in reaction conditions could be identified and advantages and disadvantages of the processes highlighted. The results show that C₂ selectivity can be improved by both PBMR and CLR in comparison to conventional PBR, possibly reducing cost-intensive downstream units. While a PBMR can slightly improve selectivity (23%) while keeping the same conversion compared to a PBR, the use of a CLR allows for achieving exceptionally high selectivities of up to 90%. In order to address the low conversion, CLR tests were carried out with an additional O₂ carrier material, which led to a significant improvement in terms of C₂ yield. In addition to an evaluation and comparison of the different reactor concepts, the findings at the miniplant scale provide estimates of their potential use and scalability.

Keywords: oxidative coupling of methane; OCM; packed bed reactor; chemical looping; packed bed membrane reactor



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1. Introduction

The global demand for ethylene, a key building block in the petrochemical industry, is increasing and is expected to exceed 200 million tons by 2025 [1], while conventional naphtha-based ethylene production faces challenges related to energy consumption, environmental impact, and feedstock availability [2].

The Oxidative Coupling of Methane (OCM) offers a promising alternative for ethylene production by leveraging methane, the primary component of natural gas and biogas, as a widely available and potentially renewable feedstock. Originally proposed by Keller and Bhasin in the 1980s [3], OCM involves the direct conversion of methane into higher (C₂₊)

hydrocarbons, primarily ethane and ethylene, through oxidative reactions in the presence of a catalyst, usually a metal oxide [4,5].

The conventional OCM process involves the simultaneous feeding of methane and oxygen, at near atmospheric pressure into a Packed Bed Reactor (PBR), where the heterogeneous reaction takes place in the presence of a metal oxide catalyst at temperatures of 650 to 950 °C [3,5]. This co-feed approach results in a complex interplay of heterogeneous and homogeneous reactions, leading to the conversion of methane into C₂₊ hydrocarbons (see Figure 1). However, the desired selectivity towards C₂ products is hindered by competing side-reactions favoring the formation of CO and CO₂ [6–8], along with the risk of hotspot formation due to the exothermic nature of the reactions [9].

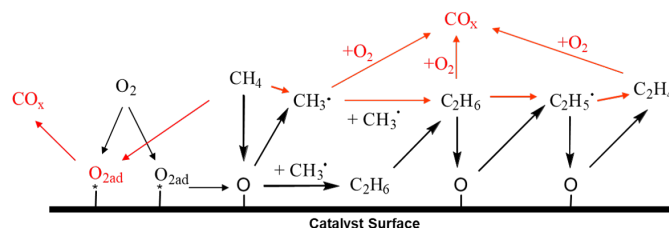
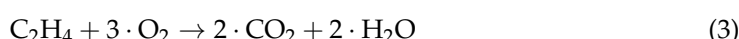
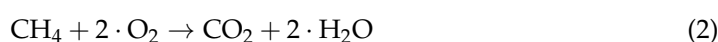
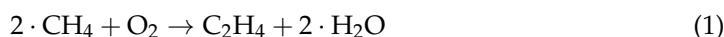


Figure 1. OCM reaction network of surface and gas phase reactions (black: desired pathway, red: side reactions, * = Active site) [8].

The production of CO and CO₂ is further caused by the oxidation of C₂ products. This deep oxidation occurs mainly in the gas phase, as side reactions are more thermodynamically favored, but can also occur due to heterogeneous catalytic deep oxidation [8,10,11]. Figure 1 displays the schematic OCM reaction network with the desired reaction route (black) as well as the most important side reactions (red).

The overall reaction equation of the OCM reaction, as well as the equations of the main side reaction and the total oxidation of C₂H₄, are given in Equations (1)–(3).



The consecutive deep oxidation of the C₂ products causes an inverse relationship between CH₄ conversion and C₂ selectivity, which underscores the challenge of optimizing process parameters to maximize product yield while minimizing undesirable by-products [6]. On one hand, enough O₂ must be present to ensure sufficient CH₄ conversion, but the local O₂ concentration must always be kept minimal to avoid non-selective gas phase reactions and local temperature hot-spot formation.

Ensuring that CH₄ and O₂ react mainly selectively on the catalyst surface, while providing a sufficiently large amount of O₂ to the reaction, is crucial and one of the main challenges in the design and optimization of reactor and reaction concepts for OCM. To tackle this challenge, innovative solutions for catalyst design and reactor engineering have been investigated over the past years [4,12–14]. There is general consensus that a yield of about 30% would be necessary for a first industrial application, a goal that has not yet been achieved in a robust, steady-state operation despite intensive research efforts [11,15].

Catalyst development is a key area of research in OCM. Researchers have explored various metal oxide catalysts, including supported and unsupported systems, to enhance activity and selectivity [5,16–19]. The Mn-Na₂WO₄/SiO₂ catalyst has emerged as a promising candidate for OCM, exhibiting high activity, stability, and selectivity towards C₂ products [15,20–22].

The Packed Bed Reactor (PBR) is the most investigated reactor concept for OCM [23–25]. The main advantage of this reactor concept is the simple and cost-effective setup and operation. Reactors at lab scale are assumed to operate under isothermal conditions. However, due to the exothermic reactions in OCM, the behavior is different at larger scales, leading to a steep temperature profile inside the reactor and potential hot-spot formation [6].

Another approach, which was considered early on [26] is the use of Packed Bed Membrane Reactors (PBMRs) to improve oxygen dosage and distribution [27]. As the reaction order of deep oxidation of methane and C₂ products is higher than that of the actual OCM reaction [6], a specific strategy for an improved oxygen dosage is necessary to keep the local O₂ concentration low and to suppress side reactions [28,29]. The more uniform O₂ distribution along the entire catalytic bed in such a PBMR can also improve heat management compared to a PBR [30], since a consistent reactant-to-oxygen ratio can be ensured. PBMRs also find applications in other partial oxidation reactions, such as the oxidative dehydrogenation of alkenes to olefins or methanol to formaldehyde [31,32]. PBMRs can be equipped with dense/selective or porous/non-selective membranes. In this work, the focus is solely on those PBMRs using porous membranes.

Lu et al. demonstrated that using a membrane reactor can increase C₂ yield and selectivity by up to 10% and 30%, respectively, due to more uniform oxygen dosing and a broader distribution of the reaction zone compared to a PBR [33]. Godini et al. achieved 18% and 24% C₂ yield in a PBMR with a modified α -alumina membrane and a Mn-Na₂WO₄/SiO₂ catalyst [34,35]. Building on these findings, the EU-funded Horizon 2020 project MEMERE (Methane activation via integrated MEMbrane REactors) aimed to develop an innovative pilot-scale PBMR for OCM [36]. A factor to consider when operating a PBMR with porous membranes is that the local air/O₂ flow through the membrane strongly depends on the trans-membrane pressure gradient (ΔP_{mem}) [30,37]. Therefore, a primary focus in selecting and operating a membrane reactor is to adjust this pressure gradient to avoid back-permeation of reactants into the air-feeding side, which leads to a performance decrease and the risk of forming explosive atmospheres [26]. Surface modification of the membrane is an approach, aiming to set the right ratio of pore number and diameter for the most homogeneous oxygen flow possible [13,38]. Because of the dense catalyst packing, there is also an axial pressure gradient along the reactor bed. Adjusted membrane modification and/or adjusted inert packing on the inert side must compensate for this effect; otherwise, bypass streams towards the reactor end can occur [30,37,39].

A Chemical Looping Reactor (CLR) presents a further promising alternative to conventional OCM, leveraging oxygen carriers to facilitate methane conversion and increase C₂ selectivity [17,40]. In contrast to PBR or PBMR which are operated steady state, this cyclic process involves the constant circulation of oxygen carriers between a fuel reactor and an air reactor, enabling the direct conversion of methane to C₂ hydrocarbons via oxygen carrier reduction [11,41]. By utilizing lattice oxygen from the carriers, Chemical Looping circumvents direct contact between gaseous oxygen and methane, reducing gas phase reaction to a bare minimum and enabling very high C₂ yields [19,42]. This approach results in a reaction effluent containing very little nitrogen, thus improving the efficiency of subsequent processes and reducing their size and cost [2].

CLR offers several advantages over conventional OCM in PBRs, including the elimination of energy-intensive air separation units, enhanced safety by preventing methane–oxygen mixtures, and potential for higher C₂ yield through reduction of gas-phase reactions [4,43,44]. Recent advancements have demonstrated successful lab-scale implementation of CLR for OCM, highlighting its potential for scale-up [11,42].

In CLR, efforts have focused on developing multifunctional catalysts with high C_2 selectivity and oxygen storage capacity [41,44,45]. Studies showed that the $Mn-Na_2WO_4/SiO_2$ catalyst can provide a decent oxygen storage capacity [19,46].

In this work, a parametric study is performed on the influence of temperature and gas hourly space velocity (GHSV) to investigate the three mentioned reactor concepts at miniplant scale under comparable reaction conditions. Operating at higher gas flow rates and catalyst volumes, the applied setup allows exploration of a broader range of operational parameters. This enables consideration of thermal effects, such as heat generation and removal, which significantly influence reactor performance during strongly exothermic reactions but are negligible at laboratory scale.

In the case of CLR and PBMR, efforts are made to maximize performance within a limited range by adjusting concept-specific parameters, for instance, introducing small amounts of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) to the inert material in the CLR in order to enhance O_2 storage capacity. The present study provides an assessment and estimation regarding the scalability potential of the OCM processes.

2. Materials and Methods

2.1. Catalyst Preparation

A $Mn-Na_2WO_4/SiO_2$ catalyst was used for all experiments in our work, as previous studies have shown its very good performance and high temperature stability [22]. The catalysts were prepared using the incipient wetness impregnation method (IWI). An appropriate amount of the precursors listed in Table 1 was dissolved in distilled water and impregnated drop by drop on SiO_2 . After each impregnation, it was dried at 120 °C for 8 h, and finally calcined at 900 °C for 1.5 h.

Table 1. Chemicals used for catalyst preparation.

Chemical	Supplier	Purity
SiO_2	Sigma-Aldrich	Davisil Grade 646
Na_2WO_4	Alfa Aesar	>99.5%
$Mn(NO_3)_2 \cdot 4 H_2O$	Sigma-Aldrich	>97%

2.2. Experimental Setup

All tests were performed in a miniplant at TU Berlin. A sketch of the miniplant and its three main sections—gas feed, reactors, and gas analysis—are shown in Figure 2.

For the gas feed, the reactants are dosed through individual Bronkhorst mass flow controllers (IN-FLOW) and are (partially) pre-mixed before entering the reactor. The reactor is located and heated inside a HTM-Reetz (Berlin, Germany) electric split tube furnace (2 kW). The entire process control and display of the measured values are realized by means of a Siemens PCS7 process control system.

For the PBR and CLR tests, the reactor consists of a dense alumina tube by Rauschert (Scheßlitz, Germany) with dimensions OD/ID = 10/8 mm. A layer of inert Silicon Carbide (SiC) is placed before and after the reaction zone to ensure a homogeneous gas distribution and smoother temperature gradients. The length of the catalytic bed is 160 mm, which corresponds to a catalyst mass of 10 g (diluted 1:1 with SiC).

The PBMR tests employed an in-house manufactured stainless-steel reactor made of high-temperature alloy Alloy 800 HT from Voite Edelstahl (Erkrath, Germany), which can withstand OCM conditions for several hundred hours of operation without deformation or material loss. The reactor holds and seals a tubular porous membrane that serves as the reactor vessel and as a diffusor at the same time. The membrane is a porous α -alumina tube from Rauschert with dimensions OD/ID = 10/7 mm and a pore diameter of

200 nm. To avoid pre-mixing of the reactants, the front and back areas of the membrane are made impermeable to gases by coating with a ceramic glaze by BOTZ (Münster, Germany) (Steinzeug) resulting in a 60 mm permeable zone that defines the reaction area. Additionally, 12 g catalysts, diluted with SiC, are used for the experiments. The O₂ or air is fed from the outer side (shell side) to promote a homogeneous distribution in the inner side (tube side) where the catalyst is located. CH₄ is fed through the tube side to the reaction zone (Figure 3).

To limit thermal stress on the ceramic tube/membrane, the system is first heated with a moderate temperature gradient of 10 K/min up to 650 °C. During the first heating phase, both zones of the reactor (tube and shell) are flushed with a low inert N₂ flow (20 mL/min). Subsequently, the system is further heated to reaction temperature with a lower gradient (<5 K/min) while simultaneously feeding air to tube and shell side to condition the catalyst with oxygen. The reactor is then briefly purged with N₂ before starting the CH₄ flow first, followed by the O₂ flow shortly after.

Reaction temperature is measured using type-K thermocouples. In PBR and CLR setups, a single-point thermocouple is mounted externally, 1 cm below the start of the reaction zone. In PBMR tests, a WIKA multi-point thermocouple (Klingenberg, Germany) is inserted directly into the catalytic bed and enclosed in a thin-walled dense alumina tube to prevent direct contact between reactants and the metallic sensor.

After the reactor, the gas stream is quenched, de-watered, and enters the gas analyzers. Its composition is measured with an IR spectroscope (SICK S700/710, Waldkirch, Germany) and a micro-GC (Agilent 490, Santa Clara, CA, USA) with thermal conductivity detectors (TCD) and equipped with a 20 m Molsieve 5 Å column and a PoraPLOT Q column.

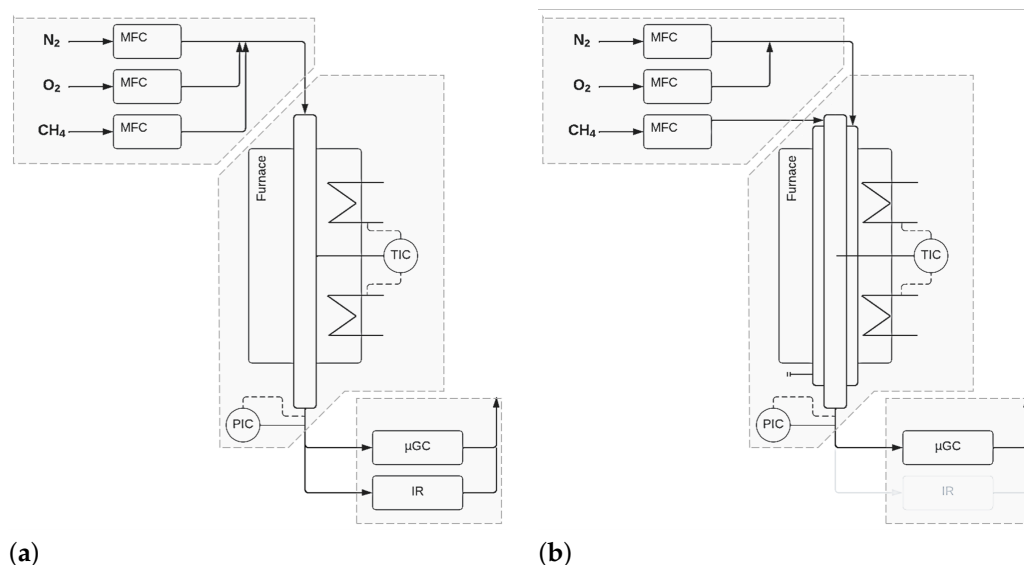


Figure 2. Schematic overview of the Miniplant in its configurations for PBR, and CLR tests (a) and for PBMR tests (b).

The evaluation and comparison of the experiments and reactor concepts are mainly done by the key performance indicators methane conversion (X_{CH_4}), C₂ selectivity (S_{C_2}), and C₂ yield (Y_{C_2}), which are—for PBR and PBMR—defined as follows:

$$X_{\text{CH}_4} = 1 - \frac{\dot{n}_{\text{CH}_4, \text{out}}}{\dot{n}_{\text{CH}_4, \text{in}}} \quad (4)$$

$$S_{\text{C}_2} = \frac{2 \cdot \dot{n}_{\text{C}_2\text{H}_4, \text{out}} + 2 \cdot \dot{n}_{\text{C}_2\text{H}_6, \text{out}}}{\dot{n}_{\text{CO}_2, \text{out}} + \dot{n}_{\text{CO}, \text{out}} + 2 \cdot \dot{n}_{\text{C}_2\text{H}_4, \text{out}} + 2 \cdot \dot{n}_{\text{C}_2\text{H}_6, \text{out}}} \quad (5)$$

$$Y_{\text{C}_2} = X_{\text{CH}_4} \cdot S_{\text{C}_2} \quad (6)$$

where $\dot{n}$ is the molar flow rate of the respective species. Because of the non-stationary nature of the CLR concept tested in this work, these reaction metrics for the CLR are calculated by integrating the molar fluxes over three complete reaction cycles.

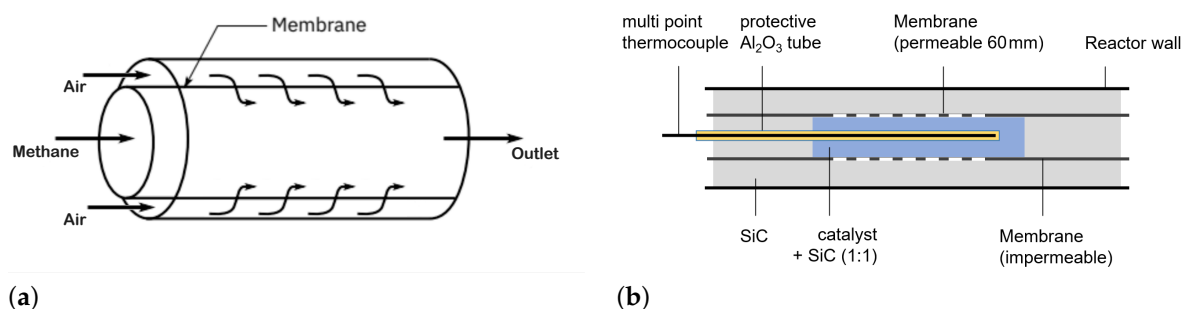


Figure 3. Functional principle of membrane as as O₂ distributor (a) and internal assembly of PBMR used for tests (b).

2.2.1. Packed Bed Reactor (PBR)

The PBR tests serve as a reference point and build the basis for comparing and evaluating the other reactor concepts. To enable the best possible comparison of the results from the different reactor types, the reaction parameters for each experimental point were selected to achieve identical or at least comparable values in terms of GHSV and reactant ratio. A summary of the experimental parameters is given in Table 2.

Table 2. Experimental conditions for PBR, PBMR, and CLR.

Parameter	PBR	PBMR	CLR
catalyst mass in g	10	12	10
catalytic bed in mm	160	160	160
permeable zone in mm	-	60	-
inert material	SiC	SiC	SiC
cat. dilution ratio	1:1	1:1	1:1
total gas feed in mL/min	70, 140	80, 250, 340	70, 140
CH ₄ -feed tube in mL/min	-	26, 76, 105	-
N ₂ /O ₂ -feed shell in mL/min	-	60, 170, 235	-
CH ₄ :O ₂ :N ₂ – Ratio	2:1:4	(1.5–2.5):1:(2–5)	-
Temperature in °C	780, 830	780, 820, 835, 840	780, 830
inlet pressure in bar(a)	2	tube: 1.5 shell: 2.5–3	1.7
outlet pressure in bar(a)	1.2	1.2	1.2
BSCF content in %	0, 20	0	0, 10, 20
Duration reaction cycle in min	-	-	5, 10

2.2.2. Packed Bed Membrane Reactor (PBMR)

The general configuration for the Packed Bed Membrane Reactor (PBMR) is similar to the conventional Packed Bed Reactor (Figure 2). The main difference is the additional tubular membrane used for air/O₂ dosing and which also houses the catalyst bed (Figure 3).

To achieve a similar pressure drop along the shell side compared to the catalytic bed and therefore to ensure a homogeneous O₂ flow across the whole permeable zone, the shell side is filled with inert SiC particles. Those particles are of the same grain size as the catalyst. Without the inert filling, back-permeation of CH₄ towards the shell side could occur. This would reduce performance and could lead to explosive CH₄ to O₂ mixtures. The inert packing also helps provide a more homogeneous heat distribution.

Carefully controlling the permeation rate as well as the pressure gradient through the membrane and along the reaction length via the membrane's pore size and distribution and the overall gas feed is the biggest challenge in operating an OCM PBMR. A negative pressure gradient towards the tube side must always be ensured.

A very thin layer of the ceramic glaze was applied to the permeable zone, blocking a certain proportion of the pores, to increase the trans-membrane pressure drop. In this way, pressure drop could be increased from 0.15–0.3 bar to approximately 1 bar at GHSV = 120 and up to 1.5 bar at GHSV = 500.

The membranes used were prototypes, and full reproducibility could not be guaranteed by the manufacturer. Therefore, all experiments were performed with membranes from the same production batch. In addition, the pressure drop of each membrane was measured after modification and prior to reactor installation using N₂ flow rates of 20–500 mL/min. Membranes showing significant deviations were excluded from testing.

Another approach to manipulating the pressure regime is by increasing or decreasing the inert gas feed. This allows the gas flow through the membrane to be adjusted while keeping the ratio of CH₄ to O₂ constant. The reaction and test conditions are given in Table 2.

2.2.3. Chemical Looping Reactor (CLR)

The original operation principle of a Chemical Looping Reactor (CLR) consisting of two separated fluidized bed reactors is illustrated in Figure 4. In this setup, the oxygen carrier (Me_xO_y) circulates between two reactors. In the first reactor, it is oxidized with air or pure oxygen (Equation (8)). The oxygen-loaded carrier is then transferred to the second reactor, where it reacts with the CH₄ feed (Equation (9)). Afterwards, the depleted carrier is recirculated and the cycle repeats. The OCM catalyst can serve directly as the carrier material. Therefore, the reaction with O₂ is almost completely limited to the catalyst surface, preventing non-selective gas phase reaction and providing high C₂ selectivity.

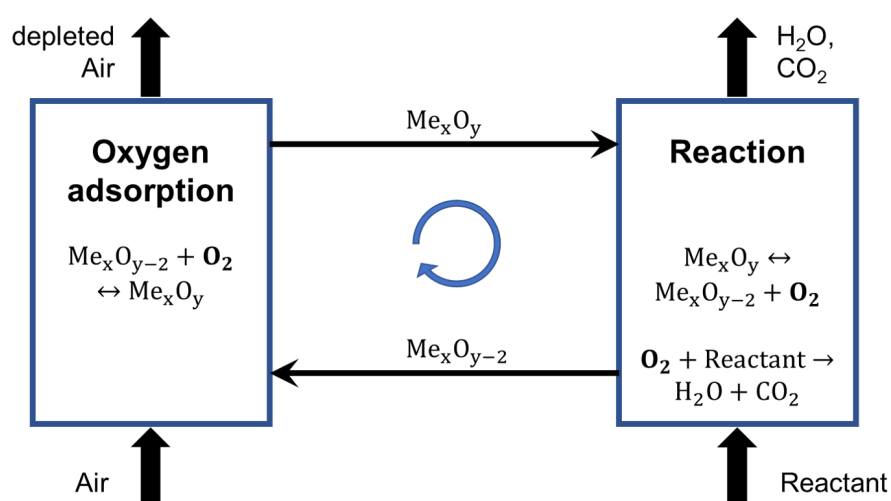
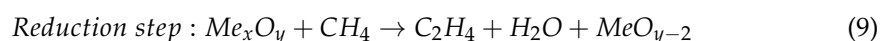
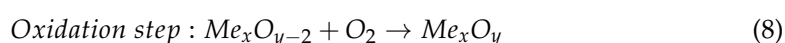
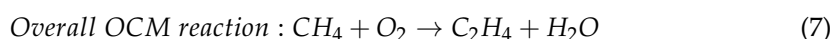


Figure 4. Basic working principle of a Chemical Looping Reactor setup (thick arrows: gas flow, thin arrows: oxygen carrier transport).

A poly-cyclic operation mode was used, to resemble Chemical Looping in the Packed Bed Reactor system (Figure 2a). In this system, only one PBR is used, but instead of the steady-state gas feed described before, in this setup, the gas feed varies over time.

Both operation modes rely on the same fundamental alternating oxidation and reduction. An advantage of the poly-cyclic mode is that it provides information about oxygen-carrier and gas composition, which are relevant for a later continuous CLR.

O₂ is fed to the reactor to oxidize the catalyst. Afterwards, the O₂ flow stops and the CH₄ feed starts. After that, the CH₄ flow is stopped and the cycle starts from the beginning. To avoid mixing of the reactants and to eliminate gas phase reaction, the two steps are separated by a inertization phase where the reactor is purged with nitrogen. To moderate the reaction in terms of heat control, the nitrogen flow remains constant throughout the entire cycle. Figure 5 shows the temporal sequence of the feed gas flows for the Chemical Looping mode.

After reaching the desired temperature, the catalyst is first oxidized in an air stream until the measured (IR and μGC) outlet concentration stabilizes and the system reaches a steady state. Subsequently, the O₂ flow is stopped until the O₂ concentration at the outlet falls below 1%_{Vol}. The methane flow is started and the actual OCM reaction is started as shown in Figure 6. A total of five complete cycles are conducted before the reaction is stopped and the catalyst is reconditioned. All experimental points with the same BSCF concentration are performed within one week using the same catalyst. For experiments with a different concentration of BSCF, the same production batch of catalyst is used.

In line with the reference PBR experiments, the operating variables temperature and gas feed are varied and investigated in the same value range. In addition, the influence of varying the duration of the reaction phase ($\Delta t_{\text{reaction}}$) is examined.

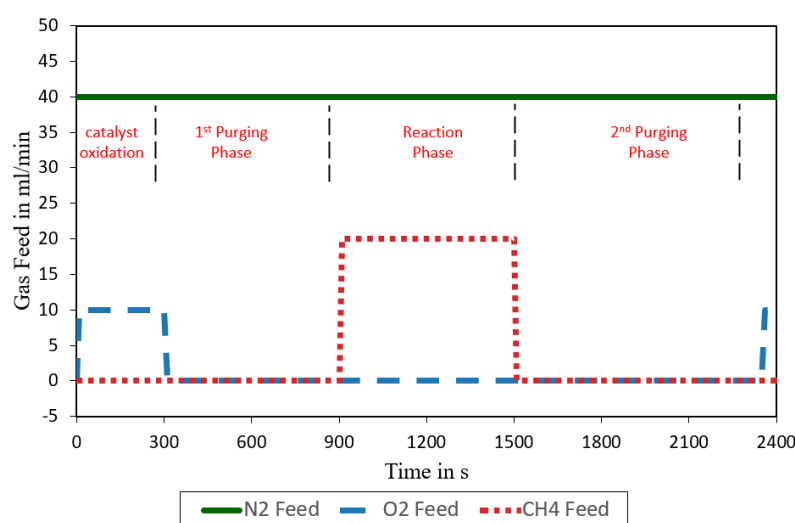


Figure 5. Feed gas sequence for poly-cyclic operation mode for CL in a PBR.

The storage capacity for O₂ in the catalyst material is limited, capping the overall CH₄ conversion. Trying to increase the total amount of bound O₂, a certain amount of BSCF (Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ}) is added to the inert material. This material is also used for the production of O₂-selective (dense) membranes and can bind considerable amounts of O₂ at high temperatures [47]. The influence of BSCF addition on the O₂ uptake as well as on selectivity and yield are also to be investigated. Table 2 shows an overview of the experimental conditions that were investigated.

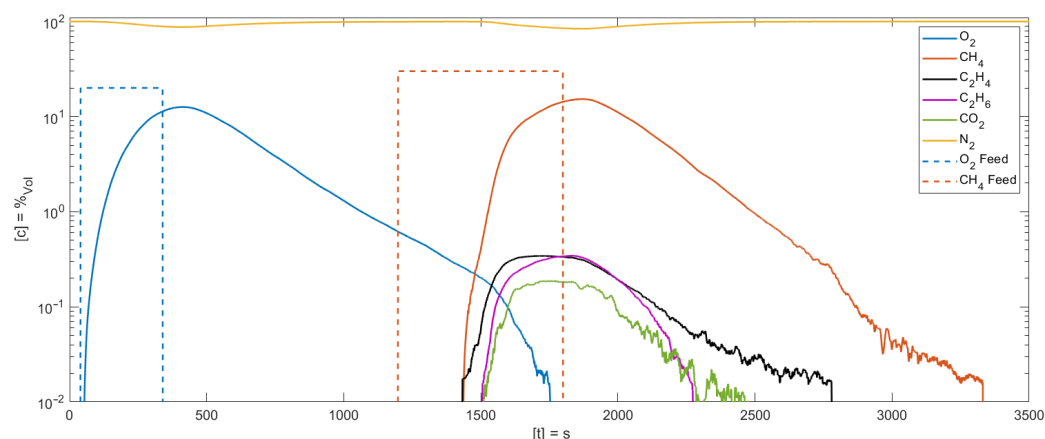


Figure 6. CLR—Exemplary outlet concentration profile of the IR-spectroscope.

3. Results

3.1. Packed Bed Reactor

The results of the reference tests in the Packed Bed Reactor (PBR) are shown in Figure 7, which shows the impact of the variations in temperature and total feed amount on the reaction. Overall, a maximum C_2 yield of 17.9% can be achieved with the set parameters, which is in line with values reported in the literature and depicted in Figure 8. An increase in temperature is observed to enhance conversion, selectivity, and yield. However, previous studies have reported that temperatures higher than 850 °C result in irreversible loss of active catalyst surface area [48].

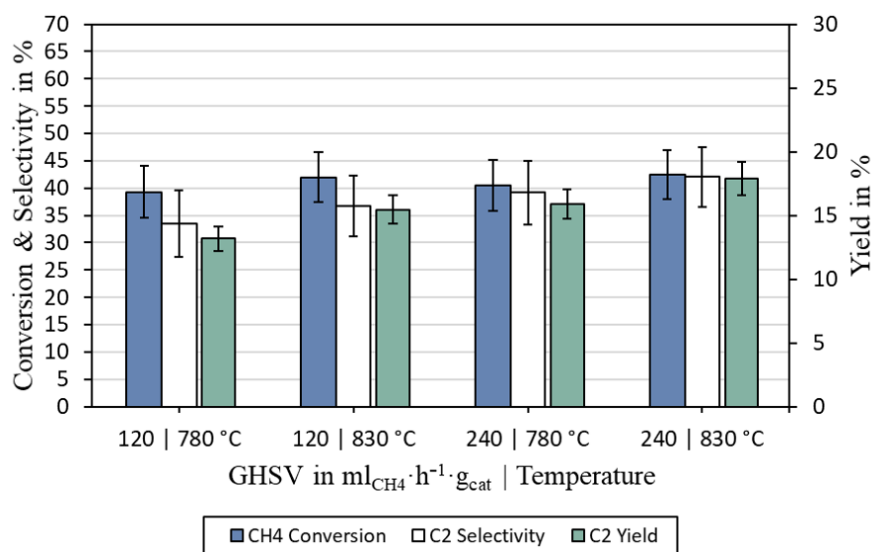


Figure 7. PBR—Influence of GHSC and Temperature on X, S, Y. ($CH_4:O_2:N_2 = 2:1:4$, total feed = 70/140 mL/min (for GHSV = 120/240 mL_{CH4} · h⁻¹ · g_{Cat}⁻¹)).

The results also indicate that an increase in total gas flow is beneficial, as it improves selectivity. By increasing the volumetric gas flow, the residence time of the reactants decreases and the main reaction zone is enlarged and spans a larger area, resulting in less steep temperature gradients. However, the parallel slight increase in conversion may also indicate a rise in the internal catalyst temperature due to higher reaction heat, which may not be fully captured by the external thermocouple position.

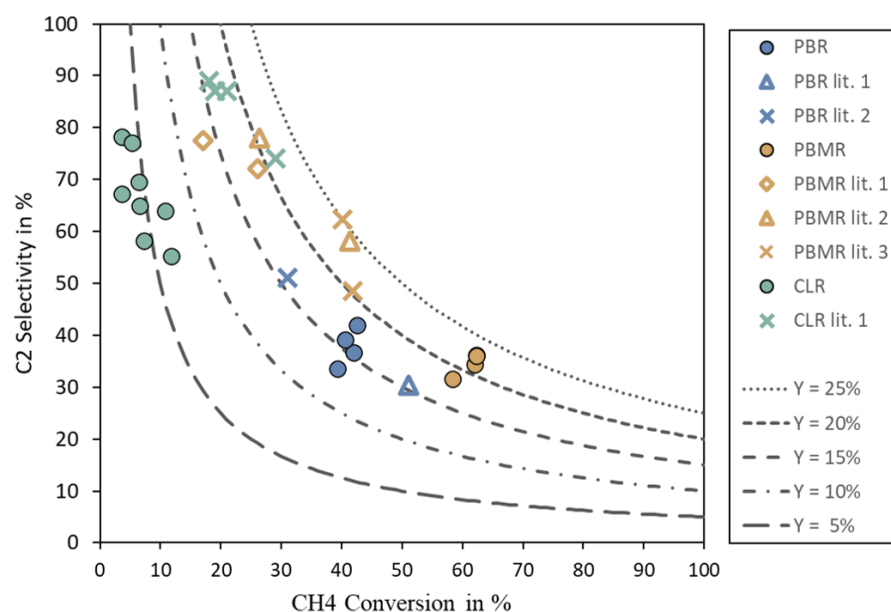


Figure 8. X vs. S diagram—Comparison of the three reactor concepts with exemplary results from literature (blue: PBR lit.1 = [4], PBR lit.2 = [6]; yellow: PBMR lit.1 = [33], PBMR lit.2 = [49], PBMR lit.3 = [34]; green: CLR lit. 1 = [42]).

3.2. Packed Bed Membrane Reactor

Figure 9 shows the results of the membrane reactor tests at different temperatures. Analogously to the PBR, there is a strong dependence of the performance on the temperature. With an increase in reactor temperature, both conversion and selectivity increase. Only at temperatures close to the critical catalyst temperature, the selectivity begins to drop. This results in a maximum C₂ yield of 22.6% in the range between 820 and 850 °C.

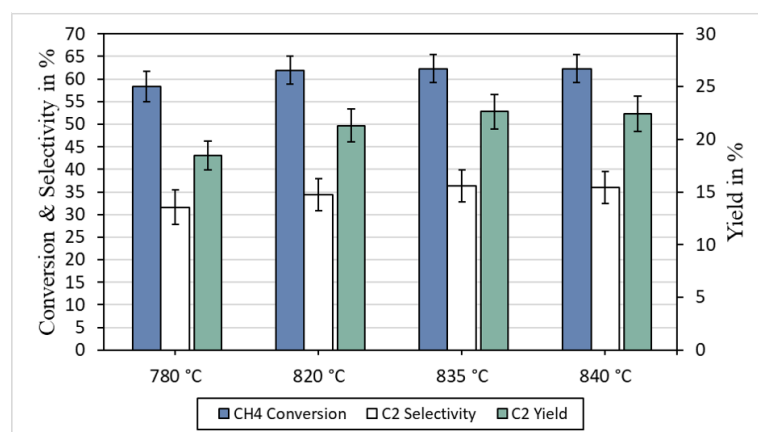


Figure 9. PBMR—Influence of Temperature (GHSV = 300 mL_{CH₄} · h^{−1} · g_{Cat.}^{−1}, CH₄:O₂:N₂ = 2:1:4).

As mentioned previously, the prevailing pressure regime, specifically the trans-membrane pressure gradient and its distribution across the catalytic bed or permeable zone, is a critical process parameter. Figure 10 illustrates the behavior when the GHSV is increased while maintaining the same reactant ratio and temperature. Up to a certain point, C₂ selectivity—and, consequently, the C₂ yield—improves. However, with further increases in the gas flow rate, the slightly better selectivity is offset by decreasing conversion. Due to the different cross-sections, the pressure in the tube side increases more than in the shell side when the GHSV is increased. Therefore, the positive effect of better heat removal is counteracted by maximizing the pressure gradient at the very end of the permeable zone,

promoting bypass flow. The corresponding pressure differences at reactor inlet and outlet are depicted in Figure A1 in the Appendix A.

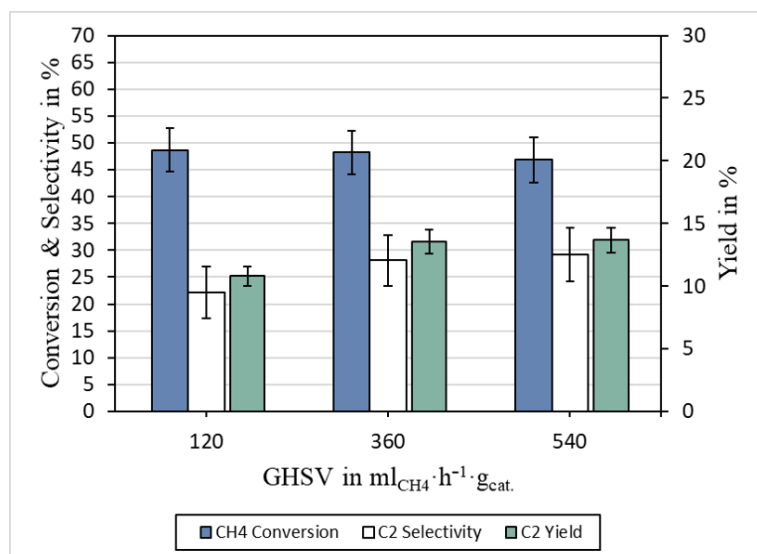


Figure 10. PBMR—Influence of gas feed at constant reactant ratio ($T = 830\text{ }^{\circ}\text{C}$, $\text{CH}_4:\text{O}_2:\text{N}_2 = 2:1:3.5$, $\Delta P_{mem} = 2.2/2/1.5\text{ bar}$ (for $\text{GHSV} = 120/360/540\text{ mL}_{\text{CH}_4} \cdot \text{h}^{-1} \cdot \text{g}_{\text{Cat}}^{-1}$), total feed = $85/250/340\text{ mL/min}$).

A significant improvement can be achieved by increasing the amount of inert gas, which is also fed through the shell side (Figure 11). An increase in the inert gas flow leads to a decrease in conversion with a simultaneous increase of the selectivity. Several reasons are related to this. On the one hand, the pressure profile in the shell side is changed to a more uniform O_2 dosage. Secondly, the O_2 concentration in the gas phase is reduced, leading to less non-selective gas phase reaction. However, down-stream units will have to become bigger when a larger amount of inert gas has to be separated.

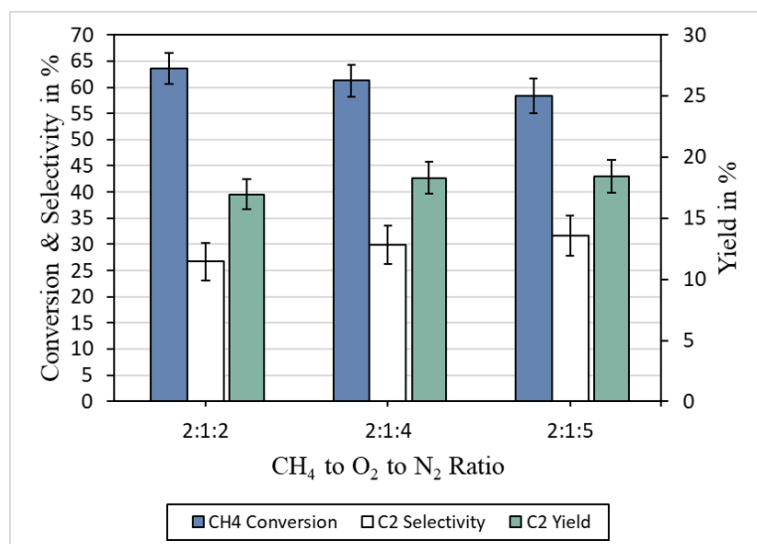


Figure 11. PBMR—Influence of additional inert gas ($T = 780\text{ }^{\circ}\text{C}$, $\text{GHSV} = 300\text{ mL}_{\text{CH}_4} \cdot \text{h}^{-1} \cdot \text{g}_{\text{Cat}}^{-1}$, $\Delta P_{Mem} = 1.8/2/2.3\text{ bar}$).

3.3. Chemical Looping

Figure 6 shows an example of the concentration curve of the IR spectroscopy at the outlet of the reactor over the duration of a complete Chemical Looping cycle.

It can be seen that the formation of CO_2 is considerably lower than the amount of C_2 products that formed, which leads to the high selectivity of the process. In the two other

reactor concepts, the ratio of the outlet concentrations of C₂-products and by-products, namely, CO₂, is around 1:2 to 1:3, while in the CLR, it is almost 3:1. Another noteworthy observation is that, for all tested process parameters, the outlet streams of the PBR and PBMR consistently contained measurable amounts of CO and H₂. In contrast, during CLR experiments, no CO or H₂ was detected in the product gas stream, or their concentrations were so low that they remained below the detection limit of the μ GC (0.01%_{vol}). This observation indicates that side reactions such as the partial oxidation of methane do not occur, or occur only to a negligible extent, which is consistent with the high selectivity achieved under these conditions.

In Figure 6, the resulting selectivity is approximately 77% with a C₂ yield of 4.2%. The IR signal indicates that the majority of the reaction is completed after approximately 2600 s. Subsequently, the product concentrations fall below the detection limit of the analyzer.

Conversion and yield are calculated for one entire cycle. When the duration of the reaction step is adjusted and shortened, yield and conversion can be expected to improve while maintaining almost the same level of selectivity. Such a process could be profitable despite the low conversion due to the higher selectivity. The resulting low amount of by-products can reduce the need for costly and energy-intensive downstream processes for product purification.

To address the inherent low oxygen availability, it was investigated whether the addition of BSCF to the inert material could increase the overall oxygen storage capacity (Figure 12). By adding more O₂ carrier material, the amount of O₂ in the system and thus the CH₄ conversion can be increased as expected. The selectivity simultaneously decreases due to the larger amount of O₂ and the associated amount of O₂ in the gas phase. At even higher concentrations of BSCF, the yield remains constant as selectivity deteriorates so that the optimum is likely to be found between 0% and 20% admixture. The further considerations in this section are made with a BSCF content of 10%.

Figure 13 shows the results obtained by increasing the temperature from 780 °C to 830 °C for the two different stages of feed and duration. As expected, the CH₄ conversion is very low (4–12%) compared to the other two concepts, but almost double the high selectivity, of over 80%, can be achieved. The maximum C₂ yield, at a selectivity of 70%, is around 7%. It can be seen that, in contrast to the PBR and PBMR, an increase in temperature has a negative effect on the performance, since the selectivity decreases significantly in all the settings considered. Since the desorption rate of O₂ from the catalyst is a function of temperature, it can be assumed that, at higher temperatures, more O₂ is desorbed in a shorter time and is more present in the gas phase, leading to side reactions and deep oxidation.

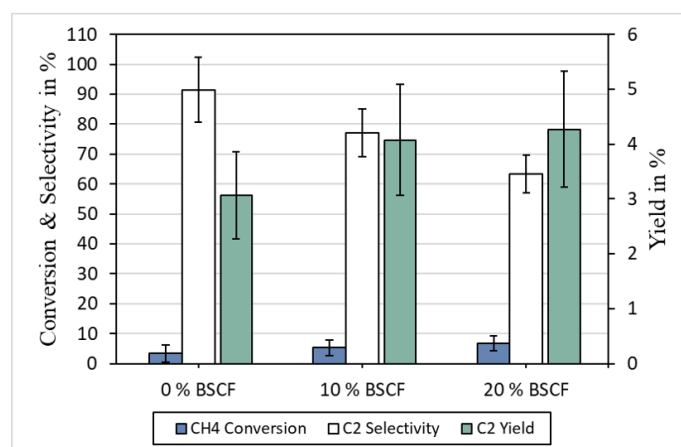


Figure 12. CLR—Influence of different BSCF concentrations in the catalyst mixture. (GHSV_{t_{Reaction}} = 240 mL_{CH₄} · h^{−1} · g_{Cat.}^{−1}, Feed = 40 mL_{CH₄} /min, Δt_{reaction} = 5 min, T = 780 °C).

To quantify the influence of the BSCF material on the OCM, tests were performed under reference conditions in the PBR where BSCF was mixed with the catalyst (up to 20%). No significant influence could be observed on these tests compared to the reference tests (see Figure A2 in the Appendix A).

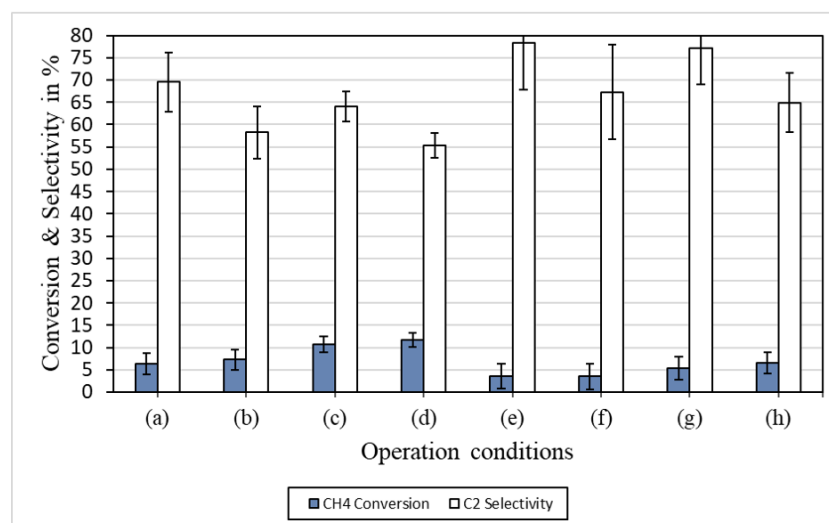


Figure 13. CLR—variation in gas feed, duration of reaction phase, and temperature. (a) 780°C, $\Delta t = 10$ min, 20 mL_{CH₄}; (b) 830°C, $\Delta t = 10$ min, 20 mL_{CH₄}; (c) 780°C, $\Delta t = 5$ min, 20 mL_{CH₄}; (d) 830°C, $\Delta t = 5$ min 20 mL_{CH₄}; (e) 780°C, $\Delta t = 10$ min, 40 mL_{CH₄}; (f) 830°C, $\Delta t = 10$ min, 40 mL_{CH₄}; (g) 780°C, $\Delta t = 5$ min, 40 mL_{CH₄}; (h) 830°C, $\Delta t = 5$ min 40 mL_{CH₄}.

Increasing the total amount of feed gas from 20 mL CH₄ (a–d) to 40 mL CH₄ (e–h) results in a lower conversion at nearly constant selectivity, as can be seen in Figure 13. Since, in particular, the first phase, in which a certain amount of the residual gas phase O₂ is still present, is passed through more quickly, the selectivity can be increased, but the amount of O₂ stored on the catalyst is too small to convert the additional amount of CH₄.

Examination of the duration of the reaction phase reveals that the shorter reaction phase may result in a significant increase in yield. As can be seen in the graph of the IR spectroscope in Figure 6, the formation of ethane and ethene occurs primarily in the first few minutes after the start of the reaction. Although CO₂ is also formed exclusively at the beginning, the significant decrease in conversion cannot be compensated for by the slight increase in selectivity with longer reaction times.

4. Discussion

Figure 8 shows the characteristic results of the three concepts plotted in an X-S diagram, together with the isolines of constant C₂ yield and some exemplary data from the literature for the same or similar reactor types.

The results achieved in the PBR are comparable to previous tests and results in the literature as depicted in Figure 8. It turns out that with a suitable catalyst and adapted process conditions, C₂ yields of up to 20% are easily achievable. However, the gap to the targeted 30% is still evident here as well.

The PBMR aims to combine these two aspects through a homogeneous O₂ dosing, keeping the local concentration low while achieving a homogeneous temperature profile over the entire catalyst. It still provides a fairly high total O₂ quantity to ensure a decent CH₄ conversion.

The PBMR has the advantage that the homogeneous O₂ supply avoids the very high initial O₂ concentrations and with it the steep temperature gradient. The total reactor

temperature can therefore be higher than in a PBR without risking to exceed the critical catalyst temperature.

The results of the PBR and PBMR show very similar behavior in terms of conversion and selectivity when varying the reaction temperature. Only the influence of the GHSV, or regulation of the same, is clearly more complex with the PBMR due to the above-mentioned need for a certain pressure regime between the tube and shell side.

The PBMR results are in line with the values from previous studies and lie along the isoline of similar C_2 -Yields in the X-S diagram. Using a PBMR instead of a PBR increases the conversion while keeping selectivity relatively constant. This led to a notable improvement in the C_2 yield.

A critical point concerning comparability is the differing thermocouple positions in PBMR compared to PBR (and CLR). While negligible at low flow rates, temperature deviations of up to 15 K were observed at higher flow rates of $> 300 \text{ mL}_{\text{CH}_4} \cdot \text{h}^{-1} \cdot \text{g}_{\text{Cat}}^{-1}$, as confirmed by tests with both external single-point and internal multi-point thermocouples. Future comparative studies should therefore ensure consistent sensor placement.

In both the PBMR and CLR experiments, the reaction was moderated by dilution with inert N_2 , which enhanced selectivity but posed challenges for industrial application since the inert gas must be separated from the product stream. Given that side reactions are significantly reduced in the CLR, future work should investigate whether and how the use of inert gas can be minimized. Alternative strategies could include moderating the high local heat release through diluting the catalyst bed itself. If inert gas cannot be fully avoided, inert gases that can be more easily separated from the product stream, such as H_2O or CO_2 —which are formed during OCM anyway—should be considered.

The CLR takes a completely different route by attempting to completely eliminate the gas phase O_2 and thus achieve enormously high selectivity and product purity, even at the expense of overall yield.

To some extent, the low CH_4 conversion is inherent in this system. However, the poly-cyclic operation in the PBR considered here also plays a non-negligible role in this. Because of the necessity to purge the gas phase between oxidation and reaction, many reactants are discharged. In an industrial plant with two interconnected reactors, this would not be necessary, leading to higher yields.

The results from the miniplant CLR are considerably lower than those reported in the literature, where in a similar poly-cyclic CLR setup higher selectivities were achieved. Those tests utilized pulsed CH_4 dosing and were conducted on a laboratory scale with significantly smaller gas and catalyst volumes [42]. Reasons for the lower performance in the miniplant setup lay in the continuous reactant dosing and in the larger dead volumes, resulting in a delayed and slower process response. However, this will likely not be an issue in an industrial-scale setup with two separate and interconnected reactors, as these reactors operate under a continuous feed flow.

Taking into account the investigated conditions of the miniplant setup, higher selectivities and yields are expected, when the reaction time is optimized and the purging time is prolonged to avoid the remaining 0.1% O_2 concentration at the start of the reaction. The results of [50] also suggest that a pure CH_4 feed can fully exploit the performance of the CLR.

It is noticeable that the efficiency of the OCM reaction decreases with increasing temperature instead of continuing to increase up to the critical catalyst temperature, as is the case with PBR and PBMR. This can have a positive effect on the stability of the catalyst and the economic feasibility if the reaction can be operated at a lower temperature.

The PBR setup is the concept with the lowest equipment and control technology complexity. The disadvantage is the large proportion of side reactions, which reduces the yield and makes downstream units more complex and cost-intensive.

The equipment requirements for a PBMR are considerably higher. The ceramic membrane poses sealing challenges; techniques such as Reactive Air Brazing (RAB) can withstand harsh reactive conditions, but are complex to manufacture.

Scaling up both PBR and PBMR presents certain challenges that need to be addressed. First, the punctual heat of reaction could become too high, potentially exceeding the catalyst's maximum temperature. Second, particularly in the case of PBMR, areas with limited to no O₂ exposure may lead to catalyst deactivation. To achieve higher production volumes, a numbering-up approach would be required, increasing the number of membranes or tube reactors. This circumvents these problems but increases the system's complexity.

Tests in the miniplant demonstrated that the membranes remained stable over several hundred hours of operation and tolerated temperature and load changes well. Nevertheless, the possibility of membrane failure must be accounted for in reactor design, along with associated maintenance and replacement costs. Cruellas et al. [49] showed that for a PBMR-OCM plant with a throughput of 1 million-ton of ethylene per year, membranes account for about 6% of total CAPEX. The integration of steam-generation tubes for heat removal and power production has only a minor impact on CAPEX. In contrast, operating costs—mainly energy and feedstock prices—play a far more decisive role, especially under European conditions [51]. The largest cost contribution being product gas separation, particularly the de-methanizer [49,52] to re-cycle unreacted CH₄. These costs decrease with increasing methane conversion, which is especially advantageous for the PBMR [52].

The Chemical Looping Reactor initially has the highest technical complexity. Although the throughput is extremely low in comparison, since the proportion of by-products in the output stream is very low, the downstream units would be considerably smaller. The possibility of using air instead of O₂ eliminates the need for an air-separation unit [49]. Moreover, due to the observed absence of CO and H₂ in the product gas, a methanizer to reconvert these species back into CH₄ may not be required. Further studies are needed to also evaluate the economic viability of downstream separation for this reactor concept.

The two alternatives shown to PBR both have their respective advantages and disadvantages, and their economic feasibility is highly dependent on the availability and cost of the feedstock. In recent years, numerous efforts have been made to bring PBR and PBMR closer to the desired target of 30% C₂ yield. And while some significant progress has been achieved [28,37], it appears that the existing gap may not be fully bridged until there are new groundbreaking developments in catalyst technology. In this context, CLR for OCM emerges as a promising alternative. Although the yield yet remains quite low, the exceptionally high selectivity has the potential to offset this limitation and drive future advancements in the process.

Because the catalyst is of particular importance for OCM in general, with future new and better catalysts, the advantages and disadvantages of the individual processes may shift. Similarly, changing demands or feedstock availability, along with an increased focus on processes with lower CO₂ emissions, could lead to a different assessment of those concepts in the future. It should be noted that the same catalyst, optimized primarily for high-temperature selectivity, was used across all three experimental series. Thus, further optimization tailored specifically to each reactor concept could be beneficial.

5. Conclusions

Three reactor concepts for the OCM, a Packed Bed Reactor (PBR), a Packed Bed Membrane Reactor (PBMR), and a Chemical Looping Reactor (CLR) were successfully implemented and tested on a miniplant scale with larger gas and catalyst volumes.

In both the membrane reactor setup and the Chemical Looping mode, a wider range of temperatures (780–840 °C) and GHSV could be tested to compare these concepts with the reference configuration. These two alternatives to conventional PBR can help tackle the difficult challenge of bringing the two reactants into contact preferably on the catalyst surface.

PBMR, compared to PBR, can increase C₂ selectivity due to the more homogeneous O₂ distribution. It can increase the conversion at a lower CH₄-to-O₂ ratio at the same level of selectivity as the PBR, leading to higher yields (up to 23%).

The Chemical Looping Process could be simulated with a poly-cyclic operation in the PBR. Due to the consequent elimination of the gas phase O₂, the reaction of O₂ and CH₄ was reduced almost exclusively to heterogeneous catalysis and therefore very high selectivities of up to 90% could be achieved. It could be shown that a certain addition of BSCF as O₂-storing material increases the CH₄ conversion with a moderate drop in selectivity. A maximum yield of 7% could be achieved with a selectivity of >70%.

In future work, optimizing the purging step of the CLR will be essential to effectively eliminate residual gas-phase oxygen and further increase selectivity. Additionally, fine-tuning the time ratio between the reaction phase and the oxidation phases has the potential to maximize performance. Regarding PBMR, comparative studies should be conducted using dense, O₂-selective membranes. Those membranes completely prevent back-permeation and can overcome the above-mentioned pressure limitations associated with porous membranes.

Some limitations in the process scale-up assessment concern downstream separation units, which require further consideration with respect to the specific characteristics of each reactor concept—for example, the elevated CO and CO₂ concentrations in PBR and PBMR systems, or the high CH₄ content in CLR configurations.

Building on the results of this study, a more detailed techno-economic assessment should be conducted in future work. Such an analysis should also account for recent developments in natural gas and electricity prices.

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Abbreviations

The following abbreviations are used in this manuscript:

OCM	Oxidative Coupling of Methane
PBR	Packed Bed Reactor
PBMR	Packed Bed Membrane Reactor
CL	Chemical Looping
IWI	Incipient Wetness Impregnation
CLR	Chemical Looping Reactor
GHSV	Gas Hourly Space velocity in $\text{mL}_{\text{CH}_4} \cdot \text{h}^{-1} \cdot \text{g}_{\text{Cat}}^{-1}$
BSCF	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
μGC	micro Gas Chromatograph
SiC	Silicon Carbide

Appendix A

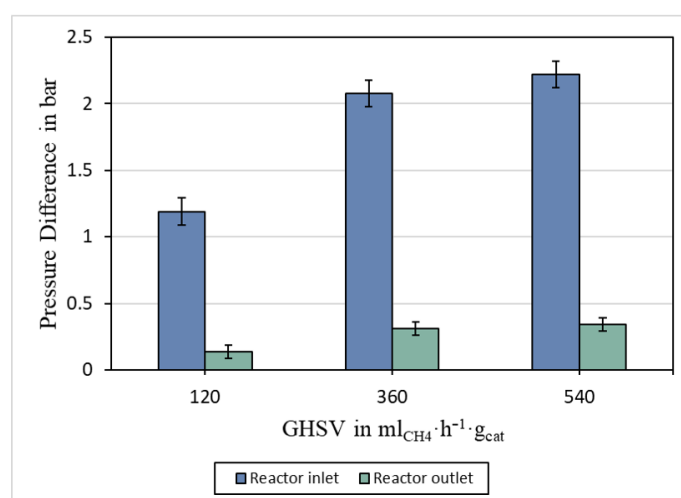


Figure A1. Pressure difference ($P_{\text{Shell}}-P_{\text{Tube}}$) at different GHSV in PBMR ($T = 830\text{ }^{\circ}\text{C}$, $\text{CH}_4:\text{O}_2:\text{N}_2 = 2:1:3.5$, $\Delta P_{\text{mem}} = 1.5/2/2.2\text{ bar}$ (for $\text{GHSV} = 120/360/540\text{ mL}_{\text{CH}_4} \cdot \text{h}^{-1} \cdot \text{g}_{\text{Cat}}^{-1}$), total feed = 85/250/340 mL/min).

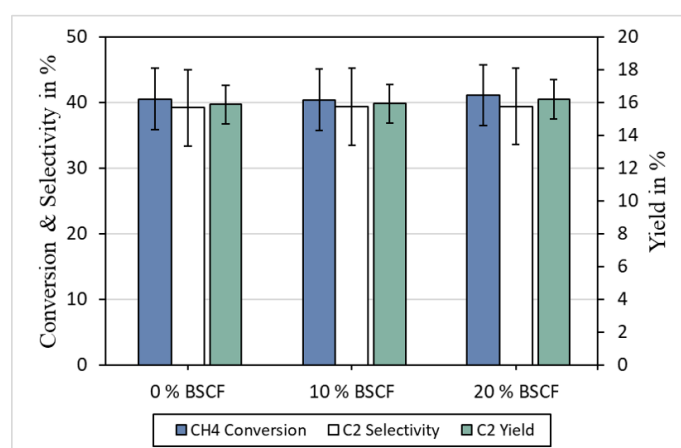


Figure A2. CLR—Influence of different BSCF concentrations in the catalyst mixture. Reference test in with pre-mixed reactants ($\text{GHSV}_{t_{\text{Reaction}}} = 240\text{ mL}_{\text{CH}_4} \cdot \text{h}^{-1} \cdot \text{g}_{\text{Cat}}^{-1}$, Feed = 40 mL_{CH₄}/min, $\Delta t_{\text{reaction}} = 5\text{ min}$, $T = 780\text{ }^{\circ}\text{C}$).

References

1. Ethylene Global Supply Demand Analytics Service | Wood Mackenzie. 2024. Available online: <https://www.woodmac.com/news/editorial/ethylene-global-supply-demand-analytics-service/> (accessed on 12 September 2024).
2. Layritz, L.S.; Dolganova, I.; Finkbeiner, M.; Luderer, G.; Penteado, A.T.; Ueckerdt, F.; Repke, J.U. The Potential of Direct Steam Cracker Electrification and Carbon Capture & Utilization via Oxidative Coupling of Methane as Decarbonization Strategies for Ethylene Production. *Appl. Energy* **2021**, *296*, 117049. [\[CrossRef\]](#)
3. Keller, G. Synthesis of Ethylene via Oxidative Coupling of Methane I. Determination of Active Catalysts. *J. Catal.* **1982**, *73*, 9–19. [\[CrossRef\]](#)
4. Cruellas, A.; Bakker, J.; Van Sint Annaland, M.; Medrano, J.; Gallucci, F. Techno-Economic Analysis of Oxidative Coupling of Methane: Current State of the Art and Future Perspectives. *Energy Convers. Manag.* **2019**, *198*, 111789. [\[CrossRef\]](#)
5. Zavyalova, U.; Holena, M.; Schlögl, R.; Baerns, M. Statistical Analysis of Past Catalytic Data on Oxidative Methane Coupling for New Insights into the Composition of High-Performance Catalysts. *ChemCatChem* **2011**, *3*, 1935–1947. [\[CrossRef\]](#)
6. Stansch, Z.; Mleczko, L.; Baerns, M. Comprehensive Kinetics of Oxidative Coupling of Methane over the $\text{La}_2\text{O}_3/\text{CaO}$ Catalyst. *Ind. Eng. Chem. Res.* **1997**, *36*, 2568–2579. [\[CrossRef\]](#)
7. Tiemersma, T.; Tuinier, M.; Gallucci, F.; Kuipers, J.; Annaland, M.V.S. A Kinetics Study for the Oxidative Coupling of Methane on a $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ Catalyst. *Appl. Catal. A Gen.* **2012**, *433–434*, 96–108. [\[CrossRef\]](#)
8. Parishan, S.; Nowicka, E.; Fleischer, V.; Schulz, C.; Colmenares, M.G.; Rosowski, F.; Schomäcker, R. Investigation into Consecutive Reactions of Ethane and Ethene Under the OCM Reaction Conditions over $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ Catalyst. *Catal. Lett.* **2018**, *148*, 1659–1675. [\[CrossRef\]](#)
9. Kondratenko, E.V.; Peppel, T.; Seeburg, D.; Kondratenko, V.A.; Kalevaru, N.; Martin, A.; Wohlrab, S. Methane Conversion into Different Hydrocarbons or Oxygenates: Current Status and Future Perspectives in Catalyst Development and Reactor Operation. *Catal. Sci. Technol.* **2017**, *7*, 366–381. [\[CrossRef\]](#)
10. Chung, E.Y.; Wang, W.K.; Nadgouda, S.G.; Baser, D.S.; Sofranko, J.A.; Fan, L.S. Catalytic Oxygen Carriers and Process Systems for Oxidative Coupling of Methane Using the Chemical Looping Technology. *Ind. Eng. Chem. Res.* **2016**, *55*, 12750–12764. [\[CrossRef\]](#)
11. Parishan, S.; Littlewood, P.; Arinchtin, A.; Fleischer, V.; Schomäcker, R. Chemical Looping as a Reactor Concept for the Oxidative Coupling of Methane over the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ Catalyst, Benefits and Limitation. *Catal. Today* **2018**, *311*, 40–47. [\[CrossRef\]](#)
12. Cruellas, A.; Melchiori, T.; Gallucci, F.; Van Sint Annaland, M. Advanced Reactor Concepts for Oxidative Coupling of Methane. *Catal. Rev.* **2017**, *59*, 234–294. [\[CrossRef\]](#)
13. Godini, H.R.; Gili, A.; Görke, O.; Simon, U.; Hou, K.; Wozny, G. Performance Analysis of a Porous Packed Bed Membrane Reactor for Oxidative Coupling of Methane: Structural and Operational Characteristics. *Energy Fuels* **2014**, *28*, 877–890. [\[CrossRef\]](#)
14. Jašo, S.; Sadjadi, S.; Godini, H.; Simon, U.; Arndt, S.; Görke, O.; Berthold, A.; Arellano-Garcia, H.; Schubert, H.; Schomäcker, R.; et al. Experimental Investigation of Fluidized-Bed Reactor Performance for Oxidative Coupling of Methane. *J. Nat. Gas Chem.* **2012**, *21*, 534–543. [\[CrossRef\]](#)
15. Arndt, S.; Otremba, T.; Simon, U.; Yildiz, M.; Schubert, H.; Schomäcker, R. $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ as Catalyst for the Oxidative Coupling of Methane. What Is Really Known? *Appl. Catal. A Gen.* **2012**, *425–426*, 53–61. [\[CrossRef\]](#)
16. Horn, R.; Schlögl, R. Methane Activation by Heterogeneous Catalysis. *Catal. Lett.* **2015**, *145*, 23–39. [\[CrossRef\]](#)
17. Sung, J.S.; Choo, K.Y.; Kim, T.H.; Greish, A.; Glukhov, L.; Finashina, E.; Kustov, L. Peculiarities of Oxidative Coupling of Methane in Redox Cyclic Mode over $\text{Ag-La}_2\text{O}_3/\text{SiO}_2$ Catalysts. *Appl. Catal. A Gen.* **2010**, *380*, 28–32. [\[CrossRef\]](#)
18. Cheng, Z.; Baser, D.S.; Nadgouda, S.G.; Qin, L.; Fan, J.A.; Fan, L.S. C_2 Selectivity Enhancement in Chemical Looping Oxidative Coupling of Methane over a Mg-Mn Composite Oxygen Carrier by Li-Doping-Induced Oxygen Vacancies. *ACS Energy Lett.* **2018**, *3*, 1730–1736. [\[CrossRef\]](#)
19. Fleischer, V.; Simon, U.; Parishan, S.; Colmenares, M.G.; Görke, O.; Gurlo, A.; Riedel, W.; Thum, L.; Schmidt, J.; Risse, T.; et al. Investigation of the Role of the $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ Catalyst Composition in the Oxidative Coupling of Methane by Chemical Looping Experiments. *J. Catal.* **2018**, *360*, 102–117. [\[CrossRef\]](#)
20. Li, S. Reaction Chemistry of $\text{W-Mn}/\text{SiO}_2$ Catalyst for the Oxidative Coupling of Methane. *J. Nat. Gas Chem.* **2003**, *12*, 1–9.
21. Wang, J.; Chou, L.; Zhang, B.; Song, H.; Zhao, J.; Yang, J.; Li, S. Comparative Study on Oxidation of Methane to Ethane and Ethylene over $\text{Na}_2\text{WO}_4\text{-Mn}/\text{SiO}_2$ Catalysts Prepared by Different Methods. *J. Mol. Catal. A Chem.* **2006**, *245*, 272–277. [\[CrossRef\]](#)
22. Yildiz, M.; Aksu, Y.; Simon, U.; Otremba, T.; Kailasam, K.; Göbel, C.; Girgsdies, F.; Görke, O.; Rosowski, F.; Thomas, A.; et al. Silica Material Variation for the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$. *Appl. Catal. A Gen.* **2016**, *525*, 168–179. [\[CrossRef\]](#)
23. Perez Ortiz, A.; Penteado, A.; Karsten, T.; Esche, E.; Grigull, V.; Schomäcker, R.; Repke, J.U. Autothermal Oxidative Coupling of Methane: Steady-State Multiplicity Over $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ at Mini-Plant Scale. *Chem. Ing. Tech.* **2022**, *94*, 791–795. [\[CrossRef\]](#)
24. Godini, H.R.; Fleischer, V.; Görke, O.; Jaso, S.; Schomäcker, R.; Wozny, G. Thermal Reaction Analysis of Oxidative Coupling of Methane. *Chem. Ing. Tech.* **2014**, *86*, 1906–1915. [\[CrossRef\]](#)
25. Kim, M.; Arndt, S.; Yildiz, M.; Schomäcker, R.; Görke, O.; Repke, J.U.; Wozny, G.; Godini, H. Reaction Engineering of Oxidative Coupling of Methane. *Chem. Eng. Res. Des.* **2021**, *172*, 84–98. [\[CrossRef\]](#)

26. Coronas, J.; Menendez, M.; Santamaria, J. Development of Ceramic Membrane Reactors with a Non-Uniform Permeation Pattern. Application to Methane Oxidative Coupling. *Chem. Eng. Sci.* **1994**, *49*, 4749–4757. [\[CrossRef\]](#)
27. Ortiz-Bravo, C.A.; Chagas, C.A.; Toniolo, F.S. Oxidative Coupling of Methane (OCM): An Overview of the Challenges and Opportunities for Developing New Technologies. *J. Nat. Gas Sci. Eng.* **2021**, *96*, 104254. [\[CrossRef\]](#)
28. Cruellas, A.; Melchiori, T.; Gallucci, F.; Van Sint Annaland, M. Oxidative Coupling of Methane: A Comparison of Different Reactor Configurations. *Energy Technol.* **2020**, *8*, 1900148. [\[CrossRef\]](#)
29. Harold, M.P.; Lee, C. Intermediate Product Yield Enhancement with a Catalytic Inorganic Membrane—II. Nonisothermal and Integral Operation in a Back-Mixed Reactor. *Chem. Eng. Sci.* **1997**, *52*, 1923–1939. [\[CrossRef\]](#)
30. Cruellas, A.; Ververs, W.; Annaland, M.V.S.; Gallucci, F. Experimental Investigation of the Oxidative Coupling of Methane in a Porous Membrane Reactor: Relevance of Back-Permeation. *Membranes* **2020**, *10*, 152. [\[CrossRef\]](#)
31. Diakov, V.; Blackwell, B.; Varma, A. Methanol Oxidative Dehydrogenation in a Catalytic Packed-Bed Membrane Reactor: Experiments and Model. *Chem. Eng. Sci.* **2002**, *57*, 1563–1569. [\[CrossRef\]](#)
32. Ramos, R.; Menéndez, M.; Santamaría, J. Oxidative Dehydrogenation of Propane in an Inert Membrane Reactor. *Catal. Today* **2000**, *56*, 239–245. [\[CrossRef\]](#)
33. Lu, Y.; Dixon, A.G.; Moser, W.R.; Hua Ma, Y. Oxidative Coupling of Methane in a Modified γ -Alumina Membrane Reactor. *Chem. Eng. Sci.* **2000**, *55*, 4901–4912. [\[CrossRef\]](#)
34. Godini, H.; Gili, A.; Görke, O.; Arndt, S.; Simon, U.; Thomas, A.; Schomäcker, R.; Wozny, G. Sol–Gel Method for Synthesis of Mn–Na₂WO₄/SiO₂ Catalyst for Methane Oxidative Coupling. *Catal. Today* **2014**, *236*, 12–22. [\[CrossRef\]](#)
35. Godini, H.; Trivedi, H.; De Villasante, A.G.; Görke, O.; Jašo, S.; Simon, U.; Berthold, A.; Witt, W.; Wozny, G. Design and Demonstration of an Experimental Membrane Reactor Set-up for Oxidative Coupling of Methane. *Chem. Eng. Res. Des.* **2013**, *91*, 2671–2681. [\[CrossRef\]](#)
36. METHane Activation via Integrated MEMbrane REactors. 2025. Available online: <https://www.aspire2050.eu/memere> (accessed on 20 August 2025).
37. Karsten, T.; Middelkoop, V.; Matras, D.; Vamvakeros, A.; Poulston, S.; Grosjean, N.; Rollins, B.; Gallucci, F.; Godini, H.R.; Jacques, S.D.M.; et al. Multi-Scale Studies of 3D Printed Mn–Na–W/SiO₂ Catalyst for Oxidative Coupling of Methane. *Catalysts* **2021**, *11*, 290. [\[CrossRef\]](#)
38. Papavassiliou, V.; Lee, C.; Nestlerode, J.; Harold, M.P. Pneumatically Controlled Transport and Reaction in Inorganic Membranes. *Ind. Eng. Chem. Res.* **1997**, *36*, 4954–4964. [\[CrossRef\]](#)
39. Aseem, A.; Harold, M.P. C₂ Yield Enhancement during Oxidative Coupling of Methane in a Nonpermselective Porous Membrane Reactor. *Chem. Eng. Sci.* **2018**, *175*, 199–207. [\[CrossRef\]](#)
40. Baser, D.S.; Nadgouda, S.G.; Joshi, A.S.; Fan, L.S. 110th Anniversary: Indirect Partial Oxidation of Methane Using a Counter-Current Moving-Bed Chemical Looping Configuration for Enhanced Syngas Production. *Ind. Eng. Chem. Res.* **2019**, *58*, 16407–16416. [\[CrossRef\]](#)
41. Greish, A.A.; Glukhov, L.M.; Finashina, E.D.; Kustov, L.M.; Sung, J.S.; Choo, K.Y.; Kim, T.H. Oxidative Coupling of Methane in the Redox Cyclic Mode over the Catalysts on the Basis of CeO₂ and La₂O₃. *Mendeleev Commun.* **2010**, *20*, 28–30. [\[CrossRef\]](#)
42. Fleischer, V.; Littlewood, P.; Parishan, S.; Schomäcker, R. Chemical Looping as Reactor Concept for the Oxidative Coupling of Methane over a Na₂WO₄/Mn/SiO₂ Catalyst. *Chem. Eng. J.* **2016**, *306*, 646–654. [\[CrossRef\]](#)
43. Godini, H.R.; Xiao, S.; Jašo, S.; Stünkel, S.; Salerno, D.; Son, N.X.; Song, S.; Wozny, G. Techno-Economic Analysis of Integrating the Methane Oxidative Coupling and Methane Reforming Processes. *Fuel Process. Technol.* **2013**, *106*, 684–694. [\[CrossRef\]](#)
44. Baser, D.S.; Cheng, Z.; Fan, J.A.; Fan, L.S. Codoping Mg–Mn Based Oxygen Carrier with Lithium and Tungsten for Enhanced C₂ Yield in a Chemical Looping Oxidative Coupling of Methane System. *ACS Sustain. Chem. Eng.* **2021**, *9*, 2651–2660. [\[CrossRef\]](#)
45. Jiang, S.; Ding, W.; Zhao, K.; Huang, Z.; Wei, G.; Feng, Y.; Lv, Y.; He, F. Enhanced Chemical Looping Oxidative Coupling of Methane by Na-doped LaMnO₃ Redox Catalysts. *Fuel* **2021**, *299*, 120932. [\[CrossRef\]](#)
46. Stobbe, E.; De Boer, B.; Geus, J. The Reduction and Oxidation Behaviour of Manganese Oxides. *Catal. Today* **1999**, *47*, 161–167. [\[CrossRef\]](#)
47. Nauels, N. *Determination of Transport Properties of Asymmetric BSCF-Membranes and Testing of a Membrane Module for Air Separation*; Berichte aus der Verfahrenstechnik, Shaker: Aachen, Germany, 2018.
48. Matras, D.; Vamvakeros, A.; Jacques, S.D.M.; Grosjean, N.; Rollins, B.; Poulston, S.; Stenning, G.B.G.; Godini, H.R.; Drnec, J.; Cernik, R.J.; et al. Effect of Thermal Treatment on the Stability of Na–Mn–W/SiO₂ Catalyst for the Oxidative Coupling of Methane. *Faraday Discuss.* **2021**, *229*, 176–196. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Cruellas, A.; Heezius, J.; Spallina, V.; Van Sint Annaland, M.; Medrano, J.A.; Gallucci, F. Oxidative Coupling of Methane in Membrane Reactors; A Techno-Economic Assessment. *Processes* **2020**, *8*, 274. [\[CrossRef\]](#)
50. Damasceno, S.; Trindade, F.J.; Fonseca, F.C.; Florio, D.Z.D.; Ferlauto, A.S. Oxidative Coupling of Methane in Chemical Looping Design. *Fuel Process. Technol.* **2022**, *231*, 107255. [\[CrossRef\]](#)

51. Godini, H.R.; Azadi, M.; Penteado, A.; Khadivi, M.; Wozny, G.; Repke, J.U. A Multi-Perspectives Analysis of Methane Oxidative Coupling Process Based on Miniplant-Scale Experimental Data. *Chem. Eng. Res. Des.* **2019**, *151*, 56–69. [[CrossRef](#)]
52. Spallina, V.; Velarde, I.C.; Jimenez, J.A.M.; Godini, H.R.; Gallucci, F.; Van Sint Annaland, M. Techno-Economic Assessment of Different Routes for Olefins Production through the Oxidative Coupling of Methane (OCM): Advances in Benchmark Technologies. *Energy Convers. Manag.* **2017**, *154*, 244–261. [[CrossRef](#)]

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