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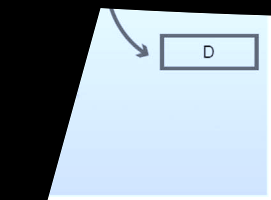

also be combined with a membrane reactor system. In conclusion, membrane reactors have the potential to play an important role in this context, although the coupling of reactions makes the systems even more complex and, moreover, thorough systems analysis is necessary in addition to existing materials issues.

Gas separation membranes feasible for such membrane reactors have been widely researched and come from all materials classes, i.e. polymers, metals, and ceramics. The nature of these materials leads to specific characteristics with respect to permeability, selectivity, and stability under certain process conditions, particularly temperature, pressure, and gas atmospheres including possibly corrosive impurities. This provides process engineers with the opportunity to choose membranes from a broad range of materials classes, for which, of course, detailed materials and process optimisation still remains to be done.

In this review, we concentrate on membrane reactor concepts using one selected type of membrane, i.e. ceramic ion-conducting gas separation membranes, because we observe huge interest in these membranes reflected in the number of publications in recent years. The major advantage of this type of membrane is the infinite selectivity towards the targeted gas due to the solid-state transport of the respective ions, here oxygen or hydrogen (i.e. protons). The driving force for the separation process is the chemical potential (i.e. partial pressure in a gas phase) gradient of the gas permeating across the membrane. The transport, i.e. diffusion, through the dense ceramic membrane layer is a thermally activated process requiring temperatures between 400 and 1000 °C [7–10]. At the high partial pressure side, the permeable ions form at catalytic surfaces, which is a multi-step process including ionisation, dissociation, and finally incorporation into the crystal lattice. The ions or the respective defects diffuse through the membrane layer and recombine at the low partial pressure side releasing the electrons again. Also the combination of oxygen ion and proton conduction in one material is possible (co-ionic conductor) and can be used for membrane reactors as well [11]. Purely ionic conductors transport only ions such as O^{2-} or H^{+} (or both). They have negligible electronic conductivity. Therefore, a voltage across the membrane is created. An external circuit is necessary in order to have a continuous ion flux. The most popular application for such a membrane is a solid oxide fuel cell or gas sensors. In reverse mode, also a voltage can be applied driving the ion flux through the membrane resulting in, for example, solid oxide electrolyser cells. The major advantage of this concept is the ability to tune the ion flux by the applied voltage, which is at the same time the major drawback due to the need for electrodes and electrical energy. Since this is a special class of membrane reactors widely investigated in the framework of Power-to-X technologies [12,13], it is not part of the scope of the present review. Here, we concentrate on mixed ionic-electronic conductors (MIECs). They have both ionic and electronic conductivity at the same time. The charge compensation takes place in the membrane. In this case, only heat and a gradient in the chemical potential of oxygen or hydrogen are needed.

To ensure a high flux through the membrane, several transport mechanisms have to be considered [14]. (i) Solid state diffusion through the dense membrane comprising bulk and grain boundary resistances is always reciprocally proportional to the membrane thickness. Therefore, the development of thin membrane layers is necessary, which for mechanical reasons need to be supported by thicker porous layers. In the case of very thin membrane layers, (ii) surface exchange kinetics become rate-limiting, comprising all steps according to ionisation and dissociation of the gas molecules as well as incorporation of the ionic species in the crystal lattice, Finally, (iii) concentration polarisation effects in the gas phase and particularly in the porous supports occur due to slow transport of the gas molecules through the pore network consisting of, for example, convection, molecular diffusion, and Knudsen diffusion depending on the support microstructure and the actual permeation rate. In conclusion, the resulting permeation rate strongly depends on material properties, microstructure, and process parameters.

The challenges involved in the development and operation of such membrane reactors are the harsh environments (high temperature and potentially reducing or corrosive atmospheres) requiring sufficient stability of the materials and reaction performance. Therefore, selective materials with long-term stability, including catalysts, must be developed in order to optimise energy and cost efficiency of the overall process. The quantitative description of the membrane reactor performance is very complex because many parameters can be used for evaluation particularly when a product mixture is desired, e.g. syngas. No uniform method has been established in the literature. Nevertheless, relevant parameters for rating membrane reactors are (i) selectivity (with respect to the desired product), (ii) conversion rate (of the educt), and (iii) yield. The selectivity quantifies how much desired product is formed in relation to all products including undesired by-products. The conversion rate corresponds to the relative amount of a reactant which has reacted, and the yield describes how much of a desired product is formed, which can be described as conversion times selectivity. Moreover, the faradaic efficiency is sometimes used, which describes the contingent of transported electrons participating in the reaction. This is particularly useful in current-assisted modes to rate the efficiency of a process and quantify the need for electrical power.

In the past few years, various review articles have been published about the use of membrane reactors, but they mostly concentrated on one particular topic (e.g. CO_2 utilisation) [3] or a single educt (e.g. CH_4) [15]. In this review, we give a broad overview of different processes, products, and materials reported for the selected class of ceramic ion-conducting membranes. Fig. 2 shows the membrane reactor

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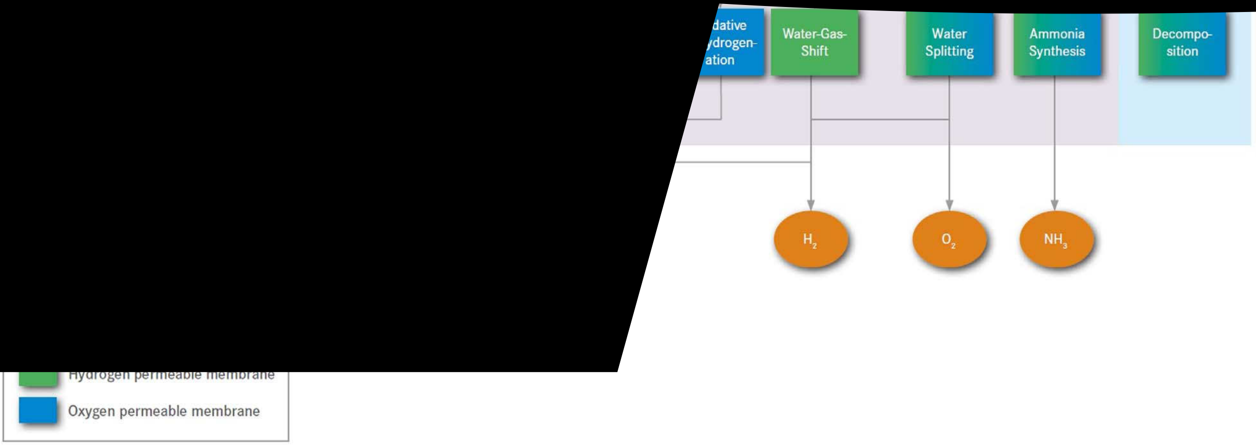

Fig. 2. Summary of selected processes where oxygen- and hydrogen-permeable membranes are applicable.

concepts reviewed. These concepts are described in detail in the following sections. The applications for the proton-conducting hydrogen transport membrane are shown in green, and the applications for oxygen transport membranes in blue. In addition, we provide an evaluation of the potential of each process from our current perspective. At this point it is not possible to assess certain processes with respect to their economic potential because most of the developments are still on a laboratory scale and need further improvement on the scientific and technological level.

2. Products

We decided to classify the various processes according to the desired products. Therefore, we chose a number of chemicals which can be synthesised in ionic-conducting ceramic membrane reactors [16–18] and we will focus mainly on the following:

- hydrogen
- syngas (mixture of H_2 and CO)
- higher hydrocarbons (C_{2+}-hydrocarbons, ethane, ethylene)
- methane
- ammonia

They represent a selection of the most common and important products for the chemical industry and will be examined in more detail in the following sections.

2.1. Hydrogen

Hydrogen is a promising future energy carrier and is already a very important raw material in the chemical industry, for example for the synthesis of ammonia and in the production of liquid fuels. It can be converted very efficiently into electricity in stationary and mobile fuel cell applications or directly combusted without harmful emissions in future designs of gas turbines. Hydrogen is one main component of power-to-gas concepts, storing fluctuating wind or solar power in a chemical form by generating a gaseous energy carrier mainly by electrolysis [19,20].

The classical method of hydrogen production is the reforming of methane or other hydrocarbons. During this process, hydrogen, CO_2 and CO have to be separated (water-gas shift reaction, autothermal reforming) to obtain a high-purity product, although this increases the complexity of the system and the costs. This classical method is mostly dependent on fossil fuels [21], which give rise to large amounts of CO_2 emissions. The simultaneous capture of CO_2 when using fossil fuels [22] could be one solution to reduce total emissions. However, there is a need for storage capacity and utilisation options for the future. The use of biogas as a raw material represents an attractive alternative in this context [23]. Suleman et al. [24] showed that hydrogen production from renewable sources has a much smaller impact on the environment than the use of fossil resources

Hydrogen can be produced through mixed-conducting ceramic membrane reactors by means of three reactions: water splitting, the water-gas shift reaction and autothermal reforming. The reactions, typical educts, membrane transport properties, temperatures, and formation enthalpies are summarised in Table 1. Due to the inherent ambipolar conduction of the membrane material, no input of electrical power is required. As the lattice diffusion of charged species is a thermally activated process, as already mentioned, transport across the membrane is suitably promoted at the reaction temperature.

For the generation of hydrogen in a ceramic membrane reactor, it is possible to use mixed oxygen ion-electron conductors as well as mixed proton-electron conductors. An advantage of dense ceramic hydrogen permeable membranes is their 100% selectivity for hydrogen. Further purification steps for subsequent processes can therefore be dispensed with. Suitable membrane materials with perovskitic and fluoritic structure can be found in [8–10,25,26]. Special attention has to be paid to their stability, particularly in acid conditions, i.e. CO_2 and H_2S. Although many perovskite materials suffer from carbonation, thermally and also chemically stable materials up to high temperatures of more than 1000 °C have been reported [25]. To further increase the stability and the performance of materials, dual-phase materials can also be used. Such materials can be cer-met or cer-cer, thus combining a purely ionic and a purely electronic conducting phase [26–29].

In the present review, we do not focus on current-assisted methods of hydrogen production (such as water electrolysis) although they offer interesting possibilities such as methane reforming or partial oxidation of hydrocarbons which are considered in [30]. For further alternative

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Hydrocarbons + H_2O + O_2	H^+ / e^- or O^{2-} / e^-

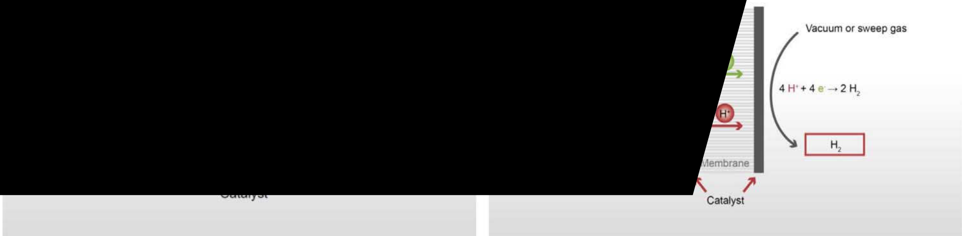

Fig. 3. Schematic of a membrane reactor for water splitting.

methods, the reader is referred to [31,32] or [33].

2.1.1. *Water splitting*

Water splitting represents an attractive pathway for generating hydrogen gas directly from water, which is a cheap and abundant source of hydrogen. However the dissociation of water is an endothermic reaction and the equilibrium constant to generate hydrogen is very low, leading to a high energy consumption of the reaction [16].

$$H_2O \leftrightarrows H_2 + \frac{1}{2}O_2 \tag{1}$$

There are two attractive configurations for the water-splitting reaction with ceramic membranes, which will be examined in more detail. With a mixed oxygen ion and electron conductor, the hydrogen is formed at the feed side and accumulates in the retentate, where it has to be separated from unreacted water. With a mixed proton- and electron-conducting membrane, hydrogen is transported from the feed side through the membrane and accumulates on the sweep side of the membrane. The hydrogen is either separated from the sweep gas or no further purification is needed if a vacuum is used. A schematic of both reaction configurations is shown in Fig. 3.

In recent years, there have been a few studies demonstrating the application of oxygen-permeable membranes for water splitting. [34] used a cermet composite membrane consisting of a Gd-doped CeO_2 (CGO) ion-conducting phase in combination with Ni, which ensured electronic conductivity. Additionally, a $SrFeCo_{0.5}O_x$ (SFC2) material was tested. In both cases, a porous layer of the corresponding membrane material was used as the catalyst. Both configurations showed promising hydrogen generation rates caused by water dissociation. 90 μm thick cermet membranes displayed a hydrogen formation rate of around 10 ml min^{-1} cm^{-2} and 1 mm thick SFC2 membranes showed formation rates of approximately 1 ml min^{-1} cm^{-2}.

In [35], a perovskite membrane consisting of $La_{0.3}Sr_{0.7}FeO_{3-\delta}$ was applied for water splitting without an additional catalytic layer. 3 mm thick membranes were used for the tests and a formation rate of 0.0145 ml min^{-1} cm^{-2} was achieved.

$BaFe_{0.5}Zr_{0.1}O_{3-\delta}$ (BFZ) and $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) were used as membranes in [36]. Both materials showed good hydrogen production rates at 900 °C (see Table 2). Polarisation effects limited the hydrogen production rate of the thin film LSCF tube.

Wang et al. indicated the potential of a cer-cer composite material consisting of $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) and $Gd_{0.08}Sr_{0.88}Ti_{0.95}Al_{0.05}O_{3\pm\delta}$ (GSTA) [37]. A variety of membrane thicknesses and different oxygen partial pressure gradients were tested. A higher steam content and an increased oxygen partial pressure gradient showed positive effects on hydrogen generation.

Franca et al. used a microtubular $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane reactor for water splitting at 900 °C. The permeating oxygen was simultaneously used to enhance the steam methane reforming on the other side of the membrane [38]. This application demonstrates the potential of water splitting not only in hydrogen generation but also for direct utilisation of the oxygen generated.

A BFZ tubular membrane for water splitting was tested by Park et al. [39]. A reactive sweep gas containing CO was channelled on the permeate side to enhance the partial pressure gradient and the oxygen flux and simultaneously to increase the hydrogen formation rate, which

Table 2
Selected examples of different membrane systems for hydrogen production via water splitting, using oxygen-permeable membranes.

Membrane material	Catalyst	Temperature [°C]	Formation rate of H_2 [ml min^{-1} cm^{-2}]	Reference
Gd-doped CeO_2 (CGO)/Ni	CGO/Ni	900	≈ 10	[34]
$SrFeCo_{0.5}O_x$ (SFC2)	SFC2	900	≈ 1 (d = 1 mm)	
$La_{0.3}Sr_{0.7}FeO_3$ (LSF)	No catalyst	860	0.0145 (d = 3 mm)	[35]
$BaFe_{0.5}Zr_{0.1}O_{3-\delta}$ (BFZ)	No catalyst	900	2.57 (d = 1.6 mm)	[36]
$La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)		900	15.4 (d = 30 μm)	
BFZ	No catalyst	900	3 (d = 1.05 mm)	[39]

[redacted]

partial oxidation of methane and reforming reactions (Sections 2.2.1 and 2.2.2). As feedstock, CO and water are used for the reaction forming H_2 and CO_2. The utilisation of biomass-derived syngas represents an environmentally friendly alternative to fossil raw materials [41].

The reaction is slightly exothermic with $\Delta H^\circ = -41.09$ kJ/mol [42]. The reaction kinetics of the WGS reaction were reviewed by [43].

$$CO + H_2O \leftrightarrows H_2 + CO_2 \tag{2}$$

The reaction is thermodynamically favoured at low temperatures and kinetically favoured at high temperatures. Therefore, on an industrial scale a two-step process is applied at the moment, a high-temperature shift up to 550 °C for fast but limited conversion followed by a low-temperature part at 200–250 °C in order to maximise conversion at a lower rate. It might be possible to reduce this to a single-step process by applying a ceramic membrane reactor at very high temperatures (approx. 900 °C). Continuous removal of hydrogen leads to a shift of the reaction to the hydrogen production side reducing the thermodynamic limitation and therefore increasing the efficiency. The extracted hydrogen has a high purity due to the theoretical 100% selectivity of the membrane for hydrogen.

A schematic of a WGS membrane reactor is given in Fig. 4.

For this reaction, only mixed proton-electron conducting membrane materials are suitable because the removal of hydrogen from the reaction zone increases the formation of hydrogen by pushing the reaction towards the hydrogen production side. Various hydrogen-permeable ceramics such as perovskites [44] or fluorites and also cermet composites [45] could therefore be used in WGS membrane reactors.

Different membrane configurations and materials, also including metal membranes, were reviewed by [46]. The authors identify some important fields which are not yet understood sufficiently, e.g. catalyst-

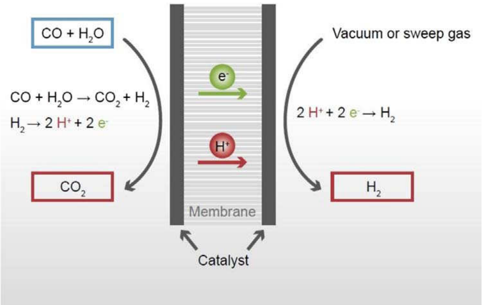

Fig. 4. Schematic of a water-gas shift membrane reactor.

Cl, KOH, NaCl and NaOH showing that $La_{5.5}WO_{12-\delta}$ was very under harsh conditions.-

order to implement the materials in a whole membrane reactor m, asymmetric membranes are a promising setup for combining hanical stability with reduced membrane thickness therefore ieving increased hydrogen permeability. However, the fabrication of ch systems is challenging as shown in [50,51].

Li et al. [52] report on the operation of a WGS membrane reactor with a tubular $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ perovskite membrane at 900 °C. The CO conversion reached up to 90% with a H_2O/CO feed ratio of 1/2. The total H_2 yield under these conditions was also 90%. About 10% of the hydrogen permeated through the membrane.

Recently, researchers have concentrated on the development of catalysts for industrial applications at up to around 550 °C. RePt/CeO_2–TiO_2 [53], Rh/La_2O_3 [54] Pt/apatite [55] Cu/ZnO/Al_2O_3 [56] and Cu/Ni/CeO_2-La_2O_3 [57] show good catalytic performance and demonstrate the great potential of further developments in this field. For use in the single-step process discussed here, catalysts are needed which operate at higher temperatures of about 900 °C.

Up to now, no performance data is available for water-gas shift membrane reactors. However, in the authors' opinion this is one of the most promising applications for proton-conducting membranes in the future.

2.2. *Syngas*

Syngas is a mixture of synthetically produced H_2 and CO. It is a very important intermediate product in the chemical industry and can be further processed into ammonia by the Haber-Bosch process or converted into synthetic fuels by Fischer-Tropsch synthesis. Hence, syngas is a step in the gas-to-liquids application to convert natural gas or coal to liquid fuels, which are usually produced from limited oil resources [58]. Depending on the final product, different ratios of H_2/CO are needed, for example 1/1 for the synthesis of dimethyl ether (DME), 2/1 for Fischer-Tropsch synthesis of liquid fuels, and 3/1 for further CO conversion for ammonia synthesis [59].

The use of ceramic membranes for the production of syngas has the advantage of high thermochemical stability of the materials, control of the oxygen supply, and reduced total oxidation and coke formation.

Syngas can be produced by partial oxidation, steam reforming, the reverse water-gas shift reaction, and dry reforming of methane. The main educts are various hydrocarbons, oxygen, water, and CO_2. Alternative feedstocks are solid materials such as coal or biomass [60] and coke oven gas [61]. The reactions need only thermal activation to run. Heat can be supplied by other chemical processes such as industrial waste heat or in a sustainable process by solar thermal energy [62]. There is no need for electrical power input. The reactions and some additional information are summarised in Table 3.

Conventional ways of producing syngas on an industrial scale are various steam reforming methods, in which usually methane and steam are converted in catalytic reactors. An overview of the processes and suitable catalysts is given in [59]. Most of the problems in the conventional process routes involve catalyst deactivation and the formation of coke [63]. Also combined fixed-bed and membrane processes are under investigation and indicate opportunities for cost reduction even for well-established large-scale production [64].

The reverse water-gas shift reaction, which is basically the back-reaction of the reaction shown in Section 2.1.2., will not be considered

[redacted]

even oxygen distribution and prevents the formation of hot spots and the total oxidation of methane to CO_2 and water. The ratio of H_2/CO obtained is around 2/1 and is significantly dependent on the CH_4/O_2 feed ratio [67]. A schematic of the membrane reactor is shown in Fig. 5.

$$CH_4 + \frac{1}{2}O_2 \leftrightarrows CO + 2H_2 \tag{3}$$

The most suitable membrane materials are perovskites with high oxygen ion and electronic conductivity [68]. However, also alternative concepts with cer-cer or cermet compounds can be used, as shown below. It is important to note that some perovskite materials display low stability in CO_2-containing atmospheres [69] and possibly need to be modified by using different doping elements [70]. Another problem which can occur during the reaction is the formation of soot, which was studied by Wei et al. [71] by performing numerical simulations. It was found that the oxygen/carbon ratio has a significant influence on the formation of solid carbon.

A large number of different studies report performance data of dense ceramic membrane reactors for the partial oxidation of methane. Almost all of the reactions were performed at high temperatures of 850–950 °C where methane conversion and selectivity for CO were usually very high.

Babakhani et al. [72] investigated a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Ni_{0.1}O_{3\text{-}\delta}$ membrane reactor at 850 °C with a Ni/Al_2O_3 catalyst and demonstrated methane conversion of 98% and a CO yield of 96%. To the best of our knowledge, this is the highest value reported at the lowest temperature.

Different groups performed partial oxidation at the slightly higher temperature of 875 °C [73–76]. All of them used Ni-based catalysts and the CO yields varied from 85% to 96%. Yang et al. [75] obtained the highest yield with a $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3\text{-}\delta}$ membrane packed with NiO/MgO catalyst.

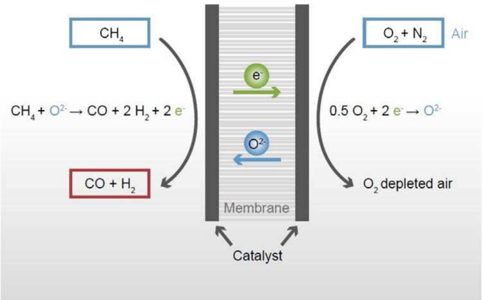

Fig. 5. Schematic of the working principle of partial oxidation of methane in a ceramic membrane reactor.

0 °C was the preferred reaction temperature applied by [77–82]
[83]. A CO yield of 96% was obtained by Wei et al. [83] with a
o$_{0.6}$Fe$_{0.2}$Ta$_{0.2}$O$_{3\text{-}\delta}$ membrane and Ni-based catalyst.

Cer-cer composite membranes were applied by [78,84–86] at tem-
ratures of 900 and 950 °C. Zhu et al. [85] again achieved a CO yield
96% with the $Ce_{0.85}Sm_{0.15}O_{1.925}$ - $Sm_{0.6}Sr_{0.4}FeO_{3\text{-}\delta}$ (SDC-SSF) com-
posite and LSC catalyst at 950 °C. However, the applied temperature was 100 °C higher than with the single-phase perovskite membrane reported above [72].

Partial oxidation of methane at a lower temperature using a composite Ag/CGO cermet membrane was reported by Ruiz-Trejo et al. [87]. The applied temperature was 700 °C and therefore the methane conversion was only 21%, which led to a CO yield of 19%. A selection of all relevant studies is listed in Table 4 for a better overview.

The development of new catalysts for partial oxidation of methane shows the potential of perovskite materials such as $La_{0.3}Sr_{0.7}Fe_{0.7}Cu_{0.2}Mo_{0.1}O_{3\text{-}\delta}$ [88] and $LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3\text{-}\delta}$ [89], which exhibit high CO selectivity. This opens up the possibility of developing and exploring a material which is suitable as both a membrane and catalyst. This may be a key to cost-efficient production because there would be no compatibility problems between the two components.

The first steps towards the industrial application of ceramic membrane reactors for syngas production were taken by Zhang et al. [90] showing the fabrication of $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3\text{-}\delta}$ tubes with a length of 560 mm in the sintered state. The authors state that the applied slip casting technique is suitable for large-scale production. Another approach was applied by Anderson et al. [91], in which a planar architecture of $La_{1-x}Ca_xFeO_{3\text{-}\delta}$ (LCF) membranes was first used for air separation and the supply of pure oxygen. 16 t_{O2}/day was produced with a test unit and experiments for partial oxidation of methane were also performed successfully.

Partial oxidation is one of the most promising applications for ceramic membrane reactors, which is reflected in the number of studies listed in Table 4. Due to the availability of high-flux membrane materials, it is at the moment the method which is the closest to industrial application.

2.2.2. *Autothermal reforming*

Steam reforming of methane is a commonly used way to produce syngas for several chemical applications. The feedstocks are not limited to hydrocarbons such as methane, but also include alcohols such as ethanol. By combining steam reforming with controlled oxidation, it is possible to control the heat balance of the reaction so that no external heat supply is needed to sustain the reaction (autothermal reforming) [93]. For steam reforming of methane, the H_2/CO product ratio is in the region of 3, as shown in the reaction equation, and the reaction is endothermic with $\Delta H^\circ = 210\ \text{kJ mol}^{-1}$ [94]. By applying the water-gas shift reaction to the product syngas, it is possible to convert the CO to H_2, which makes autothermal reforming also attractive for hydrogen production.

$$CH_4 + H_2O \leftrightarrows 3H_2 + CO \tag{4}$$

$$CH_4 + H_2O + \frac{1}{2}O_2 \leftrightarrows 3H_2 + CO_2 \tag{5}$$

[redacted]

[redacted]	[redacted]	[redacted]	0.98/0.98/0.96 (CO)	[85]
[redacted]	[redacted]	[redacted]	0.99/0.91/0.9 (CO)	[79]
[redacted]	[redacted]	900	0.99/0.95/0.94 (CO)	[80]
[redacted]	[redacted]	900	0.99/0.96/0.95 (CO)	[81]
[redacted]	[redacted]	900	0.9/0.97/0.87 (CO)	[82]
[redacted]	[redacted]	900	0.96/1/0.96 (CO)	[83]
[redacted]	[redacted]	875	0.92/1/0.91 (CO)	[73]
[redacted] (BSCFNiO)	[redacted]	850	0.98/0.975/0.96 (CO)	[72]
$Zr_{0.84}Y_{0.16}O_{1.92}$-$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (YSZ-LSCF)	Ru	950	0.9/-/-	[86]
$BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (BCFT)	Ni-based	875	0.96/0.99/0.95 (CO)	[74]
$BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN)	NiO/MgO	875	0.96/1/0.96 (CO)	[75]
$Ag/Ce_{0.9}Gd_{0.1}O_{2-x}$ (CGO)	Ni	700	0.21/0.92/0.19 (CO)	[87]
$Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN)	Ni	875	0.92/0.92/0.85 (CO)	[76]

$$C_2H_5OH + 2H_2O + \frac{1}{2}O_2 \leftrightarrows 5H_2 + 2CO_2 \tag{6}$$

There are two possible ways of using a membrane for autothermal reforming. The schematics of possible membrane reactor configurations are given in Fig. 6.

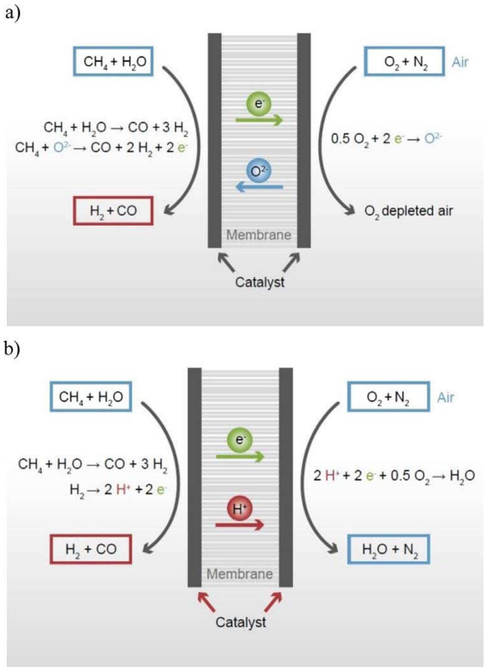

Fig. 6. Schematics of membrane reactors for autothermal reforming of methane with a mixed ion-electron conducting membrane a) and a mixed proton-electron conducting membrane b).

The first is a mixed oxygen ion and electron conductor where one part of the feed methane is "sacrificed" and reacts with oxygen in an exothermic reaction. The second possibility is the use of a mixed proton and electron conductor where part of the generated hydrogen is oxidised and used for thermal management of the system. By exactly adjusting the operating conditions, the reaction can theoretically be operated without an external heat supply.

In recent years, several research groups have reported on syngas and hydrogen generation via reforming reactions with the integration of a mixed ionic- and electronic-conducting membrane. [95,96] give an overview of reforming processes for syngas and hydrogen generation and also the use of biogas as an environmentally friendly and sustainable feedstock. In general, environmental aspects are very important in the field of hydrogen production as mostly fossil fuels such as methane are currently utilised. Another promising feedstock is coke oven gas, which is usually formed as a by-product in the treatment of coal for the steel industry [97,98]. Propane is also a conceivable alternative [99] as well as glycerol [100]. In this context, the development of recirculating and CO_2-capture technologies is important [101].

Another very attractive feedstock is ethanol, which can be easily stored and transported in a liquid state. On-site reforming for fuel cell application is possible and was discussed in [102,103]. Hung et al. [104] investigated the catalytic activity of different metals for the autothermal reforming of ethanol showing that, depending on which metal is used, different reaction pathways are possible. For the authors, Rh represented the catalyst with the best performance. Park et al. [105] performed ethanol reforming for the production of hydrogen using a dense $Ba_{0.5}Sr_{0.5}Cu_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite/Ag composite membrane and Rh as the catalyst. At 600 °C, 0.418 ml min^{-1} of hydrogen was produced using a 0.65 mm thick membrane. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was applied as a membrane material by Jin et al. [106], resulting in a yield of 3.5 mol_{H2}/mol_{EtOH}. The reaction was performed at 750 °C with a Ni/α-Al_2O_3 catalyst. $La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-\delta}$ was another membrane

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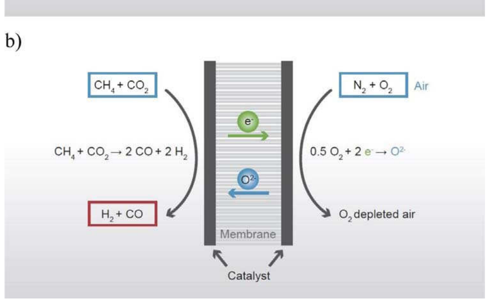

Fig. 7. Schematics of the two possible membrane configurations for dry reforming of methane.

but various alcohols such as ethanol [113], dimethyl ether (DME) [114], toluene [115], and also biomass [116] are suitable feedstocks.

The reaction can be run under autothermal conditions by the addition of oxygen via an oxygen-permeable membrane and no further external heat supply is needed. Spallina et al. [117] report the operation of a small-scale plant for the autothermal reforming of methane where a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membrane is used at 800 °C for the addition of oxygen. The total efficiency of the system is reported to be 74–78%.

To verify the high potential of the method, more research in this area is definitely needed in the future.

A selection of recent relevant studies is summarised in Table 5. For autothermal reforming there is no uniform evaluation of the performance data, so that different units are used in the literature to illustrate the formation rates of H_2.

2.2.3. *Dry reforming of methane*

Dry reforming of methane combines the partial oxidation of methane with the utilisation of CO_2 and therefore has the potential to contribute to a reduction of CO_2 emissions. The ratio of H_2/CO is 1 and therefore lower than with other methods for syngas production. The reaction is endothermic with $\Delta H^\circ = 260.5\ \mathrm{kJ\ mol^{-1}}$ [118].

$$CH_4 + CO_2 \leftrightarrows 2CO + 2H_2 \tag{7}$$

Schematics of the two possible membrane configurations are given in Fig. 7a and b.

There are two different working principles of a membrane reactor for the dry reforming of methane. In the first method, the methane/CO_2 mixture is fed in on one side of the membrane. Oxygen is added via the membrane by air separation. This method increases the catalyst activity. The second way of operating the membrane reactor is to add methane and CO_2 on the two different sides of the membrane. Here a decomposition of CO_2 to CO and O^{2-} takes place [119] and the oxygen is transported to the methane side of the membrane to perform a partial oxidation reaction.

As only the oxygen supply is important in the dry reforming of methane, mixed oxygen ion- and electron-conducting materials can be utilised for the construction of membrane reactors.

Several studies showed that the first reaction principle where oxygen is added in small amounts to a methane/CO_2 mixture has the benefit of increasing the catalyst activity. This was demonstrated by [120–122] using a $Pt/CeZrO_2$ catalyst. This means that the membrane has only an indirect influence on the reaction as the optimal amount of oxygen is below 1% [120]. Kathiraser et al. [123] fabricated $La_{0.6}Sr_{0.4}Co_{0.8}Ga_{0.2}O_{3-\delta}$ (LSCG) hollow-fibre membranes to perform dry reforming of methane and achieved a methane conversion of 93% with a CO yield of 86% using a $Ni/LaAlO_3-Al_2O_3$ catalyst at 725 °C. A slightly higher temperature of 800 °C was applied by Yang et al. [124] for the reaction using a $La_{0.6}Sr_{0.4}Co_{0.8}Ni_{0.2}O_{3-\delta}$ (LSCN) hollow-fibre membrane and a similar Ni/Al_2O_3 catalyst. In this case, the conversion of methane was around 100% and the CO yield reached 99%. It was also shown that the reaction on the feed side of the membrane was supported by the permeating oxygen.

Membrane reactors with CO_2 as the oxygen source were investigated by [125,126]. Therefore methane and CO_2 had to be fed in on different sides of the membrane. To achieve dissociation of CO_2 the reaction temperature was higher than for the previously described reaction configuration, ranging in particular from 900 °C to more than

Table 5
Summary of different membrane systems for hydrogen production via reforming reactions, using both oxygen- and hydrogen-permeable membranes.

Membrane material	Catalyst	Temperature [°C]	Formation rate	Reference
$La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)	No catalyst	700	$1.2\ \mathrm{ml\ min^{-1}}\ H_2$ (d = 22 μm)	[107]
$Ba_{0.5}Sr_{0.5}Cu_{0.2}Fe_{0.8}O_{3-\delta}$ (BSCF)/Ag	Rh	600	$0.418\ \mathrm{ml\ min^{-1}}\ H_2$ (d = 0.65 mm)	[105]
$SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$	Ni	900	$4.0\ \mathrm{ml\ cm^{-2}\ min^{-1}}\ H_2$ (d = 33 μm)	[108]
$BaFe_{0.9}Zr_{0.1}O_{3-\delta}$ (BFZ)	No catalyst	600	$0.96\ \mathrm{ml\ min^{-1}}\ H_2$	[39]
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	Ni/Al_2O_3	750	$3.5\ mol_{H2}/mol_{EtOH}$	[106]
$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{2.9}$ (BZCY)	Ni-BZCY	650	$Y_{H2} = 77\%$	[109]

[redacted]

The future perspectives for dry reforming are very good because it can directly contribute to achieving CO_2 reduction plans in the next few years. Nevertheless, at the moment only a few studies including membrane reactors have been published, as can be seen in Table 6.

2.3. Higher hydrocarbons

The term higher hydrocarbons (also called C_{2+} hydrocarbons or C_2 hydrocarbons in the literature) describes molecules with chains of two or more carbon atoms (for example alkanes, olefins, and aromatics), which are important intermediate products in the chemical industry. Higher hydrocarbons can be further processed to liquid fuels or used as basic chemicals, e.g. for polymer synthesis [133].

It is possible to convert methane into higher hydrocarbons via Fischer-Tropsch synthesis, but a direct conversion route without the intermediate syngas production step would be beneficial [134]. However, at the moment there is still no direct conversion method which can compete with Fischer-Tropsch synthesis [133]. The main products of the direct conversion are ethane and ethylene [15]. The synthesis of aromatic compounds is also very attractive.

Membrane processes are in general very promising for use in the petrochemical industry, especially for energy-efficient separation tasks [135]. Both mixed oxygen ion and electron as well as proton and electron conductors can be used in ceramic membrane reactors. Catalysts can reduce reaction temperatures (e.g. 800 °C for direct conversion of methane) [133].

The synthesis of higher hydrocarbons via mixed-conducting ceramic membranes can be performed by the coupling of methane,

Table 6
Summary of different membrane systems for the synthesis of syngas via dry reforming reactions, using oxygen-permeable membranes.

Membrane material	Catalyst	Temperature [°C]	Conversion/ selectivity/ yield	Reference
$La_{0.6}Sr_{0.4}Co_{0.8}Ga_{0.2}O_{3\delta}$ (LSCG)	Ni/ $LaAlO_3$-Al_2O_3	725	0.93/0.93/ 0.86 (CO)	[123]
$La_{0.6}Sr_{0.4}Co_{0.8}Ni_{0.2}O_{3-\delta}$ (LSCN)	Ni/ Al_2O_3	800	1/0.99/0.99 (CO)	[124]
Nb_2O_5-doped $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFNb)	Pd/Ni	900	0.84/0.97/ 0.81 (CO)	[125]
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)	No catalyst	1030	0.17/-/-	[126]

s a very energy-intensive approach.

ere are also other possible products which are not covered here, ample dimethyl ether (DME) [140–144].

1. Methane coupling

The coupling of methane to higher hydrocarbons is a very attractive y to directly transform methane (CH_4) into more valuable chemicals ch as ethane (C_2H_6) and ethylene (C_2H_4).

There are several possible reaction pathways, which can be roughly divided into oxidative and non-oxidative reactions. In the non-oxidative reactions, hydrogen is removed by a hydrogen-permeable membrane and the product is formed at the feed side of the membrane (Fig. 8a). In the oxidative reactions, the membrane serves as a distributor for oxygen, which can be utilised from air separation on the other side of the membrane (Fig. 8b).

$$2CH_4 + \frac{1}{2}O_2 \leftrightarrows C_2H_6 + H_2O \tag{8}$$

$$2CH_4 + O_2 \leftrightarrows C_2H_4 + 2H_2O \tag{9}$$

$$2CH_4 \leftrightarrows C_2H_6 + H_2 \tag{10}$$

$$2CH_4 \leftrightarrows C_2H_4 + 2H_2 \tag{11}$$

Several studies were undertaken in the 1990s on the non-oxidative coupling of methane with hydrogen-permeable membranes, also using electrochemical cells with an externally applied current. In recent years, only the oxidative case, where oxygen-permeable membranes are used, has been studied by a number of researchers. The non-oxidative coupling of methane can be performed with proton-conducting membrane materials. In terms of efficiency, the oxidative pathway is more beneficial because the reaction is exothermic and the generated heat can be used to sustain the reaction.

Chiang et al. [145] used a $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ perovskite material (SCY) with Ag electrodes and studied the methane consumption and the formation of ethane and ethylene at 750 °C. At an applied current of less than 3 mA, the selectivity for C_2 compounds was almost 100%. At a higher current, CH_4 consumption, and also the formation of CO_2, strongly increased. The same group of researchers also showed that the application of an oxygen-ion conductor such as YSZ enhanced CH_4 consumption electrochemically even though the O^{2-} charge carriers were not involved in the overall reaction [146]. Further research was performed by Chiang et al. [147], who proposed the replacement of a conventional catalyst by electrochemical cells.

Woldman et al. [148] also used an SCY membrane for methane coupling experiments. The membrane consisted of an LSM spinel, but the observed methane conversion and production of ethane and ethylene was very low. Another interesting application in the field of methane sensors was proposed by the same authors.

Langguth et al. [149] applied $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ (SCYb) as the membrane material and used silver as the electrode material. The C_2 yield was increased by applying an external current. The highest potential for improvements was found to be the electrodes and the manufacturing of thin SCYb films.

In [150], the non-oxidative conversion of methane was investigated theoretically by kinetic transport simulations. The removal of hydrogen from the reaction zone was found to be a key point in increasing the methane conversion and obtaining high yields (more than 90%) of higher hydrocarbons.

O2 (for oxidative reaction pathway)	H^+ / e^- or O^{2-} / e^- or H^+ / O^{2-} / e^-

[redacted]

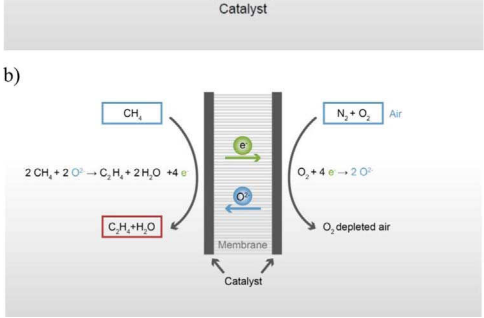

Fig. 8. Schematic of the oxidative coupling of methane with a mixed proton-electron conducting membrane a) and a mixed ion-electron conducting membrane b).

Liu et al. [151] put this principle into operation and used a mixed proton- and electron-conducting SCYb membrane where hydrogen could be removed from the reaction side thus forming water on the permeate side of the membrane. At 950 °C, a methane conversion of 58% and a C_2 yield of 13.4% were obtained.

Oxidative coupling of methane is achieved by the controlled addition of oxygen with a mixed oxygen ion- and electron-conducting membrane. Basic studies showed that it is very important to adjust several parameters such as the flow rate of methane and the oxygen flux to match the reaction rate. The products of the reaction are in general more reactive than the methane itself, which represents an additional obstacle [152,153].

The preferred membrane materials for oxidative coupling of methane are different perovskites represented by Ba-based compounds and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF).

[154–157] used different Ba-, Co- and Fe-containing perovskite membranes at temperatures of 800 – 1000 °C. The best performance was obtained with dense $Ba_{0.5}Ce_{0.4}Gd_{0.1}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCGCF) and a catalyst consisting of Na-W-Mn/SiO_2. At 850 °C, the methane conversion was 52% and the C_2 yield was 35% [154].

LSCF membrane reactors developed by Othman et al. [158] showed similar performance, achieving a methane conversion of 48% and a C_2 yield of 38% while a catalyst made from $Bi_{1.5}Y_{0.2}Sm_{0.2}O_{3-\delta}$ was applied at 900 °C. Other groups also used LSCF for their membranes, but their performance was significantly lower as shown in Table 8 [159,160].

There have been considerable activities in the development of new catalysts for oxidative coupling of methane in the past few years. Nevertheless, catalyst development is still far from commercial application and various obstacles have to be overcome. Especially the

nation of CO_2 and solid carbon seems to be the main challenge for rmodynamics [161–169].

A different reactor concept was proposed by Caravaca et al. [170]. he authors discussed a combination of solid electrolyte and fixed-bed eactor. They used YSZ for the membrane and applied Ag electrodes for external power input. The methane coupling reactions took place at the methane feed side of the membrane while on the other side of the membrane water splitting was performed to supply the oxygen through the membrane. Additionally, hydrogen was obtained as a secondary product. At 800 °C, a methane conversion of 23% and a C_2 yield of 14% were obtained using a Ce-Na_2WO_4/SiO_2 catalyst. Penteado et al. [171] used CO_2, which is a by-product of the oxidative coupling of methane, and proposed a membrane-based separation of CO_2 from the product gas.

The use of membrane reactor systems for methane-coupling reactions is summarised in Table 8. It is a promising method because it is possible to upgrade methane directly to more valuable chemicals instead of simply combusting it. The number of studies dealing with the topic shows the importance, but a great deal of research is still required to increase the product yields at feasible temperatures.

2.3.2. *Alkane dehydrogenation to olefins*

Dehydrogenation reactions make it possible to upgrade different chemical compounds such as alkanes. The most common reaction is the oxidative dehydrogenation of ethane to ethylene (ODHE). Ethylene is an important raw material for the chemical industry, e.g. in the synthesis of polymers.

By the controlled addition of oxygen, ethane is oxidised to ethylene while water is formed as a by-product. The reaction is exothermic with $\Delta H^\circ = -105$ kJ mol-1 [172]. Typical reaction temperatures are in the range of 750 – 850 °C

$$C_2H_6 + \frac{1}{2}O_2 \leftrightarrows C_2H_4 + H_2O \tag{12}$$

Fig. 9 presents a schematic of the reaction in a membrane reactor where ethane is the feedstock on the reaction side of the membrane. Oxygen is supplied by simultaneous air separation on the other side of the membrane.

An alternative method of non-oxidative dehydrogenation of ethane and simultaneously removing hydrogen from the reaction zone is also possible, but was not the major focus of the researchers. Hasany et al. [173] performed simulations in this context and showed that removing the hydrogen can shift the reaction equilibrium to the ethylene side and therefore improve the yield of ethylene.

Mixed oxygen ion and electron conductors, such as the well-known perovskites, are the preferred type of membranes considered in the present review.

Rodríguez et al. [174] compared a conventional liquid-cooled tubular reactor and a membrane reactor for the ODHE reaction. The result indicated that using a membrane reactor has benefits for heat generation along the membrane because of the controlled oxygen distribution.

For ODHE with mixed oxygen ion and electron conducting membranes, several studies have been performed in recent years in which all

[redacted]

[redacted]	[redacted]	[redacted]	–	[147]
[redacted]	[redacted]	[redacted]	0.58/0.23/0.13 (C_2)	[151]
[redacted]	[redacted]	[redacted]	-/0.62/- (C_2)	[149]
[redacted]	[redacted]	[redacted]	0.5/0.4/0.2 (C_2)	[159]
[redacted]	[redacted]	[redacted]	0.52/0.68/0.35 (C_{2+})	[154]
[redacted]	[redacted]	[redacted]	0.32/0.57/0.18 (C_2)	[155]
[redacted]	[redacted]	[redacted]	0.34/0.5/0.17 (C_2)	[156]
[redacted] (YSZ)	[redacted]	[redacted]	0.23/0.61/0.14 (C_2)	[170]
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)	$Bi_{1.5}Y_{0.2}Sm_{0.2}O_{3-\delta}$ (BYS)	900	0.22/0.68/0.15 (C_{2+})	[160]
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)	$Bi_{1.5}Y_{0.2}Sm_{0.2}O_{3-\delta}$ (BYS)	900	0.48/0.8/0.38 (C_{2+})	[158]

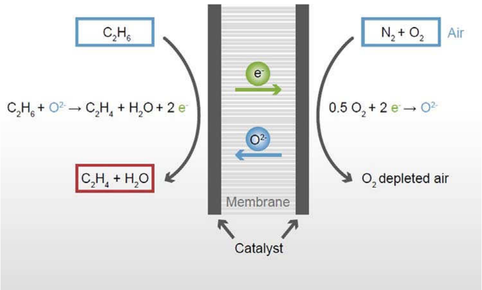

Fig. 9. Schematic of the oxidative dehydrogenation of ethane with a mixed ion-electron conducting membrane.

the researchers used perovskite materials either from BSCF [175–179] or from BCFZ [180–182]. In general, two different temperature levels were tested, below and above 800 °C. At 775 °C, the highest ethylene yield of 75% was achieved by [175,176] using BSCF and a Pd catalyst. At 850 °C, the highest ethylene yield was 83% with a selectivity of 93% [178]. In this study, again BSCF was used as the membrane material and $Ce_{0.8}Tb_{0.2}O_{2-\delta}$ as the catalyst. All relevant studies and the reported performance of the membrane reactors are summarised in Table 9.

An alternative reactor concept applying porous ceramic membranes is proposed by Shelepova et al. [183]. The authors carried out a simulation study to implement a hydrogen-permeable membrane for propane dehydrogenation. However, dense hydrogen-permeable ceramic membranes could also be utilised for this application.

Hamel et al. [184] discussed the possibility of using porous ceramic or metal membranes to distribute the reactants in a controlled manner into the catalytic zone of the reactor. Adjustment of the mass flow parameters and back diffusion of the reactants were the main issues in this study.

Propane is an alternative reactant for dehydrogenation reactions and is investigated in [185] in combination with a Pd metal membrane. The selectivity for propylene was highest in a temperature range of 450 – 550 °C, which in principle could also be covered by ceramic membranes.

Dehydrogenation is also very attractive because it implies an

Table 9
Summary of different membrane systems for the synthesis of olefins via dehydrogenation, using oxygen-permeable membranes.

Membrane material	Catalyst	Temperature [°C]	Conversion/selectivity/yield	Reference
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	V/MgO Pd	775 775	0.9/0.83/0.75 (C_2H_4) 0.88/0.85/0.75 (C_2H_4)	[175]
$BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ)	No catalyst	800	0.62/0.63/0.39 (C_2H_4)	[180]
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}$ $O_{3-\delta}$(BSCF)	V/MgO Pd	775 775	0.91/0.8/0.73 (C_2H_4) 0.87/0.86/0.75 (C_2H_4)	[176]
$BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ)	Cr_2O_3	725	0.89/0.58/0.52 (C_2H_4)	[181]
$BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ)	No catalyst	800	0.63/0.64/0.4 (C_2H_4)	[182]
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	No catalyst	850	0.9/0.85/0.76 (C_2H_4)	[177]
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	$Ce_{0.8}Tb_{0.2}O_{2-\delta}$	850	0.89/0.93/0.83 (C_2H_4)	[178]
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)	BSCF	850	0.92/0.88/0.81 (C_2H_4)	[179]

[redacted]

electron conducting membrane a) and a mixed proton-electron conducting membrane b).

upgrading of the educt, which leads to an added value without the need for intermediate products. An appreciable number of studies is already available as shown in Table 9.

2.3.3. Methane dehydroaromatisation

Methane dehydroaromatisation is a method for directly converting methane into more valuable aromatic compounds such as benzene. There are two reaction pathways which are suitable for ceramic membrane reactors. The first is the oxidative reaction path where oxygen is added as a second reactant and aromatics and water are formed. The second path is the non-oxidative reaction where hydrogen is formed as a secondary product. In Fig. 10, a schematic of possible membrane reactor configurations is shown.

$$6CH_4 + \frac{9}{2}O_2 \leftrightarrows C_6H_6 + 9H_2O \tag{13}$$

$$6CH_4 \leftrightarrows C_6H_6 + 9H_2 \tag{14}$$

The oxidative reaction path can be performed with a mixed oxygen ion-electron conductor while a mixed proton- and electron-conducting membrane material is used for the non-oxidative reaction.

Perovskite-type BSCF oxygen permeation membranes were used by [186] to perform methane dehydroaromatisation. It was shown that the membrane reactor supressed the formation of coke compared to a fixed-bed configuration. Also the methane conversion and aromatics yield were increased. Similar results were obtained in [187].

An effective method for increasing the conversion of methane is the continuous removal of hydrogen from the reaction zone [188].

The mixed proton- and electron-conducting $La_{5.5}W_{0.6}Mo_{0.4}O_{11.25-\delta}$ material was applied in a hollow-fibre membrane reactor by Xue et al. [189] to demonstrate the performance for the production of aromatics. Mo/HZSM-5 was the catalyst for the reaction and a methane conversion

[redacted]

romising new catalyst, Fe/SiO$_2$, was reported by [192] and
ed a maximum methane conversion of 48.1% and a benzene
vity of 21.5%, also over a comparatively long time of 60 h.

lorejudo et al. [11] demonstrated the formation of aromatic
pounds by using a co-ionic conducting BCZY72 membrane in
bination with a Mo/H-MCM-22 catalyst and an externally applied
rrent. The ability of the membrane material to transport both protons
d oxygen ions (in opposite directions) at an operating temperature of
10 °C was very beneficial for the performance of the system. Proton transport led to the removal of hydrogen at the reaction side of the membrane. Oxygen transport led to steam formation on the reaction side, which supressed the formation of coke and helped to keep the aromatics yield constant over a longer period of time. The conversion of methane was 11% with an aromatics yield of 10%.

In Table 10, a list of relevant studies for methane dehydroaromatisation is presented. The possibility of directly converting methane into aromatic compounds seems to be very attractive but the yields are very low at the moment. This is probably the greatest drawback of the method so far and further development is needed to increase the yield.

2.4. Methane

Methane is the major component of natural gas and at the moment one of the most important energy carriers. A well-established distribution network exists in many countries worldwide where methane is used to generate heat and electric power. Methane is also used as a feedstock for a large number of chemical applications. One example is the production of high-purity hydrogen for ammonia synthesis. An important application in the future will be the utilisation of CO_2 and surplus wind energy to produce methane as a chemical energy carrier [193].

Methane can be produced using mixed-conducting ceramic membranes by the methanation of CO_2. The main educts are CO_2 and hydrogen, which should originate from renewable sources such as water and biomass. An alternative feedstock is coke oven gas. It is possible to generate the required hydrogen by applying an external power supply to the membrane.

Reactors for catalytical methanation using biomass as a feedstock are mostly operated with a fixed catalyst bed and temperatures around 400 °C [194].

A very important point in the production of synthetic methane is the utilisation of CO_2, which can play an important role in reducing total CO_2 emissions from various chemical processes. Besides methane, there are other possible products which can be formed from CO_2 and H_2. A review of this topic is given by Saeidi et al. in [142].

Table 10
Summary of different membrane systems for the synthesis of higher hydrocarbons via methane dehydroaromatisation, using both oxygen- and hydrogen-permeable membranes.

Membrane material	Catalyst	Temperature [°C]	Conversion/selectivity/yield	Reference
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$(BSCF)	Mo/HZSM – 5	750	0.13/0.45/0.06 (aromatics)	[186]
$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ (BZCY)	Mo/zeolite	710	0.11/0.94/0.1 (aromatics)	[11]
$La_{5.5}W_{0.6}Mo_{0.4}O_{11.25-\delta}$	Mo/HZSM – 5	700	0.13/0.4/0.05 (aromatics)	[189]

[redacted]

The study by [200] is the only one to use a proton-conducting membrane made from $BaZr_{0.85}Y_{0.15}O_{3-\delta}$ + 1 wt% NiO to produce methane at 300–450 °C. CO_2 and hydrogen were fed in simultaneously on the reaction side of the membrane. Methane production was electrochemically enhanced by pumping protons out of the reaction zone and the selectivity for methane was increased to more than 60%.

In recent years, research has focused on catalyst development. Promising candidates are in particular Ru-based catalysts as shown in [66,201,202], in addition to Ni-based catalysts [201,203,204]. Also copper [205] and bimetallic Co-Fe catalysts [206] have recently been investigated.

The hydrogenation of CO_2 with a dense ceramic membrane reactor can also be interesting for products other than methane, e.g. C_2H_6O as shown by Ruiz et al. [207] at 400 °C. Oxygen-conducting YSZ was used as the membrane and Fe as the catalyst to achieve a rather low CO_2 conversion of 6% with selectivity for C_2H_6O of 50%. However, research in this direction is still at an early stage and progress can be expected in the future.

2.5. Ammonia

Ammonia is one of the most widely produced chemicals in the world. It is predominantly used as an intermediate product in fertiliser production. Other applications are pharmaceuticals and coolants. Ammonia is also a potential hydrogen storage medium as it contains three hydrogen atoms per molecule [208]. Ammonia storage is easier compared to the storage of hydrogen. It can be liquefied at pressures of a few bar [209]. The distribution of ammonia is in principle possible with the corresponding infrastructure. Additionally, it can be used as a cooling medium on board vehicles [210].

Ammonia can be utilised as a fuel in solid oxide fuel cells for stationary applications or as an auxiliary power unit. The main advantage is that it does not contain carbon and can therefore be operated CO_2-

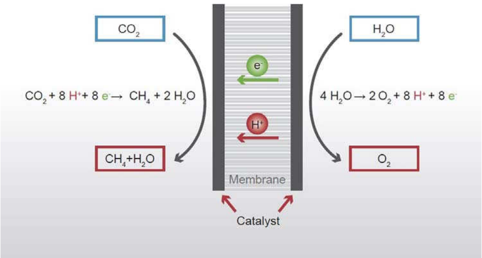

Fig. 11. Schematic of a membrane reactor for CO_2 hydrogenation.

use of membrane reactors makes it possible to reduce the re- pressure to ambient conditions. A number of review articles have ly dealt with this topic and more detailed information can be d there [209,214,215]. Calculations for the utilisation of mem- ne reactors showed that the overall energy consumption can be re- ced by 20% compared to the classical Haber-Bosch process [216]. is would be a huge improvement considering that worldwide annual mmonia production is around 200 million tonnes [209].

The production of ammonia with mixed-conducting ceramic membranes can be performed by electrochemical ammonia synthesis. The main educts are N_2 and H_2 where hydrogen can also be formed by water splitting at the membrane. The use of polymer membranes, e.g. Nafion, is also a promising alternative but will not be considered further in this review.

Electrochemical ammonia synthesis is a method of producing ammonia without high pressure at moderate temperatures of about 500 °C. Pure proton or oxygen ion conductors and an external power supply are needed to perform an electrochemical ammonia synthesis [217]. Hence, it is possible to store renewable energy from wind or solar power plants. Suitable membrane materials are various perovskites such as barium cerates and fluorites such as cerium oxide which display high proton conductivity. Apart from the pure ionic conducting ceramics, mixed ionic-electronic ceramic materials or even dual phase cermet or cer-cer materials might be of interest for future exploration in ammonia synthesis. At the moment, no studies are available covering this field and only the current-assisted process is specified.

A schematic of electrochemical ammonia synthesis is given in Fig. 12.

The first reports on electrochemical ammonia synthesis can be found in [218,219]. The membrane material was $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ perovskite with Pd electrodes. The experiments were performed at 570 °C where an ammonia formation rate of 5×10^{-9} mol s^{-1} was achieved.

In subsequent years, a number of researchers used many other proton-conducting membrane materials for electrochemical ammonia synthesis. The best performance in terms of ammonia formation rate was obtained by Li et al. [220] where $BaCe_{0.80}Gd_{0.10}Sm_{0.10}O_{3-\delta}$ (BCGS) was used as the membrane material and Ag/Pd for the electrodes. At 620 °C, the ammonia formation rate was 5.82×10^{-9} mol s^{-1} cm^{-2}.

The use of an oxygen-permeable ceramic membrane for ammonia synthesis has the advantage that wet nitrogen [221,222] or even wet air [223] can be directly utilised for the reaction. The concept behind this is to use water as a hydrogen source. In principle, at the cathode side a

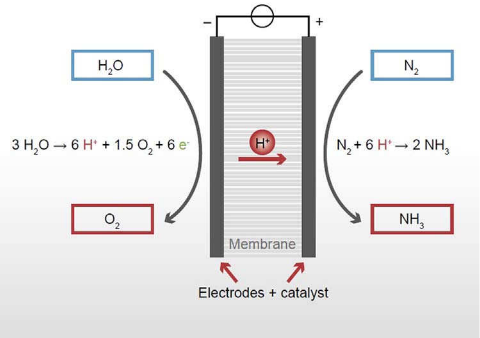

Fig. 12. Schematic of the working principle of electrochemical ammonia synthesis.

[redacted]

application could be, for example, the construction of small-scale ammonia plants. The replacement of existing large-scale facilities will be very difficult due to the high investment costs.

2.6. Coupling of reactions

One of the most attractive benefits of membrane reactors is the ability to couple different reactions and to profit from specific synergy effects. Some examples have already been given in previous sections (e.g. water splitting to provide hydrogen for ammonia synthesis). The most widely used synergy between two reactions is thermal coupling. In this case, an exothermic and an endothermic reaction are coupled and the need for an external heat supply is reduced or completely dispensed with. Heat transfer is an important issue in this case [228]. The second kind of synergy that can be used in membrane reactors is the supply of a specific reactant via the membrane which is directly produced on the other side of the membrane. The third kind of synergy is represented by the co-synthesis of different products.

Thermal coupling of two reactions can be implemented in a system for partial oxidation of methane and simultaneous thermal decomposition of CO_2 as shown by Jin et al. [229] and Zhang et al. [230]. In this case, the exothermal partial oxidation provides the heat which is directly used to decompose CO_2. Another method of thermal coupling is discussed by Kniep et al. [231] where steam reforming of methane was performed and one part of the emerging hydrogen was separated by a hydrogen-permeable membrane and combusted to provide heat for the reaction.

The combination of water splitting with other reactions can be used to provide either oxygen or hydrogen, depending on what kind of membrane is used. The case of oxygen was studied by Zhu et al. [232] by coupling water splitting with an oxidative steam-reforming reaction. Jiang et al. [233] used the oxygen obtained for the dehydrogenation of ethane. In principle, hydrogen could also be obtained as a by-product from both systems. In the case of hydrogen as a reactant, the coupling of dehydrogenation and hydrogenation seems to be most attractive. The principle was demonstrated by [234,235]. However, in these studies fixed-bed reactors were used.

The co-production of different hydrocarbons and hydrogen was presented in several studies by Kyriakou et al. [236–238] using proton-conducting membranes.

In general, the coupling of different reactions by using membrane reactors offers a wide range of synergetic possibilities and can define new fields for increasing energy efficiency and discovering niches for future commercial application.

ite membranes increased N_2O conversion from 25% to almost
by removing the oxygen arising. Even coupling with other re-
s consuming oxygen, such as the oxidative dehydrogenation of
e, is possible as shown in [239]. Research on the development of
lysts is important for this kind of reaction and was performed by
solakis et al. [240] to develop $CuO\text{-}CeO_2$ catalysts by different
thesis routes. However, more research is needed to develop opera-
onal systems for the removal of nitrogen oxides.

Another application is the decomposition of H_2S, which can also serve as a feedstock for hydrogen production assuming that it occurs in sufficient amounts. Ipsakis et al. [241] and Kraia et al. [242] demonstrated the production of hydrogen from H_2S originating from the Black Sea. Proton-conducting $BaZr_{0.85}Y_{0.15}O_{3-\delta}$ membranes have thus been successfully implemented.

4. Conclusions and outlook

After more than twenty years of research on high-temperature ceramic membrane reactors [243] there is still considerable interest in this technology although it is not yet been implemented in any industrial application. Significant progress has been made, for example, on syngas production [91,244], but some issues still remain, for instance, in materials stability, scalability, and joining and sealing of membrane components in modules. Nevertheless, interest has increased again in recent years due to the high efficiency and resulting energy savings potential of membrane reactor technology as indicated by the large number of scientific articles listed in this review article. Nowadays, the utilisation of CO_2 and (waste) heat and the coupling of different reactions are very attractive characteristics of these systems. Hydrogen can be used either as a basic chemical or an energy carrier. Water splitting, the water-gas shift reaction, and autothermal reforming are all promising processes for hydrogen production, but all of them still require further improvement in terms of hydrogen flux through the membrane and specially designed catalysts. Higher hydrocarbons such as ethylene are important feedstocks for the chemical industry. A direct synthesis route to produce ethylene via methane coupling would be very beneficial in terms of energy efficiency and would create great added value, but cannot compete with classical large-scale methods at the moment, because the development is still at an initial stage and costs and reliability are not optimal. The greatest advantage of dehydrogenation and methane dehydroaromatisation with ceramic membrane reactors is the reduction of coke formation, which is a serious problem due to catalyst deactivation. Syngas is one major intermediate product in the synthesis of various chemical compounds such as liquid fuels or in the Haber-Bosch process for ammonia production. At the moment, partial oxidation is the most advanced process for ceramic membrane reactors because oxygen-permeable membranes with high flux and sufficient stability have already been developed. Catalyst selection is comparatively easy because Ni metal is a very good candidate. The next steps towards industrialisation are now related to manufacturing and upscaling. Methanation of CO_2 combines two important goals: the utilisation of CO_2 and energy storage. The process can represent an alternative to energy storage via water electrolysis and has the advantage that existing distribution networks for natural gas could be used. Ammonia synthesis is one of the most important and also one of the oldest industrial processes. For this reason, it is already very well developed and optimised. Most ammonia production plants operate on a very large scale. Nevertheless, electrochemical ammonia synthesis has

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shown in this review article, a great deal of progress has been made in materials research, including joining and sealing technology, so that the authors have a positive outlook with regard to this technology. Nevertheless, significant efforts (and time) will need to be devoted to this topic.

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