Catalysis Today 142 (2009) 34–41

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Oxidative coupling of methane using catalyst modified dense perovskite membrane reactors

Louis Olivier, Stéphane Haag, Claude Mirodatos, Andre C. van Veen *

Institut de Recherches sur la Catalyse et l'Environnement de LYON, UMR 5256 (CNRS - Université Claude Bernard Lyon 1), 2 avenue Albert Einstein, 69626 Villeurbanne Cédex, France

ARTICLE INFO

Article history:
Available online 13 February 2009

Keywords:
Dense membrane
BSCFO perovskite
Lanthanum oxide
Strontium oxide
Productivity

ABSTRACT

A comparative study modifying an ionic oxygen conducting membrane reactor for the oxidative coupling of methane to higher hydrocarbons with 3 different catalytic surface modifications is presented. Dense $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) membrane disks were wash-coated with a Pt/MgO model catalyst as well as with more efficient Sr/La_2O_3 and LaSr/CaO catalysts. The role of the catalyst is underlined by the fact that the LaSr/CaO shows that highest yield between 900 and 1000 °C while yields decline for the Sr/La_2O_3 catalyst at temperatures above 900 °C. The latter observation agrees well with observations on conventional catalytic reactors using hydrocarbon/oxygen co-feeding at lower temperature and seems to relate to the formation of highly reactive oxygen species formed at the La_2O_3 surface. Operating a LaSr/CaO modified membrane reactor at 950 °C with a CH_4 concentration of 34%, a C_2-hydrocarbon yield of more than 18% was achieved (at a selectivity of more than 65%). Given the interesting performance, it is obvious that future membrane reactors should employ efficient catalyst systems and development should focus on maximizing the exposure of catalytically modified membrane surfaces.

1. Introduction

The valorization of natural gas is a domain of permanent research but nowadays renewed interest emerged for routes, which were practically abandoned in this area, due to the recent high oil prices. Abundant resources of natural gas available at still reasonable prices and foreseeable future shortage of petroleum have reactivated research on the oxidative coupling of methane (OCM) yielding ethane and ethylene, as value-added and easy to liquefy products. Nevertheless, operating conditions are difficult to optimize because C_2 products (C_2H_4 and C_2H_6) are more reactive than the reactant (CH_4) [1]. Typically, the higher the methane conversion, the lower the C_2 selectivity is. In previous literature studies assuming lower oil prices it has been estimated that a single-pass conversion of 35–37% and selectivity of 88–85%, equivalent to a C_2 yield of $>$30%, is required to attain commercial competitiveness for OCM [2]. In fact, results obtained are still far away from this expectation while the limit of the C_2 yield in a fixed bed reactor is found to be around 25% [3,4]. Despite extensive research efforts in the past, investigated process concepts considered mainly fixed bed reactors. Thus, alternative reactor concepts with inherent need for adapted catalysts have to be explored and eventually invented. One of the most promising design solutions could be catalytic membrane reactors allowing a cost cutting use of air instead of oxygen. Possibly these devices allow even higher productivity as flammability issues for reactant mixtures close to combustion stoichiometry could be avoided by the distributed oxygen supply.

Inorganic membranes for gas separation can be divided in two classes: porous and dense membranes. Porous membranes exhibit high permeability combined with relatively low selectivity. On the other hand, dense membranes show much better selectivity, however, at lower permeability than porous membranes. Within the category of dense membranes, ionic oxygen conducting membranes (IOCM) offer the unique advantage to provide activated oxygen at its surface while preventing hydrocarbon losses to the trans-membrane side.

First published works [5] in the domain of OCM used either porous membranes combined with catalysts in form of a centered fixed bed [6,7] or dense membranes without catalysts. In the former case, the porous membrane was used only as a gaseous oxygen distributor along the catalyst bed, without significant yield improvement. In the latter case, all attempts suffered from comparably low productivity [2,8–13]. Previous work in our group dedicated to oxidative dehydrogenation of ethane (ODHE) [14] indicated the interest to use an IOCM membrane feeding directly a layered catalyst on top of the membrane without passing oxygen via the gas-phase.

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* Corresponding author. Present address: Ruhr-University Bochum, Universitätsstraße 150, D-44801 Bochum, Germany. Tel.: +49 234 32 24217; fax: +49 234 32 14182.
E-mail address: andre.vanveen@rub.de (A.C. van Veen).

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doi:10.1016/j.cattod.2009.01.009

Mixed-conducting oxide membranes such as perovskite based systems are well known for their abilities to separate oxygen from air due to mobile oxygen defects in their lattice being only susceptible for oxygen transportation [15–21]. The performance of dense membranes can be affected by many structural factors such as grain size, e.g. altered by sintering conditions, membrane thickness and microstructure or bulk density. Furthermore, the temperature at which those membranes are operating, the chemical potential gradient of oxygen and different membrane compositions can cause over magnitudes different oxygen permeation fluxes [15].

Among dense perovskite membranes, $Ba(Co,Fe)O_{3-\delta}$ based perovskites such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ or $Ba(Co,Fe,Zr)O_{3-\delta}$ exhibit stable oxygen fluxes at high temperatures, in the presence of an air/He gradient of the oxygen chemical potential [22,23] and during a membrane reactor based partial oxidation of methane (POM) [24,25] or ODHE [14]. Shao et al. [26] studied the influence of the barium content in $BaSrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and showed that the addition of barium results in higher oxygen permeability and lower activation energy for oxygen transportation at high temperature.

In this study, three kinds of catalysts modifying the BSCFO membrane were used to study their influence in terms of permeation properties (oxygen supply rates for the OCM reaction) and catalytic performance at given temperatures. The different oxygen permeability was previously identified as important feature altering the OCM performance. Furthermore, the way to prepare wash-coated catalysts impacts on the stability of the catalytic layer and has herewith crucial importance for the reactor performance. It should be noted that the studied catalysts were comprising a Pt/MgO model system, but also efficient systems for the OCM reaction such as Sr/La_2O_3 and LaSr/CaO.

2. Experimental

2.1. Membrane materials

Membrane reactor experiments employed 1 mm thick dense $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) disks prepared by sintering pressed powder samples according to the densification procedure described previously [27]. Briefly, the perovskite synthesis proceeded by the so-called citrates method using citric acid and EDTA as complex formation agents [22] to dissolve the barium nitrate. Citric acid was added in 1:1 molar ratio with respect to the sum of metal ions. The resulting powder was calcined in air at 900 °C for 4 h and ball milled in iso-propanol suspension for achieving a smaller grain size, which improves the material properties of the final disks in terms of bulk density and mechanical stability. Then, the membrane was prepared by isostatic pressing of green disks with a pressure of 220 MPa applied for 2 min to the powder. Approximately 0.5 g of perovskite powder yielded a black colored, 1 mm thick, 15 mm-diameter disk. Densification of the disk was achieved by sintering in air for 8 h at 1160 °C with a heating and cooling ramp of 2 °C/min. The final diameter of the disk was decreased to 13 mm by shrinkage during sintering.

2.2. Membrane characterization

As in the previous work [27], formation of perovskite structure was checked by X-ray diffraction (not shown), using a Bruker D5005 system in the 2θ range 3–80°, a step width of 0.02° and a counting time of 1 s and Cu $K_{\alpha1+\alpha2}$ radiation (1.54184 Å). The microstructure of the membranes was observed by scanning electron microscopy (not shown).

2.3. Membrane surface modification

In a previous work [14], parameters for a model describing the oxygen permeation through the BSCFO membrane were determined and the modeling study underlined the importance of surface exchange processes for oxygen permeation. The impact of both, the perovskite membrane material and the catalyst coating, on the oxygen permeability was demonstrated in a recent work [27]. Results suggested wash-coating of catalysts as more promising approach for the high temperature OCM than a previously explored sol–gel approach, which is leading to only incomplete membrane coverage. Thus, the present study focusing on the impact of different catalysts modifying the membrane employed only wash-coating. For reference purpose the non-optimized but temperature stable Pt/MgO was included in the present study. Two other catalyst formulations were chosen according to their promising performances in fixed-bed high-throughput screening [28] assisting in a more global context the development of new catalytic membrane reactors for the OCM reaction.

Wash-coating of BSCFO membranes involved the deposition of a catalyst-containing suspension on one surface. The suspension was based on an aqueous slurry of the catalyst powder using additionally two organic agents. Tylose® (Clariant) acts as binding agent, has a role to adjust the viscosity of suspension and improves initial adhesion on the membrane surface prior to calcination. Acetic acid impacts on the dispersion of the particles and on the spreading behavior of suspensions on the surface of membrane. Catalyst and Tylose® powders were first dry-mixed and the mixture was added to a continuously stirred aqueous solution of acetic acid maintained at 40 °C for several minutes. The slurry was kept stirring at ambient temperature in a closed beaker to avoid water loss by evaporation during three days. Aging is required to obtain a homogeneous suspension. One droplet of suspension was spread on the surface of the membrane and following membrane drying for 2 h in nitrogen atmosphere at 120 °C calcination proceeded for 6 h in air at 900 °C.

In the case of the Pt/MgO model system, MgO was wash-coated on the membrane surface and Pt was added by impregnation, using tetraammine platinum(II) nitrate as metal precursor (Sigma–Aldrich). The estimated loading of Pt was about 2% on the MgO support. The deposition of LaSr/CaO and Sr/La_2O_3 catalysts involved first the preparation of the entire catalyst phase by co-precipitation and then a preparation of suspensions from obtained catalyst powders. The nominal composition of the LaSr/CaO system was 10 wt% La, 20 wt% Sr on CaO and 12.5 wt% Sr on La_2O_3 for the case of the Sr/La_2O_3 catalyst.

2.4. Oxygen permeability

Information on oxygen permeability, key property of mixed conducting membranes, was acquired in the temperature range of 800–1000 °C. An O_2/N_2 mixture presenting reconstituted air was fed to the oxygen-rich membrane compartment, while helium was used as a sweep gas on the permeate side. The about 1 mm thick membrane disk was sealed with gold rings in between two dense alumina tubes (outer diameter: 12 mm, inner diameter: 8 mm) by heating to 900 °C for 48 h. The total pressure at the oxygen-rich side was adjusted to 1.1 bar and investigations used a constant total flow rate of the mixed O_2 and N_2 streams controlled by mass flow controllers. Gas chromatography (HP 5890 Series II, 13X packed column) allowed complete analysis of gases at both sides of the membrane.

2.5. Catalytic membrane reactor testing

The experimental device for catalytic tests was detailed in previous work [27]. The air feed supplied the mixed conducting membrane with oxygen allowing the dense perovskite membrane to provide activated oxygen for the OCM. Mass flow controllers adjusted the flow rates of helium used as carrier gas and methane on the reactant side. Two gas chromatographs (TCDs) were used to analyze all gases. The CH_4/He mixture flow rate was fixed to 85 mL min^{-1} and the reconstituted air flow rate was set to 100 mL min^{-1}. The methane concentration in the reactant flow was varied between 10 and 34%. The experiments were conducted in a temperature range of 800–1000 °C for obtaining a highly efficient OCM reaction and for the fact that high selectivity was only observed at such high temperatures.

3. Results and discussion

3.1. Wash-coating of the membrane surface

Making use of a direct supply of ionic oxygen from the membrane to the catalyst, adhesion and well interfacing of the catalyst is crucial for the catalytic performance. Having abandoned sol–gel coating approaches due to insufficient results obtained in a previous study [27], we concentrated our efforts on the wash-coating of catalysts. The considered metal oxide based catalysts have very good thermal stability and the only deterioration of coating occurred during calcination when cracks appeared in the catalyst layer, even detaching it partially. The problem was tracked down to a too high layer thickness and brittle coatings could be avoided depositing thinner layers at the expense of lower specific catalyst loadings. The optimization task consists of finding a compromise between mechanical resistance towards thermal dilatation or shrinkage of layers and availability of sufficient catalyst. The amount of catalyst deposited on the membrane was varied using syringes with different needle diameter and altering the catalyst content in the suspension. The optimal quantity of deposited material on the membrane surface of approximately 0.5 cm^2 was found between 5 and 10 mg, depending on the catalyst. The resulting layer thickness is well below half a millimeter. Details on the approximate maximum catalyst masses for those catalysts used in the present work are reported in Table 1. The gain in weight after deposition of the catalyst was about ∼7.2, ∼5.8 and ∼8.6 mg for the Pt/MgO, LaSr/CaO and Sr/La_2O_3 catalysts, respectively. However, despite well elaborated results, further enhancements in terms of increasing the specific catalyst loading of the membranes remain possible when the slurry preparation could be improved. For example, the particle size of catalyst impacts strongly on the suspension properties and satisfying results were currently achieved with a particle size distribution centered around 80 μm for the three selected catalysts. Referring to coating micro-structured devices [29], however, the particle size seems rather high and improvement could be possible achieving smaller catalyst gain sizes in the slurry prior to its deposition. It is therefore expectable that the exact maximum amount of each catalyst could still be increased, depending on the nature of catalyst and other optimization of the organic additives.

3.2. Oxygen permeability for bare and catalyst modified membranes

Given the importance of oxygen permeability demonstrated in a recent work [27], Fig. 1 reports oxygen permeability data for reference membranes (bare and wash-coated Pt/MgO) and those modified with the efficient OCM catalysts Sr/La_2O_3 and LaSr/CaO. It comes clear that the catalytic membrane modification leads for some materials to enhanced permeability reaching for the case of Pt/MgO and LaSr/CaO almost doubled values as compared to a bare membrane. Interestingly, a modification with Sr/La_2O_3 is not beneficial and the permeability is even slightly lower that observed for the bare membrane. The latter observation might be related to two explications: First, the porous wash-coated catalyst layer might be an obstacle to the oxygen permeation as the mobility of oxygen is surely lower in the catalyst layer than that in the perovskite membrane material. Second, La is known to adsorb a multitude of oxygen species [30–33] potentially leading to a more difficult oxygen release and/or stronger re-adsorption of oxygen onto the membrane surface.

In order to obtain a hint which of the two above explanations is more probable, permeation data was subject of an analysis using the Arrhenius plots depicted in Fig. 2. First, it is obvious that the highest slope corresponding to an activation energy of 79 kJ mol^{-1} at low temperature and 47 kJ mol^{-1} at high temperature, respectively, is observed for the bare membrane. The switch over temperature is for the bare $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane at around 725 °C. Catalytic modification leads to lower activation energies for the oxygen permeation process, especially at lower

Table 1
O_2 permeation data for bare and surface-modified BSCFO membranes.

	Inlet air flow/sccm	Inlet He flow/sccm	*T*/°C	Mass of catalyst/mg	$J(O_2)$	
					mL/cm^2 min	mol/cm^2 s
BSCFO	50	100	700	0	0.44	3.27×10^{-7}
			750	0	0.78	5.8×10^{-7}
			800	0	1.09	8.11×10^{-7}
			850	0	1.37	1.02×10^{-6}
			900	0	1.70	1.26×10^{-6}
LaSr/CaO	50	100	800	5.8	2.13	1.59×10^{-6}
			850	5.8	2.56	1.9×10^{-6}
			900	5.8	3.16	2.35×10^{-6}
			950	5.8	4.30	3.2×10^{-6}
			1000	5.8	5.52	4.1×10^{-6}
Pt/MgO	50	100	800	7.2	1.47	1.09×10^{-6}
			850	7.2	2.20	1.64×10^{-6}
			900	7.2	2.84	2.11×10^{-6}
			950	7.2	3.35	2.49×10^{-6}
			1000	7.2	3.81	2.83×10^{-6}
Sr/La_2O_3	106	100	800	8.6	0.72	5.38×10^{-7}
			850	8.6	1.14	8.48×10^{-7}
			900	8.6	1.57	1.17×10^{-6}
			950	8.6	2.00	1.46×10^{-6}
			1000	8.6	2.64	1.97×10^{-6}

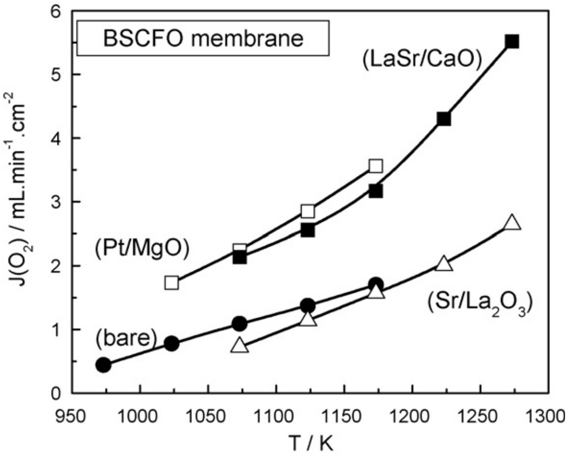

Fig. 1. Oxygen permeation through BSCFO bare and BSCFO based modified membranes (gradient established between reconstituted air: 50 mL min^{-1}/He: 100 mL min^{-1}).

temperature where higher values are observed. In the case of the Pt/MgO model catalyst activation energies decrease by 10 kJ mol^{-1}, keeping however the behavior that the activation energy is split into a domain with a higher value at low temperature and one with a lower value at high temperature. Here the temperature at which the change between the permeation domains happens is shifted up to approximately 850 °C. The latter change in the activation barrier was previously reported for the bare BSCFO membrane and related membranes with different catalyst coating [14]. According to literature reports [14,27] permeation of the oxygen through BSCFO is limited by surface steps at $T < 725$ °C and for $T > 725$ °C diffusion through the bulk becomes the rate limiting step. The change assigned to a switch in the rate limiting step from oxygen surface release at lower temperature to ionic oxygen bulk migration at higher temperature is in good agreement with the fact that it occurs at higher temperature for the Pt/MgO modified sample obviously allowing for a stronger interaction with oxygen.

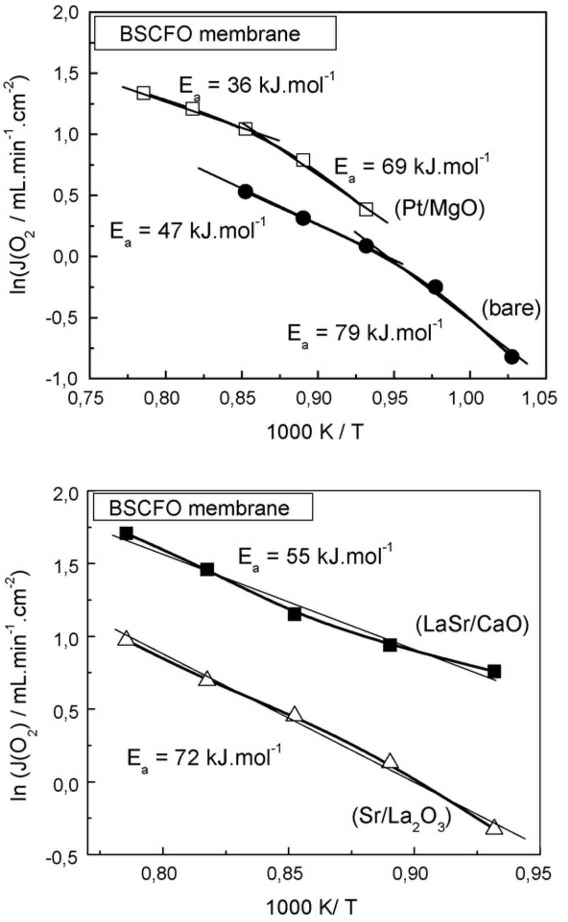

Fig. 2. Arrhenius plots and estimation of activation energy for BSCFO-based membranes for the oxygen permeation applying an air/helium gradient.

As mentioned above and indicated in previous work [14], the rate limiting step may change according to the temperature range investigated. However, for the case of the catalyst formulations LaSr/CaO and Sr/La_2O_3 it is hard to establish different domains and only one global activation energy was estimated in the investigated temperature range, amounting to 55 and 72 kJ mol^{-1} for LaSr/CaO and Sr/La_2O_3, respectively. The identical reactor configuration and use of the same perovskite material implies that the nature of the catalyst impacts on the surface release of oxygen. The missing switch in activation energies makes it highly probable that the membranes operated in the whole temperature range in a regime limited by the oxygen release from the catalyst and the comparably high activation energies suggest that the transfer of ionic oxygen in the catalyst phase itself is the rate limiting step.

In order of facilitate the comparison of results, permeability data of the four tested membranes are presented in Table 1. In fact it comes clear that the Sr/La_2O_3 modified membrane exhibits the lowest permeability. This is noteworthy as this sample had the most catalyst wash-coated and it seems reasonable that rather large exchange surfaces were developed from the porous catalyst layer. However, the high activation energy of permeation seems clearly to penalize the oxygen separation performance of this membrane.

3.3. Comparison of the catalytic performances in the OCM

The performance of the different membrane reactors in terms of methane conversion and selectivity towards C_2-hydrocarbons are given in Fig. 3. The concentration of methane entering the reaction compartment was fixed to 10%. The performance of the reactor with Pt/MgO model catalyst reported in the previous work [27] was left out for the sake of clearness. It comes clear that the presence of a catalyst is highly beneficial in terms of activity as well as in terms of selectivity. While conversion and selectivity remain well below 10% for the reactor with bare $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane, conversions reach 30% and 25% for the reactors with LaSr/CaO and Sr/La_2O_3 catalyst, respectively. C_2-hydrocarbon selectivity exceeds 60% and 40% for reactors with LaSr/CaO and Sr/La_2O_3 catalyst, respectively. More in detail, however, the C_2-hydrocarbon selectivity pass a maximum at a temperature of about 950 °C, possibly due to a starting decomposition of higher hydrocarbons at very high temperature. Another striking feature distinguishing the two membrane reactors with coated OCM catalysts is the selectivity at lower temperature. While the Sr/La_2O_3 catalyst leads to no significant selectivity at 800 °C, the LaSr/CaO coating allows achieving a minimum selectivity of 40% under comparable conditions. It should also be noted that the selectivity for the Sr/La_2O_3 modified system remains at 800 °C even lower than that of the reactor with bare membrane. The most obvious explanation for this observation is linked to the oxygen permeation behavior outlined above. It is coherent that the Sr/La_2O_3 catalyst identified as system with less efficient oxygen release posses at its surface an elevated density of oxygen species, possibly not as selective as the isolated O^- or O_2^- required for activating methane to methyl radicals, further coupled in the gas phase [34,35]. This might be in line with the principle of site isolation for selective

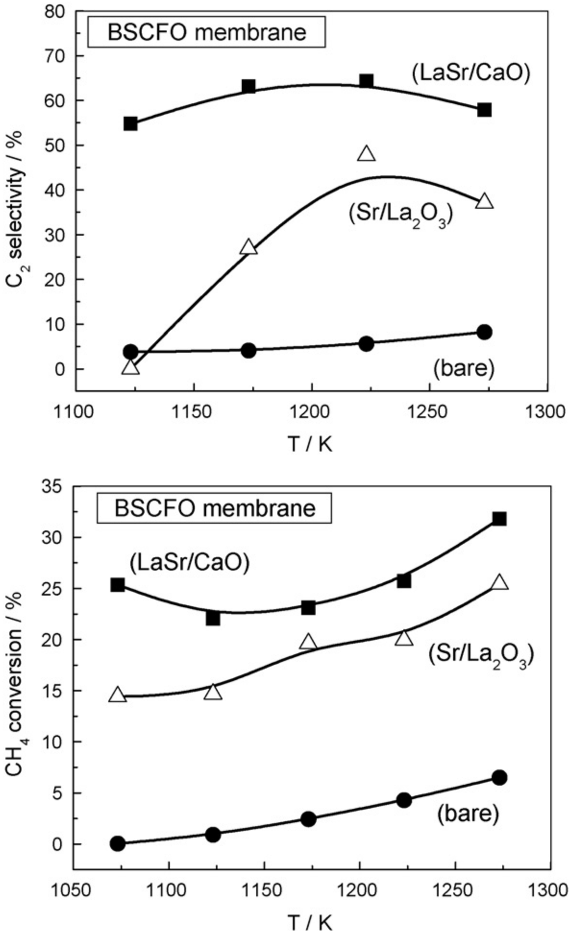

Fig. 3. Comparison of C_2 selectivity and CH_4 conversion for BSCFO based membranes at low CH_4 concentration in the reactant feed (CH_4 concentration: 10%/reactant flow rate: 85 mL min^{-1}).

oxidation of hydrocarbons [36,37]. Obviously, future work will be required for a definite decision on which property of catalyst impacts most on selectivity at the applied severe conditions.

In order to summarize on the performances of all 4 tested membrane reactors as a function of temperature, Fig. 4 reports the C_2-hydrocarbon yield. Obviously, the best performance with a yield of 18.4% at the highest temperature of 1000 °C is obtained for the LaSr/CaO modified BSCFO membrane. On the other hand, the bare BSCFO membrane shows the poorest performance with a yield not exceeding 0.5%. The Pt/MgO and Sr/La_2O_3 modified membranes display intermediate performance, with however the characteristic that Pt/MgO performs slightly better at low temperature, while Sr/La_2O_3 is superior at high temperature. It is important to remind that the poor performance of the Sr/La_2O_3 system at low temperature relates to missing selectivity at low temperature, while previous work [14] and results summarized in Table 2 indicate that the Pt/MgO catalyst lacks activity for better performance.

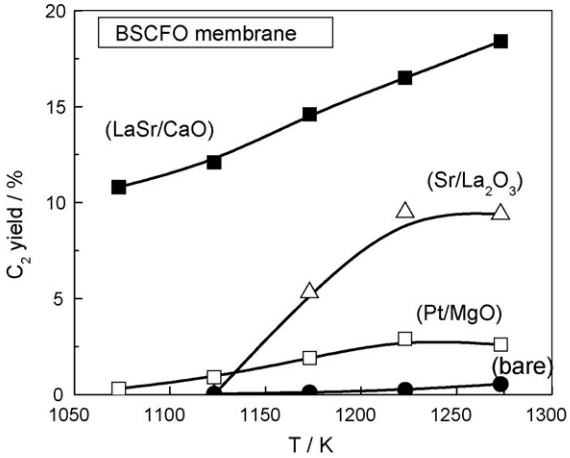

Fig. 4. C_2-hydrocarbon yield of the BSCFO bare and BSCFO-based and modified membranes (CH_4 concentration: 10%/reactant flow rate: 85 mL min^{-1}).

3.4. Impact of the CH_4 concentration on catalytic performances in the OCM

The key role of radical reactions in gas-phase [34,35] was already mentioned and motivated studying the impact of the CH_4 gas-phase concentration in view that higher concentrations were expected to enhance radical reactions. The work was carried out over the best performing LaSr/CaO modified BSCFO membrane varying the CH_4 concentration from 10% to 34% at a constant reactant flow rate of reactant flow rate of 85 mL min^{-1}. Results are depicted in Fig. 5 giving the C_2 hydrocarbon yield as a function of the methane concentration in the feed for temperatures in the range of 1073–1223 K. Indeed, C_2-hydrocarbon yields rise generally with increasing CH_4 concentration. It is worth noting however that the comparable poor performance for a CH_4 concentration of 19% at 1223 K seems exceptional and it is currently not entirely understood. This general improvement with rising methane concentration is especially visible when focusing on the C_2-hydrocarbon productivity data given in Table 2. Productivities clearly rise with increasing CH_4 partial pressure and the order of CH_4 seems in the current reactor configuration almost close to unity. However, acquiring more detailed kinetic information remains a challenging task beyond the scope of the current work. The main obstacle for a simple kinetic analysis lays in the strong coupling of the oxygen supply rates by permeation and the catalytic performance of the coated catalyst. Another reason relates to the geometry of the high temperature membrane reactor were some drawbacks originate form the disk shape of the membrane, i.e. complicated hydrodynamics of the reactor having dead volumes close to the outer alumina tube. Thus, some impact of the mass transfer from the bulk of the gas-phase to the membrane surface could hide the full intrinsic activity of the catalyst. Nevertheless, the specific mode of oxygen supply only via the membrane prevents at least the usual penalty of decreased selectivity given that oxygen is only available at the catalyst surface itself.

Table 2 reports on another important feature concerning the catalytic performance, namely the ratio between ethane and ethylene formed. Obviously, this ratio should be as low as possible given that ethylene is a more valuable product and ethane would need to be dehydrogenated in a separate unit. Generally, the ratio of ethane to ethylene declines favorably with rising temperature as this tendency would be expected considering a dehydrogenation of ethane to ethylene. However, this observation should not be over-interpreted as the availability of oxygen crossing the membrane rises also with temperature and additional oxygen could assist in an oxidative dehydrogenation as well. More in detail, it is noteworthy that the ratio of ethane to ethylene is systematically higher for the case of the Pt/MgO catalyst than that is the case for the oxide based catalyst systems Sr/La_2O_3 and LaSr/CaO, with the latter even being slightly more favorable.

Another interesting feature comparing the performance of the LaSr/CaO modified BSCFO membrane as a function of the CH_4 concentration in the reactant is the declining ratio of ethane to

Table 2
Catalytic performances of BSCFO-based membranes for the OCM.

Membrane	Inlet air flow/sccm	Inlet He flow/sccm	CH_4/% reactant	Catalyst mass/mg	T/°C	S_2/%	X_{CH_4}/%	Y_2/%	C_2H_6/C_2H_4	S_{COx}/%	$P_{C2}/10^{-5} mol\ s^{-1}\ g^{-1}$
BSCFO bare	100	85	10	0.0	850	4	1	0	N/A	96	N/A
					900	4	2	0	N/A	96	N/A
					950	6	4	0	N/A	94	N/A
					1000	8	7	1	N/A	92	N/A
LaSr/CaO on BSCFO	106	83	11	5.8	800	43	25	11	N/A	57	1.2
					850	55	22	12	N/A	45	1.3
					900	63	23	15	2.5	37	1.5
					950	64	26	17	1.0	36	1.8
					1000	58	32	18	0.4	42	2.0
LaSr/CaO on BSCFO	106	87	19	5.8	800	49	23	11	N/A	51	0.2
					850	54	24	13	N/A	46	0.4
					900	65	24	16	2.0	35	1.1
					950	61	26	16	0.7	39	2.5
					1000	50	27	13	0.3	50	3.1
LaSr/CaO on BSCFO	106	87	34	5.8	800	51	25	13	N/A	49	0.2
					850	67	24	16	5.0	33	0.7
					900	70	25	18	1.8	30	1.8
					950	66	28	18	0.7	34	3.5
					1000	53	30	16	0.2	47	4.6
Pt/MgO on BSCFO	106	83	53	7.2	800	40	1	0	18	60	0.0
					850	50	2	1	7.2	50	0.1
					900	57	3	2	3.9	43	0.2
					950	58	5	3	2.2	42	0.2
					1000	50	5	3	1.2	50	0.2
Sr/La_2O_3 on BSCFO	106	79	11	8.6	800	–	14	–	N/A	N/A	0.0
					850	0	15	0	N/A	100	0.0
					900	27	20	5	>0	73	0.4
					950	48	20	10	1.5	52	0.7
					1000	37	25	9	0.8	63	0.6

ethylene with rising CH_4 content. Obviously, increasing the CH_4 concentration is highly beneficial, both in terms of the productivity of the membrane reactor as well as in terms of the resulting product distribution. Considering an explanation for the favorable impact of higher methane concentrations two possibilities could be advanced. First, the rising partial pressure of produced C_2-hydrocarbons could lead to a stronger readsorption of ethane allowing its dehydrogenation on the catalyst surface. In this context, it should also be outlined that the strongly differing membrane reactor performances as a function of the catalytic modification or its absence prove that the OCM reaction in the given reactor configuration relates to heterogeneous catalysis and that possible thermal gas-phase contributions require to be initiated by a catalytic action. Second, higher methane concentrations could lead to thermal effects, i.e. strongly localized additional heating, in the catalyst layer which are currently not experimentally quantifiable. Such a reasoning could in addition to the chemical nature of the catalyst contribute to explain the higher ethane to ethylene ratios for the less active Pt/MgO model catalyst compared to the oxide based systems Sr/La_2O_3 and LaSr/CaO.

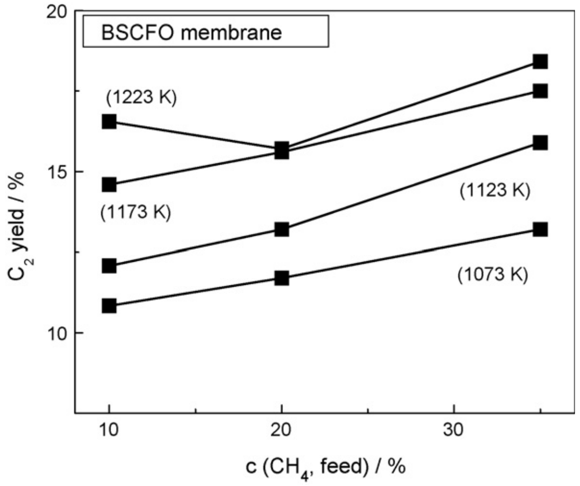

Fig. 5. C_2-hydrocarbon as a function of methane feed concentration for the LaSr/CaO modified BSCFO membrane (at a constant reactant flow rate of 85 mL min^{-1}).

3.5. Impact of the CH_4 admission on the oxygen permeation

As a matter of fact, admission of hydrocarbons is typically expected to enhance oxygen permeation rates. This can in first approximation be rationalized by the lower oxygen activity at the permeate side, given that the hydrocarbon consumes oxygen during its conversion. In turn, a steeper oxygen activity gradient is established across the membrane and according to the Wagner equation [39] higher oxygen permeation fluxes should be expected. However, such a simple regard neglects that the hydrocarbon needs to be activated in order to react with oxygen at the membrane surface and that differently active catalyst allow different hydrocarbon activation rates. In order to establish the impact of those catalysts investigated in the present study, oxygen permeation fluxes were calculated form the formation rates of oxygen containing products. The respective data is depicted in Fig. 6 relating the oxygen flux as a function of the temperature to the catalyst formulation employed at the membrane surface. Furthermore, using a membrane with the most efficient LaSr/CaO catalyst, the methane concentration was varied to establish the influence of the hydrocarbon concentration on the oxygen permeation flux.

As a matter of fact, the Pt/MgO catalyst is the least efficient material to enhance the oxygen permeation and the oxygen

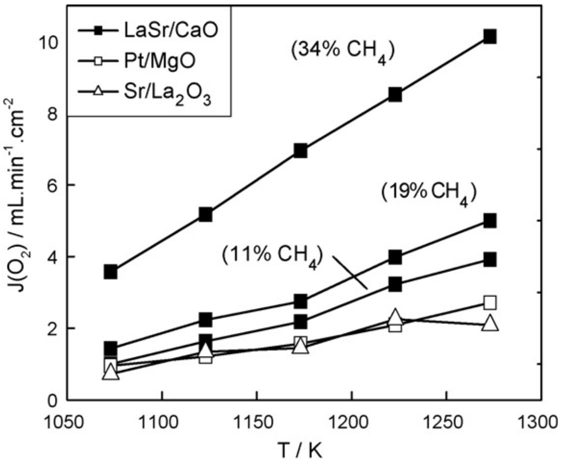

Fig. 6. Oxygen reaction permeation flows on surface-modified BSCFO membrane (at a constant reactant flow rate of 85 mL min^{-1}): ■ LaSr/CaO-coated membrane (at 11%, 19% and 34% CH$_4$ feed), □ Pt/MgO-coated membrane (at 50% CH$_4$ feed) and △ Sr/La$_2$O$_3$-coated membrane (at 11% CH$_4$ feed).

permeation under an air/50% CH$_4$ gradient were even lower than those observed under an air/He gradient. One might rationalize this observation assuming that reaction products like water or carbon dioxide decrease slightly the efficiency of the oxygen transport close to the permeation side membrane surface and the lowered oxygen activity related to methane activation does not allow to compensate. In the case of Sr/La$_2$O$_3$ and LaSr/CaO modified membranes tested at a CH$_4$ concentration of 11%, the Sr/La$_2$O$_3$ membrane does not show significant changes in oxygen permeation fluxes, while permeation fluxes across the LaSr/CaO decline by a factor of about two. Apparently the LaSr/CaO catalyst is stronger affected by the presence of the reactive atmosphere than the Sr/La$_2$O$_3$ one. Nevertheless, increasing the CH$_4$ concentration in the feed, alters the situation and oxygen permeation fluxes observed at 19% CH$_4$ feed approach those established under air/He gradient and these are even clearly over passed when the CH$_4$ concentration is further increased to 34%. In this case, the higher concentration allows to accelerate the CH$_4$ activation rate to such an extend that the resulting decline in oxygen activity at the membrane/catalyst surface leads to increased cross membrane gradients over compensating the negative effect of the reactive atmosphere on the transport efficiency.

Comparing the performance of the LaSr/CaO modified BSCFO membrane reactor with the current state of the art outlines the interest of the proposed configuration. The results obtained by Shao et al. [10] on a similar $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane (CH$_4$ conversion: 3.4%, C$_2$ selectivity: 59.5% at $T = 900\,^{\circ}C$) were already promising in terms of selectivity, however, the reported activity using a OCM catalyst as a fix-bed in a membrane did not allow to attain comparable activities. This statement holds even more considering that the authors used a higher methane concentration in the feed (50% CH$_4$/50% He) in that study, which according to the current work should be beneficial—at least in the reactor configuration proposed in this work. In comparision to those interesting yields reported by Akin and Lin [38] for another membrane reactor configuration, the current findings announce a lower yield. However, it needs to be reminded that the past study made use of CH$_4$ concentrations of only a few percent and that yields dropped rapidly with rising CH$_4$ concentration before reaching those employed in the present work. Given the beneficial impact of increasing the CH$_4$ content in the feed and the high productivities of the currently proposed surface catalyst modified membrane reactor (reported in Table 2), it seems that the present configuration could address several issues having prevented a larger scale implementation of membrane reactor based OCM.

It seems also indispensable to underline the general interest of the reported membrane configuration benchmarking it against competing strategies previously reported in literature. First, it should be noted that there is no commercial process for the OCM, which could be related to high investment cost introducing commercially such a technology. In turn, C$_2$ productivity is a key element to evaluate different concepts, which can be used to compare the performance of the membrane reactor to conventional fixed bed reactor. The present membrane configuration allows a C$_2$ productivity (ethylene and ethane) of 4.6×10^{-5} mol(C$_2$)/(g$_{cat}$ s) compared to 6×10^{-6} mol(C$_2$)/(g$_{cat}$ s) as peak performance for a 10% Li/MgO catalyst extensively well described in literature, tested in a fixed bed reactor. For the latter value, a 10% Li/MgO catalyst was tested in our laboratory [28] as reference in methane/oxygen co-feed mode and fixed bed configuration under sufficiently close conditions (6.7% methane, 3.4% oxygen, balance Ar, temperature range 600–800 °C). It should be stressed that there are general benefits related to a membrane configuration such as (i) the dispense of pure oxygen feeds, (ii) an improved safety of operation as hydrocarbon/oxygen mixtures are avoided and finally (iii) a higher productivity related to the fact that the global reactant ratio in a membrane reactor can be closer to stoichiometry than in a fixed bed reactor for flammability reasons.

4. Conclusion

Complementally to a former study altering the oxygen permeability of a membrane reactor by changing the permeability of the perovskite membrane material, the current study focused on varying the catalytic coating. Contrary to the previous work [27], no strict correlation between oxygen permeability and selectivity was established. However, it is important to underline that in line with the suggestions in our former work newly explored catalysts were selected to exhibit increased activity as compared to the model Pt/MgO system tested before. Peak performances in the current study amounted to 18.4% C$_2$-hydrocarbon yield at a selectivity of almost 60% as observed in the LaSr/CaO modified BSCFO membrane reactor. As a common feature for all catalyst modified reactors, the best selectivity is obtained at a temperature of 950 °C.

Comparing all 4 BSCFO based membrane reactors, it is obvious that a suitable catalytic modification of the membrane surface is crucial for obtaining interesting performances. In the case of the bare membrane, the developed surface of the dense membrane is probable insufficient to have a strongly beneficial impact and a release of oxygen into gas-phase could present a safety thread. The wash-coated Pt/MgO model catalyst suffers essentially from its low activity and to a smaller extent from the fact that the ethane to ethylene ratio remained comparably high. Both oxide based catalysts, Sr/La$_2$O$_3$ and LaSr/CaO, allow to attain better activities, but the slightly high conversions and higher selectivity observed despite its lower specific catalyst loading with the LaSr/CaO modified reactor suggests this latter configuration as the most suitable currently explored in our laboratory. Obviously, in order to enhance further membrane reactor performances additional effort is now required to maximize the specific catalyst loading without harming the integrity of the catalyst layer and without harming the concept of supplying the catalyst itself via the membrane with ionic oxygen.

Acknowledgement

Part of this work was supported by the European research project “TOPCOMBI” (contract NMP2-CT2005-515792).

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