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Influence of oxygen supply rates on performances of catalytic membrane reactors
Application to the oxidative coupling of methane

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Abstract

The impact of oxygen permeability using an ionic oxygen conducting membrane reactor with surface catalyst was investigated for the oxidative coupling of methane to higher hydrocarbons. Dense $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO), $Ba_{0.5}Sr_{0.5}Mn_{0.8}Fe_{0.2}O_{3-\delta}$ (BSMFO) and $BaBi_{0.4}Fe_{0.6}O_3$ (BBFO) membrane disks with Pt/MgO catalysts were prepared by sol–gel deposition or wash-coating. It is demonstrated that the oxygen supply by permeation needs to fit to the consumption during the coupling reaction. In case of insufficient oxygen supply comparably poor conversions are observed while higher oxygen fluxes lead to increased methane conversions, especially in the presence of an efficient catalyst. Generally, increasing catalytic activity leads to lower C_2 selectivity, especially for low oxygen permeation fluxes. The concept of a reactor employing dense catalytic membranes is viable, but the present study identifies further potential when the activity of the catalyst for the oxidative coupling is improved, leading to an overall enhanced performance of the membrane reactor.

Keywords: Dense membrane; Perovskite; Platinum; MgO; Oxygen permeability

1. Introduction

The valorization of natural gas is a domain of permanent research but nowadays renewed interest for routes, which were practically abandoned in this area, emerged again due to the recent high oil prices. Thus, the 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. It has been estimated in previous literature studies assuming lower oil prices 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 considering mainly process concepts based on fixed bed reactors, alternative reactor concepts with inherent need for adapted catalysts have to be invented. One of the most promising design solutions could be catalytic membrane reactors allowing a cost cutting use of air instead of oxygen and possibly higher productivity as flammability issues of the reactant mixture close to stoichiometry could be avoided.

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 but 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 opposite side.

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First published works [5] in the domain of OCM used either porous membranes combined with catalysts in form of a 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 suffer 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.

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, for temperatures 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 $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ 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 perovskites membranes with different oxygen permeability were used to study the influence of oxygen supply rates on catalytic performance at given temperatures. Furthermore, the way to prepare the coated catalysts impacting on the intrinsic catalytic properties was altered in order to study at given oxygen supply the influence of the catalyst nature on the C_2 selectivity and the methane conversion during the reaction. It should be noted that the catalyst itself was not optimized, but specifically chosen for its thermal stability when operating at temperatures until 1000 °C and the relative ease to deposit it on the membrane surface.

2. Experimental

2.1. Membrane materials

In this work, 1 mm thick dense $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO), $Ba_{0.5}Sr_{0.5}Mn_{0.8}Fe_{0.2}O_{3-\delta}$ (BSMFO) and $BaBi_{0.4}Fe_{0.6}O_3$ (BBFO) membrane disks were prepared with specific conditions of densification for each material.

The synthesis of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) oxide proceeded by the so-called citrates method using citric acid and EDTA as complex formation agents [22] (EDTA was used to dissolve the barium nitrate). Citric acid was added in 1:1 molar ratio with respect to the sum of metal salts. The resulting powder was calcined in air at 900 °C for 4 h. Recently we added a novel step conditioning the perovskite powders by ball milling in *iso*-propanol suspension, improving the material properties of the final disks in terms of bulk density and mechanical stability. The beneficial effect is related to a decreased grain size obtained prior to pelletizing. Then, the membrane was prepared by isostatic pressing with a pressure of 220 MPa applied for 2 min to the powder. Results showed that ~0.5 g of 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.

The preparation of the BSMFO membranes followed comparable steps as those ones outlined for the BSCFO membrane. The powder was calcined in air at 1200 °C for 4 h. Then, the sintering of the disk was performed at 1240 °C for 8 h (2 °C/min ramps) and its diameter after densification was 15 mm. On the other hand, the BBFO powder obtained by the citrates method was calcined at 900 °C for 4 h. The sintering of the membrane proceeded at 1000 °C for 8 h (2 °C/min ramp) and the diameter of the disk after densification was also 15 mm.

2.2. Membrane characterization

Formation of the perovskite structure was checked by X-ray diffraction (Fig. 1), 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 (Fig. 2).

2.3. Membrane surface modification

In our 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. This modeling approach was confirmed by experiments carried out under permeation conditions, showing that oxygen fluxes were

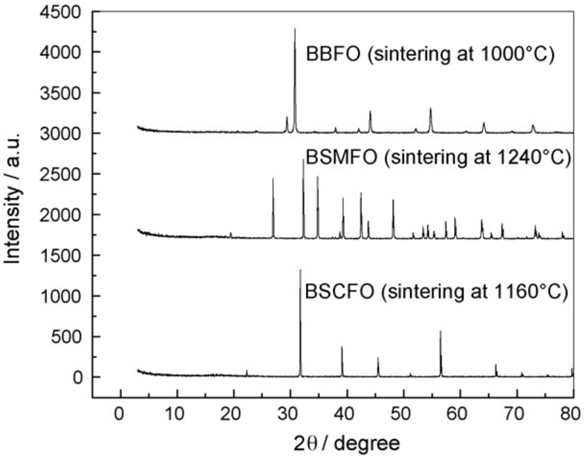

Fig. 1. XRD patterns of perovskite membranes after densification.