

Research
Green Chemical Engineering—Feature Article

Design and Fabrication of Ceramic Catalytic Membrane Reactors for Green Chemical Engineering Applications

Guangru Zhang, Wanqin Jin*, Nanping Xu

State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, China



ARTICLE INFO

Article history:

Received 13 April 2017

Revised 11 May 2017

Accepted 11 May 2017

Available online 14 November 2018

Keywords:

Dense ceramic membrane

Porous ceramic membrane

Catalytic membrane reactor

Gas separation

Heterogeneous catalysis

ABSTRACT

Catalytic membrane reactors (CMRs), which synergistically carry out separations and reactions, are expected to become a green and sustainable technology in chemical engineering. The use of ceramic membranes in CMRs is being widely considered because it permits reactions and separations to be carried out under harsh conditions in terms of both temperature and the chemical environment. This article presents the two most important types of CMRs: those based on dense mixed-conducting membranes for gas separation, and those based on porous ceramic membranes for heterogeneous catalytic processes. New developments in and innovative uses of both types of CMRs over the last decade are presented, along with an overview of our recent work in this field. Membrane reactor design, fabrication, and applications related to energy and environmental areas are highlighted. First, the configuration of membranes and membrane reactors are introduced for each of type of membrane reactor. Next, taking typical catalytic reactions as model systems, the design and optimization of CMRs are illustrated. Finally, challenges and difficulties in the process of industrializing the two types of CMRs are addressed, and a view of the future is outlined.

© 2018 THE AUTHORS. Published by Elsevier LTD on behalf of Chinese Academy of Engineering and Higher Education Press Limited Company. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

The chemical industry, which includes the petrochemical and biochemical industries, plays a key role in the global economy, and reactions and separations are key processes in the chemical industry. Unfortunately, the most conventional industrial separation processes, such as distillations, are very energy intensive. Therefore, improving the efficiency of reactions and separations is becoming essential in solving environmental and energy-related problems. Membrane separation is an alternative separation technique that can be performed efficiently on a large scale, and that is competitive in terms of both energy and overall cost [1–4]. The integration of reactions (mostly catalytic reactions) with the separation of desired products has attracted considerable attention from researchers in science and engineering. The membrane-based combination of separations with catalytic reactions is the concept behind catalytic membrane reactors (CMRs).

The most representative features of CMRs are their selective removal of a product, retention of the solid phase (such as a solid catalyst), distribution of a reactant, and catalyst support (in some cases, the membrane itself acts as a catalyst) [1–4]. CMRs do not only combine membrane separation with a catalytic process; rather, a synergy is created between the two processes that integrally couples them into a single unit. Green and sustainable chemistry and chemical engineering with lower energy consumption, lower pollution, and enhanced performance can be achieved via the implementation of CMRs. Due to the harsh conditions of most catalytic reactions, which include high temperature, high pressure, and the existence of corrosive gases or solutions (including both basic and acidic solutions), most CMRs use inorganic membranes. These inorganic membranes, which are typically ceramic membranes (e.g., metal oxides), have obvious advantages in terms of chemical and thermal stability, fouling resistance, mechanical strength, and lifetime compared with polymeric membranes. These advantages have given inorganic membranes such as ceramic membranes a wide application in CMRs.

One type of CMR is based on the dense ceramic membrane, which is a type of gas-separation membrane. Perovskite-type

* Corresponding author.

E-mail address: wqjin@njtech.edu.cn (W. Jin).

mixed ionic–electronic conducting membranes are one of the most studied dense ceramic membranes. These membranes have a generic composition of ABO_3 , where A is a lanthanide, an alkaline-earth element, or a mixture of the two, while B is normally a transition element. The properties of perovskite-type membranes are closely associated with the A- and B-site cations and their composition. At an elevated temperature (normally higher than 700 °C), these membranes simultaneously exhibit oxygen ionic and electronic conductivities, and have a theoretical 100% selectivity to oxygen. The most attractive qualities of these membranes are their high oxygen flux (and permselectivity) and high catalytic activity. Certain important gas-phase catalytic processes, such as the utilization of natural gas, the production of hydrogen, and the treatment of greenhouse gases, can be carried out in CMRs based on perovskite-type membranes. Thus, this type of CMRs has often been reviewed during the last decade. Examples of such reviews include Dixon [1], Bouwmeester [5], Sanchez Marcano and Tsotsis [2], Yang et al. [6], Liu et al. [7], Dong et al. [4], Thursfield et al. [3], and Wei et al. [8]. In addition, several excellent reviews have been written on mixed-conducting membrane materials. At present, a book chapter written by Bouwmeester and Burggraaf [9] in 1997 and a review paper written by Sunarso et al. [10] in 2008 are the definitive references for material theory and fundamental studies.

The other type of CMRs is based on a porous ceramic membrane and is mainly used for heterogeneous catalytic processes. In heterogeneous catalytic reactions in the presence of suspended ultrafine or nano-sized catalysts, a membrane with an appropriate pore size can effectively separate the catalysts from the reaction slurry. Catalyst separation and reactant distribution can be simultaneously achieved with an appropriate reactor configuration design, which can thus intensify the catalytic reaction in terms of selectivity and yield. CMRs in hybrid photocatalysis-membrane processes have often been reviewed; examples include a monograph by Ollis [11] and works by Molinari and Palmisano [12], Augugliaro et al. [13], and Mozia [14].

This article reviews the state of the art for ceramic CMRs, and includes: ① dense ceramic membrane reactors based on a perovskite-type mixed-conducting membrane and ② porous ceramic membrane reactors used for heterogeneous catalysis. We realize that a comprehensive review of this ever-widening and fast-growing field is almost impossible to provide within a single review article. Therefore, materials and theories are not discussed in detail, although some newly developed materials are briefly introduced in the discussion on special applications. In addition, this review does not cover the use of heterogeneous photocatalysis and high-performance catalysts in porous CMRs, or the use of solid electrolytes and palladium membranes in dense CMRs. Rather, we seek to review new developments in and innovative uses of dense and porous CMRs during the last decade. Within these restrictions of scope, we also intend to present the most representative work performed by our group on CMRs during that period.

2. Dense ceramic membrane reactors

This section provides a brief review of dense CMRs that are based on perovskite-type mixed ionic–electronic conducting materials. Membrane reactor design, performance, and applications related to the utilization of natural gas (e.g., the partial oxidation of methane (POM)) and biofuels (e.g., ethanol oxidative steam reforming), and the treatment of greenhouse gases (e.g., thermal decomposition of carbon dioxide (TDCD)) are presented and discussed. Reactions such as the POM and TDCD are taken as model systems to illustrate dense CMRs design and optimization for a given application.

2.1. Membrane architecture

Membrane architecture is important in determining the performance of a CMR. There are three main types of ceramic membrane architectures: disk-like (or planar) membranes, tubular membranes, and hollow fiber (HF) membranes. Disk-like membranes with a limited membrane area are usually used for kinetics studies because of their simple fabrication procedure. In contrast, a planar membrane can be fabricated on a very large scale using a tape-casting technique [15–17]. As shown in Fig. 1(a) [18], a multiple planar stack can provide a large membrane area. However, many difficulties have appeared in the engineering of such membranes, such as high-temperature sealing. For tubular membranes, which are normally prepared by a paste extrusion [19–23] or isostatic pressing [19,24–26], as shown in Fig. 1(b) [27], the sealing difficulty can be easily solved by keeping the sealing part outside of the high-temperature zone; this ensures that the temperature of the sealing part is reasonably low in order to obtain an excellent seal. In this case, low-cost polymeric sealants [28,29] are preferable to expensive metal (e.g., silver and gold), ceramic, or glass sealants [30–33]. However, a tubular membrane usually has a small packing density (defined as the membrane area per membrane tank volume) due to its relatively thick wall and large diameter. To avoid issues of small packing density and sealing difficulty, HF membranes, as shown in Fig. 1(c) and (d) [20], fabricated via a phase-inversion spinning/sintering technique are currently the most popular architecture for engineering applications, including CMRs, and will be discussed in detail later.

For a given material, the oxygen flux in a dense ceramic membrane is essentially related to the membrane thickness. The oxygen flux can be greatly increased by thinning the membrane to below a characteristic value [9,34]. However, ceramic membranes are brittle and weak to shearing and tension. A membrane cannot support itself when it is very thin (i.e., less than 500 μm). This is the main challenge for disk-like, planar, or tubular membranes. A supported membrane (or asymmetric membrane), which comprises a thin, dense separation layer fabricated on a mechanically strong porous support layer, is considered to be a promising membrane geometry to enhance the oxygen flux without sacrificing mechanical strength. This type of geometry requires a good matching of thermal and chemical compatibility—and hence a good interfacial bonding without serious solid-state reactions—between the two layers, as well as a defect-free, thin, and dense layer for a good, supported, dense ceramic membrane [35]. Jin et al. [36] and Dong et al. [37] proposed a co-sintering technique to prepare asymmetric membranes with an ultra-thin separation layer. In this technique, a precursor of the separation layer was coated onto a green support by means of spin coating or co-pressing with a substrate powder material using a uniaxial press. After high-temperature sintering, an asymmetric membrane was formed (Fig. 2(a)) [37]. This method can be extended to create planar, tubular, and HF membranes with multiple layers [38–41]. This technique shows great potential for preparing asymmetric tubular membranes and overcoming the abovementioned thickness limitation. Liu et al. [42] recently reported a $\text{SrCo}_{0.4}\text{Fe}_{0.5}\text{Zr}_{0.1}\text{O}_{3-\delta}$ (SCFZ) asymmetric tubular membrane that was fabricated by means of a co-sintering technique. A green tubular SCFZ support was coated with an SCFZ precursor using a spin-spray technique [42]. After sintering, a 20 μm dense layer was obtained (Fig. 2(b)) [42]. This work demonstrates a simple and robust strategy for the preparation of a tubular asymmetric membrane.

Over the last decade, HF membranes have garnered more attention due to their unique asymmetric multilayer structures, which are prepared using a phase-inversion spinning/sintering technique [20,43–45]. Compared with conventional planar or tubular configurations, HF membranes (Fig. 1(c) and (d)) have a

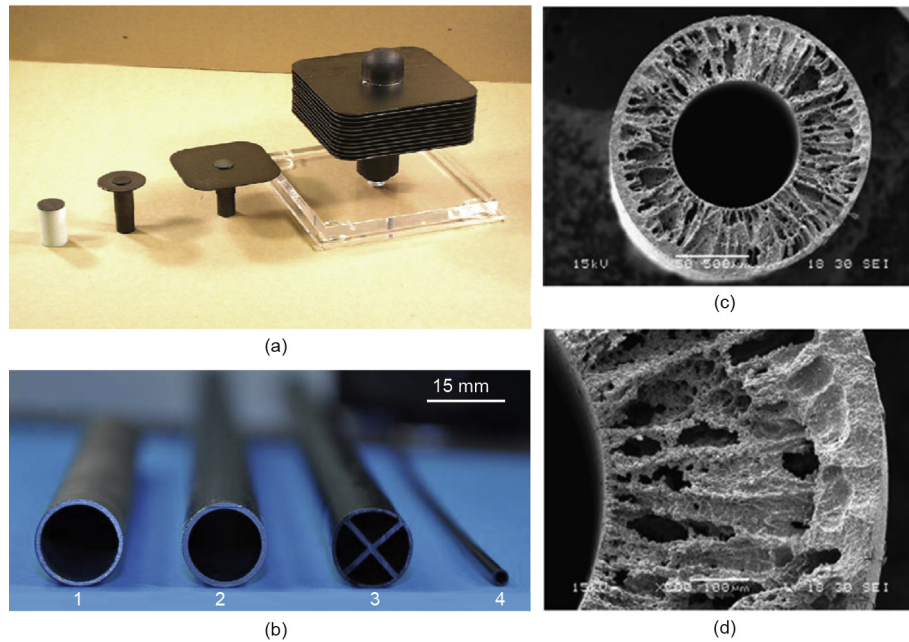


Fig. 1. (a) Mixed-conducting membranes developed by Air Products and Chemicals, Inc., from a disk-like membrane (far left) to a commercial-scale wafer-like membrane (far right) [18]; (b) tubular membrane fabricated by means of isostatic pressing (1) or extrusion (2–4) [27]; (c, d) the microstructure of HF membranes based on mixed-conducting materials [20].

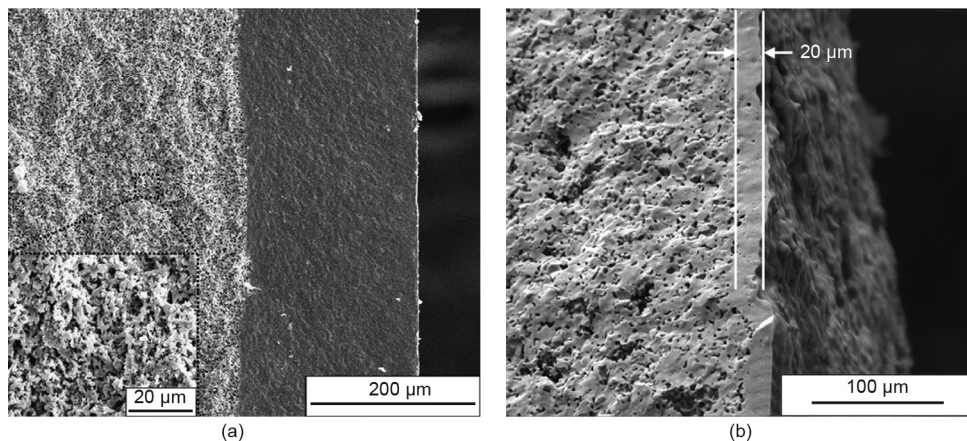


Fig. 2. Scanning electron micrograph (SEM) morphology of (a) an asymmetric disk-like membrane fabricated by means of the co-sintering technique [37] and (b) an asymmetric tubular membrane fabricated by means of a combination of the spin-spray and co-sintering techniques [42].

much greater packing density (the diameter of a single membrane is less than 1 mm) and thin separating dense layer (less than 50 μm); they also integrate different types of porous layers (i.e., finger-like layers and sponge-like layers). This architecture provides a much larger gas/membrane interface and lower mass-transfer resistance, and leads to an enhancement of surface exchange and thus permeation rates. However, the greatest disadvantage of single-channel HF membranes is their low mechanical strength, which is due to the low mechanical strength of the supporting porous layer. This disadvantage restricts the use of such membranes in further industrial applications. A multichannel design can grant an HF membrane a larger permeation area for a given volume (i.e., a higher membrane-packing density) and, most importantly, can provide greater mechanical strength (Fig. 3) [46–49]. Zhu et al. developed a multichannel hollow fiber (MCHF) membrane using $\text{SrFe}_{0.8}\text{Nb}_{0.2}\text{O}_{3-\delta}$ [47] and Nb_2O_5 -doped $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCFNb) [49]. The MCHF membrane has a breaking load that is three to six times greater than that of a

conventional single-channel HF membrane, and a higher oxygen permeation flux. This membrane is considered to be a promising architecture for CMRs.

2.2. Applications of dense CMRs

A membrane naturally separates a reactor into two chambers, and some of the species involved can selectively permeate through the membrane. Thus, the major functions of a dense membrane in a dense CMR can be classified into three categories. First, the membrane acts as a distributor for one of the reactants [50]. Given the high oxygen flux (and permselectivity) of a perovskite-type membrane, reactions can take place at the oxygen permeation side of the membrane. The dosing of oxygen can be easily and precisely controlled, which lowers the risk of thermal runaway in the case of an exothermic reaction. In addition, a better yield of intermediate oxidation products can be obtained because such reactors can work with a lower partial pressure of oxygen. Typical examples

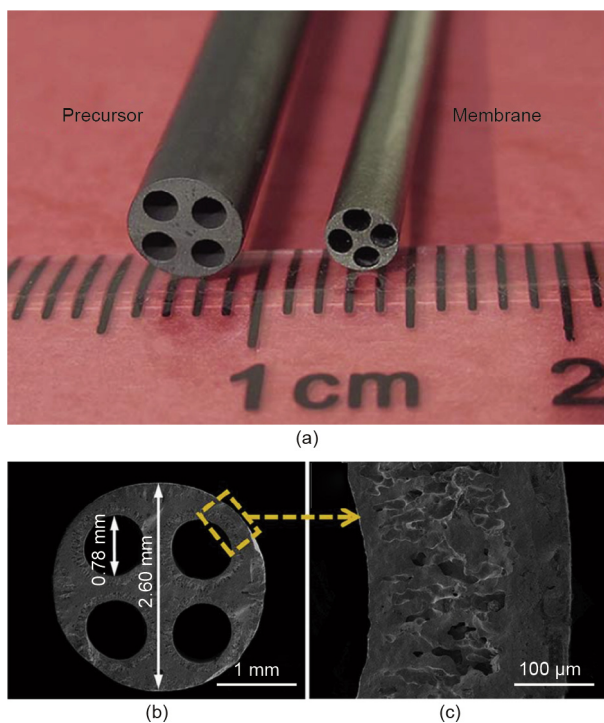
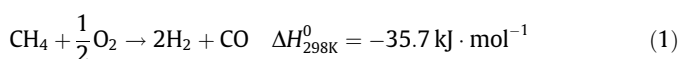


Fig. 3. (a) Image of the precursor and membrane of multichannel hollow fiber [49]; (b, c) cross-sectional SEM images of an HF membrane [47].

of processes that can benefit from these advantages include the partial oxidation of hydrocarbons [38,51–55], oxidative coupling of hydrocarbons [56–60], and oxidative dehydrogenation of hydrocarbons [61–64]. The second major function of a membrane in a CMR is to selectively remove a species. This does not simply involve separating one species from a mixture; it also—and most importantly—involves shifting a chemically equilibrated reaction in a desired direction by selectively removing one of the *in situ* products from the reaction side of the membrane. Typical reactions that benefit from this function include hydrogen production [65–68] and the decomposition of oxygen-containing compounds [55,65–75]. The third major function involves coupling reactions. A CMR comprises two chambers separated by a membrane. Reactions can take place on both sides of the membrane, which makes it possible to couple multiple reactions in a CMR. In a coupling CMR, the product of a reaction on one side of the membrane, which permeates the membrane, can be the reactant for a second reaction on the other side of the membrane. In this way, the conversions of both reactions can be enhanced. Furthermore, an auto-thermal reactor can be constructed by coupling endothermic and exothermic reactions in a CMR. A typical case is the coupling decomposition of oxygen-containing gases (CO_2 , N_2O , and H_2O) with a POM reaction [55,70–73]. In the remainder of this paper, we focus on the POM and TDCD applications, as they are very good examples to illustrate the basic functions of a dense ceramic CMR and its integration. Technical issues, membrane design, and optimizations are discussed below based on these two specific applications.

2.2.1. Syngas and hydrogen production

At present, the POM reaction, shown in Eq. (1), is considered to be the most promising process for methane (CH_4) conversion, because it is a mild exothermic reaction with high selectivity and a desirable hydrogen/carbon monoxide (H_2/CO) ratio of 2:1.



A dense CMR offers several potential advantages for the conversion of methane, and its application to this process has been extensively studied in the past several years [38,51–55]. In this process, air is supplied to one side of the membrane and methane is supplied to the other side of the membrane. In this configuration, air is used to replace pure oxygen, which is normally obtained from air-separation plants equipped with an expensive cryogenic separation unit. The POM is an exothermic reaction, and the gradual introduction of oxygen via the membrane reduces the risk of thermal runaway while simultaneously enhancing the yield of the desired products. One of the challenges in the commercialization process of this kind of membrane is long-term stability. In past years, single-layer membrane (normally consisting of only one material) reactors have received intensive attention. However, it is extremely challenging to design a single-layer membrane that has both a high oxygen permeation and a high stability when exposed to a complex gas environment (containing CO_2 , H_2 , H_2O , and H_2S) on the reaction side.

A multilayer membrane—in which the material of each layer may be the same or different—has been proposed, in which the requirements for permeability and stability are segregated into different layers [76]. As shown in Fig. 4(a), a dual-layer configuration was designed. The dense layer is made of 0.5 wt% SCFNb, which has a high oxygen permeability, and the porous layer is made of $\text{Sr}_{0.7}\text{Ba}_{0.3}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ (SBFM), which shows an excellent reduction tolerance (e.g., in hydrogen). The SCFNb layer is protected by the SBFM porous layer. A non-zero oxygen partial pressure zone was created near the porous/dense interface, which was attributed to a sufficiently high oxygen permeability of the SCFNb separation layer. This dual-layer membrane reactor design keeps the reaction site away from the surface of the dense layer and can be operated steadily for more than 1500 h with no significant performance degradation (Fig. 4(b)).

It is possible to construct an auto-thermal reactor in order to couple an endothermic POM reaction with exothermic reactions such as steam reforming in a CMR. Such a reactor also provides more flexibility for tuning the H_2/CO ratio. Zhang et al. [77] studied a combination of the POM with steam reforming in a tubular CMR based on an Al_2O_3 -doped $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCFA) membrane. Zhu et al. [78] then proposed an auto-thermal process that couples the oxidative steam reforming of ethanol (OSRE) with water-splitting (WS) reactions in a dense CMR (Fig. 5). The *in situ* oxygen is removed from the water side of the membrane and then reacts with ethanol to produce hydrogen on the other side of the membrane. At 750 °C, the hydrogen production rates from the lumen and shell sides are 6.8 and 1.8 $\text{mL} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ (standard temperature and pressure), respectively.

2.2.2. Thermal decomposition of carbon dioxide

The thermal decomposition of carbon dioxide into carbon monoxide and oxygen is considered to be a potential route for carbon dioxide capture and utilization. However, carbon dioxide decomposition is limited by its thermodynamic equilibrium. To achieve a high conversion, high-density energy inputs such as a very high temperature (> 1727 °C) are necessary in a fixed-bed reactor. Integrating the TDCD and POM reactions in a dense CMR shows a remarkable advance in the utilization of carbon dioxide to supply oxygen for the POM reaction [70,73,79–81]. As shown in Fig. 6(a), a dense CMR based on a disk-like SCFZ membrane was designed for the coupling of the TDCD and POM reactions. The TDCD reactions take place on one side of the membrane in the presence of a supported palladium (Pd)-based catalyst, and methane reacts with oxygen (which permeates from the TDCD side) over a supported nickel (Ni)-based catalyst on the other side of the membrane. At 900 °C, the carbon monoxide selectivity and carbon dioxide conversion reached 100% and 15.8%, respectively

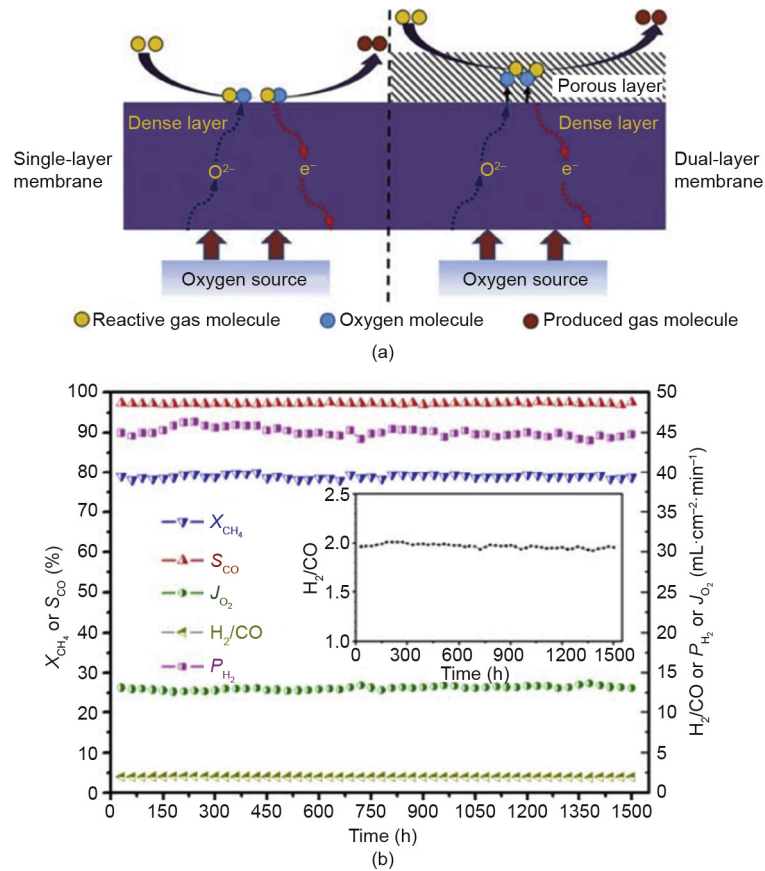


Fig. 4. (a) Schematic diagram of a porous/dense dual-layer composite membrane; (b) CO selectivity (S_{CO}), H_2 production (P_{H_2}), CH_4 conversion (X_{CH_4}), O_2 permeation flux (J_{O_2}), and H_2/CO ratio as a function of time in the dual-layer composite membrane reactor [76].

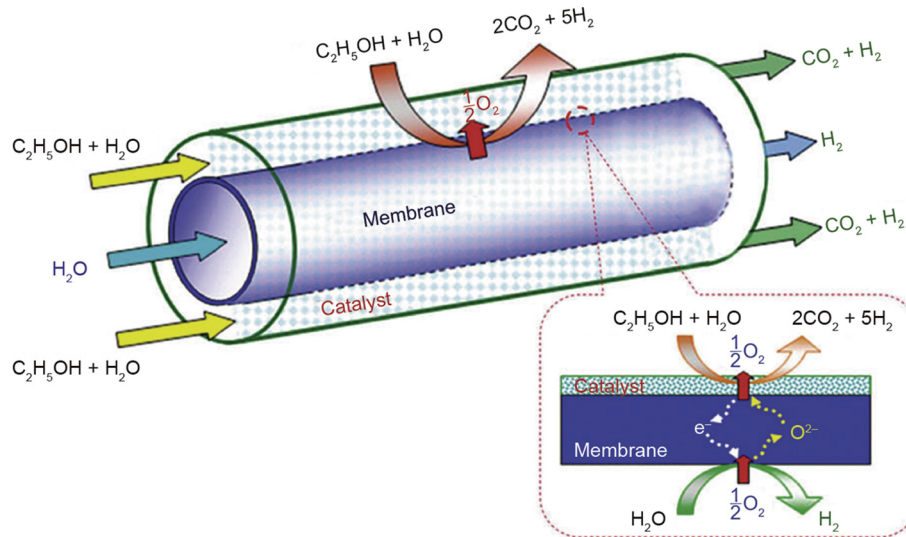


Fig. 5. Schematic diagram of the OSRE coupled with WS in a thin tubular membrane reactor [78].

[70]. For given external conditions, the decomposition of carbon dioxide benefits from the increase of oxygen permeation flux [81]. Normally, the oxygen permeation flux can be promoted by decreasing the thickness of the membrane (i.e., when bulk diffusion is the rate-determining step). Zhang et al. [79] performed coupling reactions using an SCFA thin tubular membrane with a reduced thickness, which gave it a higher oxygen flux than a

disk-like membrane. At 950 °C, the carbon dioxide conversion reached approximately 17%, which is higher than the conversion obtained when using a disc-like membrane at the same operation temperature.

Having the POM occur on the opposite side of the membrane to the TDCD can increase the driving force and promote carbon dioxide decomposition. However, the membrane in this case was

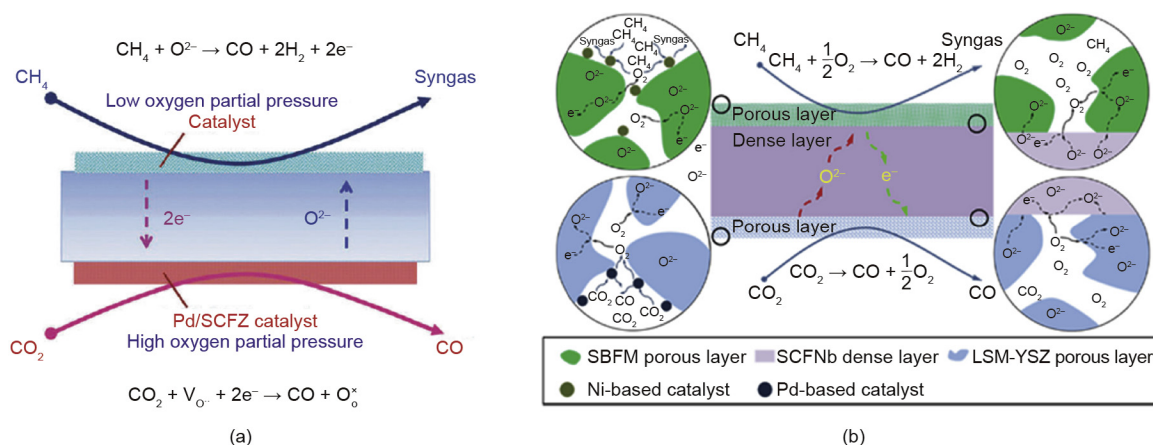


Fig. 6. Schematic diagram of membrane reactors for TDCD and POM with (a) a single-layer membrane [70] and (b) a triple-layer composite membrane [73]. V_o is the oxygen vacancy; O_o^\times is the lattice oxygen; LSM-YSZ is $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ -yttria-stabilized zirconia.

actually in a much more complicated environment, as one side was exposed to CO_2/CO while the other side was exposed to $CH_4/CO/H_2$. As discussed in the previous section, a compromise between high oxygen permeability and sufficient chemical stability is necessary in a membrane reactor. Therefore, a triple-layer composite structure (porous/dense/porous) for the TDCD and POM coupling reaction was proposed [73] (Fig. 6(b)). SBFM and $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ -yttria-stabilized zirconia (LSM-YSZ) were fabricated as porous layers on the dense SCFNb membrane, and were closed to the POM and TDCD sides, respectively. The functions of reduction resistance, carbon dioxide resistance, and high permeability were segregated to the SBFM, LSM-YSZ, and SCFNb layers, respectively. The essence of this design is that each of the layers plays its respective function and synergistically contributes to improve the stability and conversion. This novel reactor attained a 20.58% carbon dioxide conversion at 900 °C, and could be steadily operated for more than 500 h [73].

2.3. Current challenges and difficulties in dense CMRs

In addition to membrane reactor design, many technological gaps remain to be filled for the successful application of dense CMRs on industrial scales; these include high-temperature sealing and operation lifetime. One effective solution is to lower operation temperature, resulting in a lower requirement for sealing and better stability. Furthermore, the commercialization and industrialization

processes of perovskite membranes strongly rely on the large-scale fabrication method.

In the last few years, many new mixed-conducting materials have been developed. However most of these materials operate at a high temperature, normally higher than 700 °C, in order to obtain the desired oxygen flux. Clearly, a membrane that can operate at a low temperature while simultaneously having a competitive oxygen permeation as compared with a membrane that operates at a high temperature would be one of the most effective routes to ease energy consumption and pollution emission. It is commonly accepted that the metal elements of the A or B site of the typical ABO_3 structure, along with their stoichiometric coefficients, are significant in determining the properties of perovskite-type oxides [9]. Hence, most studies focus on the effects of different elements on membrane performance. In 2016, Zhu et al. [82] reported on a new route for designing membrane materials for low-temperature permeation by the rational doping of fluorine (F^-) in a perovskite oxide (Fig. 7(a)). The doped fluorine reduced the valence electron density of the oxygen ion and hence weakened the B–O–B chemical bonds, thereby creating a fast O^{2-} transport path and facilitating oxygen permeation. The oxygen flux of fluorine-doped $SrCo_{0.9}Nb_{0.1}O_{3-\delta}F_{0.1}$ (SCNF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}F_{0.1}$ (BSCFF) perovskite oxyfluoride membranes was more than two and three times greater, respectively, than those of undoped $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCN) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membranes at 600 °C (Fig. 7(b)). Many problems can be solved by operating at a lower temperature.

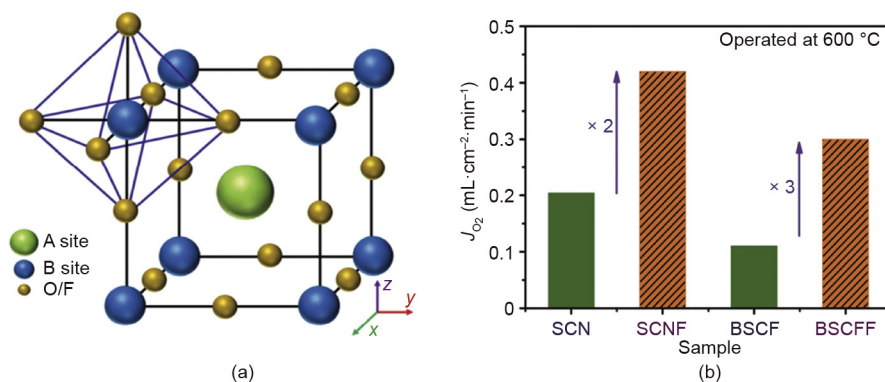


Fig. 7. (a) The cubic crystal structure of a perovskite oxyfluoride material; (b) a comparison of the oxygen permeation fluxes of a perovskite disk membrane and a perovskite oxyfluoride disk membrane at 600 °C [82].

However, for long-term operation, kinetic matching between the reaction and separation is crucial in determining the reactor performance; therefore, further research into their synergistic control are required. To date, the materials that are available for low-temperature application are far from sufficient. The development of materials for low-temperature membranes is an essential direction for future efforts. Significant achievements would be feasible if process intensification was employed in this area. In addition to heat, alternative forms and sources of energy input, such as microwaves and electric fields, could be used to intensify the separation for low-temperature applications.

Most existing studies in this area use a disk-like membrane for material screening, since such membranes are relatively easy to fabricate. Planar membranes are also used in large-scale oxygen production. However, the most significant problem is the sealing, as the membrane and sealant are in the high-temperature zone. Another major drawback is the possibility of mismatching between the membrane and sealant. As elucidated in Section 2.1, HF membranes are preferable for practical applications, as they can undertake sealing outside of the high-temperature zone. The typical fabrication procedure of perovskite HFs comprises the following steps (Fig. 8(a)): ① the high-temperature synthesis of perovskite powder (usually $> 700\text{ }^{\circ}\text{C}$) via solid-state reaction or a wet-chemistry route; ② phase inversion to spin the HF precursor; and ③ high-temperature sintering. These processes are labor-, energy-, and time-consuming as well as being environmentally unfriendly; in addition, it is usually impossible to precisely control the cation stoichiometry of the perovskite oxides. Thus, simple and reliable fabrication remains a major challenge. Zhu et al. [83] proposed a one-step thermal-processing approach that directly

introduces raw chemicals (e.g., oxides or carbonates rather than as-prepared perovskite oxides) into the phase inversion; next, the perovskite hollow fibers are obtained via a single thermal-processing step, which accomplishes the *in situ* conversion of the raw chemicals into perovskite oxides (Fig. 8(b)). This approach successfully avoids the reaction of perovskite oxide with the solvent or non-solvent used in HF fabrication and achieves a controlled stoichiometry. Consequently, the oxygen flux obtained in the fabricated HF is about 2–100 times greater than that of the HF fabricated via the traditional method. This one-step thermal processing is actually an *in situ* synthesis and sintering process. Obtaining a good match between the solid-state reaction rates in synthesis and the sintering rates is also a critical issue, so more research into optimizing the coupling process and the sintering parameters is necessary.

3. Porous ceramic membrane reactors

This section provides an introduction to the progress that has been achieved in the development of porous ceramic membrane reactors. It covers the classification of porous CMR configurations and major considerations for application-oriented ceramic membrane design, especially for ultrafine or nano-sized catalysts.

3.1. Porous ceramic membrane reactor configurations

Two main configurations of porous CMRs for heterogeneous catalysis are commonly discussed in the literature: side-stream and submerged configurations [84–88]. In the side-stream

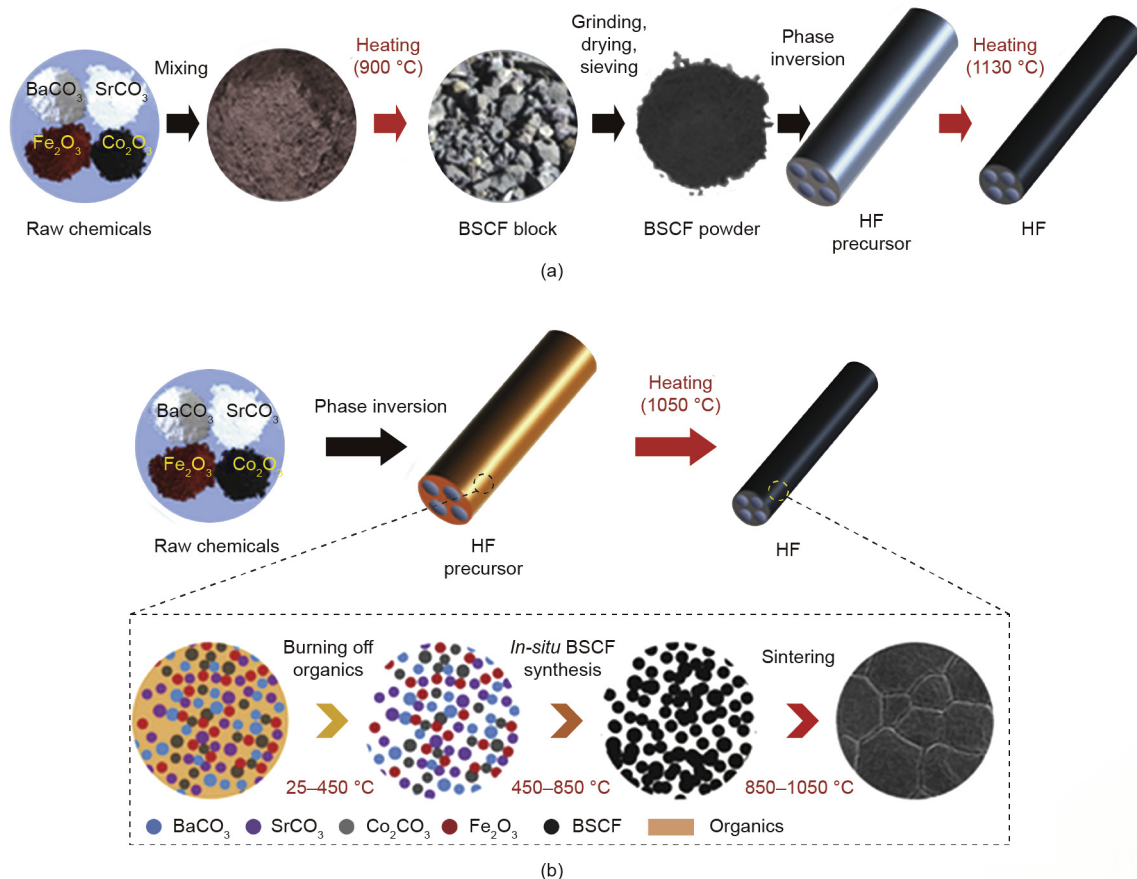


Fig. 8. A schematic of perovskite HF fabrication approaches. (a) A conventional approach with two-step thermal processing; (b) a one-step thermal-processing approach [81].

configuration, the reactions occur in a reaction vessel (which is usually stirred) and product separation is performed in a cross-flow membrane filtration unit that is placed outside of the reaction vessel (Fig. 9(a)). The reaction zone and separation zone are segregated by the membrane, which benefits membrane replacement, cleaning, and scaling up, and which permits more flexibility. However, in the side-stream configuration, significant catalyst loss can occur in the surfaces or pores of the membrane, the pipework, and the pumping system. In addition, the use of a recirculation loop increases the energy cost. In contrast, in the submerged configuration, the membrane is located in the reaction vessel, where it is submerged under the liquid (Fig. 9(b)), and the permeate is removed using a pump or gravity. Thus, a major advantage of the submerged configuration is that the catalyst loss and energy consumption are much less than in the side-stream configuration [89]. Zhong et al. [90] and Chen et al. [91] studied the hydrogenation of *p*-nitrophenol to *p*-aminophenol over nickel nanoparticles in a membrane reactor using the side-stream and submerged configurations, respectively. A much more stable reaction rate over time was observed in the submerged configuration, and it was noted that a lower surface area in the recirculating loop and a high flow rate favored the suppression of the membrane-fouling from adhesion of nickel nanoparticles. The submerged configuration provides a more compact reactor system due to the integration of the reaction and separation zones into a single unit. However, the membrane area per reactor volume is restricted due to the limited reactor volume. From this point of view, the side-stream configuration is beneficial in some circumstances for scaling up.

In an ordinary continuous-flow reactor, reactant distribution is crucial for kinetic performance. Therefore, a membrane reactor that combines the reactant distribution with catalyst separation is expected to enhance the product selectivity and yield. Two porous ceramic tubular membranes were employed in this design, with one acting as a reactant distributor controlling the supply of the reactants and the other acting as a membrane separator for the *in situ* separation of catalysts from the products [92]. Fig. 9(c) illustrates the dual-membrane configuration. The performance of phenol hydroxylation with hydrogen peroxide (H_2O_2) over a titanium silicalite-1 (TS-1) catalyst in the dual-membrane reactor was evaluated [92]. Compared with traditional H_2O_2 feeding modes, the dual-membrane configuration provides a higher dihydroxybenzene selectivity and a catalyst rejection rate of almost 100%. This study demonstrated the advantages of the dual-membrane reactor in enhancing reaction selectivity, product separation, and catalyst separation simultaneously in a continuous heterogeneous catalytic reactor.

A porous membrane can also be a good distributor for gas-phase reactants. Chen et al. [93] successfully controlled the addition of gaseous oxygen using a porous membrane as a distributor in phenol hydroxylation. Small, well-distributed oxygen bubbles generated by the porous ceramic membrane are expected to enhance the volumetric oxygen and gas-liquid mass transfer. To further improve the gas-liquid mass-transfer performance, Chen

et al. [94] proposed a novel dual-membrane airlift reactor system for cyclohexanone ammoxidation over TS-1. In this configuration, as shown in Fig. 10, the addition of gaseous ammonia was controlled by a ceramic porous tubular membrane (using the submerged configuration), and numerous small bubbles were produced. To separate the catalyst from the products, a membrane separator (a tubular porous ceramic membrane using a side-stream configuration) was employed. An obvious advantage of this configuration is the good mixing of gas and liquid, which leads to an enhanced gas-liquid mass transfer.

3.2. Porous ceramic membrane reactor design

In a membrane reactor design, combining the existing reactor with a commercial membrane with minimum modification would be the most effective strategy. However, commercial membranes may not meet the individual requirements of the application objects. Therefore, membranes must be designed and optimized for individual application, which is the concept behind application-oriented ceramic membrane design [95]. To solve problems encountered in engineering applications, this strategy develops a performance-microstructure model and a membrane structure-material model in order to optimize the membrane microstructure and the membrane fabrication, respectively. Considering the diverse sizes of the catalysts that are used in different applications, the separation efficiency and thus the CMR performance largely depend on the membrane microstructures, which include pore size and pore-size distribution, porosity, and thickness. In this section, heterogeneous catalysis based on ultrafine catalysts and heterogeneous catalysis based on nano-sized catalysts are taken as model systems in order to illustrate CMR design from a performance-microstructure perspective.

3.2.1. CMR design for an ultrafine catalyst

The use of the TS-1 catalyst, which has a high catalytic activity and selectivity, has attracted extensive attention [96,97]. In general, the particle size of TS-1 is 0.1–0.3 μm , which is too fine for effective removal from the reaction slurry by either gravity settling or porous tube filtration. Tubular membranes are commonly used in porous CMRs due to their high mechanical strength, and these membranes are commonly applied in TS-1 separation [86,88,97,98]. However, the relatively large diameter and thick wall of such membranes result in a low surface-area-to-volume ratio and a large mass-transfer resistance, and hence in a low separation efficiency for the entire membrane system. A ceramic HF membrane distributor for the distribution of reactants on the microscale in phenol hydroxylation has been proposed (Fig. 11) [99]. The small pore size of the HF membrane facilitated the generation of droplets on the microscale. Considering the particle size of TS-1, droplets with a similar size to the catalysts would benefit the reaction conversion and selectivity due to an increased contact area between the droplets and the catalyst particles. In contrast to the drop-by-drop mode (in which a reagent is added dropwise) and the one-lot mode (in which a reagent is

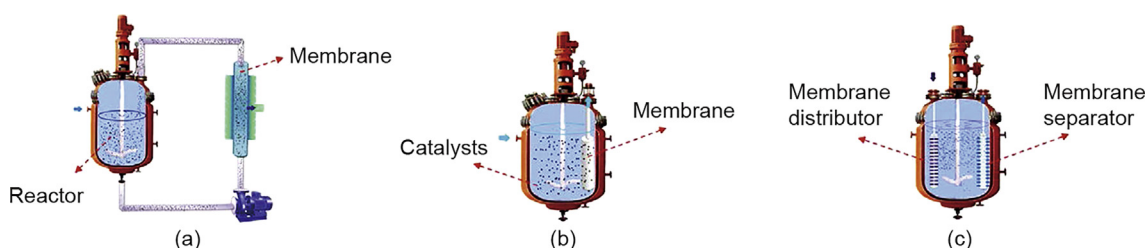


Fig. 9. Classic configurations of a porous CMR. (a) Side-stream configuration; (b) submerged configuration; (c) dual-membrane configuration.

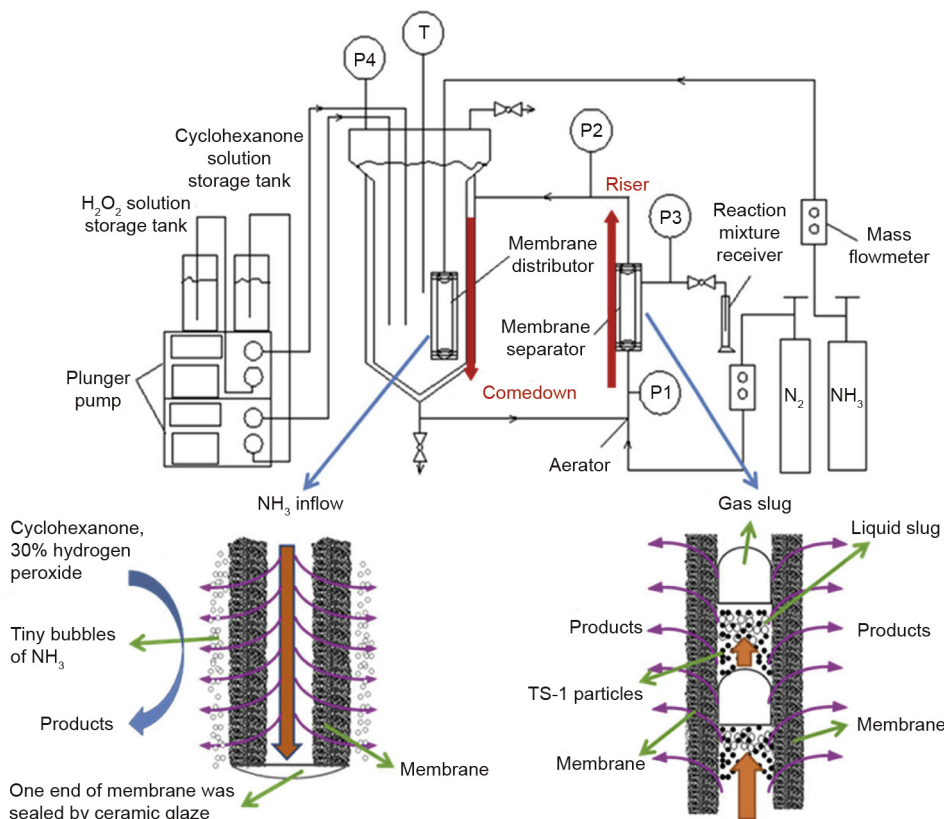


Fig. 10. A dual-membrane airlift reactor system [94]. P: pressure; T: temperature.

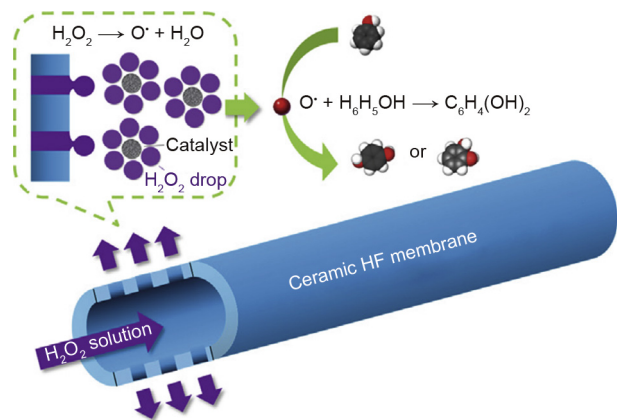


Fig. 11. A schematic of a ceramic HF membrane-based reactant distributor [98].

added all at once), the hydrogen peroxide reactant was distributed by a ceramic HF membrane with a reduced membrane pore size (2.0–0.3 μm), resulting in significant enhancement of the dihydroxybenzene selectivity. The performance of the membrane reactor was demonstrated to be closely associated with the thickness of finger-like and sponge-like pores in the ceramic HF membrane [99]. Different ceramic HF membrane structures were compared in terms of phenol conversion and dihydroxybenzene selectivity. A relatively narrow pore-size distribution and an appropriate gradient in the pore structure were found to favor the uniform formation and distribution of reactant on the microscale and nanoscale.

Several porous CMR models have been initially established to describe the relationship between membrane permeability and microstructure [95,100]. However, challenges remain in establishing models that describe HF membranes, due to their unique and

more complex microstructure in comparison with ordinary tubular membranes.

3.2.2. CMR design for a nano-sized catalyst

Compared with catalysts that are based on bulk materials, a nano-sized catalyst often exhibits superior catalytic properties. However, the high surface energy causes nano-sized catalysts to be easily adsorbed onto the components of the system during catalyst recovery. It has been demonstrated that porous ceramic membranes can completely remove nano-sized nickel catalysts (~ 60 nm) from a reaction slurry [101]. However, the loss of nano-sized nickel particles in the slurry and the formation of caking on the membrane surface cause a degradation of the permeation flux. Loading metal nanoparticles onto membrane surfaces or into membrane pores is considered to be a promising method for solving the abovementioned problems [102–107]. However, poorly adhered metal particles can easily be removed from the membrane surface during operation. Chen et al. [102] developed an improved fabrication technique to enhance the adhesion of metal particles, such as palladium (Pd), to the membrane surface by silanizing the membrane with γ -aminopropyltriethoxysilane. A more uniform distribution of Pd nanoparticles and a smaller particle size were obtained. The research group then proposed a flow-through method [104] to increase the loading amount of Pd. Pd nanoparticles can be deposited not only on the membrane surface, but also in the membrane pores, by letting the solution flow through the membrane. The combination of both surface silanization and the flow-through method resulted in a significant improvement of the catalytic reduction of *p*-nitrophenol to *p*-aminophenol, compared with the traditional impregnation method [104].

Because of their high mechanical strength and easy fabrication, tubular membranes were first chosen for porous membrane

reactors with immobilized nano-sized catalysts. However, tubular membrane supports cannot compete with powder supports in terms of the surface-area-to-volume ratio. A membrane configuration with a higher surface-area-to-volume ratio is therefore preferable. As discussed previously, the most important features of HF membranes are their much higher surface-area-to-volume ratio, in comparison with most of their disk-like and tubular counterparts, and their much lower mass-transfer resistance. As a support, HF ceramic membranes can provide more surface area per unit of volume, and can significantly benefit the deposition of nano-sized particles. The hydrogenation rate of an HF CMR loaded with Pd is at least 44% higher than that of a tubular CMR loaded with Pd [103].

3.3. Current challenges and difficulties in porous CMRs

Some successful industrial applications of porous CMRs have been achieved. A side-stream membrane reactor was designed in Zhejiang province, China, for cyclohexanone ammoxidation over TS-1 (Fig. 12(a)). The membrane model consists of 241 tubular porous ceramic membranes through which the catalyst was retained and recycled (Fig. 12(b)). Less than $1 \text{ mg}\cdot\text{L}^{-1}$ of catalyst was found in the permeation, and the conversion and selectivity were higher than 99.5%. The greatest advantage of a ceramic membrane is that it can be easily cleaned using strong basic and acidic solutions, which is all but impossible in a polymeric membrane system. Another industrial application of a porous CMR has been achieved for *p*-aminophenol production. A microfiltration membrane based on a porous ceramic membrane (from Jiangsu Jiuwu Hi-Tech Co., Ltd.) was successfully employed to recover nano-sized catalysts. This project yields a *p*-aminophenol production of $30\,000 \text{ t}\cdot\text{a}^{-1}$ in Anhui province, China (Fig. 12(c)). Many issues

are yet to be resolved from the industrial point of view, especially in terms of reactor scaling up. Computational fluid dynamics (CFD) simulation would be a powerful tool to realize the real-time measurement of multiscale dynamic behavior that includes the multiphase flow and the synergy between the reaction and transfer. Most CFD models focus on the membrane separation process [108–113]. However, CFD can also be used to predict the fluid flow pattern with the introduction of a ceramic membrane [114]. For example, in a three-blade impeller system, the maximum homogeneity of solid particles was achieved at a blade angle of 30° . The model provides a visualization of the flow field distribution in a multiphase system along with in-depth details about the fluid flow.

4. Conclusions and prospects

Many recent investigations have demonstrated that ceramic-based CMRs show great potential in a wide range of applications for chemical reactions and separations under harsh conditions in terms of both temperature and the chemical environment. The aim of this article was to review current research—mostly from the last decade—on the two most important types of CMR: those based on the dense mixed-conducting membrane for gas separation, and those based on the porous ceramic membrane for heterogeneous catalytic processes. This article mainly focused on new developments and innovative uses of these CMRs from the perspective of membrane reactor design and optimization. CMRs do not only integrate various membrane operations simply into one unit; they also intensify the process by operating in a synergistic fashion. Examples of reactions that benefit from dense CMRs include the POM to syngas, steam reforming to produce hydrogen, and the TDCD. Examples of reactions that benefit from porous CMRs include the heterogeneous catalysis of phenol hydroxylation with hydrogen peroxide or oxygen, cyclohexanone ammoxidation, and the hydrogenation of *p*-nitrophenol to *p*-aminophenol. Emerging challenges and great opportunities still exist for both types of CMR, as described below.

4.1. Challenges affecting dense CMRs

The following challenges are still encountered in the industrialization of dense CMRs:

(1) Engineering the membrane. Membrane architecture is important in determining the performance of a CMR. Disk-like (or planar), tubular, and HF membranes are good choices. The major considerations in good membrane geometry are the ease of high-temperature sealing, permeation flux, and mechanical strength. The biggest problem for the disk-like membrane is high-temperature sealing, which is also the most crucial challenge for other high-temperature membranes. Clearly, tubular and HF membranes are good candidates; however, both still have drawbacks in terms of permeation flux (membrane thickness) and mechanical strength, respectively. A combination of co-sintering and spin-spray techniques to fabricate asymmetric tubular membranes and the novel design of multichannel HF membranes are expected to be the most effective solutions. However, the precise control of structures and components during fabrication and sintering still represents a challenge.

(2) Lowering the operation temperature. A lower operation temperature would result in dramatic benefits, such as better stability, easier sealing, fewer equipment requirements, lower energy consumption, lower pollution, and greater safety. In addition to considerations of membrane geometry (e.g., ultra-thin separation layers), the development of membrane materials with low cost and high performance at low temperatures is an effective route.

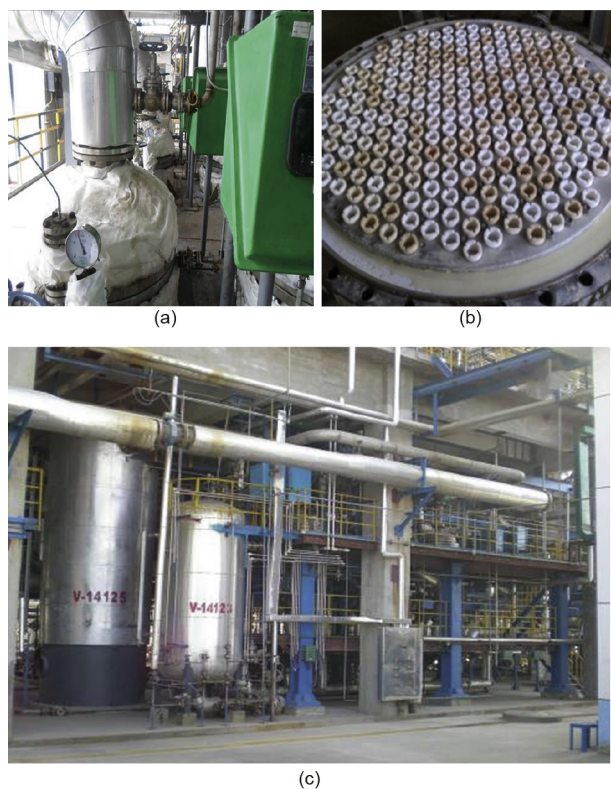


Fig. 12. Industrial applications of porous CMRs. (a) A side-stream membrane reactor for cyclohexanone ammoxidation; (b) a 241-channel membrane model; (c) *p*-aminophenol production.

Traditional strategies associated with A or B site tailoring cannot fully meet these requirements. Oxygen-site doping with fluorine has been considered, and was demonstrated to be a good choice. However, the stability of the fluorine-containing material, especially within a complex environment (e.g., in the presence of oxidizing, reducing, and/or sulfur-containing species) requires further evaluation and optimization.

(3) Large-scale membrane fabrication. Simple and reliable fabrication remains the greatest challenge for the commercialization of membrane reactors. Traditional HF membrane fabrication has been labeled as a labor-, energy-, and time-consuming process. One-step thermal-processing techniques obviously provide a breakthrough opportunity in terms of low cost and reliable large-scale membrane fabrication. In fact, one-step thermal processing is an *in situ* synthesis and sintering process. Obtaining a good match between the solid-state reaction rates in synthesis and the sintering rates is a crucial issue, and additional research into the optimization of the coupling process and sintering parameters is therefore required.

4.2. Challenges affecting porous CMRs

The following challenges are still encountered in the industrialization of porous CMRs:

(1) Membrane reactor design. The major drawback of the side-stream configuration is the adsorption of catalyst in the loop, whereas the submerged configuration has many advantages that include a small footprint, reduced catalyst adsorption, and significantly reduced energy consumption. Better performance was obtained in a dual-membrane reactor, which introduces an additional membrane distributor, due to good distribution of the reactants. Combining a dual-membrane reactor with an airlift membrane reactor provides another opportunity in gas–liquid heterogeneous catalysis by improving the gas–liquid mass transfer.

(2) Engineering the membrane. Tubular membranes are commonly used and studied for use in porous CMRs. However, their relatively large diameter and thick wall result in low surface-area-to-volume ratios and large mass-transfer resistance, and hence in a low separation efficiency for the entire membrane system. HF membranes appear to overcome these limitations. For practical application, an appropriate pore size and distribution are essential in order to generate uniform droplets at the micro-scale. Because of the large surface-area-to-volume ratio of HF membranes, they can support nano-sized catalysts. A combination of surface silanization with the flow-through method results in a uniform and smaller particle size and in better adhesion of a nano Pd catalyst on an HF membrane.

(3) Process simulation. Most CFD models consider the catalytic reaction and the membrane separation process separately. Therefore, integrally linking the two processes is essential in establishing CFD models that help us to understand the process in a way that is close to reality. Three levels of mass transfer exist in a membrane reactor: microscale, mesoscale, and macroscale mass transfers. A combination of these mass transfers and chemical reactions with multiphase hydrodynamics and kinetic models will be one of the most important research directions for porous CMRs.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20990222, 21006047, 21706117, and 21706118), the Natural Science Foundation of Jiangsu (BK20170978 and BK20170970), the State Key Laboratory of Material-Oriented Chemical Engineering (ZK201609), and the Innovative Research Team Program by the Ministry of Education of China (IRT17R54).

Compliance with ethics guidelines

Guangru Zhang, Wanqin Jin, and Nanping Xu declare that they have no conflict of interest or financial conflicts to disclose.

References

- [1] Dixon AG. Recent research in catalytic inorganic membrane reactors. *Int J Chem React Eng* 2003;1(1):R6.
- [2] Sanchez Marcano JG, Tsotsis TT. Catalytic membranes and membrane reactors. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2004.
- [3] Thursfield A, Murugan A, Franca R, Metcalfe IS. Chemical looping and oxygen permeable ceramic membranes for hydrogen production—a review. *Energy Environ Sci* 2012;5(6):7421–59.
- [4] Dong X, Jin W, Xu N, Li K. Dense ceramic catalytic membranes and membrane reactors for energy and environmental applications. *Chem Commun (Camb)* 2011;47(39):10886–902.
- [5] Bouwmeester HJM. Dense ceramic membranes for methane conversion. *Catal Today* 2003;82(1–4):141–50.
- [6] Yang W, Wang H, Zhu X, Lin L. Development and application of oxygen permeable membrane in selective oxidation of light alkanes. *Top Catal* 2005;35(1–2):155–67.
- [7] Liu Y, Tan X, Li K. Mixed conducting ceramics for catalytic membrane processing. *Catal Rev Sci Eng* 2006;48(2):145–98.
- [8] Wei Y, Yang W, Caro J, Wang H. Dense ceramic oxygen permeable membranes and catalytic membrane reactors. *Chem Eng J* 2013;220:185–203.
- [9] Bouwmeester HJM, Burggraaf AJ. Dense ceramic membranes for oxygen separation. In: *The CRC handbook of solid state electrochemistry*. Boca Raton: CRC Press; 1997. p. 481–553.
- [10] Sunarso J, Baumann S, Serra JM, Meulenberg WA, Liu S, Lin YS, et al. Mixed ionic-electronic conducting (MIEC) ceramic-based membranes for oxygen separation. *J Membr Sci* 2008;320(1–2):13–41.
- [11] Ollis DF. Integrating photocatalysis and membrane technologies for water treatment. *Ann N Y Acad Sci* 2003;984:65–84.
- [12] Molinari R, Palmisano L. Photocatalytic membrane reactors in water purification. In: Lehr JH, Keeley JW, Lehr JK, editors. *Water encyclopedia: domestic, municipal and industrial water supply and waste disposal*. New Jersey: John Wiley & Sons, Inc.; 2005. p. 791–7.
- [13] Augugliaro V, Litter M, Palmisano L, Soria J. The combination of heterogeneous photocatalysis with chemical and physical operations: a tool for improving the photoprocess performance. *J Photochem Photobiol Photochem Rev* 2006;7(4):127–44.
- [14] Mozia S. Photocatalytic membrane reactors (PMRs) in water and wastewater treatment, a review. *Separ Purif Tech* 2010;73(2):71–91.
- [15] Geffroy PM, Reichmann M, Kilmann L, Jouin J, Richet N, Chartier T. Identification of the rate-determining step in oxygen transport through $\text{La}_{(1-x)}\text{Sr}_x\text{Fe}_{(1-y)}\text{Ga}_y\text{O}_{3-\delta}$ perovskite membranes. *J Membr Sci* 2015;476:340–7.
- [16] Fernández-González R, Molina T, Savvin S, Moreno R, Makradi A, Nunez P. Characterization and fabrication of LSCF tapes. *J Eur Ceram Soc* 2014;34(4):953–9.
- [17] Reichmann M, Geffroy PM, Fouletier J, Richet N, Chartier T. Effect of cation substitution in the A site on the oxygen semi-permeation flux in $\text{La}_{0.5}\text{A}_{0.5}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_{3-\delta}$ and $\text{La}_{0.5}\text{A}_{0.5}\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_{3-\delta}$ dense perovskite membranes with A = Ca, Sr and Ba (part I). *J Power Sources* 2014;261:175–83.
- [18] Repasky JM, Foster EP, Armstrong PA, Stein VE, Anderson LL. ITM oxygen development for advanced oxygen supply. San Francisco: Gasification Technologies Council; 2011.
- [19] Gromada M, Trawczynski J, Wierzbicki M, Zawadzki M. Effect of forming techniques on efficiency of tubular oxygen separating membranes. *Ceram Int* 2017;43(1):256–61.
- [20] Wu Z, Hidayati Othman N, Zhang G, Liu Z, Jin W, Li K. Effects of fabrication processes on oxygen permeation of Nb_2O_5 -doped $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ micro-tubular membranes. *J Membr Sci* 2013;442:1–7.
- [21] Salehi M, Pfaff EM, Junior RM, Bergmann CP, Diethelm S, Neururer C, et al. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) feedstock development and optimization for thermoplastic forming of thin planar and tubular oxygen separation membranes. *J Membr Sci* 2013;443:237–45.
- [22] Cruz RT, Bragança SR, Bergmann CP, Graule T, Clemens F. Preparation of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) feedstocks with different thermoplastic binders and their use in the production of thin tubular membranes by extrusion. *Ceram Int* 2014;40(5):7531–8.
- [23] Zhang C, Xu Z, Chang X, Zhang Z, Jin W. Preparation and characterization of mixed-conducting thin tubular membrane. *J Membr Sci* 2007;299(1–2):261–7.
- [24] Xu N, Li S, Jin W, Shi J, Lin Y. Experimental and modeling study on tubular dense membranes for oxygen permeation. *AIChE J* 1999;45(12):2519–26.
- [25] Nagendra N, Bandopadhyay S. Room and elevated temperature strength of perovskite membrane tubes. *J Eur Ceram Soc* 2003;23(9):1361–8.
- [26] Li S, Jin W, Huang P, Xu N, Shi J, Lin Y. Tubular lanthanum cobaltite perovskite type membrane for oxygen permeation. *J Membr Sci* 2000;166(1):51–61.
- [27] Kaletsch A, Pfaff EM, Broeckmann C, Modigell M, Nauels N. Pilot module for oxygen separation with BSCF membranes. In: *2nd International Conference on Energy Process Engineering*; 2011 Jun 20–22; Frankfurt, Germany. Frankfurt: DECHEMA; 2011.

- [28] Tan X, Wang Z, Meng B, Meng X, Li K. Pilot-scale production of oxygen from air using perovskite hollow fibre membranes. *J Membr Sci* 2010;352(1–2):189–96.
- [29] Meng B, Wang Z, Tan X, Liu S. SrCo_{0.9}Sc_{0.1}O_{3-δ} perovskite hollow fibre membranes for air separation at intermediate temperatures. *J Eur Ceram Soc* 2009;29(13):2815–22.
- [30] Vivet A, Geffroy PM, Coudert V, Fouletier J, Richet N, Chartier T. Influence of glass and gold sealants materials on oxygen permeation performances in La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_{3-δ} perovskite membranes. *J Membr Sci* 2011;366(1–2):132–8.
- [31] Chen Y, Qian B, Hao Y, Liu S, Tade M, Shao Z. Influence of sealing materials on the oxygen permeation fluxes of some typical oxygen ion conducting ceramic membranes. *J Membr Sci* 2014;470:102–11.
- [32] Faaland S, Einarsrud MA, Grande T. Reactions between calcium- and strontium-substituted lanthanum cobaltite ceramic membranes and calcium silicate sealing materials. *Chem Mater* 2001;13(3):723–32.
- [33] Qi X, Akin FT, Lin Y. Ceramic-glass composite high temperature seals for dense ionic-conducting ceramic membranes. *J Membr Sci* 2001;193(2):185–93.
- [34] Bouwmeester HJM, Kruidhof H, Burggraaf AJ. Importance of the surface exchange kinetics as rate limiting step in oxygen permeation through mixed-conducting oxides. *Solid State Ion* 1994;72:185–94.
- [35] Chang X, Zhang C, Jin W, Xu N. Match of thermal performances between the membrane and the support for supported dense mixed-conducting membranes. *J Membr Sci* 2006;285(1–2):232–8.
- [36] Jin W, Li S, Huang P, Xu N, Shi J. Preparation of an asymmetric perovskite-type membrane and its oxygen permeability. *J Membr Sci* 2001;185(2):237–43.
- [37] Dong X, Zhang G, Liu Z, Zhong Z, Jin W, Xu N. CO₂-tolerant mixed conducting oxide for catalytic membrane reactor. *J Membr Sci* 2009;340(1–2):141–7.
- [38] Wu Z, Wang B, Li K. Functional LSM-ScSZ/NiO-ScSZ dual-layer hollow fibres for partial oxidation of methane. *Int J Hydrogen Energy* 2011;36(9):5334–41.
- [39] Liu T, Chen Y, Fang S, Lei L, Wang Y, Ren C, et al. A dual-phase bilayer oxygen permeable membrane with hierarchically porous structure fabricated by freeze-drying tape-casting method. *J Membr Sci* 2016;520:354–63.
- [40] Liu ZK, Zhu JW, Jin WQ. Preparation and characterization of mixed-conducting supported hollow fiber membrane. *J Inorg Mater* 2015;30(6):621–6.
- [41] Meng X, Ding W, Jin R, Wang H, Gai Y, Ji F, et al. Two-step fabrication of BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-δ} asymmetric oxygen permeable membrane by dip coating. *J Membr Sci* 2014;450:291–8.
- [42] Liu Z, Zhang G, Dong X, Jiang W, Jin W, Xu N. Fabrication of asymmetric tubular mixed-conducting dense membranes by a combined spin-spraying and co-sintering process. *J Membr Sci* 2012;415–416:313–9.
- [43] Wang H, Werth S, Schiestel T, Caro J. Perovskite hollow-fiber membranes for the production of oxygen-enriched air. *Angew Chem Int Ed Engl* 2005;44(42):6906–9.
- [44] Tan X, Liu Y, Li K. Mixed conducting ceramic hollow-fiber membranes for air separation. *AIChE J* 2005;51(7):1991–2000.
- [45] Leo A, Smart S, Liu S, da Costa JCD. High performance perovskite hollow fibres for oxygen separation. *J Membr Sci* 2011;368(1–2):64–8.
- [46] Chi Y, Li T, Wang B, Wu Z, Morphology Li K. performance and stability of multi-bore capillary La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} oxygen transport membranes. *J Membr Sci* 2017;529:224–33.
- [47] Zhu J, Guo S, Liu G, Liu Z, Zhang Z, Jin W. A robust mixed-conducting multichannel hollow fiber membrane reactor. *AIChE J* 2015;61(8):2592–9.
- [48] Zhu J, Liu Z, Guo S, Jin W. Influence of permeation modes on oxygen permeability of the multichannel mixed-conducting hollow fibre membrane. *Chem Eng Sci* 2015;122:614–21.
- [49] Zhu J, Dong Z, Liu Z, Zhang K, Zhang G, Jin W. Multichannel mixed-conducting hollow fiber membranes for oxygen separation. *AIChE J* 2014;60(6):1969–76.
- [50] Saracco G, Neomagus HWJP, Versteeg GF, Swaaij WPM. High-temperature membrane reactors: potential and problems. *Chem Eng Sci* 1999;54(13–4):1997–2017.
- [51] Tsai CY, Dixon AG, Moser WR, Ma YH. Dense perovskite membrane reactors for partial oxidation of methane to syngas. *AIChE J* 1997;43(511):2741–50.
- [52] Wang H, Tablet C, Feldhoff A, Caro J. A cobalt-free oxygen-permeable membrane based on the perovskite-type oxide Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-δ}. *Adv Mater* 2005;17(14):1785–8.
- [53] Shao Z, Dong H, Xiong G, Cong Y, Yang W. Performance of a mixed-conducting ceramic membrane reactor with high oxygen permeability for methane conversion. *J Membr Sci* 2001;183(2):181–92.
- [54] Jin W, Li S, Huang P, Xu N, Shi J, Lin Y. Tubular lanthanum cobaltite perovskite-type membrane reactors for partial oxidation of methane to syngas. *J Membr Sci* 2000;166(1):13–22.
- [55] Jiang H, Wang H, Werth S, Schiestel T, Caro J. Simultaneous production of hydrogen and synthesis gas by combining water splitting with partial oxidation of methane in a hollow-fiber membrane reactor. *Angew Chem Int Ed Engl* 2008;47(48):9341–4.
- [56] Tan X, Pang Z, Gu Z, Liu S. Catalytic perovskite hollow fiber membrane reactors for methane oxidative coupling. *J Membr Sci* 2007;302(1–2):109–14.
- [57] Tan X, Li K. Oxidative coupling of methane in a perovskite hollow-fiber membrane reactor. *Ind Eng Chem Res* 2006;45(1):142–9.
- [58] Wang H, Cong Y, Yang W. Oxidative coupling of methane in Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} tubular membrane reactors. *Catal Today* 2005;104(2–4):160–7.
- [59] Zeng Y, Lin Y, Swartz SL. Perovskite-type ceramic membrane: synthesis, oxygen permeation and membrane reactor performance for oxidative coupling of methane. *J Membr Sci* 1998;150(1):87–98.
- [60] Elshof JET, Bouwmeester HJM, Verweij H. Oxidative coupling of methane in a mixed-conducting perovskite membrane reactor. *Appl Catal A Gen* 1995;130(2):195–212.
- [61] Lobera MP, Escalístico S, Serra JM. High ethylene production through oxidative dehydrogenation of ethane membrane reactors based on fast oxygen-ion conductors. *ChemCatChem* 2011;3(9):1503–8.
- [62] Jiang H, Cao Z, Schirmeister S, Schiestel T, Caro J. A coupling strategy to produce hydrogen and ethylene in a membrane reactor. *Angew Chem Int Ed Engl* 2010;49(33):5656–60.
- [63] Czuprat O, Werth S, Caro J, Schiestel T. Oxidative dehydrogenation of propane in a perovskite membrane reactor with multi-step oxygen insertion. *AIChE J* 2010;56(9):2390–6.
- [64] Czuprat O, Werth S, Schirmeister S, Schiestel T, Caro J. Olefin production by a multistep oxidative dehydrogenation in a perovskite hollow-fiber membrane reactor. *ChemCatChem* 2009;1(3):401–5.
- [65] Balachandran U, Lee TH, Dorris SE. Hydrogen production by water dissociation using mixed conducting dense ceramic membranes. *Int J Hydrogen Energy* 2007;32(4):451–6.
- [66] Nalbandian L, Evdou A, Zaspalis V. La_{1-x}Sr_xMO₃ (M = Mn, Fe) perovskites as materials for thermochemical hydrogen production in conventional and membrane reactors. *Int J Hydrogen Energy* 2009;34(17):7162–72.
- [67] Song S, Moon JH, Ryu HW, Lee TH, Dorris SE, Balachandran U. Non-galvanic hydrogen production by water splitting using cermet membranes. *J Ceram Proc Res* 2008;9(2):123–5.
- [68] Evdou A, Nalbandian L, Zaspalis VT. Perovskite membrane reactor for continuous and isothermal redox hydrogen production from the dissociation of water. *J Membr Sci* 2008;325(2):704–11.
- [69] Itoh N, Sanchez MA, Xu WC, Haraya K, Hongo M. Application of a membrane reactor system to thermal-decomposition of CO₂. *J Membr Sci* 1993;77(2–3):245–53.
- [70] Jin W, Zhang C, Chang X, Fan Y, Xing W, Xu N. Efficient catalytic decomposition of CO₂ to CO and O₂ over Pd/mixed-conducting oxide catalyst in an oxygen-permeable membrane reactor. *Environ Sci Technol* 2008;42(8):3064–8.
- [71] Jiang H, Wang H, Liang F, Werth S, Schiestel T, Caro J. Direct decomposition of nitrous oxide to nitrogen by *in situ* oxygen removal with a perovskite membrane. *Angew Chem Int Ed Engl* 2009;48(16):2983–6.
- [72] Franca RV, Thursfield A, Metcalfe IS. La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} microtubular membranes for hydrogen production from water splitting. *J Membr Sci* 2012;389:173–81.
- [73] Zhang K, Zhang G, Liu Z, Zhu J, Zhu N, Jin W. Enhanced stability of membrane reactor for thermal decomposition of CO₂ via porous-dense-porous triple-layer composite membrane. *J Membr Sci* 2014;471:9–15.
- [74] Liang W, Megarajan SK, Liang F, Zhang Y, He G, Liu Z, et al. Coupling of N₂O decomposition with CO₂ reforming of CH₄ in novel cobalt-free BaFe_{0.9}Zr_{0.05}Al_{0.05}O_{3-δ} oxygen transport membrane reactor. *Chem Eng J* 2016;305:176–81.
- [75] Jiang H, Wang H, Liang F, Werth S, Schirmeister S, Schiestel T, et al. Improved water dissociation and nitrous oxide decomposition by *in situ* oxygen removal in perovskite catalytic membrane reactor. *Catal Today* 2010;156(3–4):187–90.
- [76] Jiang W, Zhang G, Liu Z, Zhang K, Jin W. A novel porous-dense dual-layer composite membrane reactor with long-term stability. *AIChE J* 2013;59(11):4355–63.
- [77] Zhang C, Chang X, Dong X, Jin W, Xu N. The oxidative stream reforming of methane to syngas in a thin tubular mixed-conducting membrane reactor. *J Membr Sci* 2008;320(1–2):401–6.
- [78] Zhu N, Dong X, Liu Z, Zhang G, Jin W, Xu N. Toward highly-effective and sustainable hydrogen production: bio-ethanol oxidative steam reforming coupled with water splitting in a thin tubular membrane reactor. *Chem Commun (Camb)* 2012;48(57):7137–9.
- [79] Zhang C, Jin W, Yang C, Xu N. Decomposition of CO₂ coupled with POM in a thin tubular oxygen-permeable membrane reactor. *Catal Today* 2009;148(3–4):298–302.
- [80] Zhang C, Chang X, Fan Y, Jin W, Xu N. Improving performance of a dense membrane reactor for thermal decomposition of CO₂ via surface modification. *Ind Eng Chem Res* 2007;46(7):2000–5.
- [81] Jin W, Zhang C, Zhang P, Fan Y, Xu N. Thermal decomposition of carbon dioxide coupled with POM in a membrane reactor. *AIChE J* 2006;52(7):2545–50.
- [82] Zhu J, Liu G, Liu Z, Chu Z, Jin W, Xu N. Unprecedented perovskite oxyfluoride membranes with high-efficiency oxygen ion transport paths for low-temperature oxygen permeation. *Adv Mater* 2016;28(18):3511–5.
- [83] Zhu J, Zhang G, Liu G, Liu Z, Jin W, Xu N. Perovskite hollow fibers with precisely controlled cation stoichiometry via one-step thermal processing. *Adv Mater* 2017;29(18). Epub 2017 Mar 6.
- [84] Zou Y, Jiang H, Liu Y, Gao H, Xing W, Chen R. Highly efficient synthesis of cumene via benzene isopropylation over nano-sized beta zeolite in a submerged ceramic membrane reactor. *Separ Purif Tech* 2016;170:49–56.
- [85] Zou Y, Jiang H, Gao H, Chen R. Efficient recovery of ultrafine catalysts from oil/water/solid three-phase system by ceramic microfiltration membrane. *Korean J Chem Eng* 2016;33(8):2453–9.

- [86] Jiang H, Jiang X, She F, Wang Y, Xing W, Chen R. Insights into membrane fouling of a side-stream ceramic membrane reactor for phenol hydroxylation over ultrafine TS-1. *Chem Eng J* 2014;239:373–80.
- [87] Mao H, Chen R, Xing W, Jin W. Organic solvent-free process for cyclohexanone ammoximation by a ceramic membrane distributor. *Chem Eng Technol* 2016;39(5):883–90.
- [88] Jiang X, She F, Jiang H, Chen R, Xing W, Jin W. Continuous phenol hydroxylation over ultrafine TS-1 in a side-stream ceramic membrane reactor. *Korean J Chem Eng* 2013;30(4):852–9.
- [89] Fane AG. Submerged membranes. In: Li NN, Fan AG, Winston Ho WS, Matsuura T, editors. *Advanced membrane technology and applications*. New Jersey: John Wiley & Sons, Inc.; 2008. p. 239–70.
- [90] Zhong Z, Xing W, Jin W, Xu N. Adhesion of nanosized nickel catalysts in the nanocatalysis/UF system. *AIChE J* 2007;53(5):1204–10.
- [91] Chen R, Du Y, Wang Q, Xing W, Jin W, Xu N. Effect of catalyst morphology on the performance of submerged nanocatalysis/membrane filtration system. *Ind Eng Chem Res* 2009;48(14):6600–7.
- [92] Jiang H, Meng L, Chen R, Jin W, Xing W, Xu N. A novel dual-membrane reactor for continuous heterogeneous oxidation catalysis. *Ind Eng Chem Res* 2011;50(18):10458–64.
- [93] Chen R, Bao Y, Xing W, Jin W, Xu N. Enhanced phenol hydroxylation with oxygen using a ceramic membrane distributor. *Chin J Catal* 2013;34(1):200–8.
- [94] Chen R, Mao H, Zhang X, Xing W, Fan Y. A dual-membrane airlift reactor for cyclohexanone ammoximation over titanium silicalite-1. *Ind Eng Chem Res* 2014;53(15):6372–9.
- [95] Xu N, Li W, Zhao Y, Xing W, Shi J. Theory and method of application-oriented ceramic membranes design (I). *J Chem Ind Eng* 2003;54(9):1284–9.
- [96] Wells DH Jr, Delgass WN Jr, Thomson KT. Evidence of defect-promoted reactivity for epoxidation of propylene in titanosilicate (TS-1) catalysts: a DFT study. *J Am Chem Soc* 2004;126(9):2956–62.
- [97] Shetti VN, Srinivas D, Ratnasamy P. Enhancement of chemoselectivity in epoxidation reactions over TS-1 catalysts by alkali and alkaline metal ions. *J Mol Catal A-Chem* 2004;210(1–2):171–8.
- [98] Lu C, Chen R, Xing W, Jin W, Xu N. A submerged membrane reactor for continuous phenol hydroxylation over TS-1. *AIChE J* 2008;54(7):1842–9.
- [99] Meng L, Guo H, Dong Z, Jiang H, Xing W, Jin W. Ceramic hollow fiber membrane distributor for heterogeneous catalysis: effects of membrane structure and operating conditions. *Chem Eng J* 2013;223:356–63.
- [100] Li W, Zhao Y, Liu F, Xing W, Xu N, Shi J. Theory and method of application-oriented ceramic membranes design (II). *J Chem Ind Eng* 2003;54(9):1290–4.
- [101] Zhong Z, Li W, Xing W, Xu N. Crossflow filtration of nanosized catalysts suspension using ceramic membranes. *Separ Purif Tech* 2011;76(3):223–30.
- [102] Chen R, Jiang Y, Xing W, Jin W. Fabrication and catalytic properties of palladium nanoparticles deposited on a silanized asymmetric ceramic support. *Ind Eng Chem Res* 2011;50(8):4405–11.
- [103] Chen R, Jiang Y, Xing W, Jin W. Preparation of palladium nanoparticles deposited on a silanized hollow fiber ceramic membrane support and their catalytic properties. *Ind Eng Chem Res* 2013;52(14):5002–8.
- [104] Li H, Jiang H, Chen R, Wang Y, Xing W. Enhanced catalytic properties of palladium nanoparticles deposited on a silanized ceramic membrane support with a flow-through method. *Ind Eng Chem Res* 2013;52(39):14099–106.
- [105] Xu J, Bhattacharyya D. Modeling of Fe/Pd nanoparticle-based functionalized membrane reactor for PCB dechlorination at room temperature. *J Phys Chem C* 2008;112(25):9133–44.
- [106] Ouyang L, Dotzauer DM, Hogg SR, Macanas J, Lahitte JF, Bruening ML. Catalytic hollow fiber membranes prepared using layer-by-layer adsorption of polyelectrolytes and metal nanoparticles. *Catal Today* 2010;156(3–4):100–6.
- [107] Dotzauer DM, Abusloua A, Miachon S, Dalmon JA, Bruening ML. Wet air oxidation with tubular ceramic membranes modified with polyelectrolyte/Pt nanoparticle films. *Appl Catal B* 2009;91(1–2):180–8.
- [108] Wiley DE, Fletcher DF. Computational fluid dynamics modelling of flow and permeation for pressure-driven membrane processes. *Desalination* 2002;145(1–3):183–6.
- [109] Rahimi M, Madaeni SS, Abbasi K. CFD modeling of permeate flux in cross-flow microfiltration membrane. *J Membr Sci* 2005;255(1–2):23–31.
- [110] Ghidossi R, Veyret D, Moulin P. Computational fluid dynamics applied to membranes: state of the art and opportunities. *Chem Eng Process* 2006;45(6):437–54.
- [111] Coroneo M, Montante G, Catalano J, Paglianti A. Modelling the effect of operating conditions on hydrodynamics and mass transfer in a Pd-Ag membrane module for H₂ purification. *J Membr Sci* 2009;343(1–2):34–41.
- [112] Brannock M, De Wever H, Wang Y, Leslie G. Computational fluid dynamics simulations of MBRs: inside submerged versus outside submerged membranes. *Desalination* 2009;236(1–3):244–51.
- [113] Brannock M, Leslie G, Wang Y, Buethorn S. Optimising mixing and nutrient removal in membrane bioreactors: CFD modelling and experimental validation. *Desalination* 2010;250(2):815–8.
- [114] Meng L, Cheng J, Jiang H, Yang C, Xing W, Jin W. Design and analysis of a submerged membrane reactor by CFD simulation. *Chem Eng Technol* 2013;36(11):1874–82.