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Limitations and potentials of oxygen transport dense and porous ceramic membranes for oxidation reactions

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Abstract

This overview focuses on both dense and porous ceramic membranes for high temperature oxidation reactions, i.e. partial and total oxidations. Non-permselective porous membranes are efficient contactors for total oxidation of VOC or soot. They are also still attractive as oxygen distributors for the partial oxidation of long chain alkanes, although dense mixed conducting membranes are now on the way to be commercialized for methane involving reactions. By a proper selection of the ion conducting materials composition, structure and thickness, and by combining in a suitable way both dense and porous layers, the oxygen flux, performance and stability of dense ceramic membranes can be considerably improved. In view of the large number of material challenges and scientific approaches found in the literature, it is clearly difficult to be exhaustive. New developments in the field of advanced membranes constantly contribute to improve the potential of membrane reactors, through the development of new preparation methods, of optimized layer stacking and of new membrane materials with original or improved properties. After a rapid overview on both dense and porous membranes used for oxidation reactions, examples of the developments in the field of membrane materials, structures, architectures, synthesis methods and reactor designs are reported, coming from either our Institute or from the recent literature on both membrane reactors and SOFCs.

Keywords: Ceramic membranes; Membrane reactors; Oxidation reactions; Oxygen transport

1. Introduction

The concept of combining membranes and reactors is being explored in various configurations, which can be classified in three groups, regarding the role of the membrane in the process [1]. The membrane can act as an *extractor* (the removal of product(s) increases the conversion by shifting the reaction equilibrium), as a *distributor* (the controlled addition of reactant(s) along the reactor wall limits side reactions), or as an active *contactor* (the controlled diffusion of reactants to the catalyst can lead to an engineered catalytic reaction zone). In the two first cases the membrane has usually no catalytic properties and is combined, for example, with a fixed bed of catalyst placed on one membrane side [2].

In the active contactor mode, the membrane acts as a diffusion barrier and plays the role of a catalyst whereas separation properties are usually not required. The concept can be used with a forced flow-mode or with an opposing reactant mode. The forced flow contactor mode has been applied to the total oxidation of VOC [2].

The distributor mode is usually well adapted to limit consecutive and parallel deep oxidation reactions for partial oxidation, oxidative dehydrogenation of hydrocarbons and oxidative coupling of methane [2,3]. For these reactions, the local oxygen concentration at the catalytic site greatly influences both hydrocarbon conversion and product selectivity. Indeed strong oxidizing conditions promote the total combustion responsible for hot spots in the catalytic bed [2,3]. Using membrane supported concepts, oxygen can be dosed in a controlled manner so that the hydrocarbon–

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oxygen ratio is tuned along the catalyst bed. Providing the kinetics of the oxidation reaction are known, an optimal oxygen partial pressure profile can be controlled along the reactor [2,3]. The derived ideal oxygen permeation profile allows the design of optimized membranes in terms of permeability or thickness gradients [2,3]. In addition, the oxygen–hydrocarbon feed separation helps to overcome flammability and explosion limits. It results in a greater catalytic activity while the controlled oxygen supply avoids the catalysts to be deactivated in reducing conditions. The concept of tuned oxygen supply has also a beneficial role in mitigating the temperature rise in the reactor [2], which is a key issue in alkane partial oxidation. The O_2 permselectivity of the membrane is also an important economic factor because air can be used instead of pure O_2. The extremely high permselectivity of dense ionic conducting ceramics, coupled with their ability to generate highly reactive/selective O^* species, explains their impressive development for these applications over the last 15 years [4]. However, due to the very poor conductivity/permeability of dense membranes below 800 °C, further improvements are still needed for applications in the range 400–700 °C, for which to date poorly permselective porous membranes have to be used [2,5].

A large number of recent review articles and books seeks to review literature and new developments on membrane reactors over the last 10 years [1–10]. Research directions that were previously considered promising have been recently reconsidered, and new ideas have emerged [9]. The present paper highlights several specific aspects in the field of membrane materials for high temperature oxidation reactions. New material developments constantly contribute to improve the potential of membrane reactors, through the implementation of new preparation methods, new shapes and new membrane materials with original or improved properties (composition, crystallographic structure, architecture, porous structure, reactivity, transport mechanisms, oxygen flux, permselectivity, long-term stability, . . .). Recent developments in SOFCs, involving thin supported electrolyte films, with composition and porosity gradients (from the dense electrolyte to the electrodes) are also directly applicable to membrane reactors for partial oxidation reactions.

2. Dense membranes for oxidation reactions

Dense membranes (cf. Fig. 1a and b) are of particular interest for oxygen transport applications [4,11,12] because of their high permselectivity compared to porous membranes (cf. Fig. 1c). Oxygen ions are selectively transported through the non-porous ceramic membrane that is tight to other species. Different types of electrochemical membranes can be developed and in all cases the dissociation of an oxygen molecule must occur at the cathode side of the cell, usually the high oxygen partial pressure compartment, according to the interfacial reaction ($1/2\,O_2 + V_o^{\cdot\cdot} + 2e^- = O_o^x$), in which $V_o^{\cdot\cdot}$ is an oxygen vacancy [12]. After migration of the oxygen anions through the electrolyte, the reverse reaction must necessarily occur at the opposite (anodic) side in order to restore the O_2 molecule in the anodic gas phase. The way by which the electrons are transferred from the anode to the cathode determines the different membrane concepts [11]. The ion flux is driven either by an electrical field (cf. Fig. 1a) or by an oxygen pressure gradient (cf. Fig. 1b).

Most materials of interest to produce these membranes are based on fluorite (AO_2) or perovskite (ABO_3) related structures [11,12]. Dual phase membranes based on metal–ceramic combinations can also be used in the configuration of Fig. 1b [11]. Ion transport is via oxygen vacancies and the total flux of oxygen species is determined by both the bulk permeability and the reaction rate of molecular oxygen at the interface membrane/external gas phase. Many conducting oxides have a sufficient ionic conductivity to be used as oxygen distributors in oxidation reactions at temperatures higher than 700 °C. This is typically an adapted temperature range for CH_4 involving reactions (oxidative coupling or conversion to syngas) [13]. Two impressive US-DOE programs led by the two major American industrial gas companies (Air Products & Chemicals, and Praxair) have rapidly driven this "energy key-technology" to the prototype level [14]. If successful, this would be the first radically new reforming technology in over 3 decades.

A number of materials including perovskite derived structures have been identified as promising candidates to transport oxygen at relatively low temperature. Obviously

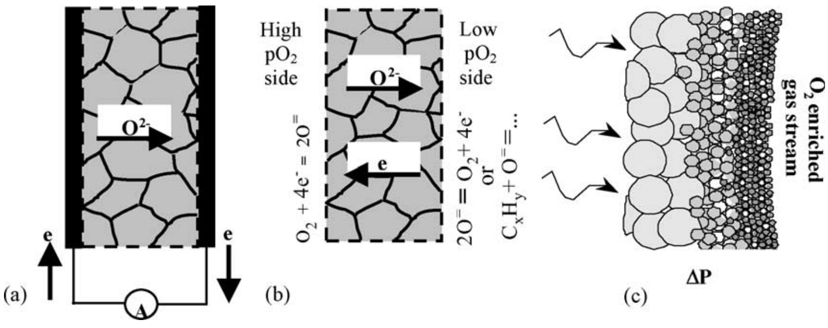

Fig. 1. Different membrane concepts for oxygen distribution in a reactor: (a) solid electrolyte cell (oxygen pump), (b) mixed ionic-electronic conductor (MIEC), (c) asymmetric porous membrane with a graded porosity.

the lanthanum cobaltites $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) and their substituted compounds $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ (LSFC), together with the Sr doped lanthanum manganites $LaMnO_3$ have been the most investigated perovskite systems. The precise composition may be tailored for a specific application. Apart from the well know (La,Sr)-(Co,Fe)$O_{3-\delta}$ structures reported for the first time in 1985 by Teraoka et al. [15], a number of derived and different structures were developed and studied. Most of the conducting ceramic materials developed as membranes were reviewed in articles and book chapters [4,11,12]. The insertion of small quantities of metals such as Ag for enhancing the O_2 permeability of $SrFeCo_{0.5}O_3$ oxide has been recently patented [16].

Doped fluorite (A_4O_8) and perovskite ($A_2B_2O_6$) structures can accommodate significant concentrations of oxygen ion vacancies. However there are constraints on the tolerated anion vacancies at intermediate temperatures due to ordering/clustering phenomena which reduce the concentration of mobile vacancies [17]. Attention was also paid to associated structures such as the pyrochlore ($A_2B_2O_7$) and brownmillerite systems ($A_2B_2O_5$) which can be considered as structures having oxygen vacancies already within the undoped formulation [4,11]. Other more complicated intergrowth structures were also investigated, such as the Ruddlesden–Popper phases (e.g. $SrO(La_{0.7}Sr_{0.3}MnO_3)_2$ or $Ln_2NiO_{4+\delta}$) or the Aurivillius-type materials based on bismuth-vanadium oxides (BIMEVOx) [4,18]. Specific details related to BIMEVOx, pyrochlore and brownmillerite structures are given below. The interest of Ruddlesden–Popper phases is discussed in Section 5.

In the mid 1980', bismuth based electrolytes were reported as catalytically active phases towards oxygen dissociation, and more recently the new BIMEVOX oxide family was reported as attractive electrolytes with very high oxide ion conductivity at moderate temperature (e.g. $10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 300 °C for BICUVOX.10 derivatives) [18]. The main drawback of Bi_2O_3-based compounds is their poor stability in reducing conditions. For example, BICUVOX.10 is irreversibly reduced below −375 mV versus air at 823 K (CuO/Cu redox system) [18]. The high sensitivity of BIMEVOX materials for irreversible electrochemical reduction has ruled out their use for long-term oxygen pumping.

Oxides of the composition $A_2B_2O_7$ often show the pyrochlore structure type, a superstructure based upon the fluorite-type structure of cubic ZrO_2 [19]. Depending on composition, doping and oxygen partial pressure, such materials display a remarkable variety of properties and applications (catalytic, electro-optic, piezoelectric, magnetism, semiconducting behavior ...). The oxygen ion conductivity of certain pyrochlores (e.g. $Y_2(Zr_yTi_{1-y})_2O_7$) can exceed 10^{-2} S/cm at 1000 °C [19]. Appropriate doping can produce either predominantly p- or n-type electronic conduction. This makes possible the design of a monolithic fuel cell in which the cathode, electrolyte and anode are chemically compatible as a consequence of being comprised of the same pyrochlore oxide, appropriately doped to create electronic conductivity in the electrodes and ionic conductivity in the electrolyte [4].

The vacancies in the perovskite lattice are formed either through doping of the lattice or through oxygen loss when the material is exposed to low O_2 partial pressures. Both of these vacancy formations may present problems [20]. Indeed, doping of cations into the lattice can cause association between the dopants and the resulting oxygen vacancies. This leads to high activation energies for oxygen anion conduction. Loss of oxygen by reduction modifies the lattice parameters and eventually results in phase decomposition [11]. In order to overcome these problems, membranes with a brownmillerite structure ($A_2B_2O_5$) have been preferred by Eltron [20] whose ion-conducting membranes are now on the way of being commercialized by the Air Products & Chemicals consortium [4,11]. The brownmillerite structure is comparable to the perovskite one, except that B metal atoms occupy only octahedral sites with no inherent oxide ion vacancy. The structure can support a large population of oxide ion vacancies, both ordered and disordered, as well as a variety of substituents in the A and B lattice sites. According to recently published results [13] the composition $La_{0.3}Sr_{1.7}Ga_{0.6}Fe_{1.4}O_{5+\delta}$ remained stable ($J_{O_2} = 6{-}7\ ml\ cm^{-2}\ min^{-1}$) even after 1000 h at 900 °C. The exact formula is classified, but the material contains neither expensive Ga nor easily reducible Co. We have to note that two times higher fluxes were obtained at the same temperature for the perovskite formulation $La_{0.8}Sr_{0.2}Co_{0.1}Fe_{0.8}Cr_{0.1}O_{3-\delta}$, tested for 340 h, and that very attractive and stable performances were obtained for the composition $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ developed by the team of Dalian [13]. It is also mentioned in [4] that very high oxygen fluxes (20–30 ml cm^{-2} min^{-1}) were reported by Statoil with perovskite type membranes developed in collaboration with BP, Sasol and Praxair. However, the corresponding temperature and the test duration are not mentioned.

Recent developments aim to obtain high O_2 flux at intermediate temperature ($600 < T < 800$ °C) in order to overcome technological issues due to the corrosion and material degradation at high temperatures. It is generally admitted that oxygen fluxes (J_{O_2}) of at least 5–10 ml cm^{-2} min^{-1} (STP) are required to achieve potential benefits in syngas production [13]. The perovskite or perovskite related-structures SrCoFe, and BaSrCoFe at 800 °C typically exhibit oxygen fluxes lower or equal to these values [4,13]. When an hydrocarbon or CO is used on the fuel side, the almost complete oxygen conversion results in very low oxygen partial pressure on the fuel side (typically 10^{-20} to 10^{-22} atm). The enhanced oxygen gradient through the membrane then results in an increase of the oxygen permeation, typically by one order of magnitude [21]. Therefore, for the best membranes mentioned above the required oxygen flow of 10 ml cm^{-2} min^{-1} can be achieved under reaction conditions.

3. Porous membranes for oxidation reactions

Although being less permselective than dense membranes, porous membranes offer a higher permeability and have been extensively used in catalytic reactors. Indeed, the high, stable and controllable permeability of porous membranes is attractive for a number of low temperature oxidation reactions (≤700 °C). The membrane can be either ''inert'' and only play the role as an oxygen distributor (Inert Membrane Reactor) or catalytically active (Catalytic Membrane Reactor) and act both as a separator and a catalyst [2,5].

In porous membranes, the gas transport mechanisms are determined by the ratio between the pore size and the mean free path length of the gas molecules [22,23]. The contribution of the different mechanisms depends on the membrane and gas properties, as well as on temperature and pressure. Then, the barrier effect can be optimized by an appropriate selection of the membrane porous structure and the operating conditions [24]. In some cases, the poor permselectivity of porous membranes towards O_2 can be significantly increased or modulated thanks to a mastered membrane design, composition and microstructure [5]. When the membrane combines catalytic properties, the objective is to increase the reaction selectivity via reactant and/or product separation. It is also possible to combine layers of different materials to carry out consecutive reactions, or to obtain an optimum catalyst distribution within the membrane [2,3,9].

3.1. Membranes as oxygen distributors

Inert porous membranes were largely used as oxygen distributors in partial oxidation or oxy-dehydrogenation of alkanes, or in the oxidative coupling of CH_4 [2,5,24]. They play the role as a barrier achieving the desired trans-membrane flux while avoiding the back-diffusion of the second reactant in the oxygen rich compartment. This latter function is usually achieved by an imposed pressure gradient [24]. The membranes used for these applications are generally mesoporous (Vycor glass [25] or obtained by filling the pores of a macroporous support with γAl_2O_3 or SiO_2 [26,27]); or even microporous (ZSM-5 zeolite [29]).

In spite of the poor permselectivity of the porous membranes, attractive performance can be obtained in many cases, provided that the operation conditions are carefully selected. It has been recently demonstrated that by optimizing the operation conditions in oxidative coupling of CH_4, 30% yield of C_2 hydrocarbons at 53% C_2 selectivity can be obtained with a mesoporous alumina membrane distributor [28].

The best results obtained with tubular porous membranes for ODH reactions usually involve membranes showing a high pressure drop (i.e. a relatively large thickness) [2,27]. A non-uniform thickness, decreasing from the entrance to the exit of the reactor, compensates the non-uniform O_2 flux generated by a significant pressure drop along the catalyst bed [27].

A number of low temperature oxidations (in the range 200–300 °C) have been explored with metallic macroporous membranes, for example ODH of methanol [30] or epoxidation of ethylene [31]. Industrial groups are currently evaluating the commercial interest of the MR concept for this type of reactions.

3.2. Contribution of material chemistry to an improvement of the O_2 permselectivity of porous membranes

Besides the above mentioned porous (non-permselective) membrane materials investigated during the last 10 years, several concepts for improving the role and permselectivity of inert porous membranes in oxidation reactions were recently studied in our group.

The first one is a chemical valve membrane designed in order to better regulate the O_2 profile in the reactor. The idea was to use a reactive V_2O_5 based membrane whose permeability was controlled by the red/ox properties of the gas phase [32]. The red/ox properties of V_2O_5 crystallites, which transform reversibly to V_2O_3 in a reducing atmosphere at 500 °C, drastically and reversibly modify the membrane morphology (cf. Fig. 2), its porous

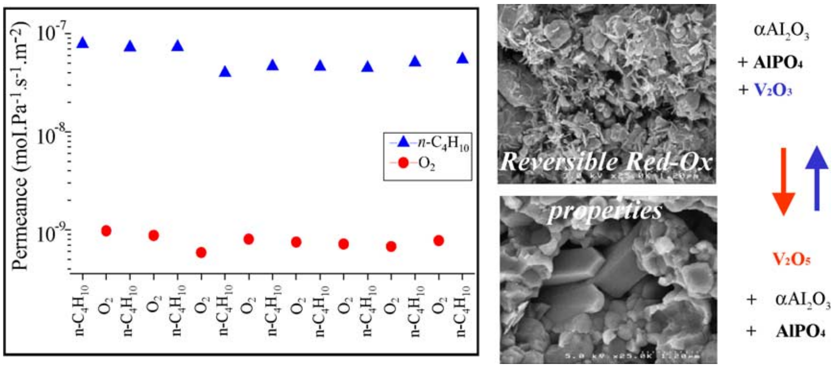

Fig. 2. Evolution of permeance of pure n-butane and pure oxygen, at 500 °C, during red/ox cycling of the chemical valve membrane. The corresponding changes in membrane morphology and crystallographic phases are shown on the right side (adapted from [32]).

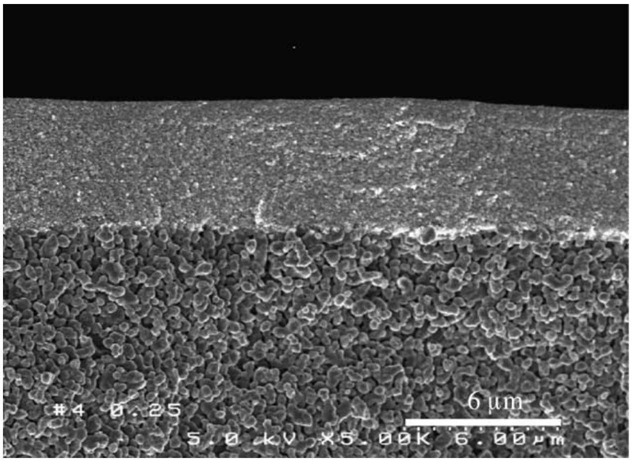

Fig. 3. FESEM observation of a mesoporous ceria based nanophase membrane ($0.25CeO_2$–$0.73Al_2O_3$–$0.02CaO + 1.5$ wt.%Pd) supported on a commercial αAl_2O_3 tube supplied by Pall-Exekia.

structure and consequently its gas permeation properties. The permeance is high when the membrane is reduced whereas it drops when it is oxidized: the ratio between the permeances of pure n-C_4H_{10} and pure O_2 is about 70 at 500 °C (cf. Fig. 2). This type of infiltrated composite membrane is reproducible, thermally, chemically stable and potentially attractive for MR applications [33].

In another study, we considered the potential contribution of nanophase ceramics and metal/ceramic nanocomposites for designing membranes with high surface reactivity and improved oxygen permselectivity [5]. Due to the large fraction of grain boundaries in nanostructured materials, grain surface properties tend to overwhelm bulk properties. For example the space charge phenomena and quantum confinement regime in nanograins strongly influence electrical conductivity of solid electrolytes [34]. Then, other oxygen diffusion mechanism can be expected in nanophase mesoporous oxygen conducting membranes in addition to Knudsen diffusion [35]. This was demonstrated with a CeO_2/Al_2O_3/Pd top layer containing 10 nm ceria crystallites deposited on an α-Al_2O_3 support (cf. Fig. 3). When increasing the temperature up to 450 °C, the measured ideal selectivity $\alpha^*(O_2/N_2)$ and $\alpha^*(O_2/Ar)$ gradually increases over the Knudsen value α_K, although $\alpha^*(N_2/Ar)$ decreases and remains lower than α_K (cf. Fig. 4). The preferential oxygen transport activated by temperature was attributed specifically to the presence of both ceria nanograins and Pd nanoparticles in the alumina matrix [35].

3.3. Catalytically active membranes

3.3.1. Dispersion of catalytic particles in an inert matrix

When the catalyst is located within the pores of an inert membrane, the catalytic and separation functions are engineered in a very compact fashion and the combination of the open pore path and transmembrane pressure provides easier access of the reactants to the catalyst. It is estimated that a membrane catalyst could be ten times more active than in the form of pellets [36], provided that the membrane thickness and porous texture, as well as the quantity and location of the catalyst in the membrane, are adapted to the reaction kinetics [22].

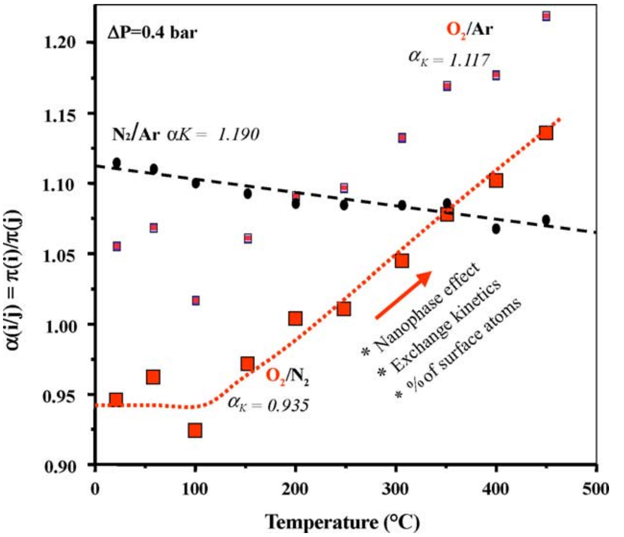

Fig. 4. Variation of single gases permeation ratios (O_2/N_2, O_2/Ar and N_2/Ar) vs. temperature for the Ceria based composite membrane shown in Fig. 3.

For biphasic applications (gas/catalyst) the membrane pore structure must favor gas–wall interactions (i.e. reactant-catalyst contacts). For catalytic consecutive-parallel reactions, such as the selective oxidation of hydrocarbons, the non-selective gas–gas molecular interactions must be limited because they lead to a total oxidation of reactants and products. Consequently, small pore mesoporous or microporous membranes, in which the dominant gas transport is Knudsen or micropore activated diffusion [23], are typically favored for contactor applications in biphasic reactions.

Noble metals can be easily dispersed in porous ceramic membrane matrices. The combustion of VOC has been typically investigated with Pt-γAl_2O_3 membranes (flow-through contactor mode) [37]. Other types of catalysts have been also impregnated or dispersed in inert membranes [5], e.g. Fe_2O_3 in SiO_2, and V_2O_5, MoS_2, Os, Ru, Cr_2O_3, SmO_2, or NiO in Al_2O_3.

3.3.2. Intrinsically catalytic membranes

In the case of inherently catalytic membranes, the catalyst has to be designed in order to control both the catalytic reaction and the separation function. As in the previous case these active contactors improve the access of the reactants to the catalyst. The membrane needs to be highly active for the considered reaction, to contain a sufficient quantity of active sites, to have a sufficiently low overall permeability and to operate in the diffusion controlled regime [22]. The membrane composition, activity and porous texture have to be optimized for each considered reaction and remain stable upon use. In most cases, new synthesis methods or precursors have to be developed for preparing these membranes, particularly when the catalyst composition is complex. This challenge explains the limited number of examples in the literature related to intrinsically catalytic membranes for MRs [5]: alumina, titania, zeolites with acid sites, V-ZSM-5, rhenium oxide, LaOCl, RuO_2–TiO_2 and RuO_2–SiO_2, VMgO, CeO_2 or La-based perovskites. We have also to mention that attractive results can be obtained in some cases with multilayer catalytic membranes [9].

The catalytic properties of oxygen conducting oxides have been pointed out for either total or partial oxidation reactions [38,39]. The surface of dense membranes, delivering active O^* species, is often a very selective catalyst for partial oxidation reactions [21,40,41]. However, as reported in [42] the membrane material must be carefully selected. Indeed, when comparing a $SrFeCo_{0.5}O_3$ dense membranes with a non-combustion material such as $BaCe_{0.8}Gd_{0.2}O_3$, for the oxidative coupling of methane, a higher C2 yield (16.5%) was obtained with the latter [42]. This result shows that the surface properties of dense membranes have an important catalytic effect. The know-how developed for preparing nanophase porous catalytic membranes [5] could be of great interest for depositing porous nanophase layers on dense membranes in order to increase the surface exchange kinetics and also to optimize the near surface reactivity/selectivity of partial oxidation reactions. This will be further detailed in Section 4.

3.3.3. The four way catalyst: a good example of multifunctional membrane contactors with a complex composition and a hierarchical structure

Among the current systems used to reduce diesel particle emissions, the CRT-system of Johnson Matthey, consists of an oxidation catalyst followed by a particle filter, on which temperatures >270 °C enable an oxidation of the deposited particles. Due to the accumulation of soot and oil ashes in the filter (cf. Fig. 5b), the exhaust back pressure in the system can lead to an increase of fuel consumption [3]. This behaviour is in strong discrepancy with the CO_2-emission reduction goals. Therefore a number of research teams focus on the development of a continuous, non-blocking, soot particle oxidation trap for the reduction of Diesel-vehicle particle emissions (cf. Fig. 5c) [3]. It can be achieved by the development of infiltration methods to deposit a homogeneous catalytic layer on the ceramic grains, without generating a too high pressure drop and with a high surface area and reactivity. Such ceramic contactors can be designed to perform only the oxidation of soot, CO and C_xH_y whereas NO_x are treated separately. In the four way catalyst, the ceramic contactor should perform continuously the oxidation of fly-ash within its pores, the removal or reduction of noxious gases, and the oxidation of CO and hydrocarbons [3]. The abatement of NO_x can be performed either by storage in, e.g. barium oxide, or by simultaneous reduction of NO_x and soot oxidation over specific catalysts and through a series of complex reactions, including the following ones [43]:

$$2NO(g) + O_2(g) \leftrightarrow 2NO_2(g) \tag{1}$$

$$2NO_2(g) + C(s) \rightarrow CO_2(g) + 2NO(g) \tag{2}$$

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g) \tag{3}$$

This type of catalytic membrane contactor has reached an advanced state of technological development with the perspective of large scale industrial applications in the coming years.

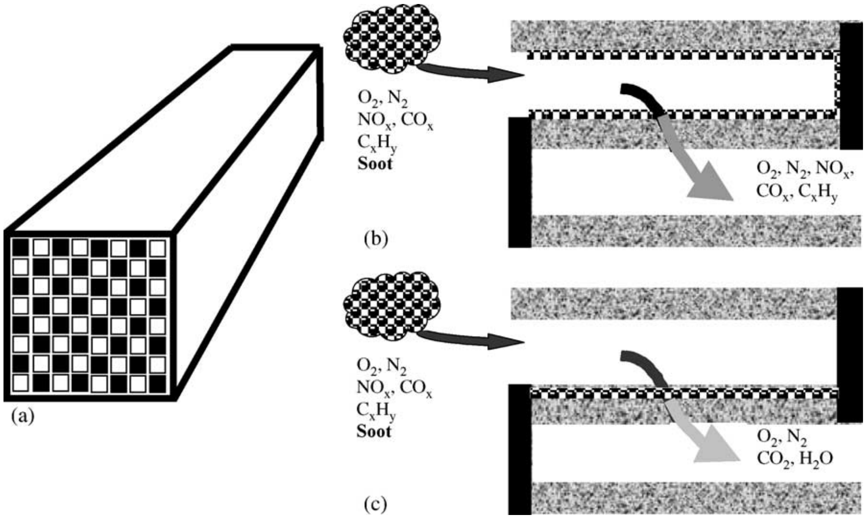

Fig. 5. Schematic representation of a diesel particle trap with monolith configuration and one channel occluded over two (a). Principle of the classical soot filtration with formation of a cake at the surface of the porous wall (b). Principle of the four ways catalytic contactor (c).

4. At the frontier between dense and porous membranes

In order to overcome the technological problems of high operating temperatures of to date's dense conducting ceramics, considerable interest has been paid to the preparation of conducting oxide materials with appropriate transport properties at intermediate temperatures in order to extend this technology to lower temperature reactions.

Decreasing dense membrane thickness is a way of increasing the oxygen flow, but only to a certain extend, i.e. until surface reactions become rate limiting [11]. Indeed, the oxygen surface exchange process involves a series of individual reaction steps including: adsorption, dissociation, charge transfer, surface diffusion of intermediate O^* surface species (O_{ad}, O^-_{2ad}, O^-_{ad}, O^{2-}_{ad}, ...) and finally incorporation into vacancies in the surface layer [17]. Oxygen diffusion and surface exchange can be measured by isotope exchange or conductivity relaxation techniques [44]. One can also consider that the enhancement of the oxygen flow by reducing the thickness could improve the stability of perovskite-based membrane performances. In fact, if the lattice oxygen involved in the oxidation reaction can be promptly replaced by new oxygen coming through the membrane, it could prevent significant oxygen depletion in the perovskite lattice and reduce the risk of fracturing. Ultathin and defect-free supported perovskite membranes are under development in several multidisciplinary research programs.

The kinetics of the surface exchange process (which also occurs reversibly at the opposite side of the membrane) can be measured by the oxygen exchange coefficient (k) [17]. Consequently there is no gain by manufacturing very thin membranes unless steps are taken to improve the flux through the interfacial regions. Relevant improvements could include an increase of the effective surface area, or the deposition of catalytically active surface species [17]. On the other hand the displacement of the thermodynamic equilibrium by converting the oxygen at the fuel side is highly beneficial for the oxygen flux [21]. Therefore, the more oxygen is consumed at the surface of the membrane, the higher is the oxygen trans-membrane pressure, and hence the greater is the oxygen flux.

Corrugation of the membrane surface or asymmetric membrane structures with porous interfaces and a dense core have been investigated to increase the oxygen surface exchange coefficient [11]. This typically leads to the SOFC reactor concept [45] which involves the deposition of porous anode (catalyst) and cathode layers on a dense ceramic electrolyte. This concept was patented by Exxon with a $Co_{0.8}Fe_{0.2}SrO_3$ dense membrane and two porous layers acting as an oxygen activation catalyst and a hydrocarbon partial oxidation catalyst, respectively [46]. Eltron Research Inc. patented the concept with a brownmillerite dense material, a [Pd (5 wt.%) on $La_{0.8}Sr_{0.2}CoO_{3-x}$] layer as the oxidation catalyst and a layer of [Ni (20 wt.%) on $La_{0.8}Sr_{0.2}MnO_3$] as the reduction catalyst [47]. As in the SOFC, a nanophase LSM based material (La/Sr/Mn) [48] or nickelate based structures [49] are good candidates for the reduction of oxygen. The catalytic activity and the nanostructure of the top layer, in which the electrochemical oxygen is delivered, play a key role on the reactor performance. As mentioned in [50] the surface modification of perovskite type MIEC materials ($LaSrGaFeO_3$) with a porous $LaSrCoO_3$ layer (by screen-printing) was found to enhance significantly the oxygen permeability of LSGF dense membranes.

A recent work reported in [51,52] confirms the above results and also clearly demonstrates the importance of both dense membrane thickness and careful surface modification for increasing the yield of partial oxidation reactions such as ODHE (cf. Fig. 6). In this work, the dense membrane surface ($Ba_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ disk) was covered either with a sol–gel-derived VMgO catalyst or with Pd nanoclusters. The membrane was used without any fixed bed of catalysts on top of it as it is usually the case. The deposited dispersed catalyst increases the numbers of triple point boundaries (interface gas phase–catalyst–membrane) which facilitates high oxygen desorption and alkane adsorption in the vicinity of O^* species. This improved membrane reactor design has been studied for ODH of ethane at intermediate temperature. At 700 °C, the presence of the catalytic layer induces an

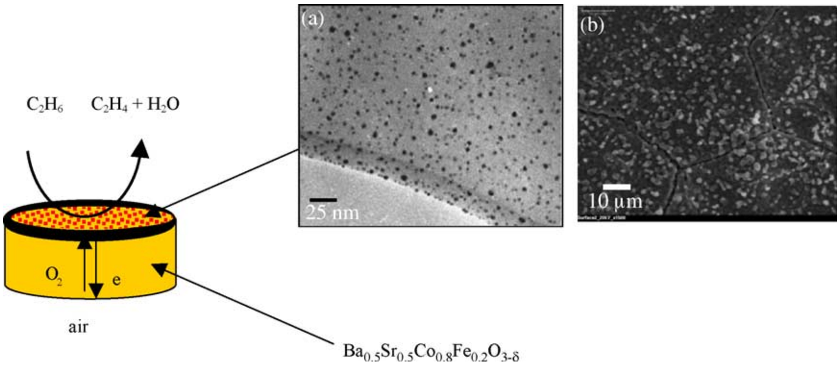

Fig. 6. Surface modification of a BSCFO dense support with either Pd nanoclusters deposited by laser vaporisation (a) or with VMgO deposited from alkoxide precursors (b) (adapted from [51]).

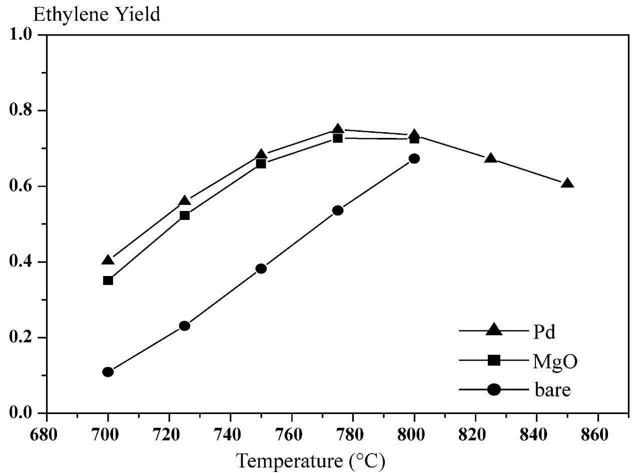

Fig. 7. Evolution of the ethylene yield as a function of temperature, for different surface modifications. Total feed on the reaction side: 37 ml min^{-1} at $pC_2H_6/p_0 = 0.255$ (adapted from [52]).

increase of the ethylene yield from 10 to 40% and the maximum yield reaches 75% at 780 °C (cf. Fig. 7). A space time yield of about 100–150 kg of C_2H_4/m^2 of membrane and per hour can be achieved which is at least one order of magnitude faster with respect to a fixed bed at comparable reactor volume. In addition the membrane reactor process did not show any deactivation after weeks.

The above result is attributed both to an adapted membrane thickness, which allows high O_2 fluxes, and to the improved surface exchange kinetics. Oxygen ion transport through the bulk is a material property, while the oxygen transfer from the gas phase into the solid and back depends on available surface area and activation barriers for chemisorption and desorption. The extremely high surface area and number of surface atoms in highly porous nanophase materials can reduce the activation barriers [35]. A dispersion of noble metal particles (playing the role of an electrode) at the surface of ion conducting oxide grains are known to enhance the oxygen exchange rate of the material by influencing the oxygen adsorption equilibrium at the surface of the electrolyte [53]:

$$0.5O_2(g) + 2e^- \text{ (metal)} \leftrightarrow O^{2-} \text{ (electrolyte)}$$

Nanophase membrane materials (electronic, ionic or mixed ionic electronic conductors) can then be efficient when used as surface layers deposited on dense conducting membranes for enhancing O_2 surface exchange kinetics (adsorption/desorption) and for getting attractive catalytic properties [51,52].

An important problem occurring during the utilisation of SOFC and dense membrane reactors is the gradient of oxygen partial pressure which is applied between the fuel and the oxidizing chambers. This can generate a number of problems in the membrane materials such as structural modification, phase segregation, loss of O_2 flux, delamination and sometimes structural failure [13]. In order to overcome these problems, a decrease of film thickness is considered: ultra-thin electrolyte layers are supported on catalytically active anodes [54]. However, the use of a protective intermediate layer, generally based on Sm doped ceria (MIEC behavior in reducing atmosphere, seems to be required for increasing the system stability during long term operation [54].

If we now consider the bulk dense material itself, the influence of grain boundaries on the electrical, diffusive and defect properties of electroceramics has been recognized for some time [34]. Given the recent and rapidly growing interest in nanocrystalline solids, the impact of that change in scale, involving high densities of interfaces has also been widely investigated, due to the enhanced ionic conduction observed in these materials [11,34]. According to [34] the impurities which contribute to ion blocking in grain boundaries are diluted in nanocrystalline oxides, giving rise to a substantial reduction of the specific grain boundary resistance. This is coupled to high levels of non-stoichiometry and electronic carrier generation. The synthesis of nanophase materials and the selection of adapted shaping methods for maintaining the nanophase structure in the final dense materials are typical material challenges to deal with.

5. Recent developments in the field of material science, with high potentials for oxidation reactions

5.1. New material structures and compositions

Although most of the ceramic structures studied up to now transport oxygen in their vacancies, new materials were developed whose structure is able to accept oxygen overstoichiometry. These oxides (Ruddlesden–Popper phases) follow the stoichiometry $A_2MO_{4+\delta}$ with the K_2NiF_4 type-structure. The structure (cf. Fig. 8) consists of sheets of (MO_6) octahedral sharing corners with interleaved A_2O_2 layers, in which the additional oxygen is localized. The oxygen overstoichiometry in these materials mainly results from structural stress arising from competing A–O and M–O bonds. The value of δ may reach 0.25 in $La_2NiO_{4+\delta}$. In addition, $Ln_2NiO_{4+\delta}$ compounds show a capability of reversibly adsorbing or desorbing oxygen in air atmosphere already at temperatures as low as 377 °C. Compared to the perovskite compounds, the oxygen transport in these materials is anisotropic and involves interstitial oxygen atoms instead of oxygen vacancies. The $La_2Ni_{1-x}Cu_xO_{4+\delta}$ phase has been studied as a SOFC cathode material [49]. Around 650 °C, the oxygen diffusion coefficient D^* and surface exchange coefficient (k) were one order of magnitude higher than those of the best perovskite materials due to lower activation energies. Although several compositions were recently studied as dense oxygen conducting membranes, such as $La_2NiO_{4+\delta}$ [55,56], $La_2Ni_{1-x}Cu_xO_{4+\delta}$ [49] and $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ [57], the pure nickelate $La_2NiO_{4+\delta}$ seems to show very promising properties.

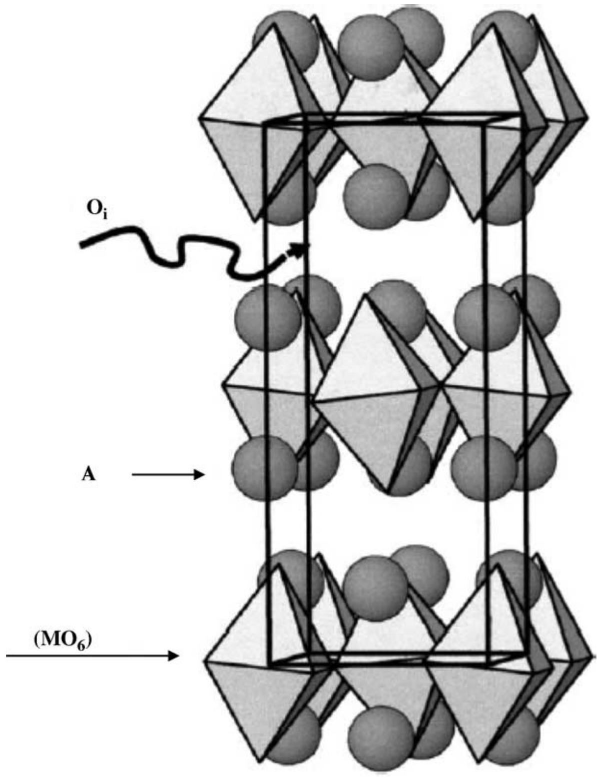

Fig. 8. Structure of $A_2MO_{4+\delta}$ materials showing the location of the interstitial oxygen atoms [49].

The combinatorial strategy based on high-throughput experimentation fulfils the current needs for significantly higher speed and efficiency in material discovery and development. Progress in these methods for catalysis research has reached an impressive rate and the combinatorial approach is now also considered for discovering new material precursors for dense oxygen-conducting membranes [58].

5.2. Wet chemistry methods for the synthesis of nanophase conducting ceramic powders

Nanophase conducting ceramics are often prepared by wet chemistry methods such as precipitation, coprecipitation, solvothermal synthesis, or sol–gel process. These low temperature processes generate large specific surface areas and porosities. The precursors can be either salts or alkoxides, dissolved, respectively, in water or organic media. The Pechini type methods involving metal complexation with citric acid or EDTA [59,60], as well as the glycine-nitrate process [61] are interesting variations of the sol–gel process, typically adapted to the synthesis of conducting oxides nanophase powders. Among the very recent developments of sol–gel methods, one can mention the use of supercritical (SC) fluids as ''green'' solvents for the precursors [62] and the assistance of microwave (MW) heating for the rapid crystallisation of ceramic oxide powders [63]. Processing of ceramic precursors in SC CO_2 media considerably decreases the required solvent quantity but also improves reaction kinetics and allows to control the morphology and size of particles. Lower crystallisation temperatures and nanophase structures with a high sintering capability are typical characteristics which can be obtained by either SC CO_2 or MW assisted synthesis methods [62,63].

5.3. Methods for membrane shaping

Spark plasma sintering (SPS) has received considerable attention as a new pressure consolidation technique leading to novel materials [64]. SPS furnaces are produced by Sumitomo Coal Mining Co. in Japan. The sample to be densified is held within a cylindrical graphite die, and a pulsed DC voltage (typically a few volts) is applied between an upper and lower graphite punch. The high heating rates that can be achieved (up to 600 °C/min), allow to reach rapidly the desired temperature and minimize the time for which the powder is exposed to lower temperature. This avoids coarsening of the powder prior to densification, limits the diffusion of species and yields fully dense ceramics with fine grained microstructures within a few minutes.

The development of large scale preparation of dense supported thin films (<100 μm) for ion transport applications is currently an international challenge. The classical techniques basically used for SOFC or sensors applications include tape casting, extrusion, slip casting, calendaring, pressing and screen-printing or other thick film techniques. Asymmetric structures with porosity and composition gradients bring up a number of problems related to classical uniform dense membranes (metastability of structures, interdiffusion of components resulting in degradation; mismatch of thermal expansion coefficients, non-uniform shrinkage of layers . . .). Such structures can be prepared by phase inversion with a ceramic-loaded polymeric phase [65] and also by casting of slurries [66].

Although a number of very thin supported YSZ dense membrane (about 100 nm thick) were recently reported [54], to date no publication reports successful deposition of really dense ultra-thin (1–10 μm) supported layers of perovskite materials on porous supports. The main problem is to prepare a completely dense thin layer with a controlled composition and crystalline structure, stable under working conditions.

Possible thin film deposition technologies are physical processes like sputtering or vacuum evaporation, low pressure MO-CVD, plasma-enhanced CVD, pulsed laser deposition, magnetron sputtering and also electrochemical vapor deposition (e.g. EVD) or wet chemistry, namely sol–gel or pyrosol methods (ultra-sonic spray pyrolysis of sols).

The sol–gel process is typically used for the deposition of thin porous nanophase membranes [5]. It is also adapted to generate composition or porosity gradients within the material and compact layers can be obtained by multi-impregnation processes from sols loaded with ceramic powders. Among the simple, low cost and high deposition rate methods, the pyrosol process [67,68] is a very attractive

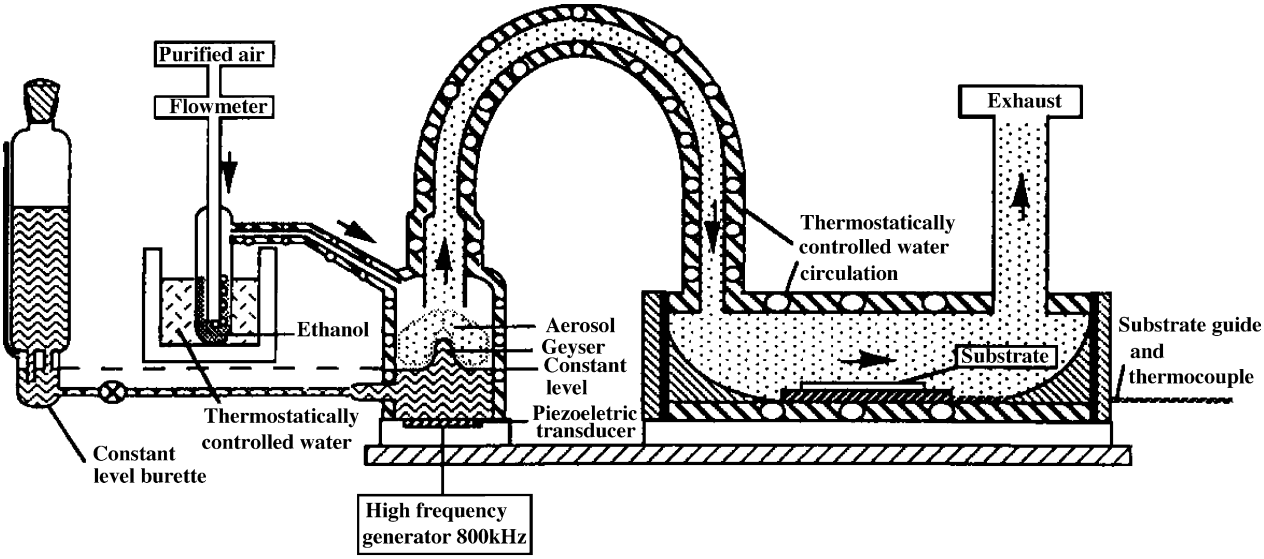

Fig. 9. The ultrasonic sol–gel device for the deposition of supported thin films by pulverisation of aerosols [68].

technique for the deposition of either porous or dense supported thin films with high quality and thicknesses ranging from 100 nm to a few microns. The method (cf. Fig. 9), initially devoted to the synthesis of sensors, capacitors, transparent electrodes and films for optical application, could become of great interest for the membrane reactor technology [51].

5.4. New reactor designs

In addition to material development, oxygen flux can be significantly increased by the membrane reactor design. Compact arrangement of tubes or stacks significantly increases the membrane surface per unit volume of the reactor. Most of the membrane reactor studies to date adopted tubular or planar configurations. The planar configuration can be made compact and is potentially cheaper than the tubular design. However a planar stack is more sensitive to both thermal stress and gas composition gradients and is also more difficult to pressurize.

In SOFC technologies, planar, monolithic and tubular configurations have been considered [17]. The most important progress to date has been achieved with the tubular geometry pursued by Siemens-Westinghouse in the United States and Mitsubishi Heavy Industries in Japan. The planar configuration is also rapidly progressing for SOFC stacks with integrated reformers. For membrane reactors, a multilayer wafer-like planar membrane configuration with slotted backbone structure is one of the options selected by Air-Products for their perovskite mixed conducting membranes [4].

Finally, the monolith configuration which was considered as too complicated to co-sinter a number of years ago [69] is now being reconsidered [4,70,71]. Apart from the honeycomb technology, improved production techniques have become available in recent years leading to either microreactors [72] or hollow fibre modules with potential surface to volume ratios in modules larger than 1000 m^2/m^3.

Although ceramic hollow fiber membranes are still in their early stage of development, very important improvements have been recently reported for this new ceramic membrane shape. Hollow fibre precursors can be produced by a number of methods such as the extrusion of ceramic pastes, vapor deposition on degradable wires, pyrolysis of polymeric wires and more recently by phase inversion/sintering, a technique inspired from the polymer hollow fibers technology [65,73].

During the past decade, both porous (Al_2O_3, ZrO_2, TiO_2) and dense perovskite fiber membranes have been developed by various teams and different methods. Porous alumina-based fibers are now commercially available as modules for high temperature applications (CEPAration-TNO). These materials can be used as prepared or for the deposition of other selective/reactive layers. On the other hand, very few results have been published on dense oxygen conductive ceramic fibers. Dense $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ perovskite fibers for proton conduction were recently published by Li and coworkers [65]. This team has also extended their know-how to the synthesis of LSCF perovskites hollow fibers for air separation and oxidative coupling reactions [74]. A German consortium (ConNeCat, Competence Network on Catalysis) is also actively working in this field [75].

6. Conclusion

Porous catalytic membranes are efficient contactors for total oxidation of VOC or soot. This niche application is expected to undergo a promising development in the car industry in the coming year. Porous membranes are still studied as oxygen distributors for the partial oxidation of long chain alkanes, although dense mixed conducting membranes perform much better for methane or ethane involving reactions and are now on the way to be commercialized. By a proper selection of the material composition, structure, thickness and by combining in a relevant way both dense and porous layers, the oxygen flux, performance and stability of dense ceramic membranes can be considerably improved. The key-challenge which is posed to material scientists consists of the development of efficient, stable and affordable dense membranes with good performance at both high and moderate temperatures, and with long-term reliability under real operating conditions. Important breakthroughs have been obtained during the last decade, further ones are expected from the very recent developments in material science.

Major identified hurdles preventing a wide spread application of ceramic membranes for reactor applications are the complex and expensive preparation and the relatively low specific areas obtained with existing module techniques. A need for simple synthesis methods adapted to mass production of high quality membrane materials is still needed. Improved concepts and production techniques have become available in recent years leading, e.g. to ceramic hollow fibre modules with potential surface to volume ratios in modules larger than 1000 m^2/m^3. Of course the mechanical resistance of such fibre modules has to be evaluated and the sealing problems have to be solved. Detailed modelling studies will also be required in order to improve the design and efficiency of the new generations of reactors.

The achievement of a technological success is more probable when the initial idea is process "pulled" rather than material "pushed". The very huge needs for innovative, efficient, robust and sustainable systems such as cheap alkane conversion processes, reformers and fuel cells, are so efficient economic "pullers" that the success of high temperature membrane reactors is now on the way to explode. There is no doubt that today's pushers in material science, catalysis and chemical engineering will contribute to this success and even facilitate its rapid transfer to H_2 related separations.

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