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Catalytic reactors based on porous ceramic membranes

J. Coronas, J. Santamaría*

Department of Chemical and Environmental Engineering, Faculty of Science, University of Zaragoza, 50009 Zaragoza, Spain

Abstract

This overview discusses some of the developments and outstanding opportunities in the field of catalytic reactors based on porous ceramic membranes, both inert and catalytic. This is an emerging area, where inputs from heterogeneous catalysis, material science and reactor engineering are playing the key roles. Rather than attempting a thorough review of the relevant literature, this work deals with some general concepts and then concentrates on a few selected examples that illustrate the application of membrane reactors. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic reactor; Porous ceramic membrane

1. Introduction

Inorganic membranes were industrially developed five decades ago with the aim of separating UF_6 using gas phase diffusion processes. In the 1980s, non-nuclear industrial applications were in place mainly oriented towards microfiltration and ultrafiltration processes. A fast development ensued, which helped to obtain standardised processes for membrane production and control of the porous structure. The application of porous ceramic membranes as catalytic reactors also starts in the 1980s. The driving force for this change was the possibility of integrating reaction and separation, which had already been achieved in the field of biochemical reaction engineering using polymeric membranes. These, however, were not applicable at the temperatures used in most of the processes of interest in the chemical process industry. The intense research activity that now takes place in the field of membrane reactors has been possible and thanks to the availability of materials that can be used as membranes, while being able to withstand severe reaction conditions.

Commercial ceramic membranes currently in use usually have an asymmetric structure consisting of a support layer (generally α-alumina) with large pores and a low pressure drop, and a separation layer made of a different material (γ-alumina, zirconia, silica, etc.), which controls the permeation flux. Since the materials used in the manufacture of ceramic membranes are also commonly used as conventional catalyst supports, there has been a strong interest in the development of membrane reactors by researchers with previous experience on heterogeneous catalysis, who adapted many of the preparation and characterisation techniques used in this field.

The traditional meaning of the term *membrane* is associated to the concept of a device which is capable of imposing certain restrictions on the permeation flux of some substances. Thus, in *selective permeation* membranes only certain molecules meet the permea-

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*Corresponding author. Fax: +34-76-762142; e-mail: iqcatal@posta.unizar.es

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tion requirements, and the membrane acts as a barrier for the rest. From a review of the literature, it is clear that only part of the research published to date on membrane reactors conforms strictly to the above definition. In fact, there are numerous examples of interesting membrane reactors which deviate considerably from that strict membrane concept. Such is for instance the case of flow-through membranes, where permeation of the whole reactant stream takes place, or of some instances of catalytic membranes in which the reactants converge on the membrane rather than permeating across it.

There have been excellent reviews on the field of membrane reactors in the last few years [1–7], and this work does not attempt to add one more to the list. Instead, it discusses specific aspects of the association between catalytic reactor engineering and porous ceramic membranes with the aim of highlighting some interesting applications of membrane reactors.

2. Types of membrane reactors

Table 1 classifies inorganic membranes according to their nature and to their most important characteristics: selectivity and permeability. Both are determined by the interaction between the membrane and the permeating molecules which gives rise to different transport mechanisms. Dense membranes, which are not addressed in this work, offer the highest selectivities for specific gases via transport processes that involve solution–diffusion or ionic conductivity mechanisms. In return, permeation fluxes through selective, defect-free dense membranes are low. The composite membranes in Table 1 are a special case since they attempt to obtain simultaneously moderately high fluxes and high selectivities. To this end, a mesoporous substrate with a low resistance to permeation is covered with a thin metallic layer which provides the desired selectivity. The methods used to attain this objective, such as electroless plating, chemical vapour deposition or ion sputtering [8–11], are far from being fully developed, and the thin metallic layer on the composite membranes frequently develop cracks and pinholes that render it useless. This problem may be exacerbated by thermal cycling of the composite membranes, which may cause metal migration and reduced adherence to the ceramic surface [5]. In spite of this, composite membranes hold the promise of a selectivity equivalent to that of dense Pd membranes at higher permeation fluxes, and a good deal of research will undoubtedly be devoted to them in the near future.

This work is concerned with porous membranes in which transport mechanisms include viscous flow Knudsen diffusion, surface diffusion, capillary condensation, and molecular sieving. In the already discussed trade-off between selectivity and permeability, porous membranes aim for higher values of the latter, which often means sacrificing selectivity. A notable exception are zeolite membranes with a promising future of applications to catalytic reactors, even though these are still scarce today. On the other hand, in spite of their lower selectivity, mesoporous membranes have given rise to interesting developments in the laboratory, which are discussed below.

2.1. Microporous (zeolite) membranes

Many laboratories are involved today in the preparation and characterisation of more selective and

Table 1
Classification of inorganic membranes

Type of membrane	Material	Selectivity	Permeability
Dense	Metallic Solid electrolytes	High (H_2, O_2)	Low to moderate
Porous (oxides, carbon, glass, metal, zeolites)	Macroporous	Non-selective	High
	Mesoporous	Low to moderate	Moderate to high
	Microporous	Can be very selective	Moderate
Composite	Glass–metal Ceramic–metal Metal–metal	Can be very selective	Moderate

continuous microporous (i.e., with pore size smaller than 2 nm) membranes. Some of these membranes can be prepared using modified sol–gel techniques as in the case of microporous silica membranes [12–14]. Other microporous membranes have been produced by controlled pyrolysis processes. Thus, the pyrolysis of polyfurfuril alcohol has been used to obtain microporous membranes of carbon on porous graphite [15], while pyrolysis of polycarbosilane produced Si–C–O membranes on porous α-alumina in which a H_2/N_2 ideal selectivity above 60 was achieved [16]. Tetraethoxysilane (TEOS) and methyltriethoxysilane were co-polymerized on a porous support, and densified by a final heat treatment giving rise to a microporous silica membrane with a CO_2/CH_4 separation factor of 12 [17]. In this case, subsequent reaction of the membrane with TEOS allowed fine tuning of the monolayer pore size increasing the separation factor to 71.5. Sometimes, mesoporous membranes can be converted into microporous membranes using deposition of supplementary material to fill mesopores. For instance, Megiris and Glezer [18,19] used chemical vapour deposition to deposit silica and silica/C films that constricted the pore openings of Vycor glass alumina supports; the resulting membranes had H_2:N_2 flux ratios between 30 and 250. Other non-zeolitic microporous materials can also be added to glass or alumina supports in order to attain the desired selectivity. Among these, pillared clay membranes are especially promising because of the versatility that using different pillaring cations allows in tailoring the membrane pore size between 0.3 and 5 nm. Vercauteren et al. [20,21] have recently synthesised hydrophilic Al_2O_3-pillared montmorillonite membranes, which were used for alcohol dehydration by means of water pervaporation.

In spite of the above and other developments of microporous membranes, zeolite materials constitute the main group of microporous membranes with regard to potential membrane reactor applications. This is so because zeolites have a regular structure with pores of molecular size, resist acid attack, are thermally stable at least up to 600–700°C and have inherent catalytic activity. Zeolite membranes are able to separate organics with close boiling points [22], with separation efficiencies that are often comparable and higher than those achievable by traditional distillation. They can also perform separations of molecules with the same molecular weight [23–26] that cannot be achieved by mesoporous membranes operating under the Knudsen diffusion regime. In addition, the selectivity of zeolite membranes towards separation and their catalytic activity can be modified by processes such as vapour [27] deposition and ion exchange [28].

The hydrothermal synthesis of zeolites on porous materials (alumina, stainless steel) have been reported for silicalite [23–25,29–31], ZSM-5 [26,32,33], mordenite [34,35], zeolite A [36–39], zeolite Y [40,41], ferrierite [34,42,43], ZSM-35 [44], analcime [42], and zeolite P [45]. There are also reports [46] which deal with composite hydrophilic membranes comprising a mixture of zeolites: mordenite, ZSM-5 and chabazite. Only a fraction of the above synthesis was reported on tubular supports [23,26,29–32,37–41,45,46], most of them for the silicalite/ZSM-5 system. It seems clear that tubular membranes are more interesting than flat ones because of their easier integration in a reactor or separator module, however, defect-free tubular membranes are more difficult to obtain due to the development of mechanical tensions during the drying/calcination steps that often lead to defects in the zeolite layer. It is difficult to make general statements about the zeolite membranes synthesised to date: key features such as their permeance values, the trends observed with temperature and composition, and the possibility of separation of mixtures depend strongly on the support porosity, composition, stability and viscosity of precursor gel for the hydrothermal synthesis as well as the mode of contact between the support and the precursor gel [26].

Both ZSM-5 and silicalite membranes have the same MFI framework structure with two different types of channels [47]: straight channels with an opening size of 0.54×0.56 nm intersecting with sinuous channels with openings of 0.51×0.55 nm. While for ZSM-5 the Si/Al ratio is about 20–1000, it is infinite for silicalite membranes. However, it must be noticed that ZSM-5 rather than pure silicalite membranes are likely to be obtained when the synthesis of silicalite membranes is carried out on porous alumina supports due to partial dissolution of the support in the synthesis medium. An interesting feature of the ZSM-5 as well as of other Al-containing zeolites is that their defect of positive charge can be compensated by metallic cations. This can be used to give specific catalytic activity to the zeolite membrane.

Most of the applications of zeolite membranes reported in the literature have been directed to separations in the absence of chemical reaction. Firstly, zeolite membranes, particularly MFI membranes, separate gases or vapours attending to their differences in kinetic diameters. In this case, transport is controlled by molecular sieving, as for instance in the case of the separations of *n*-butane/*i*-butane [24–26] and *n*-hexane/2,2-dimethylbutane [23,48–50] mixtures, where linear alkanes with a smaller kinetic diameter (0.43 nm for *n*-butane and *n*-hexane, 0.5 nm for *i*-butane and 0.62 nm for 2,2-dimethylbutane) permeate faster. The same principle applies in the separation of the methanol/metil-*tert*-butyl ether mixture, where methanol with a smaller kinetic diameter (0.39 versus 0.62 nm) is selectively separated on both silicalite [51] and zeolite Y [41] membranes. In addition to molecular sieving, the processes of preferential adsorption must be considered to explain the permeation of mixtures through zeolite membranes. This separation mechanism (that often coexists/competes with molecular sieving) implies that one of the components in the mixture adsorbs preferentially on the zeolite. In this case, the adsorbed molecules are selectively transported, blocking the pass through the membrane of the other species in the mixture, even though the pore size would have permitted the transport of any of them as a single component. This is the case of the following gas phase mixtures separated with MFI membranes: methanol/H_2 [29], *n*-butane/H_2 [23,26], ethanol/O_2 and propanol/O_2 [52], and CO_2/H_2 [25], where permeation of hydrogen or oxygen was hindered by the more strongly adsorbed molecule. The selectivity involved in this mechanism can reach very high values, e.g., a propanol/O_2 selectivity around 7500 was found using a silicalite membrane [52]. Also, it seems clear that in addition to molecular sieving, preferential adsorption also plays a significant role in suitable systems, such as the already mentioned *n*-butane/*i*-butane separation on MFI zeolites.

In some instances, which are obviously related to the preferential adsorption mechanism just discussed, the main factor controlling the separation is the organophilic or hydrophilic character of the zeolite and the polarity of the permeating molecules. Silicalite, the MFI-form without aluminium, is organophilic, and the hydrophilic character increases as the aluminium content in the ZSM-5-form increases. Thus, the organophilic character of the zeolite played a key role in the separation of ethanol/water mixtures with silicalite membranes [53]. In this case, it was found that the amount of ethanol adsorbed on silicalite was about three times larger than that of water because of the hydrophobicity of silicalite, giving an ethanol/water separation factor higher than 60. A similar situation has been found for other mixtures such as acetic acid/water [54,55] and acetone/water [55]. On the other hand, the permeance of water through hydrophilic zeolite membranes (zeolite A, zeolite Y and mordenite/ZSM-5/chabazite) was faster: in mixtures of water with methanol, ethanol or acetone [38], separation factors of 2500, 16 000 and 6800, respectively, were achieved; other works report a water/ethanol separation factor of 125 [41]. With hydrophilic membranes a small proportion of water in the feed mixture is often sufficient to produce a substantial blockage of the other permeating species. Thus, when a ternary gas phase mixture containing water, propanol and O_2 at atmospheric pressure with 2.5 kPa of water was subjected to permeation through a hydrophilic mordenite/ZSM-5/chabazite membrane [56], a water/propanol selectivity of 149 was observed.

It seems reasonable to predict that in the near future zeolite membranes will replace some conventional membranes on account of their efficiency to carry out certain separations. It can also be anticipated that new applications will be developed that use zeolite membranes as part of catalytic membrane reactors to perform simultaneously reaction and separation. In the literature however, only a few examples can be found of membrane reactors that incorporate zeolite membranes. Among these, Casanave et al. [57] studied the dehydrogenation of isobutane to isobutene using a silicalite tubular membrane enclosing a Pt–Sn/γ-Al_2O_3 catalyst bed. The membrane was used to selectively remove hydrogen from the reaction environment, increasing the isobutane conversion. Another report from the same laboratory [58] deals with the oxidative dehydrogenation of propane to propene using a silicalite membrane as oxygen distributor. In this case, though, a zeolite membrane might not be required since, as will be discussed below, a mesoporous membrane can efficiently distribute oxygen to a catalyst bed often with higher yields in oxidative dehydrogenation reactions.

In recent works, Maier et al. [59,60] used a non-zeolitic microporous Pt/TiO_2 catalytic membrane to carry out the selective hydrogenation of 2-hexyne and hexadiene. This was a non-separative application in which the hydrocarbon reactant and the dissolved hydrogen were fed to one side of the catalytic membrane, and copermeated through it, while products were removed at the other side. By a careful selection of the operating conditions, an unusually high semi-hydrogenation selectivity was obtained. The authors explained this high selectivity by a single-file diffusion transport mechanism operating through the membrane. Under this regime, the probability of further hydrogen contact with the semihydrogenated molecule decreased, and as a consequence overhydrogenation could be almost completely avoided.

There are also examples of applications of membrane reactors in the patent literature. Suzuki [61] reported reactor operation using several cation-exchanged A and Y zeolite membranes, in which the reaction (e.g., cracking, hydrogenation) took place on one side of the membrane and products were selectively removed at the other, thus coupling reaction and separation. Although some of the examples examined in that report are likely to run into problems in relation to matching permeances to reaction rates in the systems considered, and to the stability of membrane reactor operation (due to problems such as coke formation), they successfully show the potential of zeolite membranes for reactor applications. Also in the patent literature, Haag and Tsikoyiannis [62] proposed a wide array of hydrocarbon conversion reactions as candidates for the application of zeolite membranes.

2.2. *Mesoporous membranes*

Mesoporous ceramic membranes provide a very broad array of opportunities regarding the choice of materials for the membranes, their catalytic properties and possible applications. Table 2 gives a classification of catalytic reactors based on ceramic membranes, according to the role played by the membrane. When an inert membrane reactor (IMR) is used, the catalytic material does not form part of the membrane (a typical configuration is a tubular membrane enclosing a fixed bed of catalyst, Fig. 1(A)). In this case, the membrane does not participate in the reaction directly, but it is used to add or remove certain species from the reactor. The most widely used application involves equilibrium displacement by removal of at least one reaction product (corresponding to configuration A of Table 3). Most often, the removal of hydrogen in dehydrogenation reactions has been the process of choice, although configuration A has also been applied to other processes such as decomposition (H_2S, H_2O) and production of synthesis gas [63–68]. Product removal may be selective (i.e., H_2 permeation through a composite Pd-ceramic membrane), or preferential (i.e., preferential permeation of H_2 versus higher molecular weight products using a Knudsen-diffusion membrane). Regarding the latter, as several authors have demonstrated [69,70], dilution effects (i.e., a more diluted stream on the feed side due to

Table 2
Classification of catalytic reactors based on ceramic membranes

Inert membrane reactors (IMRs)	The role of the membrane is to remove products or to add reactants. The catalyst is located apart from the membrane structure
Catalytic membrane reactors (CMRs)	The membrane material itself is catalytic, or becomes catalytically active during preparation by the addition of active precursors
Combined	There is catalytic material both inside and outside the membrane

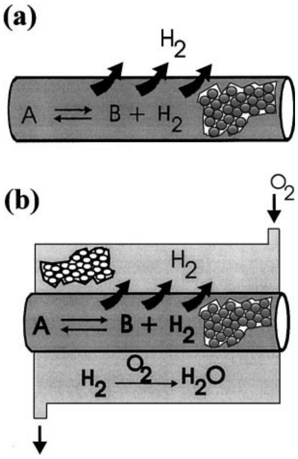

Fig. 1. Application of membrane reactors. Configurations A and B in Table 3.

Table 3
Some possible configurations of porous membrane reactors

Configuration	Advantages sought	Type of membrane
A: Inert membrane reactor (IMR) – permeation of products	Increased reaction yield by equilibrium displacement	(i) Selective. Thin metallic layers (e.g., Pd or Ag-based alloys on ceramic substrates). (ii) Nonselective. Porous membranes: silica, alumina, titania, glass, etc. (iii) Other: zeolitic membranes
B: IMR – permeation of products plus reaction coupling	As above, although higher yields can be expected due to the thermal/chemical coupling of reactions	As above
C: IMR – distribution of reactants	Increased selectivity through control of the concentration of selected species along the reactor. Increased reactor safety	Meso- or microporous membranes
D: Catalytic membrane reactor (CMR) – Mobile and active lattice oxygen	Control of the oxygen distribution in the reactor. In principle, it is possible to avoid the presence of gas phase oxygen	(i) Thin layers of Ag-based alloys on top of porous ceramic membranes. (ii) Thin layers of dense oxide on top of porous ceramic membranes
E: CMR – Segregation of reactants on both sides of the membrane	Confinement of reaction to a finite thickness zone inside the membrane. Reactant slip is avoided. Improved safety	Porous catalytic membranes
F: Inert/catalytic composite membrane	Control of the concentration of a reactant by means of mass transfer resistance in the IMR zone	Composite membranes: inert (diffusion) zone plus catalytically active zone
G: CMR – Segregation of liquid and gaseous reactants	Improved mass transfer in G–L–S reactions	Porous catalytic membranes
H: CMR – Joint permeation of reactants	Improved G–S contact, higher conversions	Porous catalytic membranes

counterpermeance of the sweep gas) also contribute to increasing the conversion of equilibrium-limited reactions to the point that it is sometimes difficult to assess whether the preferential H_2 removal has a net positive effect by itself. Equilibrium displacement can be enhanced through reaction coupling (configuration B in Table 3). In this case (e.g., [71–74]), on both sides of the membrane complementary processes are run that use either the permeated species (chemical coupling, e.g., dehydrogenation/hydrogenation, or dehydrogenation/combustion reactions), or the heat generated in the reaction (thermal coupling, exothermic/endothermic processes). The reactions often use different catalysts, which would be packed on opposite sides of the membrane tube.

A second application of IMRs consists in using the membrane to distribute a reactant to a fixed bed of catalyst packed in the opposite side. The most frequent case corresponds to a series–parallel reacting network where there is a favourable kinetic effect regarding the partial pressure of the distributed reactant (configuration C in Table 3, Fig. 2). Thus, it has often been found in selective oxidation processes that a low partial pressure of oxygen favours the selective oxidation reaction versus the deep oxidation to CO and CO_2. Since oxygen is a necessary reactant, its presence in

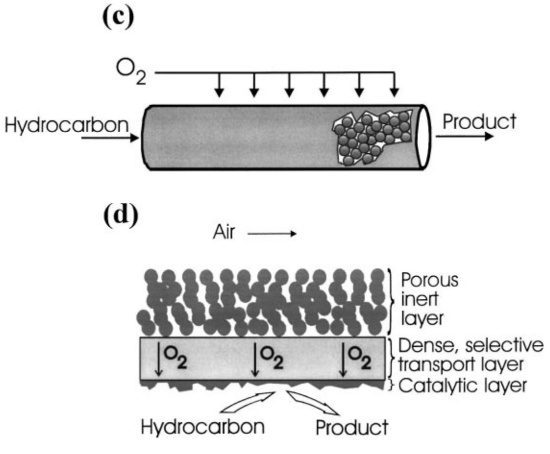

Fig. 2. Application of membrane reactors. Configurations C and D in Table 3.

the reaction environment cannot be completely avoided, but its partial pressure can be lowered by distributing it through a porous membrane. IMRs have been used successfully as oxygen distributors in a number of oxidations [75–88] including methane oxidative coupling and the production of olefins and oxygenates (e.g., maleic anhydride [86,87]) from the oxidation of alkanes. A potentially interesting configuration for oxidations with a valuable intermediate product was proposed by Lu et al. [89] consisting of a two-membrane reactor system in which the first membrane was used to distribute oxygen, and the second to remove intermediate reaction products.

In general, the use of a membrane for the distribution of oxygen in oxidation processes produced not only greater selectivities with respect to conventional feed arrangements, but also a safer operation with reduced formation of hot spots and a lower probability of runaway [81,82,85,90,91]. The avoidance of hot spots can give additional increments of selectivity by suppressing undesired reactions that take place at high temperatures, and in any case helps to extend catalyst life. The distribution of oxygen also allows a wider range of operating conditions: by distributing the oxygen feed in the IMR it is possible to operate at overall hydrocarbon to oxygen ratios that would be within the explosive region if the same composition was fed at the entrance of a fixed bed reactor.

It is worth noting that obtaining a true IMR is not always an easy task, since the membrane itself, or the components used to modify its permeation properties (e.g., pore-filling materials), can sometimes make an undesired contribution to the reaction. Thus, the membranes used in selective oxidation reactions often had to be significantly modified (by using controlled sintering to reduce surface area, or by doping with alkaline compounds to decrease surface acidity), in order to reduce non-selective catalytic activity (e.g., [77,85,92]).

Reactant distribution can also be achieved using porous membranes with a thin but dense permselective layer. In the case of oxidation reactions, this would have the important advantage of using air instead of oxygen in the oxygen-supply side. However, there are few results reported to date, which is mainly due to the difficulties in attaining sufficiently high permeation fluxes (which is usually achieved by reducing the thickness of the dense layer), while at the same time maintaining the membrane properties during prolonged exposure at operating conditions. The only clear advantage with respect to reactant distribution using porous membranes would be the case of composite, catalytically active membranes (configuration D, Fig. 2), where at least in principle, the oxygen species transported through the membrane could react before recombination and desorption takes place. This would completely avoid the presence of gas phase oxygen, and could certainly represent a valuable alternative provided that a membrane with sufficiently high reaction selectivity and permeability to oxygen can be developed [93–95]. A considerable research effort is being conducted in order to develop dense membranes capable of simultaneous oxygen anion and electron conductivity. These membranes could be used in catalytic reactors for syngas production by partial oxidation of natural gas [96]. In this case the reaction on one side of the membrane acts as an efficient oxygen sink resulting in an enhanced oxygen transport across the membrane.

A porous catalytic membrane can also be used to keep reactants segregated on either side of it (Configuration E, Fig. 3). Under certain conditions (fast

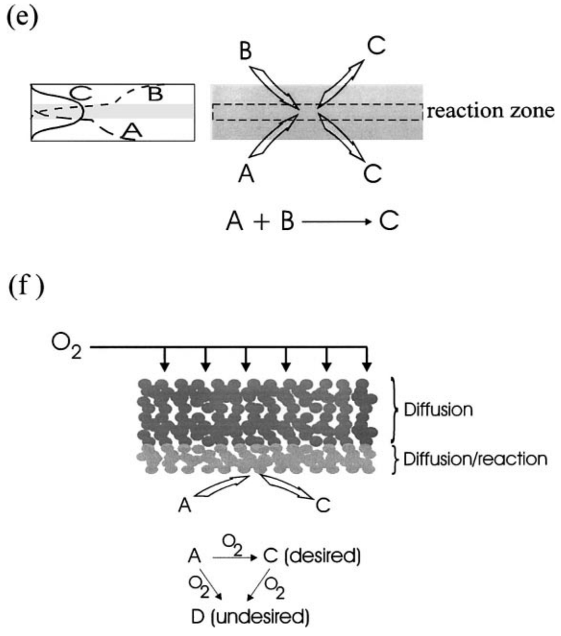

Fig. 3. Application of membrane reactors. Configurations E and F in Table 3.

reaction compared to mass transport), this is useful to confine the reaction in a finite reaction zone inside the porous structure, avoiding the slip of reactants to the opposite side. Further, the reactants arrive at the reaction zone in a stoichiometric ratio, which helps to reduce unwanted side reactions. This concept is also interesting for oxidation processes providing a safer operation by avoiding any premixing of reactants. In the case where a pressure difference is applied over the membrane, the products can be shifted preferentially towards the low-pressure side, which gives a lower residence time in the reaction zone, and reduces further reaction of valuable partial oxidation products [90,97,98].

Configuration F of Table 3 corresponds to a form of reactant distribution, which is an alternative to configuration C for oxidation reactions [99–101]. In this case, the goal is the same (reduce the concentration of oxygen in the reacting environment), although the oxygen partial pressure is now lowered by feeding it through a diffusion layer of sufficient resistance. Oxygen diffusion can take place by itself or in the presence of a stagnant fluid filling the pores of the membrane. This can be achieved by feeding an inert species at approximately the same partial pressure to both sides of the membrane. The diffusion zone is followed by a catalytic layer, where the reaction of oxygen and the reactant permeated from the opposite side takes place. The key to the success of such a configuration is the ability to obtain a sufficiently well-defined sharp distribution of the active component across the membrane radius, which is not always achieved. A different concept also using configuration F was proposed by Vicente et al. [101] to provide in situ the heat necessary for dehydrogenation reactions by using oxygen-assisted dehydrogenation rather than an oxidative dehydrogenation process. In this case, an oxygen-containing stream permeated from the reactor shell side, while a butane-containing stream flowed on the tube side. The catalytic membrane contained a relatively thin (ca. 1 mm) layer of a dehydrogenation catalyst (Cr_2O_3), which also has significant combustion activity. A transversal cut of this membrane can be seen in Fig. 5. The hydrogen produced during dehydrogenation would be preferentially burnt, displacing the dehydrogenation equilibrium and providing the heat necessary to drive the reaction.

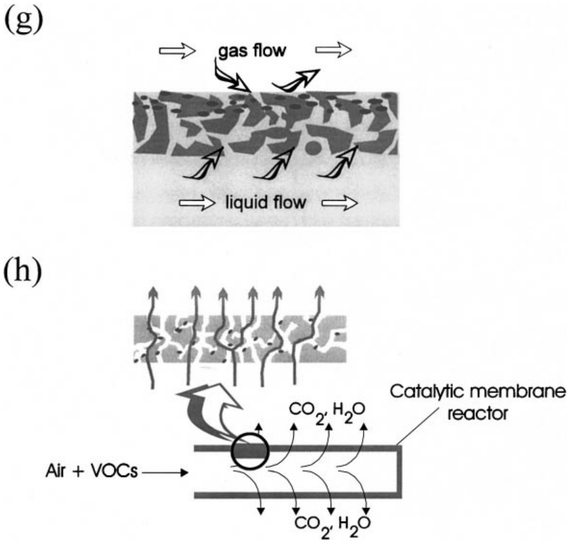

Fig. 4. Application of membrane reactors. Configurations G and H in Table 3.

The last two configurations in Table 3 use catalytic membranes to improve contact efficiency with the objective of attaining higher conversions by decreasing mass transfer resistances. Configuration G (Fig. 4) aims to improve the contact in gas–liquid–solid systems by providing a well-defined contact region: the liquid-filled pores of the catalytic zone of the membrane in close proximity to the gas interphase. This does not require a permselective membrane and avoids the problem of catalyst recovery that appears in slurry reactors. The concept has been demonstrated for instance in hydrogenation reactions over Pt/Al_2O_3 catalysts [102,103].

Finally, configuration H involves a flow-through membrane, in which, unlike the cases discussed above, the permeation of a premixed feedstream takes place. This was the approach employed in works by Saracco et al. [104,105], who used catalytically modified fly ash filters for alcohol dehydration and for the reduction of nitrogen oxides with NH_3. Pina et al. used Pt/Al_2O_3 [106,107] and perovskite-containing membranes [108] operating in the Knudsen regime for the purification (by catalytic combustion) of air streams containing volatile organic compounds in low concentrations. Since in the Knudsen diffusion regime the probability of collisions between the molecules and the wall of the pores is maximised, this type of membrane would be expected to give a high contact efficiency in the reaction of diluted streams, such as those commonly encountered in VOC removal. The results showed that the membrane could perform very efficiently in the combustion of VOCs at low temperatures, although at the expense of a significant pressure drop. The industrial application of this type of combustor would require optimisation of the membrane structure aimed to reducing the pressure drop. Otherwise, its use would be restricted to applications involving reaction simultaneous with gas filtration, where the pressure drop is already present. Another application of co-permeation through a catalytically active membrane operating in the Knudsen diffusion regime is related to the case where gas phase reactions are detrimental to selectivity. Binkerd et al. [109] demonstrated this concept by using a Knudsen-diffusion radial-flow membrane for methane oxidative coupling. This mode of operation had the additional advantage of reducing the contact of products with oxygenated surfaces.

2.3. Preparation of mesoporous catalytic membranes

As indicated in Table 2, with catalytic membrane reactors (CMRs), the reaction (or at least part of it) takes place directly on the membrane. There is a strong ongoing research effort aimed to devising new methods of preparation for catalytic membranes. In that respect, it must be emphasised that in the same way as the membrane reactor provides new modes of contact in the field of reactor engineering, it also brings about a host of new opportunities in the field of catalyst preparation. Some of these will be briefly outlined below.

Porous ceramic membranes can be made, in whole or in part, of alumina, silica, titania, zirconia, zeolites, etc., materials which are catalytically active under suitable operating conditions. In this case, we have intrinsically active membranes, where the membrane itself is the catalyst. From the examples discussed in the previous section, it is clear that during the preparation procedure, we can give specific properties to this catalyst which are not normally encountered in conventional reactors: the fact that a continuous catalyst structure exists can be used to segregate reactants; the asymmetry of this structure, with successive layers of different porosity, can be used to facilitate the diffusion of one of the reactants, while hindering the pass of the other; a positive pressure difference can be established across the catalyst thickness, and this allows the net flow reactants/products to be directed at will towards either side of the catalyst; successive layers of different materials can be deposited across the membrane radius which, at least in principle, would allow one to carry out different consecutive reactions in different regions of the membrane, etc. Also, the permeability of the porous membrane is not necessarily uniform along its length. On the contrary, the permeability can be tailored to suit specific permeation patterns (e.g., [79]), as required by the reaction kinetics, heat transfer arrangements, etc.

When the membrane is not catalytically active under reaction conditions, an active phase can be deposited on it using the membrane material as a support. Impregnation, ion-exchange, chemical vapour deposition (CVD), and sol–gel techniques are commonly employed for this purpose. Again, most of the differences with conventional catalyst preparation procedures using the same techniques stem from the existence of a continuous porous membrane structure. Thus, Zaspalis et al. [110] prepared a thin γ-alumina membrane by slip casting on top of an α-alumina support, and obtained a membrane that was active for the oxidative dehydrogenation of methanol to formaldehyde. On the other hand, the pores of the membrane structure can be filled with appropriate precursors, which are then forced to react in a confined environment. This approach has been used to prepare catalytic membranes active for combustion by synthesising perovskite-type oxides inside porous α-alumina tubes using La, Co, Sr and Mn citrates [108]. Another avenue consists of preparing slips containing appropriate components (e.g., Sr–Fe–Co mixed oxides), which can then be extruded to fabricate membrane tubes [111].

Other researchers have used impregnation of active materials (e.g., Pt) on asymmetric porous membranes, either as received (e.g., [67,112]), or after modification of the porous structure by deposition of γ-alumina [106]. Pt/γ-alumina membranes have also been prepared by CVD by making the organic precursor flow across the porous membrane structure [107]. Here the porous structure plays, once more, an important role: the residence time of precursor molecules and the deposition temperature can be tailored to obtain a homogeneous deposition or, if desired, a sharp step distribution of the active component. On the other hand, the so-called co-condesation technique (i.e., the solvated metal atom deposition) has been proposed to prepare metallic (Pd) films on γ-alumina supports in a more homogeneous and economical way than sputtering and physical vapour deposition techniques [113].

The influence of the membrane structure becomes critical when trying to obtain a non-uniform catalyst distribution across the membrane radius. This can be achieved in a number of ways such as successive

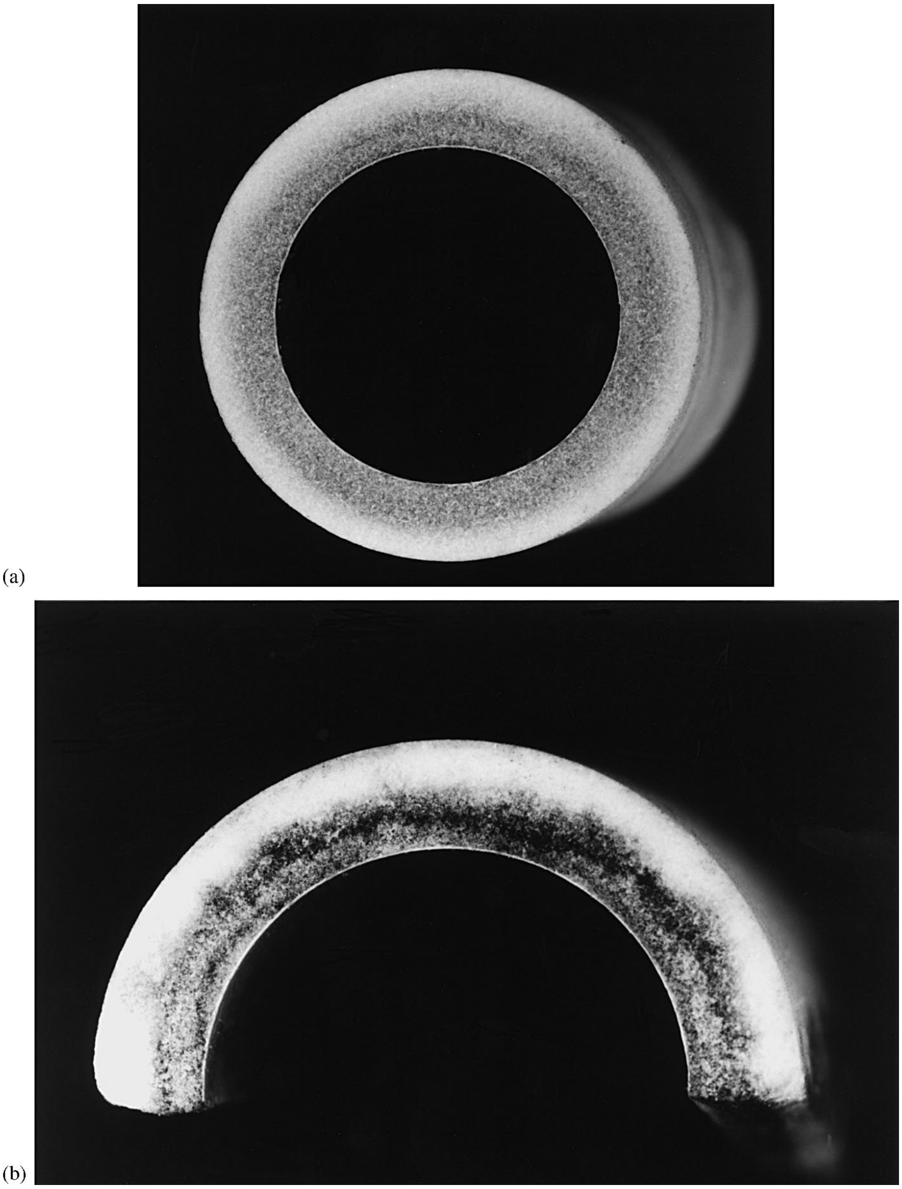

Fig. 5. (a) Step distribution of active components in a tubular Cr_2O_3/Al_2O_3 membrane obtained by impregnation from one side. (b) Step distribution of active components in a tubular V/MgO membrane obtained by impregnation from one side.

deposition of inert and active layers using sol–gel techniques. This approach was successfully employed by Yeung et al. [9] to vary the position of a narrow step distribution of Pt across the membrane radius. Along this line, Michaels [114] suggested the possibility of placing consecutive ceramic layers of different materials via sol–gel, where each layer could be loaded with a different catalyst. The flexibility of the sol–gel method allows the synthesis of thin porous catalytic films that are difficult to achieve by other means. Such is the case of the V–P–O catalytic membranes prepared by Farrusseng et al. [115] for the partial oxidation of butane.

A non-uniform catalyst distribution can also be obtained by the reaction of suitable precursors fed from opposite sides of the membrane structure, an extension of the possibilities of configuration E discussed above. Thus, Gavalas et al. [116] used the reaction between SiH_4 and oxygen at 450°C to deposit very thin films of silica within the walls of porous substrates, and Megiris and Glezer [18] used a similar procedure to deposit SiO_2/C nanostructures within the mouth of the pores of Vycor glass substrates.

However, if a sufficiently homogeneous membrane structure is present, simple impregnation may be sufficient to obtain a controlled, non-uniform distribution of active materials. For instance, Cr_2O_3/Al_2O_3 and V/MgO catalysts have been deposited in a pattern that approaches a step distribution by impregnation of the active components from one side of the membrane only (Fig. 5). This required a previous deposition of γ-Al_2O_3 in the case of Cr_2O_3/Al_2O_3 [101], and of MgO for the V/MgO catalyst [117], and optimization of the duration and number of impregnations. It is possible to obtain different active phase distributions by impregnation from both sides, by previously filling the pores with an inert liquid, or by allowing the membrane to dry from one or from both sides, which tends to concentrate the solution in the pores as the drying interface recedes.

3. Conclusions

The field of catalytic reactors based on porous membranes offers very attractive research opportunities to academic and industrial scientists working on catalysis. An important effort is still needed to develop methods of preparation and characterisation, novel membrane materials and reactor configurations, and new applications to different reaction systems. Industrial applications are not foreseeable in the immediate future, perhaps not due to lack of opportunities, but because of the formidable practical problems involved in moving from laboratory to industrial scale in such a new technology. However, even if only a few of the potential applications eventually materialize, their impact on our current approach to Catalytic Reaction Engineering would certainly be significant: membrane reactors offer the prospect of higher yields and selectivities in many different processes as well as a safer and more environmentally friendly reactor operation.

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