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The chemical valve membrane: a new concept for an auto-regulation of O_2 distribution in membrane reactors

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Abstract

An original method is proposed in this work to regulate the alkane/O_2 ratio in catalytic membrane reactors for oxidative reactions. The concept is based on the use of a "chemical valve membrane" as O_2 distributor. V_2O_5 is an attractive key constituent for such a membrane because of its reversible red/ox behavior (V_2O_5/V_2O_3) and related textural variations able to regulate membrane permeance. This work shows how membrane permeability can be controlled by the red/ox characteristics of the gas phase. We studied the influence of the reducing gas on the evolution of membrane permeance in relation to the membrane weight changes, up to 500°C. The red/ox kinetics have been compared using a series of reducing gases (i-C_4H_{10}, C_3H_8, C_2H_6, C_2H_4, CH_4 and H_2). Finally, we showed how the permeability of such a membrane, when used as an O_2 distributor in a reactor configuration, is controlled by the red/ox characteristics of the gas phase (i.e. by the alkane/O_2 ratio in the reactor).

Keywords: Ceramic membranes; Membrane reactors; Vanadium oxide; Composite ceramic membranes; Chemical valve membrane

1. Introduction

One important field of application for membrane reactors (MRs) concerns consecutive parallel reaction systems, such as partial oxidation or oxydehydrogenation of hydrocarbons or oxidative coupling of methane. For these applications the membrane, separating the alkane from O_2, is generally used to control the supply of O_2 in a fixed catalyst bed in order to by-pass the flammability area, to optimize the O_2 profile concentration along the reactor, and to maximize the selectivity in the desired oxygenate product. In such reactors, the O_2 permselectivity of the membrane is an important economic factor because air can be used instead of pure O_2. However, the limited permeability of dense O_2 permselective ceramic membranes below 800°C and problems of long-term stability has limited their development, although such membranes are now commercialized [1]. The higher, stable and controllable permeability of porous membranes is then also considered as attractive for a number of oxidative reactions [2,3]. The porous membranes used in such reactors are microporous, mesoporous or macroporous [4]. The back-permeation of the alkane to the O_2 feed-side can be limited by application of *trans*-membrane pressure, i.e. by using membranes with a viscous flow contribution for gas transport [5,6]. The gas transport mechanisms involved in porous membranes can be related to the ratio between the pore sizes and the mean free path length of gas molecules [7,8]. The contribution of the different mechanisms is dependent on the properties of the membranes and the gases as well as on the operating conditions of temperature and pressure. At high temperature, when adsorption

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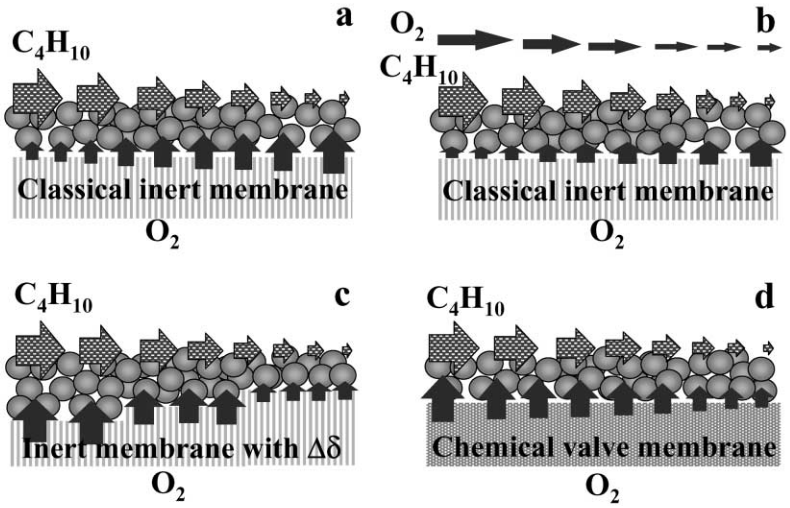

Fig. 1. Schematic representation of the O_2 concentration profile generated in a reactor for the partial oxidation of alkanes: (a) by a classical inert and uniform porous membrane; (b) by a classical inert and uniform porous membrane but with co-feeding a part of O_2 in the tube side; (c) by an inert porous membrane with a non-uniform thickness; (d) by the suggested chemical valve membrane.

is no more effective, the typical gas transport mechanisms in porous membranes are: molecular diffusion and viscous flow (macropores and mesopores), Knudsen diffusion (mesopores) and micropore activated diffusion. In these conditions, the permselectivity increases when pore sizes decrease and pressure can be used to control the transport through membranes with macropores or big mesopores.

The scenario occurring in a tubular porous MR involving a membrane with a uniform thickness and porous structure, is schematized in Fig. 1a. The progressive alkane consumption from the entrance to the exit of the reactor continuously decreases the alkane/O_2 ratio. This phenomenon is enhanced by the influence of the pressure drop generated by the catalyst bed, which tends to increase the O_2 permeation rate near the end of the reactor, due to the higher pressure gradient in that zone [4]. The important evolution of the alkane/O_2 ratio along the reactor, which is consequently not always optimized, alters the catalyst efficiency and decreases the reaction yield. Two solutions were proposed in the literature to overcome this problem: (i) co-feeding a part of the O_2 with the alkane in the reaction zone [2] (Fig. 1b) or ii) using a membrane with a thickness increasing from the entrance to the exit of the reactor [9] (Fig. 1c). In this work, a third method is proposed to better regulate the O_2 flux in the reactor. The proposed concept, shown in Fig. 1d, is based on the use of a “chemical valve membrane” whose permeability could be controlled by the red/ox characteristics of the gas phase. The V_2O_5 was found to be an attractive key constituent for this membrane because of its reversible red/ox behavior (V_2O_5/V_2O_3) and related textural variations able to regulate the membrane permeance [10]. The synthesis conditions as well as the morphological, textural and structural characteristics of this vanadium based “chemical valve membrane” are described in [10]. Both single gas permeance and gravimetric measurements have been used to evidence and study the original and reversible red/ox properties of this composite membrane. On the basis of the results reported in [10], the present work will focus on the influence of the reducing gas on the membrane permeance variation in relation to the weight changes. The red/ox kinetics will be also compared using a series of reducing gases (i-C_4H_{10}, n-C_4H_{10}, C_3H_8, C_2H_6, C_2H_4, CH_4 and H_2). Finally, we will show how the permeability of such a membrane, when used as an O_2 distributor in a reactor configuration, is controlled by the red/ox characteristics of the gas phase (i.e. as a function of the alkane/O_2 ratio in the reactor).

2. Experimental

2.1. Membrane synthesis method

The membrane synthesis method is described in [10], it will be only briefly mentioned here. Commercial alumina tubes with an asymmetric three layers structure (supplied by SCT, France) were used as supports for the membranes. The tubes are 15 cm long, enameled at each end on 25 mm, with internal/external diameters of 7/10 mm. The composite membrane was obtained from a polymeric sol derived from a mixture of di-*n*-propylphosphate and a home made oxo-alkoxide $VO(OCH(CH_3)CH_2OCH_3)_3$ in 1-methoxy-2-propanol. The following sequence: sol impregnation in the α-Al_2O_3 tubular support-air drying-firing during 4 h at 650°C in air (heating rate $2°C\,min^{-1}$) was repeated five times in the same way, until the tube reached a stable weight.

2.2. Characterizations

A number of classic characterization methods were used for studying the morphology (FESEM), structure (XRD) and porous texture (Hg porosimetry, N_2 adsorption–desorption) of the resulting composite infiltrated membranes. The methods used and related results are reported in [10]. The present work aims at further exploration of the red/ox properties of the membranes by both gravimetric and single gas permeance measurements. We mainly focused on the influence of the reducing gas on the membrane permeance variation in relation with the weight changes. The red/ox kinetics have been compared using a series of reducing gases (*i*-C_4H_{10}, *n*-C_4H_{10}, C_3H_8, C_2H_6, C_2H_4, CH_4 and H_2). We also studied the evolution of the membrane O_2 permeance when used as an O_2 distributor in a ODHP reactor configuration.

2.3. Gravimetric measurements

Thermogravimetric studies of a tubular membrane sample (3 cm long initially oxidized) submitted to a reducing atmosphere (*i*-C_4H_{10}, *n*-C_4H_{10}, C_3H_8, C_2H_6, C_2H_4, CH_4 or H_2) were carried out in a TG balance (Setaram 1000) up to 500°C. For this series of experiments, the sample was suspended to the balance cantilever through a Pt wire. The sample weight was continuously recorded during the reduction from 25 up to 500°C and with a constant gas flow rate ($40\,ml\,min^{-1}$). Before each change in the reducing gas, the membrane sample was reoxidized and the system was purged with Ar.

Isotherm gravimetric analyzes of the sample were also performed with the same TG balance, by fixing the temperature at 500°C and recording the weight variation as a function of time during the red/ox cycling (*n*-C_4H_{10}, O_2, C_3H_8, O_2, C_2H_6, O_2, *i*-C_4H_{10}, O_2, *n*-C_4H_{10}, O_2, H_2). The system was purged with Ar before each change in the flowing gas.

2.4. Single gas permeance studies

For the single gas permeance studies, membranes were sealed in a home made stainless steel module using graphite o-rings. During gas permeation measurements, one end of the membrane tube was closed and the internal pressure was typically 1.5 bar. The pressure in the permeate side (outside part of the tube) was the atmospheric pressure and no sweep gas was used. During the measurements as a function of temperature (heating rate $= 2.5°C\,min^{-1}$) the *trans*-membrane pressure was fixed to 500 mbar by a pressure regulator equipped with a pressure sensor. The membrane permeance for a given temperature was measured after stabilization of the flow rate. The measured permeances typically varied in the range 10^{-8} to $10^{-7}\,mol\,m^{-2}\,s^{-1}\,Pa^{-1}$ with a maximum error of less than 5%.

Single gas permeances were measured as a function of temperature (from 25 up to 500°C) for a series of reducing gases (*i*-C_4H_{10}, C_3H_8, C_2H_6, C_2H_4, CH_4 and H_2). Another set of experiments consisted in measuring the N_2 permeance of the membrane cooled at 25°C after each of the above-mentioned red/ox treatment at 500°C.

2.5. Regulation of O_2 distribution in a MR configuration

The interest of the “chemical valve” concept for an auto-regulation of the O_2 flux in a MR was evidenced by using the membrane, without any catalyst, as an O_2 distributor in a reactor configuration adapted to the oxidative dehydrogenation of propane. The stainless

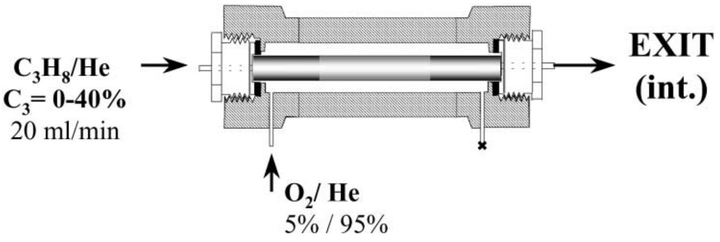

Fig. 2. Schematic representation of the membrane reactor configuration used for evidencing the auto-regulation of the O_2 flux through the chemical valve membrane (no catalyst; $P_{\mathrm{int}} < P_{\mathrm{ext}}$; $T = 500°\mathrm{C}$; $\Delta P_{\mathrm{initial}} = 485$ mbar; ΔP was measured while the C_3H_8 molar fraction was increased from 0 to 39.51% in the internal feed).

steel MR (IRC, Villeurbanne, France) was designed to operate with two separated inlet flows. In the tested O_2 distributor configuration (Fig. 2), propane was fed into the inner compartment and oxygen into the outer one, the exit was in the inner compartment. The reactant feed composition was 5.1% O_2 in He (shell-side) and X% C_3H_8 in He (tube-side). Experiments were performed at 500°C and X was varied from 0 to 39.51% while keeping constant the internal feed flux (20 ml min^{-1}). An initial *trans*-membrane pressure ($\Delta P = P_{\mathrm{int}} - P_{\mathrm{ext}}$) of 485 mbar was applied between the two compartments of the reactor (when $X = 0\%$). Because there was no exit on the shell side, the external feed flowed through the membrane. For each modification of X from 0 to 39.51% in the internal feed, the red/ox atmosphere was changed, inducing a variation of the membrane permeance and consequently of the *trans*-membrane pressure. The evolution of the (O_2 + He) permeance through the membrane as a function of the C_3H_8/O_2 molar ratio in the system, was calculated from the measured ΔP values by the using the following equation:

$$\Pi(O_2 + \mathrm{He}) = \frac{\mathrm{flux}(O_2 + \mathrm{He})}{\Delta P}$$

in which the (O_2+He) flux through the membrane was constant (20 ml min^{-1}) and ΔP was measured 30 min after each variation of the C_3H_8 partial pressure.

3. Results and discussion

The main morphological, structural and textural characteristics of the composite "chemical valve membrane" are reported elsewhere [10]. A summary of the results is presented in Fig. 3. The mixture of vanadium and phosphorous molecular precursors leads to an innovative liquid precursor able to infiltrate the pores of the commercial α-Al_2O_3 tubular support. After the thermal treatment at 650°C in air, the pores of the internal and intermediate layers of the support were entirely filled with a ceramic material containing V_2O_5 and $AlPO_4$ crystallites. The red/ox properties of V_2O_5 crystallites, which transform reversibly to V_2O_3 under reducing atmosphere, were found to control the porous characteristics of the membrane (grains morphology, pore size distribution, porous volume and S_{BET}) and consequently its permeance properties. A number of techniques (FESEM, N_2 adsorption–desorption, Hg porosimetry, TGA, TDA, XRD, LRS, NMR) were used in order to study the morphological, textural and structural characteristics of this composite membrane whose original and reversible red/ox properties were clearly evidenced by single gas permeance results. The membrane permeance is higher when it is reduced and lower when it is oxidized: the ratio between the permeances of pure n-C_4H_{10} and pure O_2 is of about 70 at 500°C. The red/ox reactivity was found to be reversible and the membrane permeance behavior was not altered after 10 red/ox cycles, even under drastic conditions (heating/cooling cycles 25/500°C pure gas switching at 500°C). This type of infiltrated composite membrane was found to be thermally and chemically stable. The reproducibility of both membrane synthesis and red/ox behaviour has been checked on a seven membranes series. Their permeance was measured at room temperature as a function of ΔP but also during red/ox cycles at 500°C. The involved gas transport mechanisms are typically in the transition regime (Knudsen diffusion and viscous flow) with a

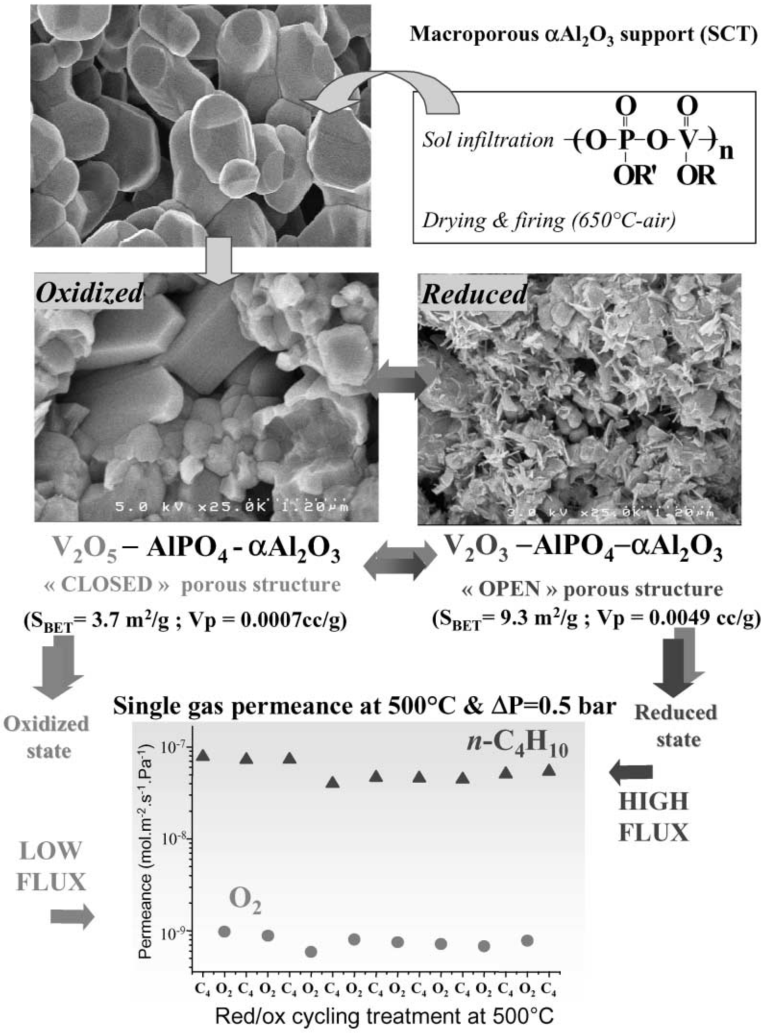

Fig. 3. Main characteristics of the chemical valve membrane, summarized from [10].

Knudsen contribution in the range 50–90%. At 25°C and with $\Delta P = 0.5 \times 10^5$ Pa, the N_2 permeance is in the range 10^{-7} to 10^{-8} mol m^{-2} s^{-1} Pa^{-1}. Concerning red/ox properties, the seven membranes behave in the same way, clearly evidencing a “chemical valve” effect when comparing the permeance of O_2 or alkanes. Indeed for the whole membrane series, the permeance was a function of the oxidation degree of the vanadium oxide particles present within the membrane material. This oxidation degree was controlled either by pre-treating the membrane (in a reducing or oxidizing atmosphere at high temperature) before the permeation tests or directly by the permeating gas at 500°C. This latter case is the one observed in the permeation curves of O_2 and n-C_4H_{10} reported in Fig. 3.

On the basis of these results, the present work focused on the influence of the type of reducing gas on the membrane permeance variation in relation with its weight variations. The red/ox kinetics have been compared using a series of reducing gases (i-C_4H_{10}, n-C_4H_{10}, C_3H_8, C_2H_6, C_2H_4, CH_4 and H_2). We also studied the evolution of the membrane permeability when used as an O_2 distributor in a reactor configuration.

3.1. Influence of the reducing gas on the membrane permeance variation

The evolution between 25 and 500°C, of the permeance of several of the aforementioned reducing gases (i-C_4H_{10}, n-C_4H_{10}, C_3H_8, C_2H_4, C_2H_6 and H_2) through the "chemical valve membrane" initially oxidized, is shown in Fig. 4. Each permeation/reducing treatment was performed with a heating rate of $2.5°C\,min^{-1}$ and 25 min plateau at 500°C. At low temperature, the evolution of permeance with temperature typically obeys the equation for gas transport in the transition regime, i.e. with both a viscous flow and a Knudsen contribution. When temperature increases, the permeance tends first to stabilize and then increases again. This leads to very unusual single gas permeation plots versus temperature. The temperature T_R for which the permeance starts increasing varies from 375 to 450°C, depending on the considered reducing gas. At room temperature, the order for single gas permeances ($\Pi_{H_2} > \Pi_{C_2H_6} > \Pi_{C_2H_4} > \Pi_{C_2H_6} > \Pi_{C_3H_8} > \Pi_{n\text{-}C_4H_{10}} > \Pi_{i\text{-}C_4H_{10}}$) is a function of the molecular weight (M_w) and the viscosity (η) of each gas. After a 25 min plateau at 500°C, the order of permeances remains unchanged.

3.2. Relation between the membrane weight and permeance variations during reduction

Fig. 5 compares the evolution of the membrane weight (measured with a TG balance on a 3 cm long membrane sample) and single gas permeances as a function of temperature, during reducing treatments with n-C_4H_{10}, C_3H_8, C_2H_6 and H_2. These curves demonstrate the direct relation between the membrane weight loss during the reduction (oxygen loss during V_2O_5 to V_2O_3 transformation) and its increasing permeance. A similar fit has been observed for treatments with i-C_4H_{10}, C_2H_4 and CH_4 (results not shown). In the series of the studied alkanes, the temperature needed to observe an increase of permeance (or a weight loss) increases when the number of carbon atoms in the alkane chain decreases. Indeed this temperature is 375, 410, 450 and 475°C, respectively, for n-C_4H_{10}, C_3H_8, C_2H_6 and CH_4. This can be attributed to a decreasing reducing power of alkanes when the carbon chain decreases. Differences in adsorption and reactivity between the considered gases and the vanadium-based membrane material have also to be taken account. For gases with short carbon chains, the reduction needs a higher temperature or takes a longer time.

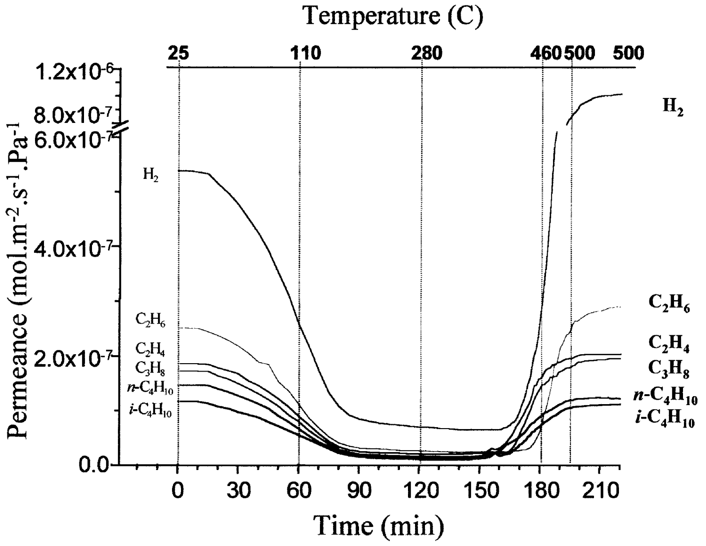

Fig. 4. Evolution of membrane permeance with temperature for different reducing gases. Heat treatment: $2.5°C\,min^{-1}$ (25 min plateau at 500°C). The membrane was reoxidized after each reducing treatment.

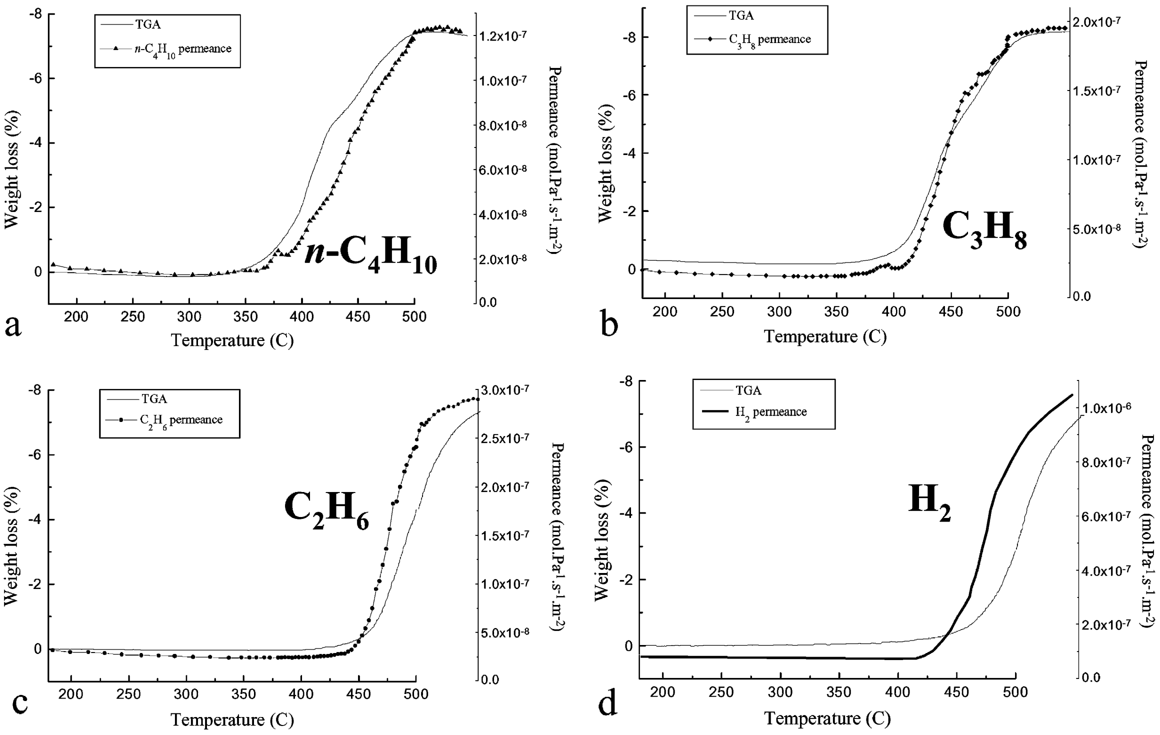

Fig. 5. Comparative evolution, for different reducing gases, of the membrane weight loss and permeance versus temperature.

3.3. Time required for completing the reduction of the membrane at 500°C

Fig. 6 gives an indication of the time needed to complete the membrane reduction at 500°C, with n-C_4H_{10}, C_3H_8, C_2H_6, i-C_4H_{10}, or H_2 as reducing gases. The time needed to obtain a stable weight (related to the reduction kinetics) increases when the alkane chain length decreases. The reduction with H_2 needs more time to be completed than the reduction with alkanes. Typically 20–30 min are needed to reduce completely the membrane with n-C_4H_{10}, although more than 2 h are needed with H_2. We have to note that the re-oxidation of the reduced membrane is very rapid: it takes less than 5 min at 500°C to completely re-oxidize the membrane. Taking into account the precision of the TG balance, we can consider that the membrane reaches approximately the same weight after stabilisation (complete reduction) for all the considered gases. This indicates that whatever the used reducing gas, the membrane material can reach the same reduction degree. But on the other hand, we will see hereafter that the permeance of the totally reduced membrane varies as a function of the gas used for the reduction.

3.4. Influence of the gas used for the reduction at 500°C, on the N_2 permeance at 25°C

The evolution of the membrane N_2 permeance at 25°C, as a function of the gas used for red/ox cycling at 500°C, is reported in Fig. 7. Before being submitted to these cycling treatments (heating–cooling cycles between 25 and 500°C under reducing or oxidizing atmosphere) the membrane has been submitted to six red/ox cycles at 500°C with n-C_4H_{10}/O_2 in order to stabilize its structure (permeance values in the reduced and oxidized states). The N_2 permeance was measured at room temperature after each of the following permeation treatment at 500°C: n-C_4H_{10}, O_2, i-C_4H_{10}, O_2, C_3H_8, O_2, C_2H_6, O_2, C_2H_4, O_2, C_2H_4, O_2, H_2, O_2, n-C_4H_{10}. During the reduction treatment the internal pressure in the tube side was 1.5 bar. In all cases, the duration of the reducing treatment has been adjusted in order to reach a stable weight for the membrane,

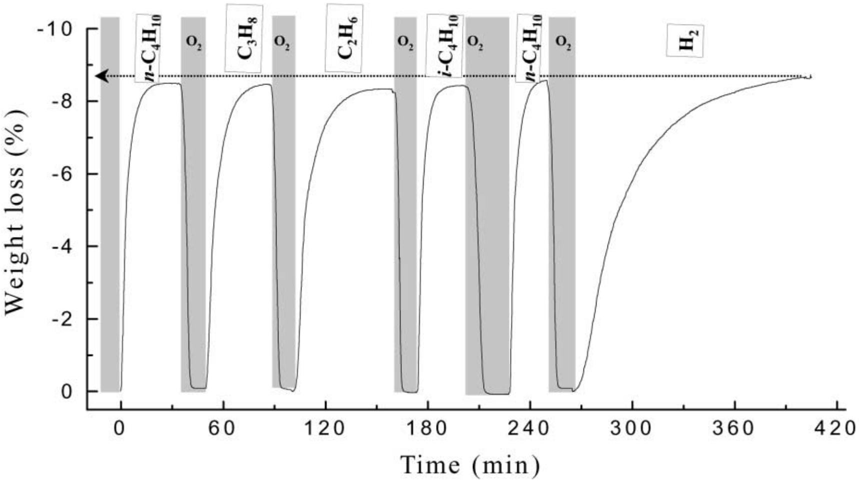

Fig. 6. Evolution of the membrane weight as a function of time during red/ox cycling at 500°C.

according to the TG results (Fig. 6). We clearly observe in Fig. 7 the typical switch-on/off evolution of the permeance during the red/ox cycling. The reversibility of the red/ox phenomena is clearly evidenced: (i) the N_2 permeance of the oxidized membrane is stable during cycling; and (ii) the N_2 permeances after the first and last treatment with n-C_4H_{10} are identical. The most remarkable result concerns the variation of N_2 permeance with the type of gas used for the reducing treatment at 500°C. If we only consider the alkane series, the N_2 permeance increases when the chain length of the alkane used for the reduction decreases: after reduction with n-C_4H_{10}, i-C_4H_{10}, C_3H_8 and C_2H_6, the values for Π_{N_2} are, respectively, 5.61×10^{-7}, 5.68×10^{-7}, 6.97×10^{-7} and $8.17 \times 10^{-7}\,\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$. The membrane permeance is then not only related to its reduction degree (which is maximum here for all the reducing gases). A possible explanation could be related to textural effects either due to the difference in the reduction kinetics which could affect the porous structure of the reduced membrane, or to the presence of coke formed during the reduction step (coking is favored with long chain alkanes).

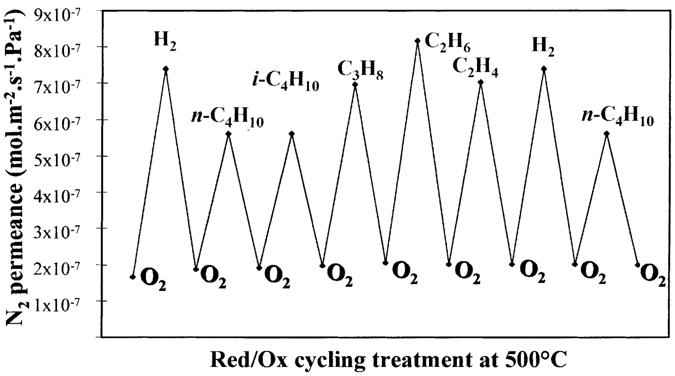

Fig. 7. Evolution of N_2 permeance at 25°C as a function of the gas used for red/ox cycling at 500°C. Membrane was first stabilized by six n-C_4H_{10}/O_2 red/ox cycling at 500°C; reduction time, t_R, fits with a weight stabilization in TGA.

3.5. Behavior of the chemical valve membrane when used as O_2 distributor in a MR configuration for the partial oxidation of alkanes

If we place the membrane, as shown in Fig. 2, in a ODHP reactor configuration (without any catalyst) fed at 500°C with a C_3H_8/He mixture (20 ml min^{-1}) in the tube-side, and with a O_2/He mixture in the shell-side, we clearly observe that the (He + O_2) permeance increases with the C_3H_8/O_2 ratio in the system (Fig. 8a). Starting from a membrane initially oxidized, the *trans*-membrane pressure ΔP was found to decrease from 485 to 90 mbar, when the C_3H_8 concentration was increased from 0 to 39.51% in the internal feed. It means that the (He + O_2) permeance increases typically by a factor × 6, when the C_3H_8/O_2 ratio increases from 0 to 7.83. For each modification of the C_3H_8 partial pressure, the red/ox atmosphere in the membrane was changed, inducing a variation of the membrane porous texture and consequently of its permeance. The (O_2 + He) permeance values reported in Fig. 8a were calculated from the measured ΔP values.

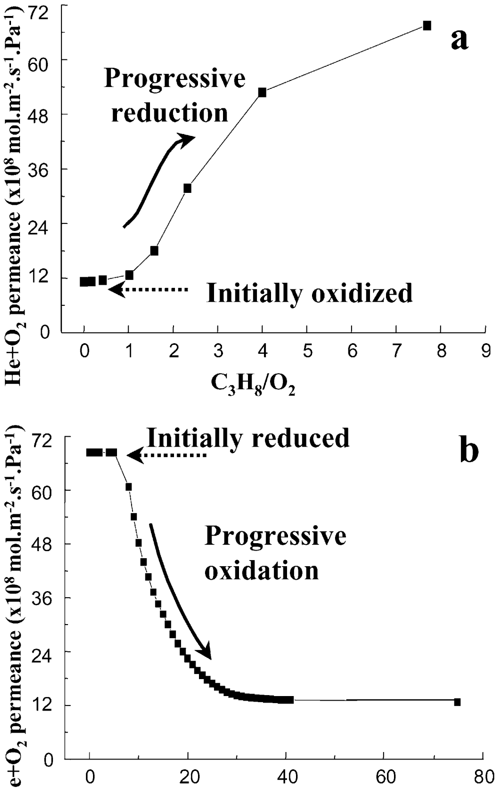

Fig. 8. Evolution of the O_2/He permeance (calculated from ΔP measurements) through the chemical valve membrane as a function of: (a) the C_3H_8/O_2 molar ratio in the reactor, when starting from an oxidized membrane; (b) time, during the re-oxidation step of the reduced membrane.

After this first test, leading to a reduced state, the reversibility of the phenomena was checked by measuring the time needed for the membrane re-oxidation. Fig. 8b shows the evolution with time of the (O_2 + He) permeance of the membrane, when submitted to the initial oxidative conditions ($C_3H_8/O_2 = 0$). The membrane permeance keeps stable during the first 5 min, then it drops rapidly to reach its initial value after about 40 min permeation experiment. The response time (5 min) measured for this membrane also includes the time needed to blow-off the pipes.

Regarding the utilization of this "chemical valve membrane" as O_2 distributor in a catalytic reactor for the partial oxidation of alkanes, the membrane will be submitted to a gas phase whose composition varies from oxidative to reductive when moving from the external to the internal side of the tubular support. We have then a gradient in the red/ox characteristics of the gas phase in contact with the membrane. As far as this membrane is meso- and macroporous with a low porosity, we can expect an efficient barrier effect (limited back-diffusion of the alkane to the shell side) and a "pneumatic control" of gas transport [6]. Indeed, this is specifically possible for membrane when a viscous flow contribution is involved for gas transport. Then, by adjusting the *trans*-membrane pressure, one can also possibly control the red/ox gradient composition within the membrane thickness. This could help in enhancing the sensitivity of the membrane and improves its textural adaptation to the gas phase composition.

Consistently, the "chemical valve" concept can be considered as potentially attractive for an auto-regulation of the O_2 concentration in a MR for the partial oxidation of alkanes. As schematically shown in Fig. 1d, the O_2 flux will be higher at the entrance of the reactor where the alkane concentration is high, although it will be lower at the exit, where the alkane concentration is low. A number of oxidative reactions requiring alkane/O_2 ratios corresponding to the range of sensitivity of the membrane could be attractive examples for testing the interest of such a concept. The partial oxidation of propane to acrolein or acrylic acid, are typically adapted as far as the required C_3H_8/O_2 ratio is about 5 [11]. On the other hand, the membrane seems less adapted to the partial oxidation of n-C_4H_{10} to maleic anhydride for which the reaction conditions with a VPO catalyst are rather oxidative (n-$C_4H_{10}/O_2 = 0.25$–0.5) [12]. Anyway, if used in adapted conditions, such a membrane could help in optimizing the alkane/O_2 ratio all along the reactor (locally and upon use), it could also limit the effects of hot-spots and then improve the reactor and catalyst efficiency.

4. Conclusion

The aim of this work was to demonstrate the interest of the "chemical valve membrane" concept for regulating the alkane/O_2 ratio in tubular reactors for partial oxidation reactions. Starting from (i) an applied objective; (ii) original concepts of "composite infiltrated membrane" and of "chemical valve"; (iii) a well known material, vanadium oxide, whose red/ox properties affects its morphology; and (iv) the well-known sol–gel synthesis process, we prepared an original "chemical valve membrane" with attractive properties. This membrane consists of a mixture of V_2O_x and $AlPO_4$ crystals occluding the pores of the αAl_2O_3 support. The red/ox characteristics of the gas phase influence reversibly the membrane morphology, weight, crystallographic structure, pore size, porosity, and consequently its permeance. We have shown in this work that the evolution (increase) of the membrane permeance versus temperature during the reduction is related to its weight variation (loss of oxygen). At 500°C, 20–30 min are needed for completing the reduction with n-C_4H_{10}, although only 3–5 min are needed to re-oxidize the membrane in pure O_2. This work also showed that the permeance of the reduced membrane is influenced by the characteristics of the gas used for the reduction at 500°C (alkane or H_2, alkane chain length). Finally, the membrane was tested as O_2 distributor in a reactor configuration fed at 500°C with a C_3H_8/He mixture in the tube-side, with a O_2/He mixture in the shell-side and without any catalyst. The $(He+O_2)$ permeance clearly increased with the C_3H_8/O_2 ratio (varying in the range 1–8) in the system. The phenomenon is reversible and the response time of the membrane to the red/ox atmosphere changes is in the range 5–30 min. A reproducible synthesis as well as reversible characteristics and permeation behavior under red/ox conditions have been proven for this original "chemical valve membrane".

Of course, a realistic evaluation of such a concept for large scale reactors and under real reaction conditions will have to be performed before really drawing conclusions about the interest of such an "academic membrane" for MR applications. Anyway, the results obtained in this work are sufficiently original and positive for claiming the validity of the "chemical valve concept" for regulating gas transport with ceramic membranes.

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