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Oxidative dehydrogenation of butane on V/MgO catalytic membranes

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Abstract

Different catalytic membranes containing V/MgO catalyst in a commercial ceramic support structure have been prepared. These membranes have been employed for the selective oxidation of butane to butene and butadiene. The effects of the vanadium concentration in the catalytic layer, the reactor configuration, the structural properties of the membrane and the operating conditions have been studied. The membrane reactor operating with segregated butane and oxygen feeds clearly outperforms (in terms of both selectivity and yield) the case of premixed feed on the same membrane. It is also shown that the structural characteristics of the membrane, (and in particular, the relative laminar and Knudsen contributions to permeation) have a strong influence on the reactor performance. Yields up to ca 20% have been obtained in this work.

1. Introduction

Vanadium supported on magnesium oxide (V/MgO) catalysts have been described in the literature as active and selective for the oxidative dehydrogenation of alkanes in general and butane in particular [1]. Also, this catalyst is stable under the usual operating conditions for this reaction. The most selective catalysts have been found to contain between 10 and 60% of V_2O_5 respect to the total catalyst weight, and in this interval the most active catalysts have 20–40% weight of V_2O_5.

A large number of studies have been devoted to the characterisation of V/MgO catalyst, as may be seen in several reviews [2,3] and recent articles (e.g. [4–8]), where a variety of experimental techniques (SEM, X-ray diffraction (XRD), ^{51}V RMN, XPS, SSITKA, HRTEM, FT-IR) have been employed. The V^{5+} atoms in tetrahedral co-ordination have been identified as the sites responsible for the selectivity in the V/MgO system [9].

In spite of the extensive research in this reaction system, the oxidation of both reactant and products to CO and CO_2 still occurs to a significant extent, resulting in an undesirable loss of selectivity. In addition to catalyst development, an alternative way to improve the selectivity is to find improved modes of contact between catalyst and reactants, and between the reactants themselves. Inert membrane reactors (IMRs), also known as membrane-enclosed packed bed reactors, have been used in catalytic oxidations as a way to improve not only reaction selectivity but also the safety of reactor operation [10]. Examples of use [11–19] include methane oxidative coupling, oxidative dehydrogenation of ethane, propane and butane and the oxidation of butane to maleic anhydride. Several reviews on the use of membrane contactors [20–22] describe in depth the proven advantages and future perspectives of membrane reactors.

In addition to IMRs, another possibility within the field of membrane reactors is the catalytic membrane reactor (CMR), where the membrane itself possesses catalytic activity. Research on this type of contactor was pioneered by Zaspalis et al. [23,24], who employed a thin layer of $V/\gamma\text{-}Al_2O_3$ catalyst deposited on a flat $\alpha\text{-}Al_2O_3$ support for the reduction of NO_x with NH_3, and a thin layer of $Ag/\gamma\text{-}Al_2O_3$ on the same support, for methanol oxidation to formaldehyde. The selectivity obtained with a segregated feed was higher than by cofeeding both reactants to the same side of the membrane. A CMR with a thin layer of $V/\gamma\text{-}Al_2O_3$ also provided improved yields in the oxidation of etilene to acetaldehyde [25].

Harold and co-workers [26,27] simulated a CMR, for a general reaction of the type:

$$A + B \rightarrow R, \quad r_1 = k_1 C_A^{n_1} C_B^{m_1}$$

$$A + R \rightarrow P, \quad r_2 = k_2 C_A^{n_2} C_B^{m_2}$$

The above reaction scheme may represent any oxidation reaction in which the desired product (R) may be further oxidised to CO_x (P). These simulation works [26,27] demonstrated that, under suitable operating conditions, and provided that some requisites are fulfilled by the reaction kinetics ($n_1 < n_2$), using a CMR with segregated feeds

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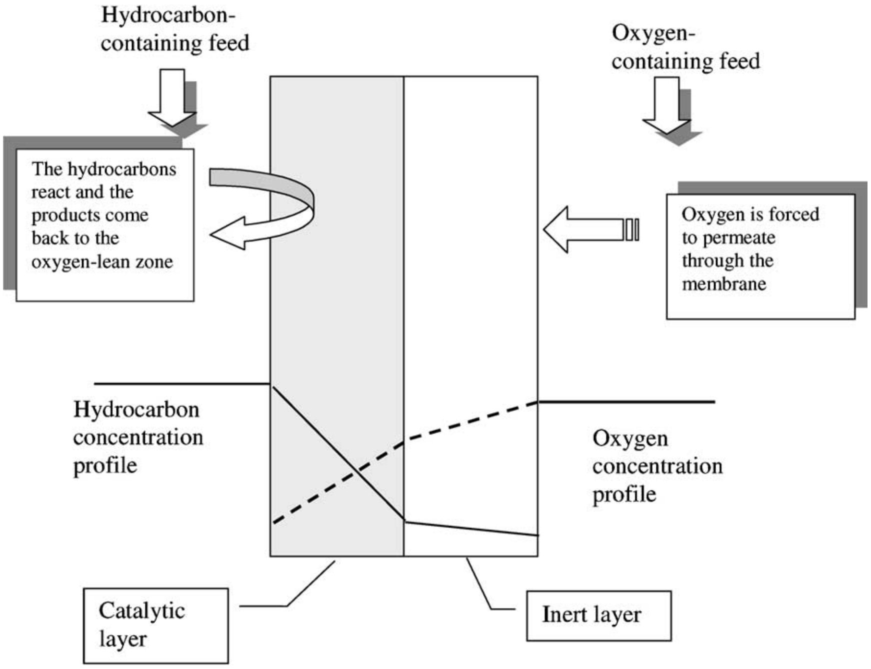

Fig. 1. Simplified scheme of a CMR used for a selective oxidation reaction.

leads to improvements in selectivity and yield. A more sophisticated model was developed recently [28], and its results also agree with this prediction.

The conceptual basis for the improvements obtained with a CMR in selective oxidations is illustrated in Fig. 1. There are two zones within the membrane contactor: a catalytic (active) layer and a diffusion (inert) layer. The feed is segregated, i.e. the hydrocarbon containing stream is fed to the side where the catalytic layer is located, while the oxygen containing stream is fed to the inert layer side. Since a partial pressure gradient exists for every reactant, both of them tend to diffuse in opposite directions. The reaction takes place at the catalytic layer, where the partial pressure of oxygen is lower than in the feed, due to the diffusion resistance of the inert layer and to the consumption of oxygen in the reaction. Because in most cases of selective oxidations the selectivity to the desired product is favoured by a low partial pressure of oxygen, the decreased oxygen partial pressure results in a higher selectivity and yield to the desired product. This effect cannot be obtained in a conventional fixed bed reactor (FBR), where lowering the oxygen partial pressure in the feed in order to increase the selectivity leads to low per pass conversion and yield. On the other hand, the permeation flux in a CMR contributes to a rapid removal of products from the vicinity of the catalyst, an important advantage with respect to the IMR in partial oxidation reactions. Therefore, a CMR has been used in this work.

Few experimental works have been published on the oxidative dehydrogenation of alkanes using CMRs [15,29–32], and they deal with the reaction of propane. Some of the

Table 1
Some results published on the oxidative dehydrogenation of alkanes using CMRs

Type of catalytic membrane	T (°C)	Propane conversion	Selectivity to propene	Yield to propene	Reference
Thin V/MgO layer on a SCT support (200 nm pore size)	600	9.8	47.8	4.7	[15]
Thin NiO layer on a SCT support (5 nm γ-alumina)	254	10	42.4	4.3	[15]
V/Al_2O_3 layer on a 160 nm membrane (SCT)	480	9	57	5.1	[29]
V/Al_2O_3 layer on a support with pores filled with silica	600	45	33	15	[30]
V/MFI zeolite both in the internal surface and the pores of a 200 nm SCT membrane	555	10.2	40.6	4.1	[31]
	579	14.7	39.7	5.9	[31]
	604	11.7	42.6	5	
	628	14.7	42.5	6.2	
	650	19.8	43	8.5	
V/Al_2O_3 and V/MgO membranes on alumina supports	585	48	31.5	15	[32]
		50	30	15	

results obtained are summarised in Table 1. Two studies [15,30] that used a thin catalytic V/Al_2O_3 layer found that the yield obtained with segregated propane and oxygen feeds was higher than when both reactants were cofed at the same side. Conversely, other works used a thin layer of V/MgO [15] or V/zeolite [31] and found no significant improvement. However, in a recent work [32], it was shown that a large increase in propene yield (up to three times) could be achieved by using a thicker V/MgO layer coupled with a diffusion layer. In this case, the results were explained by the larger catalyst load compared to previous works, and by the fact that the diffusion layer (which was not present in the other oxidative dehydrogenation studies with V/MgO) allowed to work with a lower oxygen partial pressure in the reaction zone.

Since it is well known that V/MgO is a better catalyst for the oxidative dehydrogenation of butane than V/Al_2O_3 [2], in this work a V/MgO catalytic membrane will be employed in the oxidative dehydrogenation of butane. The aim of the investigation is to study for this process the effect of the main reactor-related variables: vanadium content of the catalytic layer, permeation characteristics of the membrane and reactor feed configuration.

2. Experimental system and membrane preparation

The starting material in all cases were tubular (7 mm i.d., 10 mm o.d.) α-Al_2O_3 microfiltration membranes (SCT), with 10 mm pores and with a 10 cm long permeable zone. This material was modified by impregnation with suitable solutions, as described in more detail elsewhere [32]. Briefly, the support was impregnated repeatedly with a $Mg(NO_3)_2$ solution, and then calcined at 700 °C. The procedure was repeated until the desired weight increase was achieved, (i.e. the load of MgO in the pores of the support). To prepare the V/MgO catalyst, V was then incorporated by impregnation from the inner membrane side with a saturated NH_4VO_3 solution followed by calcination. The depth of the penetration of the V-containing solution was limited by controlling the impregnation time. Previous tests using both optical photography on reduced samples and SEM–EDX measurements [32] showed that with 6 min of impregnation the V deposit was limited to approximately half of the membrane thickness. The impregnation steps were repeated until the desired concentration of V was obtained. The membranes prepared were characterised by XRD, temperature-programmed reduction (TPR) and permeation measurements.

Several reactor feed configurations were tested, as shown in Fig. 2. Configuration 1 is a monolith-like arrangement in which the reactants are premixed and fed to the same side (inner side of the membrane), exiting from the same side. In configurations 2 and 3 oxygen is supplied to the inert-zone side of the membrane (outer side), while butane is fed to the inner (active layer) side, from which the product stream exits. The difference between configurations 2 and 3 lies in the side to which the inert gas (He) is fed, as shown in Fig. 2. All the reactants were supplied by means of mass-flow controllers and the reaction products were analysed by on-line gas chromatography. More details of the reaction system were given elsewhere [30].

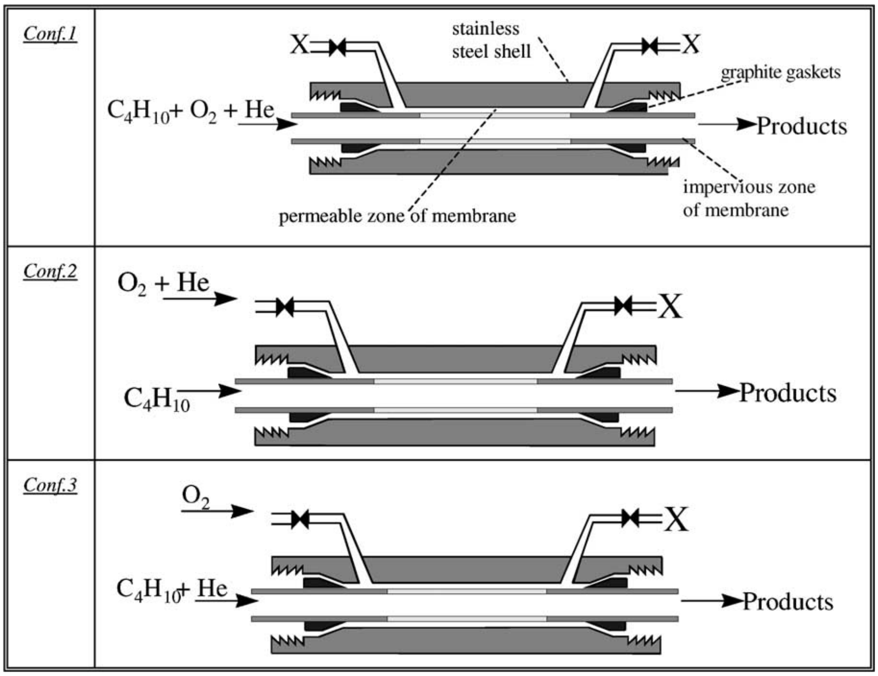

Fig. 2. Scheme of the three reactor feed configurations employed in this work. X indicates a closed inlet/outlet.

3. Results and discussion

Three membranes, with different V loadings have been prepared. They will be designated as MxV/MgO, where x is the percentage by weight of V respect to the total amount of $V_2O_5 + MgO$ added to the support. The contents in V and MgO and the total amount of catalyst in each membrane are shown in Table 2.

XRD analysis of the prepared membranes (results not shown) displayed mainly the Al_2O_3 pattern, although smaller-intensity reflections of MgO and $Mg_3V_2O_8$ could also be observed. A study of the XRD patterns also indicated that the proportion of detectable Mg vanadates on the membranes prepared in this work was lower than that observed for powdered catalysts when prepared with the same V/Mg ratio in a single treatment. The results of TPR experiments carried out on two of the membranes are shown in Fig. 3, where they are compared with the TPR pattern of a typical V/MgO catalyst (C14V/MgO), prepared as described in the literature [17]. The main peak of hydrogen consumption appears at higher temperatures in the case of membranes. Taking into account the XRD results just discussed this could be interpreted as a result of the different preparation procedure employed for the membranes, yielding a catalyst where V is less easily reduced. Reaction with the α-Al_2O_3 support (to form aluminates, although these were not detected in the XRD analysis) could also be invoked; however, in view of the low surface are of the α-Al_2O_3 (0.06 m^2/g, compared to 8.6 m^2/g for MgO), this would necessarily be a minor contribution. Finally, at least part of the displacement of the main reduction peak towards higher temperatures could be due to the sintering of the V_2O_5 phase caused by repeated heating at 700 °C involved in the preparation procedure. Larger crystallites are more difficult to reduce and, under a fixed temperature ramp, this would translate into a higher apparent reduction temperature.

Table 2
The V and Mg content in the catalytic membranes prepared

Membrane	MgO (wt.%)[a]	V_2O_5 (wt.%)[a]	V_2O_5 (wt.%)[b]	Catalyst weight (g)
M11V/MgO	5	0.6	20	1
M16V/MgO	6.5	1.2	28	1.2
M29V/MgO	5.8	3.2	52	1.3

[a] Referred to the total weight of the membrane.

[b] The catalyst weight ($V_2O_5 + MgO$), in the catalytic zone of the membrane, assuming that MgO deposits are distributed homogeneously in the membrane pores while V only penetrates the inner half of the membrane thickness.

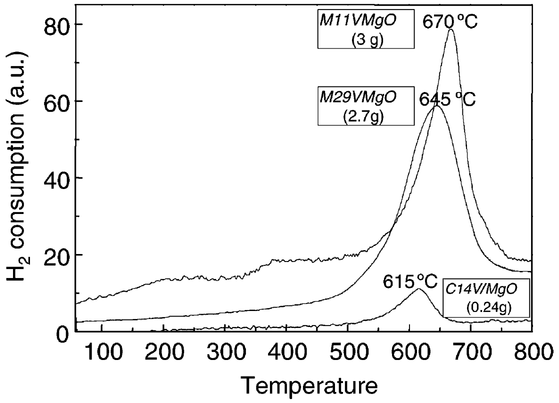

Fig. 3. TPR patterns of a conventional V/MgO catalyst (C14V/MgO) and of powder obtained by grinding some catalytic membranes used in this work.

There are several works with CMRs in which the inert gas was distributed at either side or at both sides of the membrane [15,25,30]. The optimal distribution is not obvious and probably depends on the specific reaction system investigated. In this work, a series of experiments was run by varying the amount of inert gas (He) fed at each side of the membrane, while keeping constant the total amount of He introduced. In this way, the reactor configuration varies from the configuration 2 (all the inert gas fed to the external side) to configuration 3 (all the inert gas fed to the internal side). The total pressure was approximately 1 atm in the inner side, and was varied in the outer side to obtain the desired permeation flux. The results are shown in Table 3, where the $F_{He,in}$ and $F_{He,out}$ values are the flow rates of He supplied to the internal (active layer) and external (inert layer) sides of the membrane, respectively. As more He is

Table 3
Results obtained by varying the inert gas distribution from configuration 2 ($F_{He,in} = 0$) to configuration 3 ($F_{He,out} = 0$)[a]

$F_{He,out}$ (ml/min)[b]	$F_{He,in}$ (ml/min)[b]	ΔP (bar)	$X_{C_4H_8}$	X_{O_2}	S_{C_4}	$S_{butadiene}$	$S_{butenes}$	Yield C_4
168	0	0.21	24.5	79	54.3	29.2	25.1	13.3
152	16	0.12	23.6	77.9	54.4	28.4	26	12.8
144	24	0.11	23.6	77.5	54.3	28.8	25.6	12.8
128	40	0.1	23.3	76.5	53.8	28.1	25.7	12.5
96	72	0.09	22.5	76.3	51.8	26.4	25.4	11.6
80	88	0.08	22.7	76.7	50.8	25.2	25.7	11.5
48	120	0.06	21.9	76.6	48.5	23	25.6	10.6
0	168	0.03	21.7	78.8	46.2	21	25.2	10
Co-feed (configuration 1)			22	77.2	50	23.1	27	11

[a] Membrane M29V/MgO; $T = 550$ °C; butane flowrate 16 cm^3 (STP)/min; oxygen flowrate 16 cm^3 (STP)/min.

[b] $F_{He,in}$ and $F_{He,out}$ are the flow rates of He fed to the inner (active) and outer (inert) sides of the membrane, respectively.

shifted to the inner membrane side (i.e. as we change from configuration 2 to 3), a decrease in yield to olefins is observed. While the selectivity to butenes remains almost unchanged, the selectivity to butadiene is nearly 50% higher with configuration 2 compared to configuration 3. Also, the butane conversion is slightly higher (24.5 versus 21.7), while there is little change in the oxygen conversion. The higher butane conversion can be explained by taking into account the higher average butane concentration in the inner side (i.e. in contact with the active zone), as well as the increase in residence time that takes place as more He is supplied at the outer side. As for the higher selectivity, there are at least two contributing factors. On the one hand, the oxygen feed becomes more diluted as more He is fed to the outer side, which means that the oxygen partial pressure at the inert/active layer interface decreases. On the other, as may be expected, as $F_{\mathrm{He,out}}$ increases (and therefore, the total permeation flux across the membrane increases) the pressure drop through the membrane (ΔP) becomes larger. A higher pressure gradient across the membrane reduces the back permeation of butane to the external side, and thus, the amount of butane in the zones with high oxygen concentrations also decreases, with the corresponding increase in selectivity.

From these results it can be concluded that for the system investigated the best feed arrangement consists in supplying the inert gas together with oxygen at the outer membrane side (configuration 2). This was the configuration used for the remaining experiments.

The data in Table 3 also show that the yield obtained with configuration 2 is generally higher than with configuration 1 (premixed feed). The only exceptions are the last two cases of the segregated feed arrangement, where little or no diluent is fed to the outer side, and a highly concentrated oxygen stream reaches the active zone of the membrane. The comparison between the results obtained with segregated and premixed feeds has been carried out on a wider range of operating conditions. Fig. 4 shows, as a selectivity-conversion plot, the results obtained with configurations 1 and 2, for different temperatures and total feed flow rates. It may be seen that the segregated feed (configuration 2) provided the highest selectivity throughout the experimental range investigated, except at the lowest conversion levels (which were obtained with low temperature and a high feed flow rate). Under these conditions a large amount of oxygen permeates unreacted through the catalytic zone, and the beneficial effect of the oxygen distribution is lost. At a higher temperature (580 °C) little or no oxygen escapes unreacted from the catalytic zone, and the selectivity obtained with configuration 2 is higher at any of the flowrates investigated.

However, with the second membrane used (M16V/MgO), the results were considerably different: the selectivity-conversion behaviour with the segregated feed was at best comparable, and often inferior to that observed in the premixed feed mode (Fig. 5). This cannot be explained by the different V loading on both membranes, which should have a similar effect on both feed modes. Instead, the explanation is related to the different permeation patterns of both membranes, as will be discussed next. The permeation flux of a single gas through a membrane can be represented by the following equation [33]:

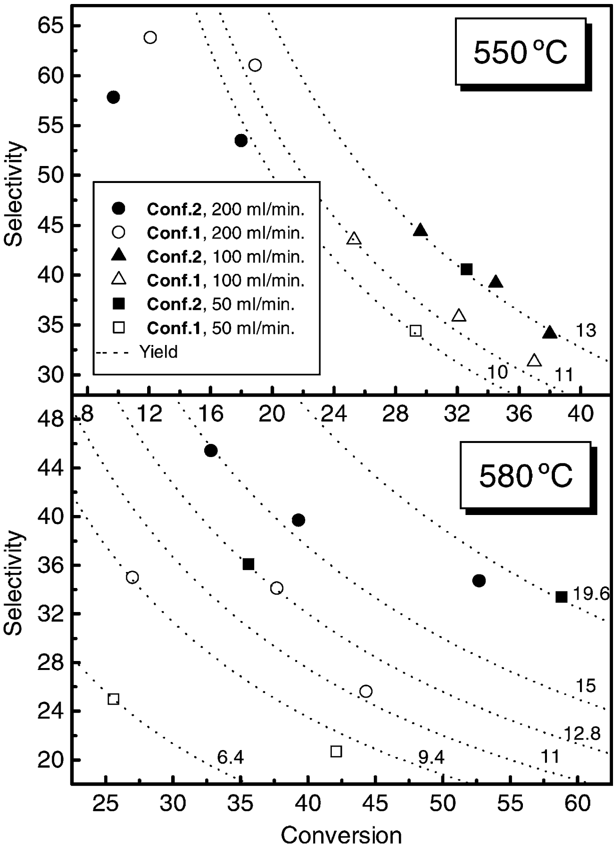

Fig. 4. Selectivity to olefins as a function of butane conversion for two different membrane configurations and temperatures. Membrane: M11V/MgO; different gas flow rates and butane/oxygen ratios.

$$F\,(\mathrm{ml/min\,bar\,cm^2}) = A + BP_{\mathrm{m}}$$

where P_{m} is the mean pressure in the membrane (the arithmetic mean of the pressure at both sides), and A and B correspond to the Knudsen and viscous contributions to the gas flow in the pores. The values of A and B for the membranes employed in this work are given in Table 4. Under a pure Knudsen permeation regime, back permeation would be unavoidable, since molecule–wall collisions prevail, rather than molecule–molecule impacts. On the other hand, as the viscous contribution increases, molecule–molecule collisions

Table 4
Permeation characteristics of the membranes used in this work[a]

Membrane	$F = A + BP_{\mathrm{m}}$ (cm^3/min cm^2 bar)	B/A
M11V/MgO	$5.4 + 2P_{\mathrm{m}}$	0.37
M16V/MgO	$3.2 + 0.6P_{\mathrm{m}}$	0.18
M29V/MgO	$5.8 + 3.6P_{\mathrm{m}}$	0.60

[a] Permeation was measured with nitrogen at ambient temperature.

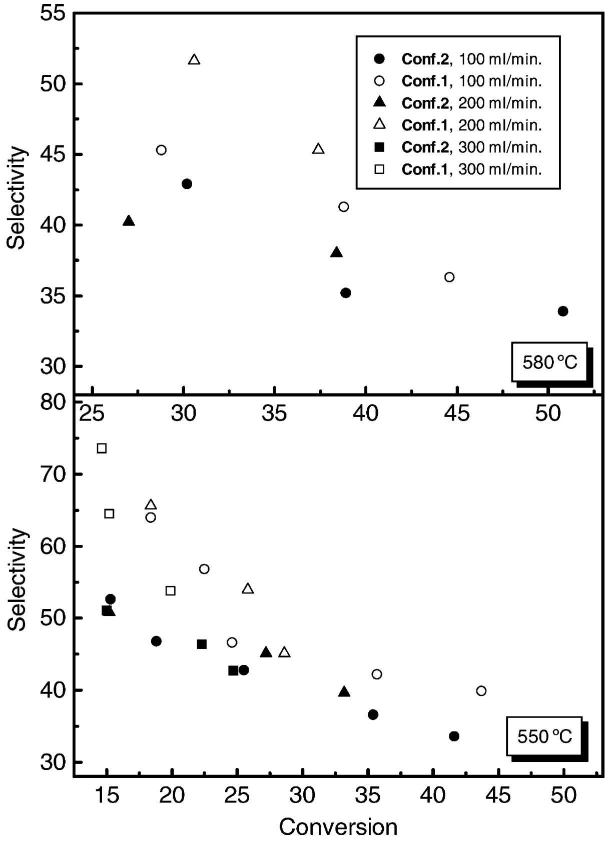

Fig. 5. Selectivity to olefins as a function of butane conversion for two different membrane configurations and temperatures. Membrane: M16V/MgO; different gas flow rates and butane/oxygen ratios.

become more important, and the convective flux from the outer side becomes effective in preventing back permeation of inner-side species.

It can be seen that the permeation in membrane M16V/MgO takes place mainly in the Knudsen regime (low value of *B*), while in membranes M11V/MgO and M29V/MgO a much larger viscous contribution exists. Therefore, the back permeation of butane in membrane M16V/MgO will not be influenced by the permeation of oxygen and He in the opposite direction. Thus, in the presence of a significant partial pressure gradient for butane (which is close to 1 bar at the reactor entrance for configuration 2) a considerable back permeation of butane (and of reaction products) towards the oxygen-rich zone can be expected, leading to a lower selectivity. Conversely, with membrane M11V/MgO, which has an important laminar contribution to the permeation flow, the back permeation of butane was strongly reduced and a higher selectivity could be obtained.

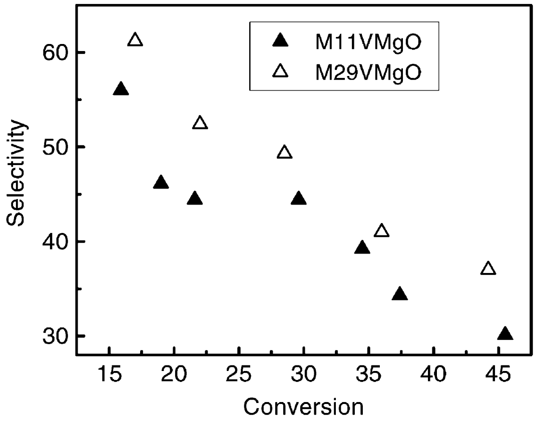

Fig. 6. Comparison of the results obtained with membranes M11V/MgO and M29V/MgO. Total feed flow rate 100 ml/min, variable butane/oxygen ratio.

Membrane M29V/MgO has the largest viscous component in the permeation flow, as shown in Table 4. This means that the back permeation of butane and hydrocarbon products is further reduced, and as a consequence this membrane should provide an even better selectivity-conversion behaviour than membrane M11V/MgO. This was the case, as shown in Fig. 6. The importance of reducing the back permeation of hydrocarbons to oxygen-rich areas in CMRs was already stressed in a recent work [30]. Several possible ways of achieving this objective were proposed: increasing the convective flow towards the product side, using a higher diffusion resistance in the support layer and increasing the catalytic activity of the active layer. Regarding the last point, the higher V content of membrane M29V/MgO also contributes to reducing the back permeation of reactants.

Finally, although the above results show that a segregated feed is more efficient than a premixed feed in a CMR, it is also useful to compare the results of the CMR with those of a conventional FBR. In order to make a direct comparison (i.e. using the same catalytic material) between the two modes of contact (CMR and FBR), the membrane M11V/MgO was ground, and the resulting powder was packed a fixed bed of catalyst inside a quartz tube. The results are shown in Fig. 7 as a selectivity-conversion plot, for two different temperatures. It can be seen that at any given conversion, the CMR

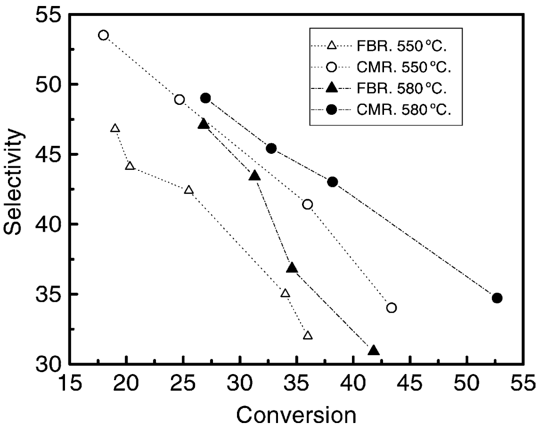

Fig. 7. Selectivity to olefins as a function of butane conversion for a CMR (M11V/MgO) and for a fixed bed reactor (FBR) packed with ground M11V/MgO membrane powder. The $\tau = 5{\cdot}10^{-3}\,\mathrm{g\,ml^{-1}\,min}$.

operating under feed configuration 2 provided a higher selectivity than the conventional FBR.

4. Conclusions

The selectivity to olefins in the oxidative dehydrogenation of butane can be increased by using a CMR, in which the catalyst is concentrated in one side of the membrane, and the feeds of hydrocarbon and oxygen are segregated. The best feed configuration for this system supplies oxygen, along with the inert diluent, to the outer (inactive) layer of the membrane, and butane to the inner (catalytically active) side. The permeation characteristics of the membrane are also important: the existence of an inert layer between the oxygen feed and the catalytic zone is necessary, and the permeation pattern should have a significant viscous contribution to be effective in preventing back permeation of reactants and products.

It is also necessary to have enough catalyst activity (and/or catalyst load) in the active layer of the membrane in order to achieve high oxygen and butane conversions, avoiding the passage of unconverted reactants to the opposite sides. This need for a sufficient catalytic activity may turn out to be in contradiction with the use of very thin catalytic layers coupled to diffusion layers of adequate resistance, suggested as a desirable option in earlier studies [26,30,32]. From the application point of view, it is also clear that a sufficient thickness of the active layer is needed to have an acceptable value of productivity per unit of reactor volume. Therefore, some compromise is necessary in order to obtain an optimum yield to olefins and a reasonable reactor design.

The membranes presented in this work have provided the highest yield to olefins reported to date with catalytic membranes in the oxidative dehydrogenation of alkanes. Further improvements are of course possible if new developments in catalytic membrane preparation methods give rise to catalytic layers with the same properties as catalysts prepared by conventional, well optimised, methods. However, with any given catalyst, a suitable reactor configuration such as that provided by the CMR, should be apt to increase the yield achievable in conventional reactors.

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