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Membrane reactor for selective oxidation of butane to maleic anhydride

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Abstract

A simulation of a packed-bed membrane reactor acting as an oxygen distributor for the selective oxidation of *n*-butane to maleic anhydride (MA) has been performed by recreating specific reactive atmospheres in a microreactor. In the membrane reactor, the oxidation state of the catalyst depends on its position in the bed, leading to an important change in the MA yield. However, this heterogeneity can be turned to an advantage using a reverse of *n*-butane flow. Co-promoted catalysts have also been developed to enhance the global performance of the membrane reactor. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Maleic anhydride; Doped catalyst; Membrane reactors

1. Introduction

For 20 years, membrane catalysis has been receiving an increasing interest. The number and variety of applications continuously grew and different classifications have been tentatively proposed. Most of them describe how catalyst and membrane are combined [1]. However, as suggested in [2,3], it is also possible to base the classification on the role of the membrane in the reactor. These two modes of classification are quite complementary and, in the following, specific names are proposed for the different types of membrane reactors.

In most cases, at least those studied at the beginning of membrane catalysis, the function of the membrane was principally to selectively remove, from the reactor, a product of an equilibrium-restricted reaction, in order to gain yield on conventional reactors. It is proposed to name this type of membrane reactor an extractor.

In other applications, the role of the membrane is to dose a reactant that may originate successive reactions. As the targeted product is often a product of primary addition, the regulation of this reactant concentration by permeation through the membrane may improve the selectivity. When compared to a conventional reactor, the same amounts of reactants can be introduced but here, one of them is distributed by the membrane along the catalyst bed. It is therefore proposed to call this type of membrane reactor a distributor.

The third type of membrane reactor takes advantage of the unique geometry of a membrane, i.e. a permeable wall separating two media. If the membrane is also a support for a catalyst, it is therefore possible to feed it from both sides with reactants (for instance gas from one side, liquid from the other) or to force a reactive mixture through the active wall. In the first case, it is possible to favour the contact between the catalyst and the reactant that is limiting the performance in conventional reactors (e.g. gas in gas–liquid–solid processes, hydrophobic reactant with

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hydrophilic catalyst, etc.). In the second case, the residence time in the active pore of reactants and products is controlled by operating parameters (pressure drop across the membrane) and not by diffusion. This may lead to a better control of activity or selectivity. In the two cases the role of the membrane is to favour contact between reactants and catalyst. It is therefore proposed to call this type of membrane reactor a contactor. The first mode being named an interfacial contactor, the second a flow-through contactor.

In this paper, we report on some aspects of membrane reactors of the distributor type, using the selective oxidation of *n*-butane to maleic anhydride (MA) as an example. This reaction is until now the only selective oxidation of light alkanes performed at an industrial scale. Most of the plants use conventional fixed-bed reactors [4] in which the flammability of the O_2/C_4 mixtures leads to a very low productivity, owing to the limited concentration of butane in the reactants (1.5%). The resulting low concentration of MA at the outlet of the reactor also leads to problems during the subsequent separation step. To limit the problems due to the exothermicity of the reaction, fluidized bed and circulating fluidized bed [5] reactors have been developed but catalysts had to be adapted due to attrition problems [6]. In all cases, the MA yield is limited to ca. 60%, the selectivity decreasing rapidly at high conversion.

Several studies have proposed the use of membrane reactors of distributor type to enhance selectivity towards primary products in catalytic selective oxidations [7–9]. In the present reaction, another advantage could be expected from the feeding separation of the two reactants by the membrane, which limits the flammability problems. This allows the use of butane-rich feed, leading to higher MA productions [10].

In the present study, special attention has been given to the effects of the oxygen distribution on the catalyst characteristics. These characteristics will indeed directly affect the membrane reactor performance.

The membrane reactor combines a tubular porous ceramic membrane and a fixed bed catalyst placed in the core volume of the ceramic tube. According to the classification proposed by Tsotsis et al. [1], it is a packed bed membrane reactor (PBMR). Combination of the two names, i.e. PBMR-distributor, gives a complete description of the reactor and its function.

2. Experimental

2.1. Catalyst

Two catalysts were used, both based on Vanadium Phosphorous mixed oxides. The common precursor of the active solids was $VOPO_4{\cdot}2H_2O$, as obtained by reacting V_2O_5 and H_3PO_4 [11]. Standard solids were obtained by direct reduction of $VOPO_4{\cdot}2H_2O$ by isobutanol leading to the vanadyl phosphohemihydrate, $VOHPO_4{\cdot}(1/2)H_2O$. For cobalt-promoted solids, reduction was performed in presence of $Co(C_5H_7O_2)$, previously dissolved in isobutanol. For experiments in the membrane reactor, in order to avoid too large a pressure drop in the catalyst bed, powders were transformed into pellets of ca. 2 mm size, using a lab extrusion machine. Activation of the samples was made under flowing reactants ($O_2/C_4 = 12$) at 670 K for 15 h.

2.2. Membrane

The MFI membrane was obtained by synthesis of zeolite crystals inside the pores of a macroporous host material (pore-plugging method) [10]. The composite membrane obtained presented several advantages when compared to conventional supported zeolite films (less long-range stresses during thermal cycling, maximum defect not larger than the pore size of the host). The chosen support was a commercial SCT-USFilter T1-70 tube, made of 3 layers of macroporous α-alumina (from outer to inner side, respective thickness: 1500, 40 and 20 μm and pore size: 10, 0.9 and 0.2 μm). The precursor solution of the MFI zeolite was obtained by mixing silica (Aerosil 380) and a template (tetrapropylammonium hydroxide, TPAOH). After a 3-day ageing period, that solution was poured in a Teflon-lined autoclave containing the SCT porous ceramic tube. Hydrothermal synthesis was then performed at 443 K for 3 days, and the membrane was calcined at 773 K under a flow of 5% O_2 diluted in N_2. Characterisation of the membrane showed it could be considered defect-free (i.e. the transport through the membrane is controlled by the micropores of the MFI structure) and that the separative layer was a composite MFI-alumina material [12]. The permeance of the membrane for oxygen was ca. $3 \times 10^{-7}\ \mathrm{mol\,Pa^{-1}\,s^{-1}\,m^{-2}}$ at 670 K

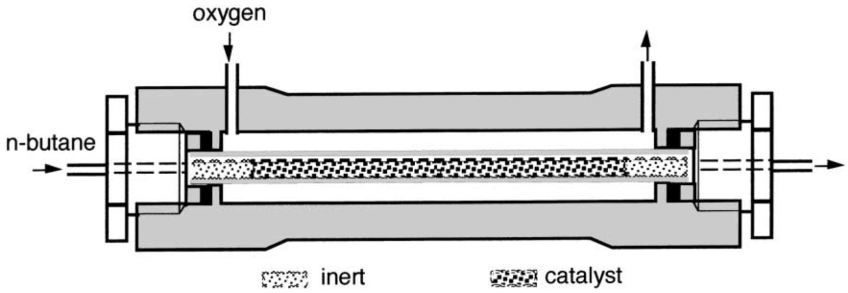

Fig. 1. Schematic of the membrane reactor (segregated feed).

(temperature of membrane reactor catalytic experiments). Other transport properties of the zeolite membrane can be found in [12].

2.3. Catalytic testings

They were performed in both the membrane reactor and the conventional microreactor at 670 K, GHSV 3000 h^{-1}.

The membrane reactor module was made of a stainless steel shell containing the composite membrane tube, which was packed with the catalyst (Fig. 1). The endings of the membrane tube were enamelled and equipped with compression fittings of graphite seals (Fargraf Cefilac), in order to ensure tightness between the inner (retentate or tube side) and the outer (permeate or shell side) compartments. The reactor temperature was measured by a thermocouple moving in a stainless steel tube (1/16 in.) installed in the central axis of the inner compartment. An electric tape wound around the stainless tube heated the membrane module. The density of whorls was adjusted along the reactor length, in order to obtain a temperature profile within ±5 K. The reactor could be fed with *n*-butane, oxygen and helium (used as dilutent) with different ratios, from both retentate and permeate inlets. All streams were mass flow (Brooks 5850E) controlled. ΔP, the pressure difference across the membrane was regulated by an automatic valve (Kämmer 800377) connected to a differential manometer (Keller DP232), whereas the pressure at the retentate outlet is measured by a manometer (Keller PAA23). Permeate and retentate outlet flow rates were measured with film flowmeters. Reaction products were analyzed on-line using a gas chromatograph (HP 5890A, Intersmat IGC) equipped with FID and TCD detectors.

Different feed configurations were compared. Butane was always introduced in the tube side, oxygen was either co-fed with butane (as in conventional reactors) or distributed through the membrane (Fig. 1). Mixed configurations (some of the oxygen reactant is co-fed with butane) were also used. The transmembrane differential pressure was fixed in order to avoid back-permeation of butane to the shell side and to control the amount of oxygen fed through the membrane.

Microreactor experiments were performed in order to simulate the local situation of the catalyst along the fixed-bed. As a matter of fact, the present membrane reactor configuration, as shown in Fig. 1, implies that the O_2/C_4H_{10} ratio continuously decreases along the catalyst bed. Butane, introduced at the inlet of the catalyst bed, was progressively consumed, when oxygen was evenly distributed along the bed (the pressure drop due to the catalyst bed being neglected). In order to characterize the catalyst under fuel rich conditions, typical of the situation at the membrane reactor inlet, some tests have been performed in a conventional (non-membrane) microreactor with $O_2/C_4 = 0.6$. This value has been calculated from oxygen permeation measurements with the MFI membrane, the ratio of the total amounts of O_2 (distributed) and C_4 introduced in the membrane reactor being 12, close to the value of conventional fixed-bed industrial processes (oxygen-rich mixture). For comparison, other experiments were carried out using the microreactor under $O_2/C_4 = 12$ (standard ratio) and 20 (simulation of the membrane reactor outlet). Results were quite similar for these two fuel lean conditions. Catalysts were characterized before and after testing.

3. Results

3.1. Catalyst

Characterizations of the solids before and after testing in the microreactor (20 h on stream) have been performed using different techniques [13]. After activation (fresh catalyst), the solids showed a specific area close to 20 $m^2 g^{-1}$ and XRD analysis disclosed in all cases the presence of vanadyl pyrophosphate $(VO)_2P_2O_7$. Fig. 2 shows the ^{31}P (SEM) NMR spectra of the standard and Co-modified catalysts before and after testing in the microreactor under fuel rich conditions (simulation of the inlet of the membrane reactor).

3.2. Catalytic measurements

3.2.1. Conventional microreactor

Fig. 3 compares the performance (MA yield) of the standard catalyst under conventional ($O_2/C_4 = 12$) and fuel rich ($O_2/C_4 = 0.6$) conditions. In the last case, a rapid deactivation occurred, and only butenes, via oxidative dehydrogenation of butane, were formed. Fig. 4 illustrates the reversibility of the catalyst

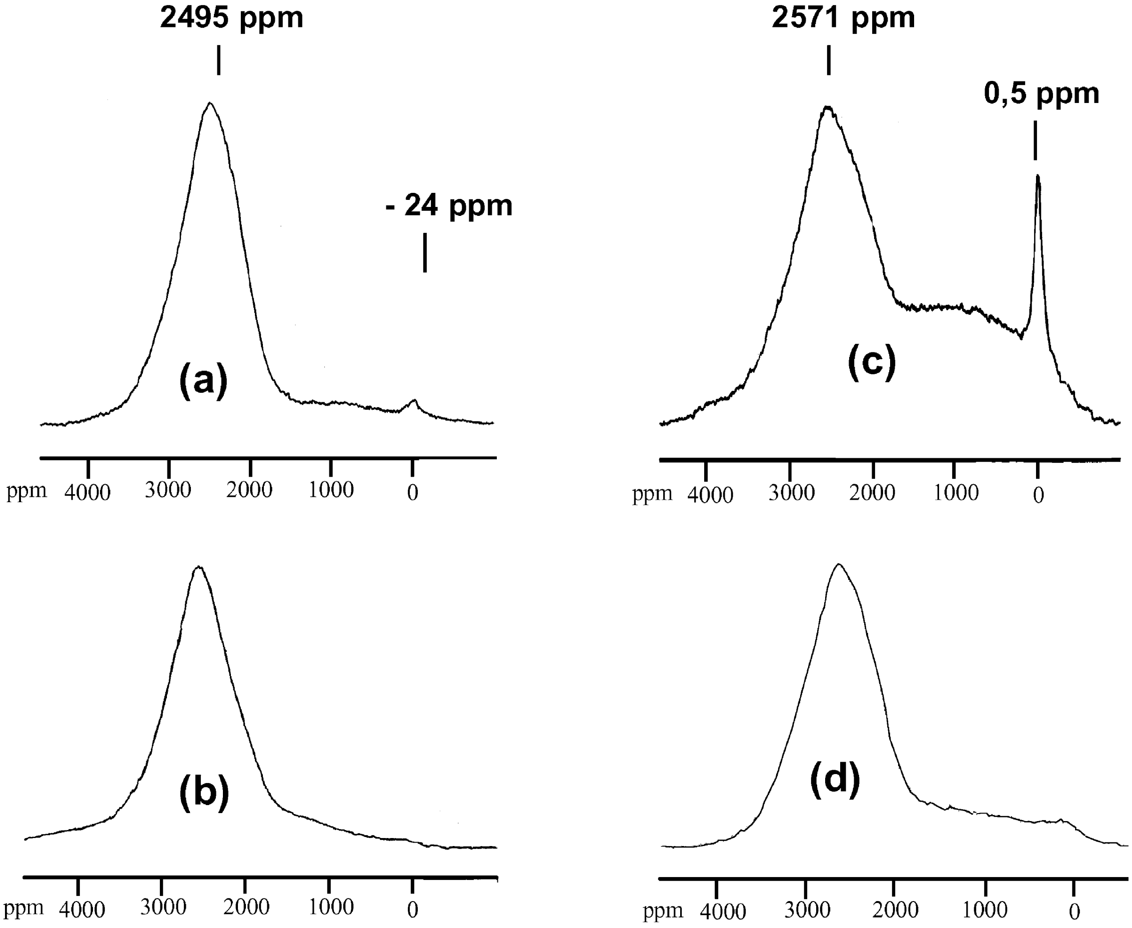

Fig. 2. ^{31}P (SEM) NMR spectra of the catalysts: (a) fresh standard catalyst; (b) standard catalyst after testing in the microreactor under fuel rich conditions; (c) fresh Co-promoted catalyst; (d) Co-promoted catalyst after testing in the microreactor under fuel rich conditions.

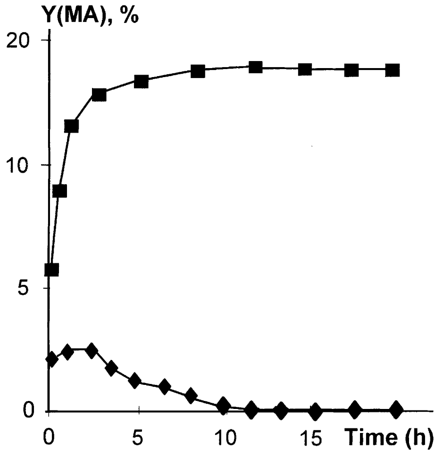

Fig. 3. Performance (MA yield) of the standard catalyst in the microreactor, $T = 670\,\mathrm{K}$, GHSV $= 3000\,\mathrm{h}^{-1}$: (■) $O_2/C_4 = 12$, conventional fuel lean conditions; (◆) $O_2/C_4 = 0.6$, fuel rich conditions.

properties when cycling the operating conditions from fuel lean to fuel rich atmospheres. Fig. 5 shows the respective behaviors of the standard and modified catalysts under fuel rich conditions. Even though the standard solid rapidly deactivated, the Co-promoted catalyst was stable.

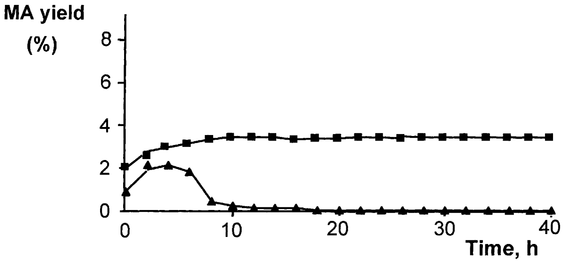

Fig. 5. Comparison of the standard (▲) and Co-promoted (■) catalysts under fuel rich conditions ($T = 670\,\mathrm{K}$, GHSV $= 3000\,\mathrm{h}^{-1}$).

3.2.2. Membrane reactor

Note that all the membrane experiments presented here have been performed with the standard catalyst. Fig. 6 represents schematics of the different feeding modes of the membrane reactor. The corresponding catalytic performances are given in Table 1. All experiments were performed with a O_2/C_4 ratio (introduced in the catalyst bed) between 8 and 9, close to the conventional fuel lean ratio. These different modes are:

1. Co-feed: oxygen and *n*-butane are mixed and fed the tube side. Permeate inlet and outlet are closed (this mimics the conventional reactor).
2. Totally segregated feed (*n*-butane to the tube side, oxygen through the membrane).
3. Mixed feed (ca. 20% of total oxygen entering the catalyst bed is co-fed with *n*-butane).
4. Similar to configuration 3, but with reversing of the feed containing *n*-butane. The performance measured 15 min after the reversal is clearly above that obtained before 30 min after reversal, the MA yield is back at steady state (Table 1).

4. Discussion

4.1. Microreactor experiments

If the standard catalyst performance was stable when operated under conventional fuel lean conditions

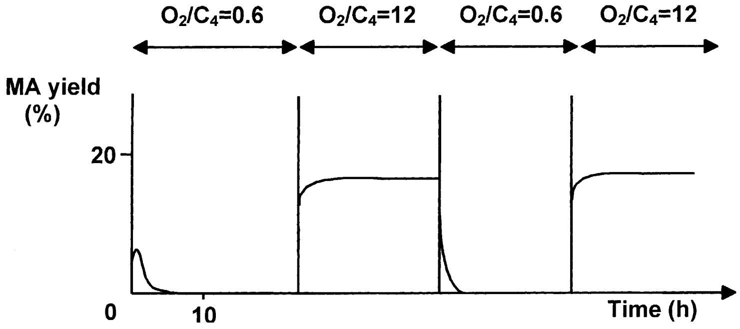

Fig. 4. Reversibility of the performance of the standard catalyst in the microreactor.

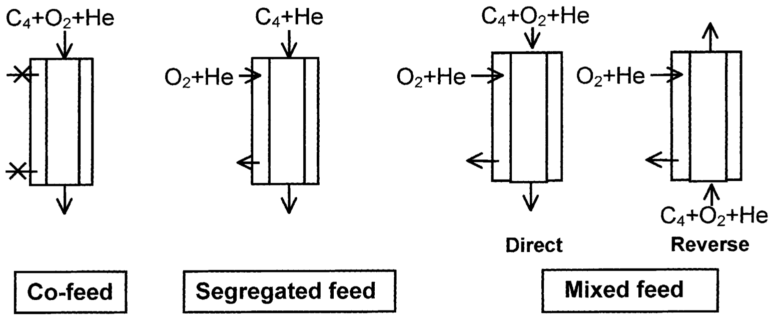

Fig. 6. Schematics of the different feed configurations of the membrane reactor.

($O_2/C_4 = 12$), the MA yield rapidly drooped to zero when placed under fuel rich atmosphere (Fig. 3). At this state, only butanes were formed via C_4H_{10} ODH.

The ^{31}P (SEM) NMR spectrum of the standard catalyst before testing shows (Fig. 2) that the fresh catalyst contained both V^{4+} (near 2500 ppm) and V^{5+} species (near 0 ppm). The very same NMR spectrum (not shown here) was observed after testing under a O_2/C_4 ratio of 12, in good keeping with the stability of the catalytic performance. This was no more the case after catalytic testing under fuel rich conditions ($O_2/C_4 = 0.6$), as only V^{4+} were then visible (Fig. 2). On the basis of similar experiments, it has been proposed that the active site for selective oxidation involves both V^{4+} and V^{5+} species [13]. In the presence of mainly V^{4+} species, only ODH takes place. When there is a large excess of V^{5+}, total oxidation may preferentially occur.

The surface state was quite reversible however, since activity rapidly changed and recovered previous values (Fig. 4).

Table 1
Catalytic results of the membrane reactor as a function of the feed conditions[a]

Feed	O_2/C_4	X_{C_4}	S_{MA}	Y_{MA}
Co-feed	8	24	67	16
Segregated feed	8	19	68	13
Mixed feed (steady state)	9	21	80	17
Mixed feed reversal + 15 min	9	24	82	20
Mixed feed reversal + 30 min	9	21	80	17

[a] O_2/C_4 is the ratio of reactants entering the catalyst bed. X_{C_4} is the butane conversion (%), S_{MA} and Y_{MA} the maleic anhydride selectivity and yield expressed in %.

After modification by cobalt addition, the performance under fuel rich conditions ($O_2/C_4 = 0.6$) was much better than that of the non-promoted system (Fig. 5). Even if the performance was lower than that obtained under fuel lean atmosphere, some MA was produced at steady state. The NMR spectrum after testing (Fig. 2) showed the presence of a small peak close to 0 ppm, indicating that, even under reducing (fuel-rich) conditions, V^{5+} species were still present in the Co-modified solid, at least enough to lead to selective oxidation. Note also that this peak was much larger in the fresh promoted catalyst than in the fresh standard one. This also suggests that cobalt favors the presence of V^{5+} species. It has also been suggested that Co is involved in the V^{4+}/V^{5+} redox equilibrium existing during selective oxidation of butane to MA [14].

XPS analyses also supported those V^{4+}/V^{5+} evolutions under fuel rich conditions for both solids [13,14].

4.2. Membrane reactor experiments

Let us first consider the reactor with co-fed reactants (Fig. 6). The performance (Table 1) was close to that observed with the microreactor (Fig. 3, $O_2/C_4 = 12$, close values of W/F). This suggests that the pellets packed in the membrane tube work similarly to the powder in the microreactor. The co-feed membrane reactor can therefore be considered as representative of the conventional fixed bed one.

For totally segregated feeds, the MA yield was about 25% lower than in the previous case. This is not surprising, as the first part of the catalyst bed was probably deactivated, due to the reductive atmosphere prevailing in this zone. Such a deactivation was also observed in the microreactor under similar fuel rich conditions.

This led us to introduce some oxygen diluted in the butane feed, as was proposed by Mallada et al. [10]. In the case of such a mixed feed, the performance of the membrane reactor was similar to that of the conventional one. A simple calculation of the O_2/C_4 ratio in the first part of the reactor (1/10th of the total length of the packed bed) gives a value in the range 2–3, which should be too low to ensure a high activity towards MA. Considering however that a significant part of the packed bed was placed in this inadequate reactive atmosphere, the global performance was still high, and there is certainly room for an optimization of the feed conditions.

Even if the performance of the mixed fed reactor was better than that of the totally segregated configuration, the oxidation state of the catalyst bed was certainly heterogeneous, the first part being too reduced, when the end of the bed was probably overoxidized. This heterogeneity can however be turned to an advantage by reversing the flow in the inner volume, leading to a transient MA yield clearly higher than that of the conventional reactor (Table 1). This is due to the fact that, just after reversal, butane first flows through the previously overoxidized catalyst, leading in this zone to a high MA yield. This however is only a transient phenomenon, as this catalyst zone was progressively reduced by butane, driving back the situation to the previous one. However, during this interval, the end of the bed was oxidized by the high O_2/C_4 ratio prevailing then in this zone. It is therefore possible, using a new reversal of the C_4 flow, to observe a new exaltation of the MA yield. This catalyst flexibility is also illustrated in Fig. 4, when cycling the microreactor between fuel rich and lean conditions.

To schematise, the catalyst bed of the reversible membrane reactor can be divided into two zones, the first being reduced by butane (MA production), while the second is reoxidized. In this way this membrane reactor looks like the CFB reactor developed by DuPont [3]. In both cases, reduction and reoxidation of the catalyst are separated, but they occur here without moving the bed.

Let us underline that these are preliminary observations, but this type of reactor, combining a membrane distributing oxygen in a continuous way to the catalyst bed and a reversal of the C_4 flow may be an interesting subject for further investigations. It is clear that the above-mentioned observations deserve more experimental studies, especially about the transient MA production. The data reported here give the situation 15 min after the reversal, and a peak in the MA production must occur during each period, which timing will be a key parameter for an optimization of the process.

Further studies are currently under way to better describe this type of membrane reactor, including possible heat transfer effects. Moreover, cobalt-promoted catalysts will be used to enhance the global performance.

5. Conclusion

The simulation in a microreactor of the catalyst bed of the PBMR-distributor showed an important heterogeneity of the catalyst oxidation state, depending on its axial position in the reactor. The active catalyst requiring an optimal V^{4+}/V^{5+} ratio, the inlet of the bed presented a poor performance, as it was excessively reduced to V^{4+} by the butane flow. This can be partly solved by diluting some of the O_2 reactant in the butane feed. For these conditions, the global performance (MA yield) of the membrane reactor was similar to that obtained using the conventional cofeed configuration. As has been shown in [10], it is then possible to take advantage of the segregated feed, which limits the flammability problems, and operate with higher butane concentrations than those used in conventional processes.

Another issue of the present study is the increase of the MA yield observed when reversing the butane flow in the membrane reactor. During a transient period the performance was higher than that observed using a conventional feed. This was due to the heterogeneity of the packed bed, which, at steady state, presented an increase of oxidation state from inlet to outlet. When reversed, the butane first flew in the oxidized zone leading to the observed increase of the MA yield, while oxygen distributed through the membrane reoxidized the end of the bed. Further studies are currently under way to better describe this type of membrane reactor that couples distribution of one reactant and sequential reverse flow of the other. It may combine two of the main interests of reverse flow operation, i.e. better heat management and exploitation of the catalyst dynamic properties [15].

As was introduced in [2], besides a proper membrane, membrane reactors may require the design of a proper catalyst, owing to the specific reactive atmosphere they create. In this study, a cobalt-promoted solid adapted to reducing atmospheres has been developed for the membrane reactor.

Acknowledgements

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