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Selective oxidation of butane to maleic anhydride in a catalytic membrane reactor adapted to rich butane feed

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Abstract

The *n*-butane selective oxidation has been studied in a membrane reactor, using high butane concentrations. Thanks to the oxygen distribution by the membrane, it is possible to keep the local composition outside the flammability zone. A MFI ceramic membrane was used to distribute oxygen (or part of it) in the catalyst bed, made of a VPO mixed oxide, either conventional or Co-doped. In a first step, the effect of the oxygen distribution has been studied, showing that, under standard reactant mixtures (O_2/butane = 12, low butane concentration), the membrane reactor performed very close to the conventional one. Under high butane concentrations, the VPO system suffered from a drastic decrease of the selectivity towards maleic anhydride (MA). The addition of cobalt to the VPO catalyst allowed keeping the MA selectivity at a high level (75%). The combination of the CoVPO catalyst and the MFI membrane was used to explore the membrane reactor performance with high butane concentrations in the feed, corresponding to the flammability zone in a conventional reactor. For these conditions, the MA productivity was three times higher than that observed with the conventional reactor.

Keywords: Butane selective oxidation; Catalytic membrane reactor; Distributor; Maleic anhydride productivity

1. Introduction

For several decades, maleic anhydride (MA) has been produced by partial oxidation of benzene over V_2O_3–MoO_3 catalysts. The conversion of such a system was 95%, and the selectivity towards MA over 75%. The main by-products are carbon dioxide and monoxide. However, from 1970s butane oxidation processes replaced the previous one, as a consequence of the lowest cost, larger availability, and safer operation of butane. Moreover, this allowed reducing harmful emission of benzene in the atmosphere. Nowadays, in industrial processes, the best yields obtained are close to 60%, corresponding to 75% butane conversion and 80% MA selectivity.

However, the flammability of butane in air makes difficult running this kind of reactors at a butane concentration over 2 vol.%. This leads to downstream MA concentrations lower than 1%. Consequently, the costs of separation and collection of the product are quite important.

At the industrial level, different types of reactors are used for MA synthesis [1,2]. They all use VPO-based catalysts which have been intensively studied in the past [3,4]. They present conversions similar to those previously mentioned, but unfortunately, each technology presents some disadvantage: the fixed bed reactor is limited to low butane concentrations (lower than 2%), besides possible hot spot and exothermic conditions. The fluidized bed reactor and the re-circulating bed reactor allow higher butane concentration operation because the fluidized bed inhibits the flame propagation, whereas in the re-circulating reactor the butane and the oxygen do not enter directly in contact with each other. Using the latter system, the catalyst can be regenerated, leading to selectivity improvements. However, with both above-mentioned technologies the catalyst attrition can be a major drawback.

All this justifies permanent efforts in the research of better selective oxidation processes. In this perspective,

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catalytic membrane reactors (CMRs) represent a very interesting option.

CMRs have been classified in previous publications from our team, into three groups, depending on the function of the membrane: extractor, distributor or contactor [5,6]. The *extractor* CMR configuration favours the yield by selectively removing from the reactor a product in equilibrium restricted reactions or consecutive reaction. For example, dehydrogenation reactions have been widely studied in such a reactor [7–11].

Contactor CMRs have been used to optimize the contact of the reactants with the catalyst. Gas–liquid applications are one of the most studied examples [12–14].

In the present case, the *distributor* CMR configuration is used to control the feed of one of the reactants, i.e., oxygen. This may lead to different advantages. First, the oxygen concentration could be kept at low values all along the catalyst bed, leading to a selectivity increase towards products of first addition. Second, a better heat management is possible due to the homogeneity of the reactant feed and therefore of the reaction exothermic conditions. Third, in the case of flammable mixtures the oxygen distribution through the membrane prevents the local formation of dangerous concentrations. Therefore, global ratios that would be forbidden in conventional reactors are allowed [15]. However, in all studies on that matter the membrane has been combined with conventional vanadium phosphate mixed oxide (VPO) catalysts [5,15–17] and those catalysts have been shown low selectivity towards maleic anhydride in the reducing atmosphere that prevails in such membrane reactors [18].

In the present study we combine a microporous zeolite membrane acting as a distributor and a cobalt-doped VPO catalyst that was previously shown to keep a high selectivity in fuel rich conditions [19].

2. Experimental

2.1. Catalyst preparation

VPO and Co-based VPO catalysts were prepared via the *organic route* [20]. Vanadium pentoxide and 85% phosphoric acid were refluxed under stirring in isobutanol for 16 h. The role of isobutanol, apart from being the solvent, is to reduce vanadium pentoxide into $VO(HPO_4)\cdot(1/2)H_2O$. The resulting precipitate was collected by filtration, washed with isobutanol and then ethanol. The obtained powder was dried in an oven at 100 °C for 24 h. It was then mixed with a small amount of water to obtain a thick paste, and extruded into 1 mm diameter filaments. Once dried, these were broken and sieved into selected particle size of 0.2–0.3 mm. This was done in order to limit mass transfer resistance in the catalyst bed.

For the preparation of cobalt-doped catalyst, cobalt acetyl acetonate was used as a precursor and introduced, with Co/V ratios corresponding to 0.5, 1 and 3 at.%, into the reaction mixture together with vanadium pentoxide and phosphoric acid. Chemical analysis performed on the resulting powders confirmed the incorporation of cobalt according to these Co/V ratios.

The obtained solids were then activated directly under reaction conditions (1.5 vol.% butane in air) at 470 °C for 72 h, before testing.

2.2. Membrane preparation

The MFI/alumina nanocomposite membrane was synthesized in the wall of a porous ceramic tubular support (Pall-Exekia T1-70), consisting of three macroporous α-alumina layers (from outer to inner side, respective average pore sizes: 12, 0.8, 0.1 μm and thicknesses 1500, 40, 20 μm). It had an outer diameter of 10 mm, inner diameter of 7 mm and an effective membrane length of 13 cm. The nanocomposite MFI/alumina membrane (Fig. 1) was obtained by synthesis of zeolite crystals inside the pores of the macroporous tubular support (*pore-plugging* method) [21–23].

The MFI zeolite precursor solution was obtained by mixing silica (Aerosil 380) and a template (tetrapropylammonium hydroxide, TPAOH). After a 3-day ageing period, the solution was poured in a Teflon-lined autoclave containing the porous ceramic tube. Hydrothermal synthesis was then performed at 443 K for 3 days, and the membrane was calcined at 773 K under air flow. Low temperature butane/hydrogen separation through the membrane showed it could be considered close to defect-free (i.e. the transport through the membrane is controlled by the micropores of the MFI structure).

2.3. Material characterizations

Chemical analyses of the catalysts were obtained by Ion Coupled Plasma Emission. The specific surface areas were measured by nitrogen adsorption at 77 K using the multipoint method and homemade equipment. The samples

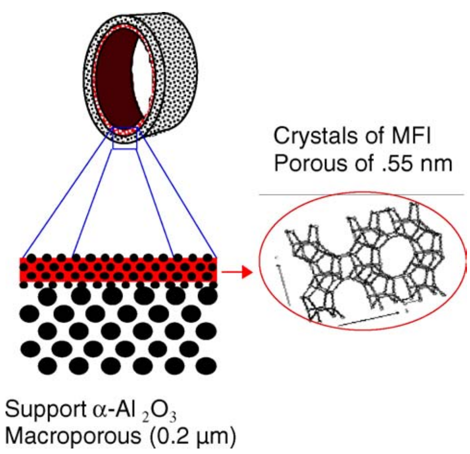

Fig. 1. Structure of the nanocomposite MFI/alumina membrane.

were previously treated at 673 K under vacuum (2.10^{-3} Pa) for 2 h. Precursor and catalyst powder X-ray diffraction patterns were recorded with a Bruker D5005 diffractometer using monochromatic Cu Kα radiation. The patterns were recorded between 3° and 80° (2θ), with a scan rate of 1.2° min^{-1}.

Programmed temperature reduction of catalyst samples were carried out under hydrogen, with a heating rate of 10 °C/min, from room temperature to 1000 °C.

Membranes were characterized by pure gas permeation at reaction temperature for oxygen and butane. However, to take into account the specific conditions of permeability in gas mixtures through zeolite membranes, measurements were also carried out in blank reaction conditions, using nitrogen instead of oxygen. This was completed in order to evaluate the amount of oxygen distributed by the membrane, as a function of differential pressure. Oxygen trans-membrane flux in gas mixture is assumed to be similar to that of nitrogen, as previously checked up in pure gas measurements [16].

2.4. Experimental set-up

The *membrane reactor module* was made of a stainless steel shell containing the composite membrane tube, which was packed with the catalyst (Fig. 2).

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. A cylindrical thermo-regulated oven was used to heat the membrane module. The temperature profile along the module was measured and checked to be homogeneous within more or less 8 °C.

A mass of 2.5 g of catalyst with uniform grain size was added to quartz powder in a 3:1 ratio, and packed in the lumen of the ceramic tube.

The reactor could be fed with the reactants, *n*-butane and oxygen, and helium was used as diluent, 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 was measured by a manometer (Keller PAA23). Permeate and retentate outlet flow rates were measured with film flow meters. Reaction products were analysed on-line using a gas chromatograph (HP 5890A, Intersmat IGC) equipped with FID and TCD detectors (see Fig. 3).

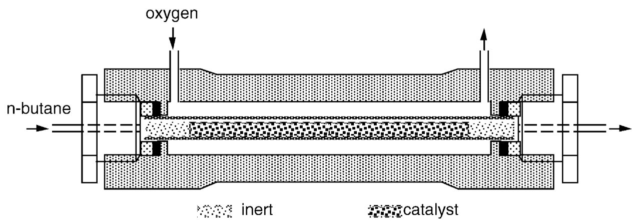

Fig. 2. Scheme of the CMR module (fully segregated feed).

2.5. Experimental reaction conditions

Different feed configurations were compared. Butane was always introduced in the tube side. Oxygen was either co-fed with butane, as in conventional reactors (CR configuration), or distributed through the membrane only (membrane reactor—MR configuration) (Fig. 1). Mixed configurations (MMR), where part of the oxygen reactant is co-fed with butane, were also used.

The trans-membrane differential pressure was fixed in order to limit the butane back-permeation to the shell side and to control the amount of oxygen fed through the membrane. Final CMR experimental conditions, particularly the oxygen feed pressure and flow rates, were settled on the basis of the blank measurement described in Section 2.3. Butane back permeation to the shell side was measured and generally found below 20%.

Feed flow rates were selected in order to avoid full conversion of either reactant.

2.5.1. Standard conditions (low butane pressure)

The standard operating conditions were 400 °C temperature, with a oxygen over butane molar ratio of 12, GHSV = 15 h^{-1} and butane at 12 hPa (partial pressure) diluted in helium with a total GHSV of 1500 h^{-1}. Oxygen over butane ratio was varied between 0.5 and 12.

2.5.2. High butane pressure conditions

In this series of experiments, the butane partial pressure was fixed at 220 hPa and its GHSV covered the range from 15 to 180 h^{-1}.

Owing to the flammability risk inherent to the use of high butane concentration in air, simple calculations were performed in order to evaluate the consequences of a membrane breakdown. The total overpressure of an internal explosion was obtained from adiabatic, i.e. pessimistic conditions. A fast security device was set up in order to (i) stop feeding butane and oxygen to the reactor, (ii) open the exhaust of the reactor to the vent and (iii) protect the pressure sensors.

2.5.3. Performance evaluation

Performances were expressed in terms of butane conversion, maleic anhydride selectivity, yield and volumetric productivity (expressed with respect to the catalyst bed volume). The conversion was calculated considering that half of the back-permeating butane was leaking before being able to react. This represents a rough average situation

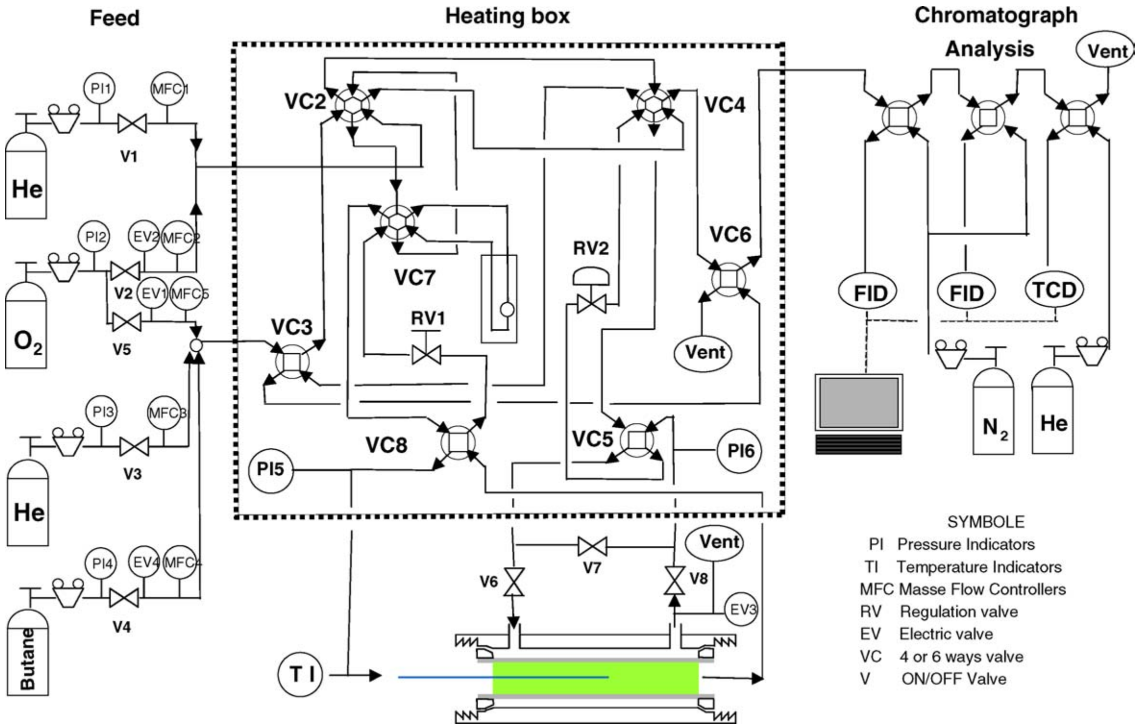

Fig. 3. Experimental set-up for the control and operation of the CMR. PI: pressure indicators, TI: temperature indicator, MFC: masse flow controllers, RV: regulation valve, EV: electric valve, VC: four- or six-way valve, V: ON/OFF valve.

between (i) the whole back-permeating butane never contacted the catalyst (i.e. it permeates at the inlet of the reactor) and (ii) it was in contact with the whole catalyst bed before permeating (i.e. it permeates at the outlet of the reactor).

3. Results

3.1. Catalyst and membrane characterization

XR diffractograms show that all samples exhibit a single $VO(HPO_4)\cdot 0.5H_2O$ phase after synthesis, and a $(VO)_2P_2O_7$ phase at 470 °C (activation temperature of the catalyst).

Table 1 presents the main physico-chemical properties of the catalyst prepared for this work. The specific area decreases with cobalt loading. However, all the systems exhibited values in the range reported in the literature [24].

TPR data show a higher hydrogen consumption in the case of the cobalt-doped samples, suggesting a higher oxygen-donor ability of these catalysts in a reducing environment.

The membrane showed pure gas permeability values for oxygen and butane in the range of 0.14 and 0.03 μmol/m^2/s/Pa, respectively.

Table 1
Characteristics of the catalysts prepared during this work

Catalyst	Co/V atomic ratio	Specific area (m^2 g^{-1})
VPO	–	20
0.5% Co/VPO	0.5	15
1.0% Co/VPO	1.0	13
3.0% Co/VPO	3.0	9

3.2. Effect of oxygen distribution in standard conditions

The goal of the set of experiments was to evaluate the influence of the oxygen distribution through the

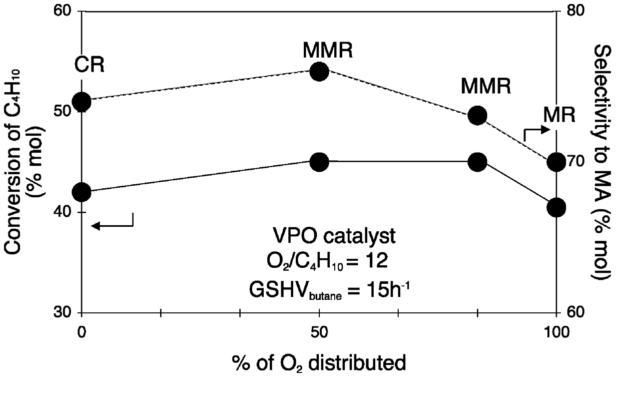

Fig. 4. Butane conversion and maleic anhydride selectivity as a function of the oxygen fraction distributed through the membrane (pure VPO catalyst, oxygen/butane ratio 12, butane GHSV 15 h^{-1}, butane partial pressure 12 hPa). CR: conventional reactor, MR: fully segregated feed membrane reactor, MMR: mixed feed membrane reactor.

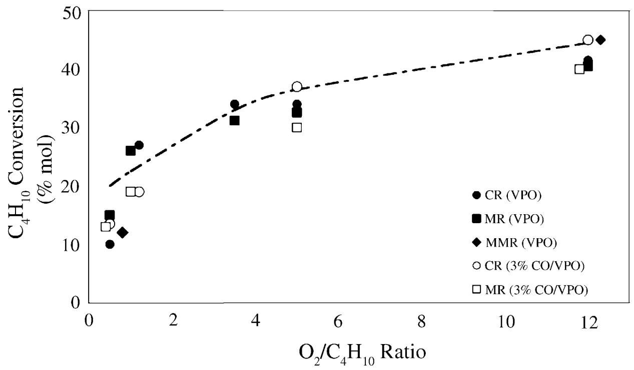

Fig. 5. Butane conversion as a function of the oxygen/butane ratio. CR: conventional reactor, MR: fully segregated feed membrane reactor, MMR: mixed feed membrane reactor. Black symbols: VPO catalyst, white symbols; 3% Co/CPO catalyst.

membrane on the reactor performances, when compared to the conventional co-feeding. Standard conditions were used.

Fig. 4 shows the results of conversion and selectivity as a function of the amount of oxygen distributed through the membrane in standard conditions.

The effect of the mode of oxygen feeding is limited (conversion range 40–45%, and selectivity range 70–75%). However, a maximum in mixed feed is found, as previously reported [5].

3.3. Effect of oxygen/butane ratio at low butane pressure

Fig. 5 shows the effect of oxygen/butane ratio on butane conversion with different reactor configurations. Only results on pure VPO and 3% Co/VPO catalysts are presented, as initial studies showed that higher cobalt doping could lead to more interesting effects.

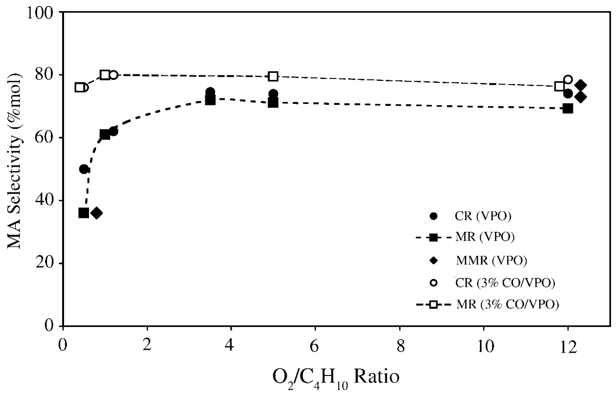

Fig. 6. Maleic anhydride selectivity as a function of the oxygen/butane ratio. CR: conventional reactor, MR: fully segregated feed membrane reactor, MMR: mixed feed membrane reactor. Black symbols: VPO catalyst, white symbols; 3% Co/CPO catalyst.

The conversion decreased when the oxygen/butane ratio decreased, whatever the catalyst and reactor feed configuration.

Fig. 6 shows the effect of the same parameter on maleic anhydride selectivity.

In contrast to the variation of the conversion, the selectivity of the two catalysts is very different, particularly at low oxygen/butane ratios, where the cobalt-doped catalyst maintains a very high maleic anhydride selectivity. These results are valid whatever the reactor feed configuration.

3.4. Effect of high butane pressures

Membrane reactors offer the possibility to work at higher butane partial pressure, while remaining out of flammable

Table 2

Catalytic performances of the 3% Co/VPO catalyst under various reactor configurations and butane feed conditions ($X_{C_4H_{10}}$: butane conversion, S_{MA}: selectivity to maleic anhydride)

Reactor mode	$P_{C_4H_{10}}$ (hPa)	GHSV (h^{-1})	O_2/C_4H_{10}	$X_{C_4H_{10}}$ (%)	S_{MA} (%)	Productivity (mol m^{-3} h^{-1})
CR	12	15	12	45	78	175
		15	5	37	79	145
		15	1	19	80	75
		15	0.6	13	76	50
MR	12	15	12	40	76	151
		15	5	30	79	118
		15	1	19	80	75
		15	0.6	13	76	48
MR	220	15	5	54	58	156
		15	3.5	43	58	127
		15	2	24	58	68
MR	220	90	3.5	20	45	267
		90	2	15	49	218
MR	220	180	3.5	17	43	435
		180	2	10.5	45	280

At high butane partial pressure the oxygen to butane ratios were limited to avoid flammable mixtures in the catalytic bed. CR: conventional reactor, MR: fully segregated feed membrane reactor.

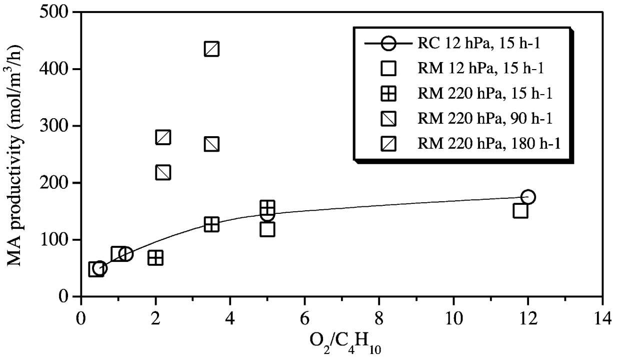

Fig. 7. Productivity of conventional and membrane reactors as a function of oxygen/butane ratio; 3% Co/VPO catalyst, under different butane partial pressures and GHSVs (see legend). CR: conventional reactor, MR: fully segregated feed membrane reactor.

compositions. However, in the present case, the mixed membrane reactor (MMR) configuration is not possible without risking explosive compositions if significant amount of oxygen is co-fed with the butane.

Table 2 and Fig. 7 compare the performances of the 3% Co/VPO catalyst in both conventional and membrane segregated feed configurations, under various butane GHSVs and partial pressures. The table includes butane conversions and MA selectivity. Other carbon containing products are CO and CO_2. Note that no butenes were detected in the exit streams, in all experiments presented in this work.

Conventional (CR) and membrane segregated feed (MR) configurations offer similar performances, as previously presented (see Fig. 5). The intrinsic rate of MA production calculated from the above data in standard conditions (first row of Table 2) is close to 5×10^{-9} mol/m^2/s. This is in agreement with common literature [25].

When changing butane partial pressure at the same GHSV (from 12 to 220 hPa at GHSV = 15 h^{-1}), the conversion increases, but the selectivity decreases, consequently leading to similar productivities and yields. When increasing the GHSV at constant high butane partial pressure, both butane conversion and selectivity to MA decrease. Nevertheless, in these high butane partial pressure and GHSVs, the productivity clearly increases up to 435 mol m^{-3} h^{-1} (Fig. 6).

4. Discussion

In this section, three main points will be addressed. The effect of oxygen feed configuration will be discussed first. Then, we will comment on the effect of catalyst cobalt doping on the reactor performances, as a function of the experimental conditions. Last, the influence of butane partial pressure on the maleic anhydride productivity in a membrane reactor will be dealt with.

4.1. Effect of oxygen distribution

The final goal of this work is to use high butane partial pressures. To avoid the flammability problem, oxygen distribution through the membrane was considered. Therefore, in a first step under standard conditions, we investigated the effect of the mode of oxygen feeding the catalyst bed.

On conventional VPO catalyst, as reported in Fig. 4, both conversion and selectivity are little affected. In the conventional reactor, where oxygen and butane are directly co-fed into the catalyst bed, the oxygen/butane ratio is moving from the initial value of 12 to about 20 (as calculated from conversion and selectivity data), which remains a fairly oxidant atmosphere. On the contrary, in the membrane reactor, the oxygen/butane ratio moves from zero to about 20 under standard conditions, changing from very reductive to oxidative media. This suggests that the first part of the catalyst bed may be placed in conditions favouring the oxidehydrogenation reactions, leading to butenes, as previously reported [18]. These butenes are commonly considered as intermediaries in the selective oxidation to maleic anhydride. They may be further oxidised in the second part of the bed, as they are not detected in the analysis. However, this likely hinders the reactor efficiency, as part of the catalyst bed does not work properly.

On the other hand, the second part of the catalyst bed would be more MA selective, due to the higher oxygen content in the atmosphere. The combination of all these effects leads to a global slight decrease in performances.

According to this hypothesis, the combined MMR oxygen feed keeps the advantages of the membrane reactor, without the drawback of a reducing atmosphere at the start of the bed. The results presented in Fig. 4 are in keeping with this idea, showing an overall slightly higher performance in the MMR situation.

Considering that at high butane concentrations, the situation at the inlet of the catalyst bed will be even worse, due to the very high local reducing conditions, a catalyst resisting to such a situation is necessary to go in this direction.

4.2. Co-doped VPO catalyst

The effect of cobalt doping on the morphology of this type of catalyst is not always consistent in the literature. However, in our case, the use of the hemihydrate route, for all samples prepared, leads to a regular decrease of the specific area with cobalt loading (see Table 1). By the way, let us underline that the 3% Co/VPO shows a higher activity, when related to its specific area.

As can be seen in Fig. 6, the Co/VPO catalyst is much more selective towards maleic anhydride in reducing atmosphere than pure VPO catalysts. This result is in keeping with that previously observed in conventional micro-reactors, under similar reducing conditions [18]. This effect was attributed to a higher state of oxidation of the vanadium species, in agreement with the above-mentioned higher oxygen-donor character (see Section 3.1).

The oxidation state of conventional VPO systems being lower in these conditions, they exhibit low selectivity towards maleic anhydride, in keeping with previous results of our group [18]. In these micro-reactor experiments, on conventional VPOs, the reaction was butene-selective. However, in the work presented here, only water, MA, CO and CO_2 were found in noticeable amounts in the exit streams.

Therefore, we have to make the hypothesis that the butenes produced on the conventional VPO surface in reducing conditions are further oxidised to carbon oxides, according to another process. Let us underline that all the reactor configurations used here, including the conventional one, were implemented in presence of the MFI/alumina nanocomposite membrane. Thus, this further oxidation of butenes could be achieved on the acidic sites of the zeolite. As a matter of fact, analytical TEM showed that the membrane zeolite material is made of HZSM-5, with extremely low silicon to aluminium ratio of 10, which makes it very acidic [26]. Acidic zeolites are known to be active for the decomposition of olefins to carbonaceous species [27], that can be further removed by oxidation.

Let us underline that here, the reaction is favoured by a competitive adsorption favourable to butenes [28]. Note that this over-oxidation process could not affect maleic anhydride production, as it is sterically hindered to enter the MFI network, when compared to butenes.

4.3. High productivity experiments

At constant GHSV (15 h^{-1}) and similar oxygen/butane ratios, a butane concentration increase leads to a general gain in conversion. This is in good keeping with an idea of a positive global order for butane in this reaction. As usually observed, this conversion increase is found together with a small drop of selectivity.

At constant high butane partial pressure (220 hPa), increasing butane GHSV from 15 to 180 h^{-1}, results in a limited decrease of conversion. This variation is, however, much lower than that based on the contact time. This suggests that high contact time (i.e. low GHSV) conditions originate some diffusion limitations. However, this conversion decrease came along with a slight decrease of selectivity to maleic anhydride, which somewhat comes against the usual selectivity versus conversion trend.

A possible explanation could be the following. Lower contact time may lead to oxidation primary products, such as butenes, that would be immediately oxidised to carbon oxides in the H-ZSM5 acidic material of the membrane, as presented in Section 4.2.

Fig. 8 illustrates the local oxygen and butane partial pressures along the catalyst bed, taking into account the experimental inlet and outlet composition on the tube side. A linear interpolation has been tentatively used to obtain the values between these two extremes. Note that, for similar inlet conditions, the conventional reactor would operate well into the flammability zone.

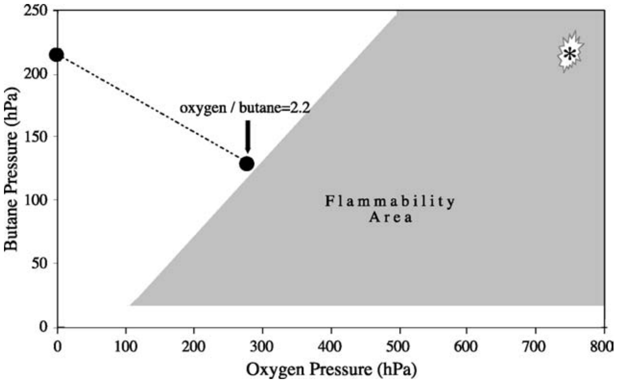

Fig. 8. Schematic of the oxygen and butane composition along the catalyst bed of the CMR. Conditions: high butane partial pressure feed (220 hPa), oxygen/butane ratio fed to the catalyst bed of 3.5, GHSV of 15 h^{-1}. Asterisk (*) indicates corresponding inlet conditions in a conventional reactor.

While allowing operative conditions out of the ordinary, the distributor CMR still needs specific reactor management considerations. As a matter of fact, keeping its reactive atmosphere out of the flammability region implies a limited range of interconnected values for the experimental parameters (feed flow rates, oxygen/butane ratios, etc.), for given reactor geometry and membrane characteristics.

Thus, in the case of high butane partial pressure feeds, these limitations imply a oxygen-lean feed of the reactor (i.e. low oxygen/butane ratios), as listed in Table 2. Therefore, a specific catalyst, able to maintain high performances in these conditions, is needed to properly operate distributor CMRs. A similar conclusion was already noticed for extractor CMRs [6,11].

5. Conclusion

This work has demonstrated the possibility to run the selective oxidation of butane to maleic anhydride in a CMR of the distributor type, using a high butane partial pressure feed. This leads to productivities well above those obtained in conventional reactor mode.

While both reactor configurations (conventional and membrane fed) must operate out of the conditions of flammability, the membrane oxygen distribution allows the introduction of much higher butane amounts. However, this implies for the distributor CMR a highly reducing reactive atmosphere. Therefore, its satisfactory operation was made possible by using a specially designed catalyst.

Further progress in the field may come from a refined modelling study combining catalyst kinetics and membrane transport equations. This would lead to an improvement in material characteristic, reactor design and optimal operating conditions.

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