Oxidative Dehydrogenation of Butane Using Membrane Reactors

C. Téllez, M. Menéndez, and J. Santamaría
Dept. of Chemical and Environmental Engineering, University of Zaragoza, 50009 Zaragoza, Spain

The oxidative dehydrogenation of butane was studied at temperatures between 450 and 550°C using a conventional fixed-bed reactor and inert membrane catalytic reactors with different feed arrangements. When inert membrane reactors were employed, a ceramic membrane was used to distribute oxygen to a fixed bed of V-Mg-O catalyst. The membrane reactor was found to be more efficient than a fixed-bed reactor under most of the conditions investigated. In addition, in the membrane reactor the formation of hot spots decreased considerably, leading to a more stable and safer operation.

Introduction

Inorganic membrane reactors are at the core of one of the fastest expanding fields of research in chemical reaction engineering during the last decade. Unlike polymeric membranes, inorganic membranes can be used in high-temperature applications, and have therefore been employed in a variety of chemical reactions. The bulk of the investigations on membrane reactors carried out to date have focused on the displacement of equilibrium by the selective removal of one of the reaction products (Saracco and Specchia, 1994). This process has often been applied to dehydrogenation reactions using Pd-based membranes, which are hydrogen permselective. In a less frequently used application nonpermselective, porous ceramic membranes operating in the Knudsen diffusion regime have been used to preferentially permeate light products (hydrogen). In this case, permselectivity is sacrificed in return for larger fluxes.

The other main field of application of membrane reactors, with which this work is concerned, uses the membrane to introduce a reactant in a controlled manner, in a reacting network where several reactions are possible. A typical example is the selective oxidation of hydrocarbons where, in addition to the desired oxidation process, deep oxidation of reactants and products to carbon oxides is also possible. In this situation, using a ceramic membrane to distribute the oxygen feed could help regulate the extent of the different reactions by lowering the oxygen partial pressure in the reactor with respect to that existing at the inlet of a fixed-bed reactor. This reduction often results in a higher selectivity for a given hydrocarbon conversion. While dense, selective membranes can be used to achieve a distributed oxygen feed (e.g., Omata et al., 1989), the fluxes obtained are generally low, which leads to a low per pass conversion. This has prompted the use of porous membranes, which are capable of larger permeation fluxes. Examples of this approach include methane oxidative coupling (Coronas et al., 1994a,b; Tonkovich et al., 1996b), and oxidative dehydrogenation of ethane (Coronas et al., 1995a; Tonkovich et al., 1995, 1996a) and propane (Pantazidis et al., 1995; Capanelli et al., 1996). In addition to improvements in selectivity, it has also been shown (Coronas et al., 1995b) that membrane reactors have significant advantages in these types of reactions where runaway behavior and explosions are possible, resulting in a more stable and safer operation.

The requirements imposed upon the inorganic membranes used in membrane reactors are by no means insignificant: (1) when the membrane is used to distribute one or more reactants, it must provide the required permeation flux (the optimum pattern may correspond to a nonuniform permeation profile along the bed (Coronas et al., 1994b)), while avoiding significant back permeation of the reacting mixture (Lafarga et al., 1994); (2) the membrane material must be stable under the reaction conditions used, which in this work include high temperatures and the presence of oxygen; (3) the pore structure and permeation flux must be stable during reaction. It is therefore important to avoid the development of mechanical defects in the membrane as well as the deposition of foreign material such as coke within its pore structure. (4) Finally, regarding the catalytic activity of the membrane, we can consider two types of reactors, namely catalytic membrane reactors (CMRs), where membrane preparation is focused on attaining catalytic activity, and inert membrane reactors (IMRs), in which the catalyst is located out of the membrane structure and the role of the membrane is limited to the transport of reactants and/or products. In this case, the membrane itself may have undesired catalytic activity that must be minimized, as is the case, for instance, with silica/alumina membranes used to distribute oxygen in methane oxidative coupling, whose nonselective activity was partly compensated by doping the membrane with alkaline compounds (Lafarga et al., 1994).

In this work, an IMR was used for the oxidative dehydrogenation of butane (ODB), over V-Mg-O catalysts. ODB offers some potential advantages over thermal dehydrogenation of butane: it is exothermic and therefore does not need an external heat input, avoids equilibrium limitations, runs at a lower temperature, and usually gives lower yields to coke and cracking products. Although ODB has been carried out over a variety of catalysts such as V-based catalysts (Chaar et al., 1987; Kung, 1994; Blasco et al., 1995) and Mo catalysts (Martin-Aranda et al., 1995; Vrieland and Murchison, 1996; Vrieland et al., 1996), probably the best results obtained to date were from the V-Mg-O catalyst, with high selectivities to butene and butadiene (Chaar et al., 1987; Bhattacharyya et al., 1992; Blasco et al., 1995). It seems well established that over V-Mg-O catalyst the reaction takes place using lattice oxygen, which is then replaced by oxygen from the gas phase. In fact, as long as there is sufficient oxygen in the gas phase to replenish the lattice, the oxygen partial pressure seems to have little or no effect on the catalytic activity (Chaar et al., 1988). However, regarding selectivity the system is still not well understood, and several factors have been suggested as being responsible for the selective (or unselective) behavior of V-based catalysts. Among these are the acidity of the catalyst (Galli et al., 1995; Blasco et al., 1995); cation reducibility and the catalyst's state of reduction (Kung, 1994); catalyst preparation (Kung and Kung, 1992); and the shape and size of the alcane molecule (Kung, 1994; Galli et al., 1995).

The dynamic equilibrium that is established between catalyst reduction due to the reaction and catalyst reoxidation from the gas phase offers interesting possibilities for a membrane reactor in which the oxygen distribution along the bed can be controlled. The use of an IMR for ODB of butane has several potential advantages over the conventional fixed-bed reactor (FBR): (1) as indicated earlier, since high partial pressures of oxygen usually favor the deep oxidation reactions, the use of a distributed oxygen feed could lead to greater selectivities by keeping a sufficiently low partial pressure of oxygen throughout the reactor; (2) the heat generation would be distributed more evenly along the bed, thereby decreasing the formation of hot spots and the probability of runaway behavior; (3) the existence of oxygen at any reactor position could also contribute to decreasing the coke formation that often takes place in the exit region of oxydehydrogenation fixed-bed reactors; and (4) in the particular case of butane oxydehydrogenation over V-Mg-O catalysts, which requires the use of lattice oxygen, it has been found that the optimal catalyst has a certain degree of reduction at steady state (Patel et al., 1990; Kung, 1994; Mamedov and Cortés Corberán, 1995). The membrane reactor offers the possibility of tailoring the oxygen feed to achieve the desired balance between the reaction (and the associated reduction) and reoxidation of the catalyst.

Experimental Studies

The catalyst was prepared along the general lines described by Chaar et al. (1987), except that commercial MgO was used as a starting material. The preparation procedure involved mixing powdered MgO with a solution containing 1 wt. % of ammonium hydroxide and 0.5% of ammonium vanadate, to produce catalysts with 20 or 24 wt. % of vanadium oxide (calculated as V_2O_5), termed 20-VMgO and 24-VMgO, respectively. The mixture was evaporated under constant stirring and the resulting solid was calcined, ground, and sieved to obtain a particle size between 250 and 500μm. The catalyst was characterized by BET surface-area measurements, temperature-programmed reduction (TPR) experiments, and X-ray diffraction (XRD). In addition, some experiments were run to estimate the overall state of reduction of the catalyst φ in a fixed-bed reactor and in membrane reactors operating under different conditions. In these experiments the reaction was carried out for a sufficient time to equilibrate the catalyst (typically 1 hour), then stopped and purged with He. The catalyst was then reoxidated using a series of pulses, each containing 0.8 Ncm^3 of oxygen, while the exit stream from the reactor was continuously monitored using a quadrupole mass spectrometer. After allowing for the combustion of the carbonaceous deposits on the catalyst surface (as measured by the amounts of CO and CO_2 evolved during oxidation of the catalyst), the average state of reduction of the catalyst in the reactor could be estimated from the total oxygen consumption.

The membranes used in the IMR were prepared from 375-mm-long, 6.6-mm-ID ceramic tubes (SCT), with a 20-nm zirconia separation layer. The required permeation flux was obtained by modification of the original α-Al_2O_3 structure via deposition of silica using sol-gel techniques, as described in previous works (Lafarga et al., 1994). The membrane was impregnated with $NaNO_3$ to reduce its acidity (which has a negative effect upon the selectivity), and enameled at both ends in order to limit the permeation to the central 14 cm of the ceramic tube. The membranes were characterized by SEM, mercury porosimetry, BET analysis, and permeation measurements. Under the conditions used in this work, the permeation flux through the membrane was predominantly of the Knudsen type (the Poiseuille and Knudsen contributions to the total flux were estimated from permeation measurements as 1/3 and 2/3, respectively).

The catalyst was located as a fixed bed of the annular section packed between the inner reactor wall and an axial quartz thermowell. The reaction system has been described elsewhere (Coronas et al., 1994a, 1995a). The reactor (membrane + catalyst bed) was enclosed in an outer stainless-steel shell, and the whole was heated by an electric furnace. When isothermal operation was attempted, the heating was provided by two independently controlled furnace sections. In addition, external refrigeration could be provided in selected zones of the reactor. In spite of this, because of the exothermicity of the reaction, temperature variations developed in the reactor, and the temperature at inner reaction positions could be significantly higher (up to 60°C, depending on the operating conditions) than the setpoint temperature, especially during FBR operation. The temperature used below when reporting the results obtained corresponds to the setpoint temperature, which is accurately maintained at each of the two ends of the catalyst bed.

The reactor could be operated as a membrane reactor

(IMR), or as a fixed-bed reactor, depending on the feed arrangement. In IMR experiments, an O_2 or O_2/He feedstream flowed on the shell side at pressures of up to 6 bars and permeated toward the catalyst bed located on the tube side, where either C_4H_6/He or C_4H_6 were fed at essentially atmospheric pressure. In FBR experiments all gases were fed simultaneously at the reactor entrance. In both cases, all streams were mass flow controlled. Total flow rates between 100 and 700 cm^3 (STP)/min were used, with an overall feed ratio He:O_2:C_4H_6 of 88:8:4, unless otherwise indicated. The exit gases were analyzed (O_2, CO, CO_2, methane, ethane, ethylene, propane, propylene, butane, *n*-butene, *cis*- and *trans*-butene, and butadiene) by on-line gas chromatography. Carbon mass balance closures were always within 5%, and usually within 2%. Butane conversion (X_{BUT}) was calculated as the ratio of the number of moles of carbon in the reaction products to the total number of moles of carbon in the exit-gas stream. Selectivities were obtained as the ratio of the number of moles of carbon in a given product to the total number of moles of carbon in the butane reacted. C_4 selectivity (S_{C_4}) denotes the total selectivity to C_4 dehydrogenation products (*n*-butene, *cis*- and *trans*-butene, and butadiene), while CO_x selectivity (S_{CO_x}) indicates total selectivity to carbon oxides.

Results and Discussion

The catalyst surface area was approximately 71 m^2/g. XRD measurements showed a well-crystallized MgO phase and a less defined magnesium orthovanadate phase, while in TPR measurements a single peak of H_2 consumption was found at 653°C and 675°C for 20-VMgO and 24-VMgO, respectively. The performance of the catalyst in terms of selectivity/conversion in experiments carried out in a conventional fixed-bed reactor was similar to the results reported in the literature for unpromoted V-Mg-O catalysts (Kung, 1994).

Preliminary experiments with empty membrane reactors showed that the intrinsic contribution of the membrane to the reaction was negligible under the conditions employed (the conversion of butane at the highest temperature used (550°C) was around 2%). When the membrane was packed with quartz chips the conversion increased to about 4% at the same temperature.

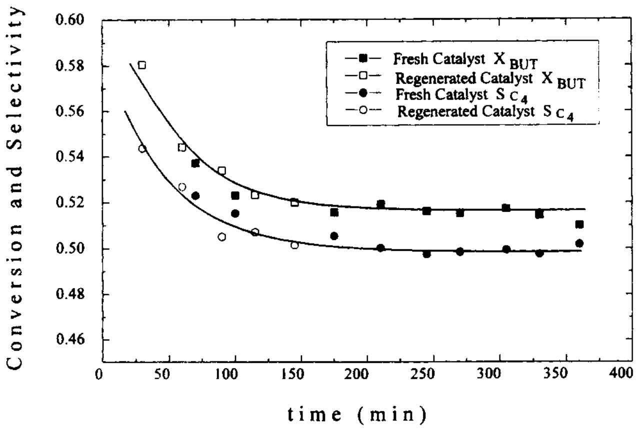

Figure 1. Stability of the catalytic membrane reactor loaded with fresh and regenerated catalyst.

$T = 500°C$, $C_4H_{10}/O_2/He = 4/8/88$, total flow rate: 200 cm^3 (STP)/min, 2.2 g of 20-VMgO catalyst. IMR, permeation of $O_2 + He$.

When the membrane reactor was loaded with the V-Mg-O catalyst, transient behavior was observed for about 2 hours, after which both the conversion and selectivities were approximately stable (Figure 1). This is probably due to the stabilization of the oxidation state of the catalyst along the reactor for a given set of reaction conditions. Figure 1 also shows that the initial catalytic performance is reproduced after the used catalyst was treated with 9% O_2 in the He stream at 525°C for 45 minutes, to remove any carbonaceous material deposited on the catalyst surface.

Regarding the stability of the membrane material, after approximately 160 hours of operation, postmortem analysis of the membranes yielded a BET surface area of 0.1 m^2/g and an average pore radius of 0.28 μm, which are similar to the original values. Unlike previous works in which the same type of membrane was used at higher temperatures (Lafarga et al., 1994; Santos et al., 1995), SEM observation of the used membranes (Figure 2) showed only a few minor cracks in the silica filling. Finally, the permeation fluxes measured for the used membranes were within 5% of the initial values, which also indicates that the physical integrity of the membrane was maintained.

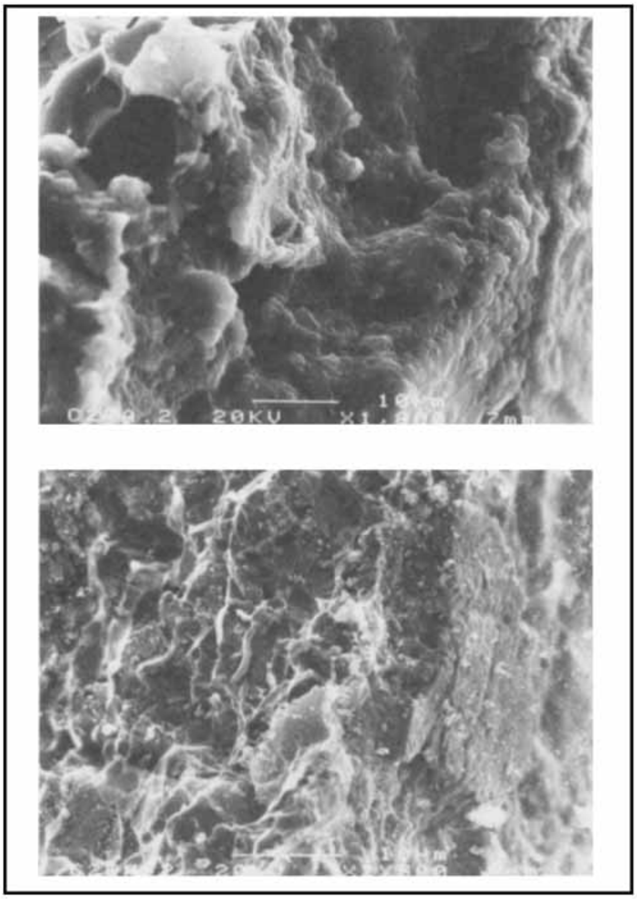

Figure 2. SEM micrographs of used membranes (after 160 h on stream).

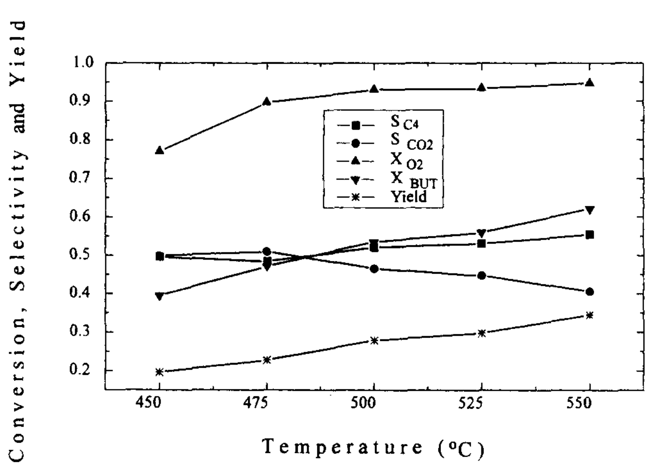

Figure 3. Effect of reaction temperature.

$C_4H_{10}/O_2/He = 4/8/88$, total flow rate: 200 cm^3 (STP)/min, 2.2 g of 20-VMgO catalyst. IMR, permeation of $O_2 + He$.

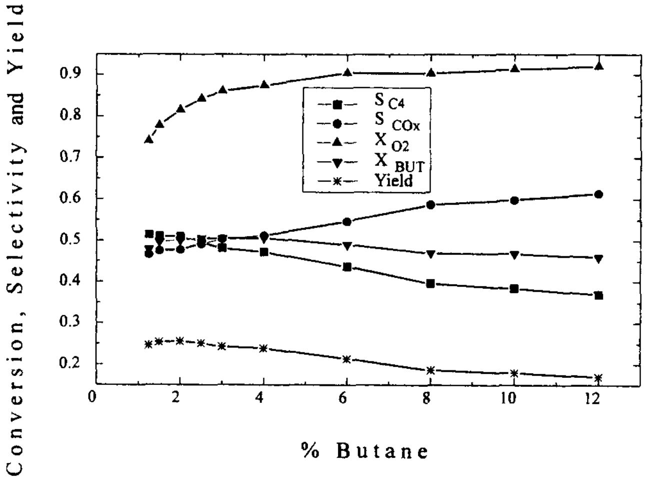

Figure 5. Effect of the reactant dilution.

$T = 500°C$, C_4H_{10} flow rate: 8 cm^3 (STP)/min, O_2 flow rate: 16 cm^3 (STP)/min, variable He flow rate. 2.2 g of 24-VMgO catalyst. IMR, permeation of $O_2 + He$.

Influence of operating conditions

Figure 3 shows the effect of reaction temperature upon the conversions and selectivities attained in a membrane reactor. As the temperature was raised in the 450–550°C interval, the butane and oxygen conversions increased, and the total selectivity to dehydrogenated C_4 products also increased slightly (the selectivity to butenes decreased, but this was compensated by an increase in the selectivity to butadiene), while the selectivity to carbon oxides decreased. A similar effect has been reported recently (Blasco et al., 1995), while other authors (Bhattacharyya et al., 1992) found varying behavior in this temperature interval, depending on the specific promoters used.

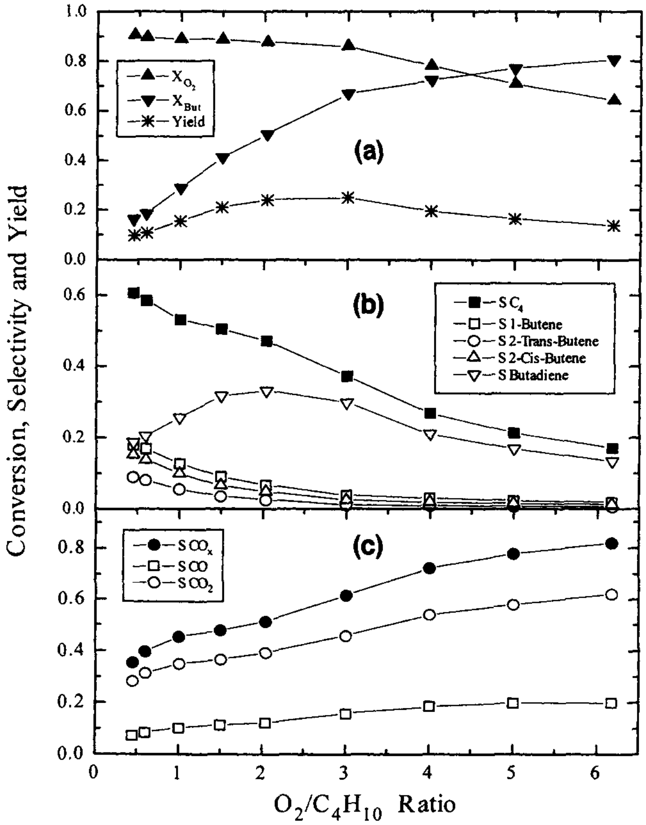

Figure 4. Effect of the O_2/C_4H_{10} ratio.

$T = 500°C$, He flow rate: 176 cm^3 (STP)/min, O_2 flow rate: 16 cm^3 (STP)/min, variable C_4H_{10} flow rate. 2.2 g of 24-VMgO catalyst. IMR, permeation of $O_2 + He$.

The effect of the O_2/C_4H_{10} ratio is presented in Figures 4a to 4c. These experiments were carried out with a constant input of He and O_2 (which were permeated through the membrane), while the flow of butane was varied. As expected, the butane conversion increases with increasing oxygen content, while the overall selectivity to dehydrogenation products decreases, in spite of an important increase in the butadiene selectivity up to a O_2/C_4H_{10} ratio of 2. The result of both tendencies is a maximum in the yield to dehydrogenation products at a O_2/C_4H_{10} ratio approximately equal to 3. The decrease in selectivity for increasing oxygen concentrations is a common feature in many selective hydrocarbon oxidations, and in fact constitutes the main reason for using inert membranes as oxygen distributors, as discussed earlier.

Another set of experiments varied the butane and oxygen concentrations in a different way (Figure 5). In this case, the butane and oxygen inputs were kept constant at 8 and 16 cm^3 (STP)/min, respectively, and the dilution gas (helium) flow was varied. It can be seen that oxygen conversion steadily increased as the reactant concentration was stepped up, while butane conversion showed only a shallow maximum. The dehydrogenation selectivity consistently decreased, while the selectivity to carbon oxides increased as the reactant concentration was increased. The increase in butane conversion was less than could have been anticipated from the results of a very similar experiment carried out in a conventional fixed-bed reactor by Bhattacharyya et al. (1992), in which the conversion of butane increased almost linearly with the concentration of reactants. The reduced influence found in this work is due to the nature of the membrane reactor used, where one of the reactants (oxygen) and the diluent are distributed throughout the catalyst bed. It is also interesting to consider the strong decrease that takes place in C_4 selectivity as the reactant concentration is increased. It should be noticed that

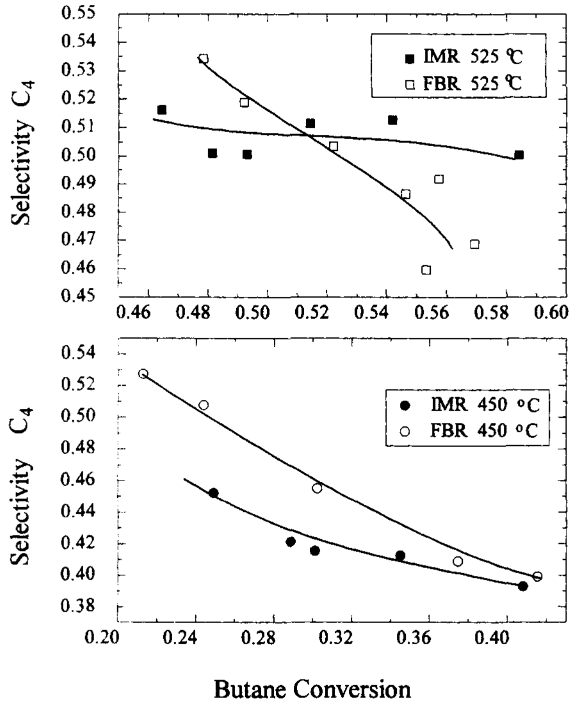

Figure 6. FBR vs. IMR with permeation of O_2+He at two different temperatures.

$C_4H_{10}/O_2/He$ = 4/8/88, 2.8 g of 24-VMgO catalyst, variable total flow rate.

increasing reactant concentration by reducing the amount of diluent input not only gives a greater concentration of oxygen, but also increases the residence time of the dehydrogenation products in the reactor, which tends to lower the selectivity.

Comparison of FBR and IMRs with different feed arrangements

The experiments reported in this section compare the results obtained with the same overall feed, $C_4H_{10}/O_2/He$ = 4/8/88, in a FBR and in an IMR with two different feed arrangements, in which butane was always fed at the tube side and oxygen at the shell side, while the diluent could be fed to either side.

Figure 6 compares the IMR with feeding He and O_2 at the shell side and the FBR at two different temperatures. In this case, the operating conditions were kept constant and the conversion was varied by changing the total gas flow rate. It can be seen that at low conversions of butane (which also means low conversions of oxygen), the FBR gives a higher selectivity than the IMR. Given the comparatively high He input flow, this is not surprising, since in the FBR the residence time is lower and a higher dilution is available from the reactor entrance. However, as the conversion increases, the favorable effect of oxygen distribution overcomes these disadvantages: although the selectivities obtained in the FBR rapidly drop with increasing conversion, the decrease is less pronounced in the IMR. As a consequence, for high butane conversions the IMR gives a clearly superior performance. Similar results (not shown) were obtained in experiments where the C_4H_{10}/O_2 ratio was varied by changing the butane input to the reactor: a higher selectivity was obtained in the IMR at butane conversions above 50%.

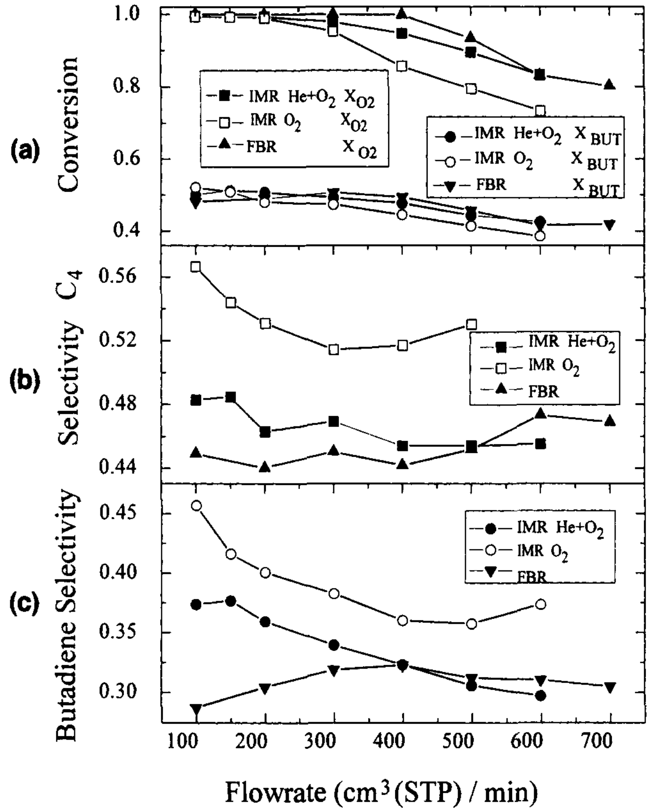

Figure 7. FBR vs. IMRs with different permeation arrangements.

T = 500°C, $C_4H_{10}/O_2/He$ = 4/8/88, 2.8 g of 24-VMgO catalyst, variable total flow rate.

The best performance, however, was given by the IMR with permeation of O_2. Figure 7 compares the performance of the FBR and the two IMRs at 500°C. It can be observed (Figure 7a) that an essentially complete conversion is obtained with any of the reactors at total flow rates below 200 cm^3 (STP)/min, and that the FBR gives the highest butane and oxygen conversions in the rest of the range investigated. The selectivity to C_4 dehydrogenation products (Figure 7b) is similar in the FBR and in the IMR with permeation of He + O_2, with higher values for the latter at low flow rates (i.e., high conversions), as discussed before. However, the highest selectivities corresponded to the IMR with permeation of O_2, in which the selectivities were on average 10 percentage points higher than those of the FBR. It can be seen that this is mainly due to the high selectivity to butadiene that is obtained in the IMR with permeation of O_2 (Figure 7c).

The selectivity-conversion curves are presented in Figures 8a and 8b, and correspond to 500 and 575°C, respectively. No results of the FBR are given for the experiment at 575°C because of temperature instabilities due to hot-spot formation near the reactor entrance (the reaction repeatedly runs away, in spite of attempts to avoid this by using extra refrigeration in the inlet region of the bed). Again, the IMR with permeation of He + O_2 gives a higher selectivity than the FBR at higher conversions (Figure 8b), while the IMR with permeation of O_2 gave a superior performance over the whole range

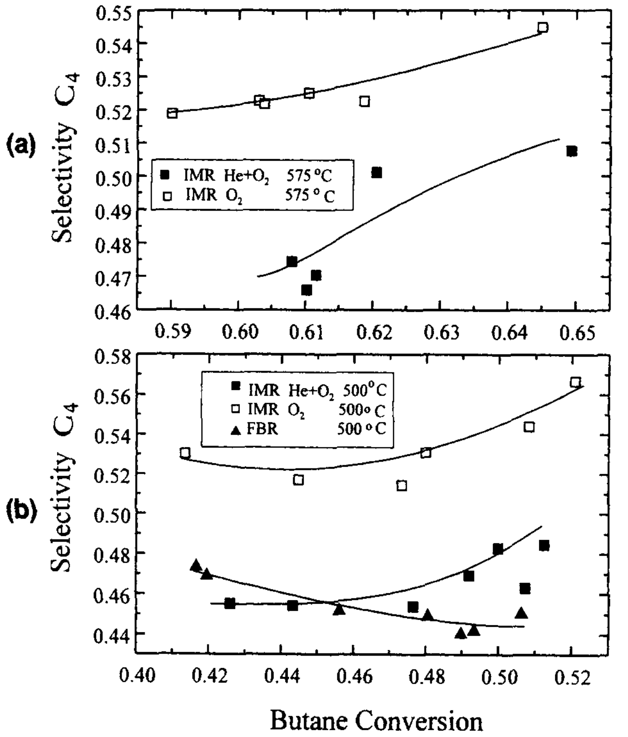

Figure 8. Selectivity vs. conversion for FBR and IMRs with different permeation arrangements.

$C_4H_{10}/O_2/He = 4/8/88$, 2.8 g of 24-VMgO catalyst, variable total flow rate. (a) 500°C; (b) 575°C.

of conversions investigated. The higher selectivity obtained in the IMR with permeation of $O_2 + He$ at higher conversions, and in the IMR with permeation of O_2 throughout the conversion range investigated, probably reflects not only the favorable kinetic effect of a low oxygen concentration throughout the reactor, but also the fact that, under conditions of high oxygen consumption, the catalyst in the FBR undergoes strong changes in its oxidation state (oxidized at the bed entrance where most of the reaction takes place, strongly reduced at the bed exit), while a more favorable intermediate state is obtained with the IMR.

The overall oxidation state of the catalyst was measured as outlined in the experimental section: the same mixture ($C_4H_{10}/O_2He = 4/8/88$) was fed to the three different reaction systems for 60 minutes, at a total flow rate of 100 cm^3 (STP)/min, or for 75 minutes, at a total flow rate of 200 cm^3 (STP)/min. After this, the reaction was stopped and the catalyst reoxidated. The amount of oxygen consumed in catalyst reoxidation was calculated using on-line mass spectrometry after allowing for the oxygen consumed in burning the carbonaceous deposits on the catalyst (estimated from the amounts of CO and CO_2 formed upon catalyst reoxidation). The results are presented in Table 1. It can be seen that the FBR and the IMR with permeation of $He + O_2$ consume more oxygen (i.e., on average the catalyst is more reduced at the end of the reaction) than the IMR with permeation of O_2. Also, under low total flow rates the catalyst is more reduced, which was an expected result given the higher oxygen conversion that is obtained. These results show that, depending on the particular feed arrangement used, there is indeed a difference in the average oxidation state of the catalyst in the same catalyst bed for a given overall feed composition.

Table 1. Amount of Oxygen Consumed (cm^3 (STP)) in the Reoxidation of the Catalyst Bed after Reaction for a Specified Period of Time

Reaction Conditions	FBR	IMR, $He + O_2$	IMR, O_2
100 cm^3 (STP)/min, 60 min on stream	33.7	29.5	22.4
200 cm^3 (STP)/min, 75 min on stream	24.4	23.9	19.7

The average degree of catalyst reduction (φ) in the bed is obviously important in a reaction such as ODB, which uses lattice oxygen. However, if the oxidation state of the catalyst is not uniform throughout the bed, the actual distribution of the oxidation/reduction state along the reactor may be a more significant parameter. We do not have a direct measurement of the φ profile in the bed. Nevertheless, some reasonable assumptions can be made that are consistent with the results obtained in this work. Thus, in a FBR the catalyst in the inlet zone of the bed would see the highest oxygen concentration. Since most of the reaction takes place in this region, as indicated by the temperature profiles discussed below, it can be concluded that much of the reaction takes place over a catalyst with a low value of φ, and thus with a lower selectivity (Kung, 1994). On the other hand, in an IMR with $He + O_2$ permeation, the entrance region of the reactor would have a very high concentration of butane, leading to significant coke formation. In this case, part of the oxygen feed would be consumed in burning the coke formed to CO and CO_2, thereby lowering the selectivity. This was confirmed by burning the coke formed on the catalyst after reaction, which showed that the coke load on the IMR with permeation of $He + O_2$ was 14 times higher than on the FBR. In the latter case, very little coke was formed because of (1) a high initial dilution with He, and (2) the formation of steam in the oxidative dehydrogenation and combustion reactions that occur mainly in the entrance region of the FBR. This steam is transported down the catalyst bed and helps to avoid coke formation throughout the reactor. Finally, an intermediate situation arose in the IMR with permeation of O_2, in which the rate of coke formation was lower than in the IMR with permeation of $He + O_2$. The distinct behavior induced by the different feed arrangements in the IMR was also confirmed in a separate experiment (not shown) at 575°C, in which the formation of cracked products (related to coke formation and also to reaction under high butane concentrations) was between 2 and 3 times higher in the IMR with permeation of $He + O_2$.

Safety and operability characteristics

The difficulty with controlling the temperature in fixed-bed reactor operation, even under conditions of high concentration of diluent, has already been pointed out. It is also important to notice that some of the experiments carried out in this work with membrane reactors would have been within the flammability range if a fixed-bed reactor with the same overall feed composition had been used. Therefore, by distributing the oxygen feed, an IMR can extend the range of safe reactor operation. Concerning this point, the membrane reactor was also less apt to run away and gave a much smoother

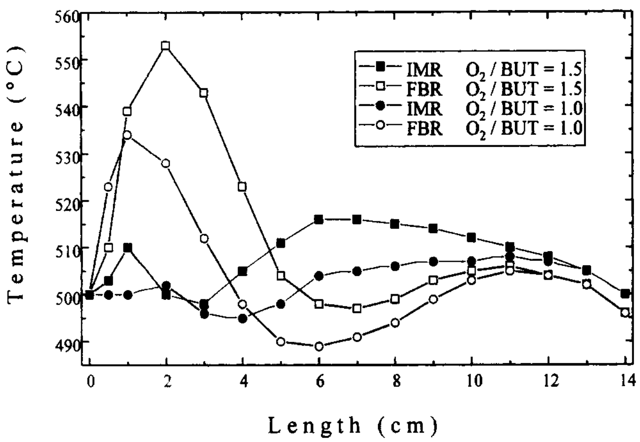

Figure 9. Temperature profiles in fixed-bed and inert-membrane reactors for different operating conditions.

C_4H_{10} concentration was 10% in all cases, O_2/C_4H_{10} as indicated in the figure. 2.2 g of 24-VMgO catalyst, total flow rate = 300 cm^3 (STP)/min. Setpoint temperature, 500°C.

temperature profile along the bed, as shown in Figure 9 where the temperature profiles for a FBR and for an IMR with permeation of $He + O_2$ are compared.

Conclusions

A ceramic membrane reactor has been used as an efficient contactor in the oxidative dehydrogenation of butane. The composite silica-alumina membrane used as a reactant distributor provided an adequate permeation flux and performed stably, with no significant degradation after 160 hours of operation and about 20 cycles between room temperature and reaction temperature.

Both of the IMRs used gave higher selectivities than the FBR at high butane conversions, and the IMR with permeation of O_2 did the same over the whole range of conversions investigated. The main disadvantage with the permeation of $He + O_2$ was related to the formation of coke and cracked products in the entrance region of the reactor, which lowers the selectivity, and also to the high values of the residence time in the reactor. In spite of this, the fact that this reactor was able to give higher selectivities than the FBR at the higher conversions shows the advantage of distributing the oxygen feed to the reactor.

From the data presented, it can be concluded that the oxygen distribution arrangement has a direct effect on the average state of oxidation of the catalyst in the reactor, and also in the variation of the degree of reduction (φ) along the bed. The results obtained can be interpreted as follows: in the FBR, the results seem to indicate that φ is low near the reactor entrance and high in the rest of the bed. This would give a relatively high average value, but a low value (and therefore a decrease in selectivity) in the entrance region, where most of the reaction takes place. In the IMR with permeation of $He + O_2$, a high φ and a high butane concentration would be present near the bed entrance, thus increasing the rate of coking in this region, which would lower the selectivity, as coke burning takes place with part of the available oxygen. However, the rest of the bed would benefit from the distribution of oxygen, giving an intermediate φ, with higher selectivity. Finally, the best results occur with an IMR in which He and butane are cofed at the reactor entrance and oxygen is diffused through the membrane wall. The advantages of this are the oxygen distribution and the low residence time, while it keeps coke formation to a minimum near the reactor entrance.

Use of the membrane also helped keep reactor operation stable and safe. The membrane reactor had relatively small temperature variations under conditions in which the fixed-bed reactor would give intense hot spots or even run away. This expands the range of conditions under which the reaction can be carried out (i.e., higher overall oxygen-to-butane ratios) and makes the reactor easier to control.

Acknowledgments

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