Oxidative Dehydrogenation of *n*-Butane in a Two-Zone Fluidized-Bed Reactor

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A fluidized-bed reactor with separate butane and oxygen feeds has been studied in the oxidative dehydrogenation of butane. Under suitable conditions, feed segregation allows the creation of separated oxidation and reduction zones in the same reaction vessel, between which a V/MgO catalyst is recirculated. The behavior of the reactor has been characterized, with the separation of oxidation and reduction zones as the focus of the study. The performance of the two-zone reactor has been compared to that of a conventional fluidized-bed reactor.

Introduction

Oxidative dehydrogenation of alkanes has been widely studied in recent years as an alternative to thermal dehydrogenation of paraffinic hydrocarbons, to obtain valuable olefin products. Of particular interest is the production of butadiene, intensively used in the manufacture of rubbers and other polymers and also as an intermediate in a number of industrial syntheses. A single-pass oxidative dehydrogenation process to obtain butadiene directly from butane would certainly be industrially attractive. Among the emerging possibilities for its application, it has recently been proposed as a novel alternative for the production of styrene from butane.[1]

Despite the search for efficient catalysts that has taken place in the past decade, the main problem in the state-of-the-art oxidative dehydrogenation of butane still is the lack of selectivity. Supported vanadium oxides are among the most active and selective catalysts studied to date,[2] but the yields obtained are too low to make the process commercially feasible, because both the reactant butane and the olefin products (butenes and butadiene) can undergo deep oxidation to carbon oxides.

In addition to the development of more selective catalysts, the influence of the type of reactor and mode of contact has also been investigated. In particular, the contribution of gas-phase oxygen is considered detrimental to selectivity, and this has led to reactor designs that avoid or minimize the existence of gas-phase oxygen in the reaction atmosphere. Examples of this practice go back to the 1950s, when Sohio researchers[3] proposed a process in which a hydrocarbon would be contacted at elevated temperature in a fluidized bed containing a supported, variable-valence metal oxide in its higher oxidation state. The hydrocarbon would then be partially oxidized to intermediate products using the catalyst lattice oxygen, which entails a simultaneous reduction of the catalyst in the fluidized bed. To restore the solid to its higher oxidation state, a separate air-fluidized bed at high temperature would be used as a regenerator. This scheme forms the basis of the ARCO

process, proposed for the oxidative coupling of methane.[4] A more recent example is the riser reactor−fluidized bed regenerator system which is currently in use for the selective oxidation of *n*-butane to maleic anhydride by DuPont.[5] The obvious drawback with this approach is the need to continuously recirculate the catalyst between reactor and regenerator. Large amounts of catalyst must be transferred to and from the regenerator, and the slip of oxygen into the reactor and of hydrocarbons into the regenerator cannot be completely avoided.

Alternatively, a parallel arrangement of catalytic reactors is possible, where anaerobic oxidative dehydrogenation would take place in one or more of the reactors while the rest undergo regeneration. Again, this was proposed for methane oxidative coupling[6] and also for the oxidative dehydrogenation of butane.[1] The main disadvantage in this case lies in the intrinsically unsteady catalytic behavior associated with anaerobic operation of fixed beds with a reducible catalyst. Steady-state operation with improved selectivity can be obtained if a low, but sufficient, oxygen concentration is maintained throughout the bed. This has been achieved by using ceramic membranes as oxygen distributors to a fixed bed of catalyst. While this does not avoid the existence of gas-phase oxygen, its concentration is reduced sufficiently so that the selectivity is significantly higher than that obtained in conventional fixed-bed reactors.[7−9]

Despite the above-discussed problems regarding the transfer of catalyst between reactor and regenerator, a fluidized-bed reactor loaded with a reducible catalyst under anaerobic conditions remains a very attractive system for oxidative dehydrogenation of butane. In addition to the higher selectivity that can be attained in the absence of gas-phase oxygen, such a system avoids in principle the formation of explosive mixtures and is ideally suited to dissipate the considerable heat evolved in the reaction. A way to circumvent the problems associated with the transfer of catalyst between reactor and regenerator would be to implement both functions in separate zones of the same reactor vessel. This could be achieved by using segregated feeds for the oxidant and the hydrocarbon in a fluidized-bed reactor. In this case, hydrocarbon oxidation would take place with lattice oxygen in the reduction zone (above the hydrocarbon inlet), and the oxygen-depleted catalyst would be regenerated by internal recirculation to the

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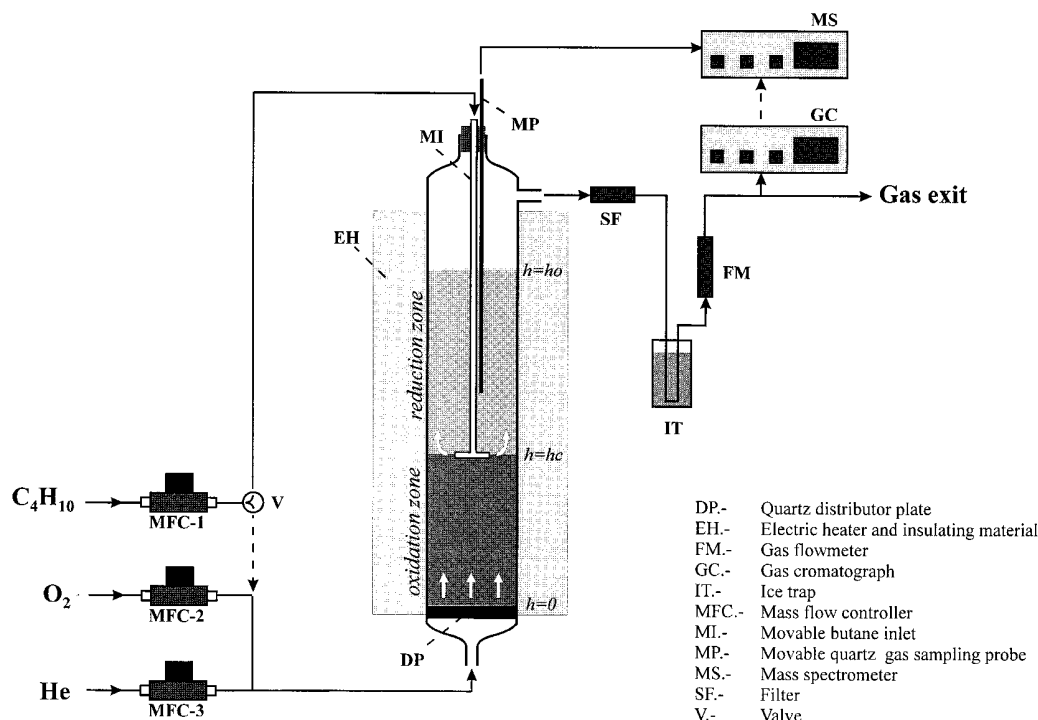‡ UPV−CSIC. E-mail: jmlopez@itq.upv.es. Fax: +34 96 387 78 09.

Figure 1. Experimental setup.

DP.-	Quartz distributor plate
EH.-	Electric heater and insulating material
FM.-	Gas flowmeter
GC.-	Gas cromatograph
IT.-	Ice trap
MFC.-	Mass flow controller
MI.-	Movable butane inlet
MP.-	Movable quartz gas sampling probe
MS.-	Mass spectrometer
SF.-	Filter
V.-	Valve

oxidation zone, at the bottom part of the reactor. When the operating conditions are chosen carefully, it should be possible to segregate reaction and regeneration zones to avoid the simultaneous presence of hydrocarbons and oxygen in the reaction atmosphere.

In the late 1970s researchers at Monsanto[10,11] proposed such a system for the oxidative coupling of toluene to stilbene. Some interesting reaction results were provided, but unfortunately the separation of reaction and regeneration zones was not studied, and no data were presented that could provide evidence of zone segregation. In a previous work at our laboratory,[12] a two-zone, redox fluidized-bed reactor was used for methane oxidative coupling using Li/Sn/MgO and Mn/P/Si catalysts. The reactor used was termed an in situ redox fluidized-bed reactor, where reaction and regeneration took place in the same vessel as opposed to having catalyst regeneration in a separate reactor (ex situ). While in that work the principle of zone segregation was demonstrated to a certain extent, complete separation of oxidation and reduction zones was not achieved and the yields obtained were under 13%. This was mainly due to the nature of the catalyst used, which presented a low redox capacity and also a low selectivity when fully oxidized. In a recent work,[13] some preliminary results were presented that indicated that, with a suitable catalytic system with sufficient redox capacity (oxidative dehydrogenation of butane over V/MgO catalysts), full segregation of oxidation and reduction zones could be achieved, and this would lead to a significantly higher yield to the desired products. In this work, an in-depth study of this system has been undertaken, with the aim of gaining insight into the behavior of the catalyst and into the main factors affecting reactor performance.

Experimental Section

Catalyst. The catalyst used was vanadium oxide supported on MgO. This was prepared by impregnation of MgO (obtained from the calcination of magnesium oxalate at 923 K for 3 h) with an aqueous ammonium metavanadate solution, according to a previously reported procedure.[2] The solid was dried at 343 K and 27 kPa and then kept at 283 K overnight. Finally, the sample was calcined in air at 873 K for 4 h. A BET surface area (N_2 adsorption using an ASAP 2000 apparatus) of 99.0 m^2 g^{-1} was obtained in the calcined sample. The initial fine powder was pressed into pellets and then crushed and sieved to the appropriate size. Chemical analysis of V and Mg by atomic absorption spectrometry showed a vanadium content of 20 wt % as V_2O_5.

X-ray diffraction patterns (XRD) were collected using a Phillips X'PertMPD diffractometer with a graphite monochromator, operating at 40 kV and 20 mA, employing Ni-filtered Cu Kα radiation ($\lambda = 0.1542$ nm).

Photoelectron spectra (XPS) were recorded on a UG-Escalab-210 electron spectrometer using Mg Kα radiation (Mg Kα = 1253.6 eV) in the constant analyzer energy mode, with a pass energy of 50 eV. To facilitate the analysis of the catalysts, 13-mm-diameter self-supporting wafers were prepared and fixed on a sample holder. Samples were outgassed at 373 K for 2 h in the preparation chamber. During analysis the pressure was maintained at 5×10^{-10} Torr. The binding energy (BE) scale was regulated by setting the C 1s transition at 284.9 eV. The accuracy of the BE was ±0.2 eV.

Diffuse reflectance (DR) spectra in the UV−visible region were collected with a Shimazdu UV-2010 PC spectrophotometer equipped with a reflectance attachment. Commercial V_2O_5 and NH_4VO_3 and specially prepared V samples supported on MgO were used as reference compounds.

Reaction System. Figure 1 presents the experimental system, showing with more detail the feed arrangement used in the fluidized-bed reactor. This was a 30-mm-i.d., 25-cm-length quartz fluidized-bed reactor, equipped with a quartz distributor plate. Two mobile

Table 1. Conditions Used in the Experimental Study

| variable	reference value	range studied
T(K)	823	823−873
u_r	1.5	1.05−2.5
P_h	4%	4−10%
R_{oh}	2	0.5−4.0
h_h (cm)	7	3−7

axial quartz probes were used respectively to introduce the hydrocarbon feed and to take samples of the reaction atmosphere at different reactor heights. At the bottom, a He/O_2 mixture was fed through the quartz distributor, while butane could be fed either premixed with He and O_2 (conventional fluidized-bed reactor) or through one of the quartz probes at a specified height (two-zone fluidized-bed reactor). All gas streams were mass-flow-controlled.

The reactor was heated by an external electrical furnace with a PID controller. Steady-state temperature profiles along the reactor were fairly homogeneous: The maximum temperature differences observed between any two reactor positions under reaction conditions were typically around 12 and 20 °C for the conventional and the two-zone fluidized-bed reactor, respectively. The higher temperature differences in the latter originated in the bottom (regeneration) part of the reactor, where the gas flow rate was lower with respect to the conventional fluidized-bed reactor.

The mobile sampling probe was connected to an on-line mass spectrometer (HIDEN HAL 2/201) to determine the evolution of the concentration of the different species along the reactor. This was essential to assess the extent of the oxidation and reduction zones in the reactor. On-line gas chromatography was employed to determine the product distribution at the reactor exit. Before entering the gas chromatograph (Varian 3400 with molecular sieve 5 A 45/60 and Chromosorb P AW 80/100 columns), the gases were passed through a glass wool filter to remove solid particles and then through a cold trap to remove water. The exit flow rate was then measured, which allowed the calculation of carbon mass balances, which were usually better than ±5% for the experiments reported in this work.

Preliminary tests in the absence of reaction were used to determine the fluidization characteristics of the catalyst used. Particle sizes below 100 μm showed cohesive behavior, with formation of channels through the bed, while good fluidization was obtained with the size range between 100 and 250 μm. The minimum fluidization velocity, u_{mf} (measured in He at 550 °C), was 1.2 cm/s. The relative velocity, u_r, defined as u/u_{mf}, was varied between 1.05 and 2.5. In this work, the gas velocity u was calculated as the ratio of the actual flows of He plus O_2 at the distributor plate (measured at the reaction temperature) to the cross-sectional area of the reactor. The typical catalyst load in the fluidized-bed reactor was 25 g, giving a total bed height of around 11 cm.

In addition to the bed temperature T and the relative velocity u_r, the main reactor-related variables investigated were the ratio of the molar feed rates of oxygen and hydrocarbon R_{oh}, the percentage of hydrocarbon in the reactor feed P_h (irrespective of whether a conventional or a two-zone fluidized bed was used), and the height at which the hydrocarbon was introduced, h_h. Table 1 shows the reference values used in the study for each of these variables.
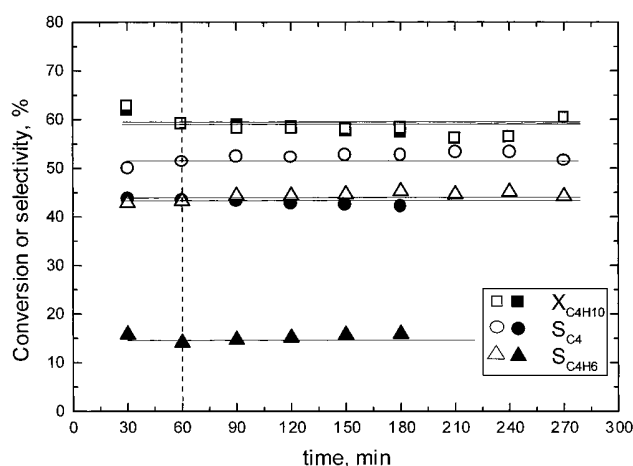
Figure 2. Evolution of conversion and selectivity with time for a cofeed (full symbols) and separate feeds (open symbols). For reference conditions, see Table 1.

Table 2. Oxidative Dehydrogenation of *n*-Butane under the Reference Conditions of Table 1[a]

|	mode of operation	
	cofeed	separate feeds
X_{C4H10}	57.3	58.1
X_{O2}	100.0	100.0
S_{C4H6}	16.3	44.4
S_{1-C4H6}	8.1	3.9
$S_{2-t-C4H6}$	10.2	2.0
$S_{2-c-C4H6}$	7.7	2.1
$S_{C4}[b]$	42.3	52.4
S_{CO}	8.7	10.6
S_{CO2}	44.1	34.8
$S_{COx}[c]$	52.8	45.4
$S_{others}[d]$	4.9	2.2

[a] Note: Conversion and selectivity were calculated as the average of data taken every 30 min, between 60 and 270 min on stream. [b] Selectivity to C_4 olefins (1-butene, 2-butenes, and butadiene). [c] Selectivity to CO and CO_2. [d] Selectivity to C_1, C_2, and C_3 hydrocarbons.

Results and Discussion

XRD patterns (not shown) indicated that both MgO and $Mg_3V_2O_8$ were present in the catalyst, before and after reaction. The sample crystallinity increased considerably after use, while the BET surface area decreased to 43.5 m^2 g^{-1}.

Figure 2 shows the evolution of butane conversion, butadiene selectivity, and total selectivity to C_4 dehydrogenation products (1-butene, 2-butenes, and butadiene) with time, both for cofeeding of butane and oxygen at the reactor entrance (conventional fluidized-bed reactor) and for separate feeds of butane and oxygen (two-zone fluidized-bed reactor). The experiment was run under the reference conditions given in Table 1, which correspond to an overall butane/oxygen/inert ratio of 4/8/88. It can be seen that, after approximately 60 min on stream, the exit compositions are constant for both configurations, which means that a dynamic equilibrium has been reached between oxidation and reduction of the catalyst in the different reactor zones. A detailed breakdown of the product distribution is presented in Table 2. Both Figure 2 and Table 2 indicate that the selectivity to dehydrogenation products is considerably higher in the separate feed mode, and this comes mainly from a much higher selectivity to butadiene (44.4 vs 16.3%). A higher selectivity implies a more effective use of oxygen, and because oxygen

Scheme 1. Possible Reaction Network for the Oxidative Dehydrogenation of *n*-Butane over V/MgO Catalyst (Adapted from Blasco et al.[2])
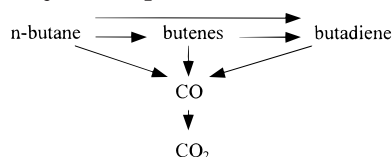
conversion is 100% in both reactors, this results in a somewhat higher butane conversion for the two-zone fluidized-bed reactor.

The higher selectivity to dehydrogenation products obtained in the separate feed mode and especially the enhanced formation of butadiene at the expense of butenes and carbon oxides seem to indicate that separation of the catalyst reduction and oxidation zones has been achieved. In this way, butane would react with oxygen from the catalyst lattice in the absence of gas-phase oxygen, which is expected to favor the consecutive reactions in the horizontal direction of the reaction scheme shown above, i.e., increasing butadiene formation and decreasing the production of carbon oxides (Scheme 1).

In addition, Table 2 shows that for the cofeed operation mode the distribution of butene isomers is close to the equilibrium ratio of 1-butene/*cis*-2-butene/*trans*-2-butene equal to 1/1/1.1, while in the separate feed mode the ratio shifts in the direction of the statistical distribution (3/1/1), which is the ratio expected when the first step in the process is the abstraction of a hydrogen atom by reaction with lattice oxygen to form a secondary butyl radical and a surface OH group. This is the mechanism proposed by Chaar et al.[14] for selective butane activation on V-based catalysts.

Separation of the Oxidation and Reduction Zones in the Reactor. A direct assessment of the separation of the oxidation and reduction zones in the separate feed mode was carried out by measuring the butane and oxygen axial concentration profiles in the reactor. To do this, steady-state operation was first established and then a mass spectrometer connected to the mobile quartz gas sampling probe was used to determine the variation of concentrations along the reactor, as shown in Figure 1. The results presented in Figure 3 concern different values of the oxygen-to-hydrocarbon ratio R_{oh}. The reference conditions just discussed correspond to Figure 3C. Under the conditions used in this work, the relative variations of the MS signals were very approximately equivalent to the relative variations of the concentration of the different species; this means that in the reference experiment gas-phase oxygen is totally consumed below the butane inlet, i.e., at $h < h_h$. Thus, above h_h the reaction takes place using mainly lattice oxygen (it is reasonable to assume that some adsorbed oxygen might be transported along with the catalyst). As could be expected, a neat separation of the oxidation and reduction zones is also obtained for higher butane-to-oxygen ratios (Figure 3A,B).

Characterization experiments were run separately in order to verify the occurrence of changes in the oxidation state of the catalyst that would correspond to a separation of the oxidation and reduction zones. After reaching steady-state conditions, the bed was suddenly defluidized (by shutting off all feed gases simultaneously) and allowed to cool under an inert atmosphere. Catalyst

samples were then taken under a He atmosphere at the top, bottom, and middle of the resulting fixed bed, with the latter sample roughly corresponding to the catalyst surrounding the hydrocarbon inlet. These samples were then analyzed using DR in the UV−visible region (Figure 4) and XPS (Figure 5). In the UV−visible region, the fresh catalyst exhibits a peak at 280 nm which indicates[15] the presence of isolated VO_4 tetrahedron with a high oxidation state, i.e., V^{5+}. After the catalytic test, the nature of V species was modified, depending on the height at which the catalyst sample was obtained. Thus, the appearance of new bands in the 500−800-nm interval indicates the presence of V^{4+} species whose intensities increase with height, from sample C-0 (bottom of the reactor) to sample C-6 (top of the reactor).

XPS data shown in Figure 5 are consistent with the above description. Thus, it can be seen that the intensity for the $V_{2p3/2}$ line (Figure 5A) shifts from 517.4 eV, in the case of sample C-0, to 516.7 eV for sample C-6. From these results it can be concluded that sample C-0 was completely reoxidized (note that the fresh catalyst presented a $V_{2p3/2}$ line at 517.0 eV), while the catalyst appeared increasingly reduced as we moved from reactor inlet to outlet. This was also confirmed from the analysis of the position of the O_{1s} line in the samples studied (Figure 5B): it can be observed that the O_{1s} line appears at 532 eV in sample C-0, and a new band at 530 eV is observed in samples with a lower oxidation state of the V species (see spectra of samples C-3 and C-6). It can therefore be concluded that, despite the strong mixing characteristic of fluidized-bed reactors, the results of catalyst characterization experiments show a progressive reduction of the catalyst in the vertical direction that agrees well with the separation of the oxidation and reduction zones and the concentration profiles observed in Figure 3A−C.

The separation of the oxidation and reduction zones becomes less clear as the oxygen-to-butane ratio increases, and in fact it was not obtained for molar ratios of 3 and above (Figure 3D,E). A delicate balance is required to obtain segregation of the oxidation and reduction zones: the reaction in the reduction zone extracts only a certain amount of lattice oxygen from the catalyst, which is then recirculated to the oxidation zone. If the oxygen input to this zone is higher than that required to replenish the catalyst lattice or if the residence time of the gas bubbles in this zone is not enough to transfer their oxygen content to the catalyst, then oxygen will not be completely consumed and mixing of butane and oxygen will occur in the reaction zone. It is clear that an increase of the oxygen-to-butane ratio in the reactor feed beyond a certain limit will cause oxygen bypass into the reduction zone. This limit depends on the catalytic system and specific operating conditions (temperature, fluidization velocity, and volumes of the oxidation and reduction zones) employed.

The mixing of butane and oxygen in the gas phase has an immediate effect on the reactor performance: Figure 6 compares the performance of the conventional and two-zone fluidized-bed reactors in terms of butadiene yield for different values of R_{oh}. While the two-zone fluidized-bed reactor outperforms the conventional reactor over the whole range explored, it can be seen that R_{oh} ratios of up to 2.0 are aligned around the +200% increase line; i.e., butadiene yields are 3 times those obtained with the conventional fluidized-bed reactor operating with the same feed. As the oxygen-to-butane
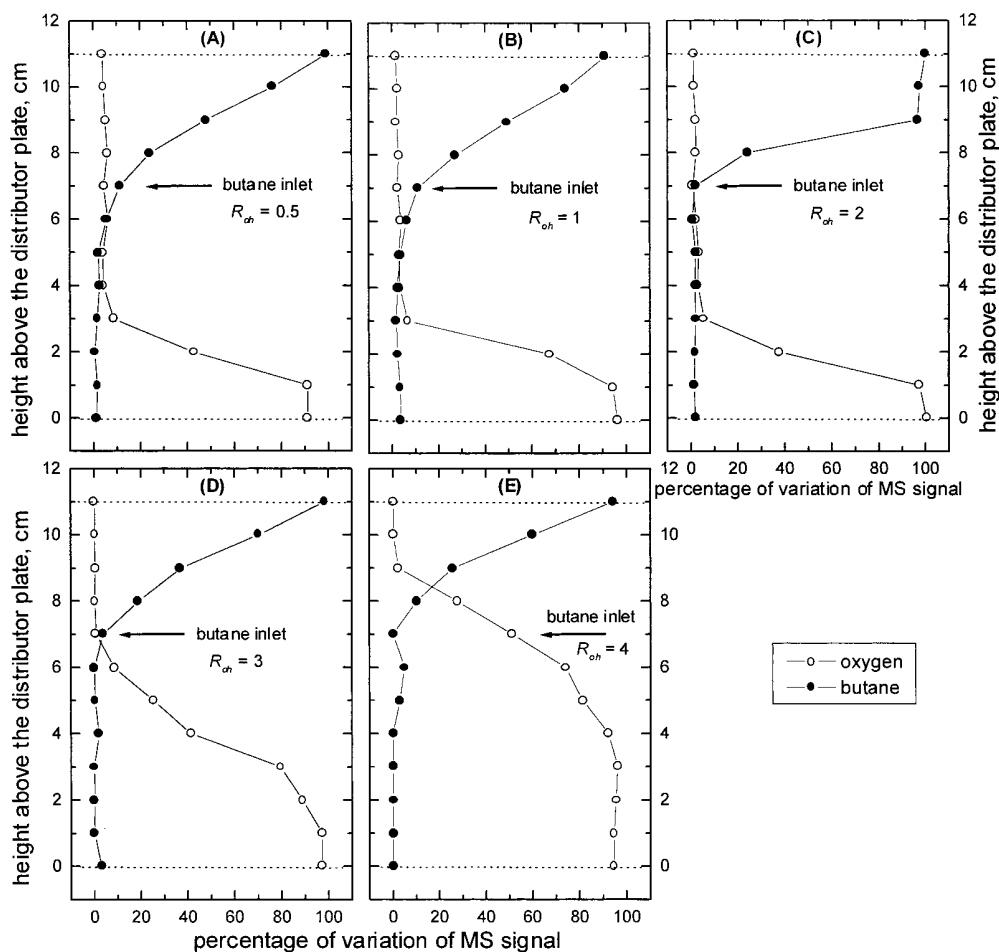
Figure 3. Variation of butane and oxygen concentrations with reactor height for different values of the C_4H_{10}/O_2/He molar ratio (indicated in the figure). Other experimental variables were set at their reference values given in Table 1.
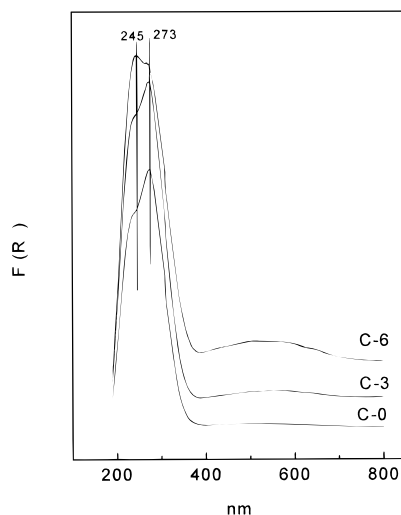

Figure 4. DR spectra in the UV–visible region of samples taken at different reactor heights: bottom (C-0), middle (C-3), and top of the reactor (C-6), after reaching steady state under a C_4H_{10}/O_2/He ratio of 4/4/92.

Figure 5. $V_{2p3/2}$ (A) and O_{1s} (B) XPS spectra of samples taken at different reactor heights: bottom (C-0), middle (C-3), and top of the reactor (C-6).

ratio increases from 0.5 to 2.0, so does the conversion, and the yield increases accordingly. A further increase to R_{oh} = 3.0 provokes a drop in selectivity that is not offset by the increase in conversion, and as a consequence the yield decreases slightly. With a further increase in R_{oh} to a value of 4, the decrease becomes
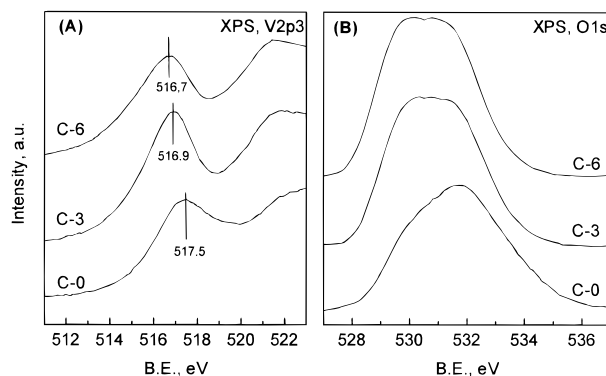
much more significant and the increase is now of only about 100%. This is clearly related to the gas-phase mixing of butane and oxygen that occurs at the higher values of the oxygen-to-hydrocarbon ratio, as shown in Figure 3E.

Butadiene is the most favored dehydrogenation product in the two-zone reactor, and thus a significant improvement is observed even at high values of R_{oh}. However, with total dehydrogenation products the two-zone reactor gives a better performance than the conventional reactor only up to R_{oh} values of 3. This is observed in Figure 7, a plot of the total selectivity to
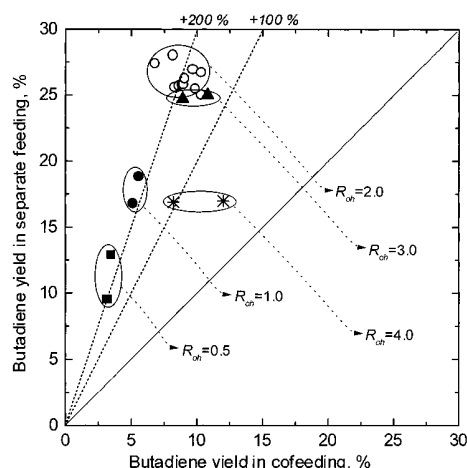
Figure 6. Comparison of the butadiene yield in the two-zone and conventional fluidized-bed reactors for different values of R_{oh}. Other variables are at their reference values.
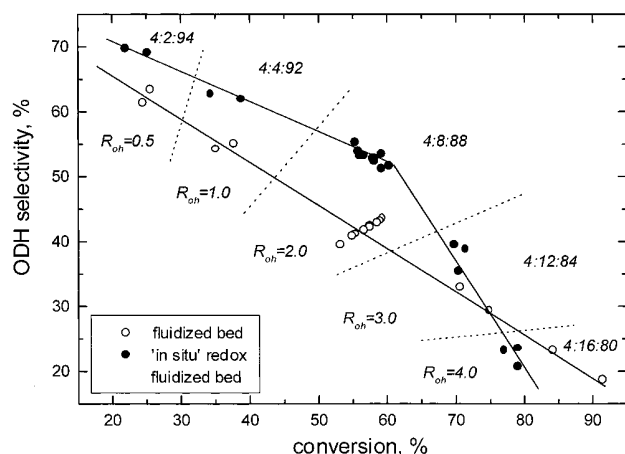

Figure 7. Selectivity−conversion plot for the conventional and two-zone fluidized-bed reactors. The data were gathered at different feed compositions, indicated in the figure as the $C_4H_{10}/O_2/$He molar ratio. Other variables are at their reference values. Note: selectivity includes all of the butene isomers and butadiene.

Figure 8. Butane conversion and butadiene selectivity for the two-zone fluidized bed as a function of u_r for different feed compositions, indicated in the figure as the $C_4H_{10}/O_2/$He molar ratio. Other variables are at their reference values.

dehydrogenation products versus butane conversion. It can be seen that the difference between the selectivity in the two-zone and conventional fluidized-bed reactors increases up to a R_{oh} value of 2 (at which point there still exists a clear segregation of oxidation and reduction zones), then decreases but continues to be higher when R_{oh} reaches a value of 3, and finally falls below the level of the conventional fluidized-bed reactor for R_{oh} values equal to 4. Therefore, the oxygen-to-hydrocarbon ratio is a key variable in the control of the segregation of the oxidation and reduction zones, and therefore of the reactor performance.

In addition to R_{oh}, other variables that could affect the separability of the oxidation and reduction zones are the height of introduction of the hydrocarbon feed, the operating temperature, and the fluidization velocity. Their effect has been investigated in specific experiments, which are described below.

Effect of the Height of the Hydrocarbon (Butane) Feed, h_h. The value of h_h was varied between 3 and 7 cm, as indicated in Table 1. Heights above 7 cm were not used in order to avoid a substantial reduction of the reaction zone volume. As could be expected, an experiment at $h_h = 0$ gave results similar to those of the conventional fluidized-bed reactor. The data gath-
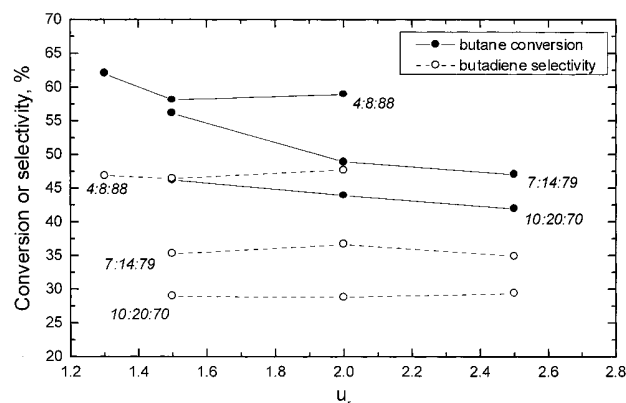
ered in experiments between 4 and 7 cm (not shown) gave the same conversion and selectivities as the reference experiment and a separation of the oxidation and reduction zones similar to that of Figure 3C. Only in the experiment at $h_h = 3$ cm a significant decrease of the selectivity was detected, which again was coincident with the overlapping of the oxidation and reduction zones. It can therefore be concluded that the reoxidation zone can be considerably smaller than the reaction zone for this process, which is in agreement with experimental observations indicating that catalyst reoxidation was considerably faster than catalyst reduction for this system.[13]

Effect of the Relative Velocity u_r and of the Concentration of Reactants. An increase of u_r has two main effects in fluidized-bed operation. On the one hand, it increases the solids recirculation rate by increasing the rising velocity of the wakes associated with bubbles. In this study, this would diminish the difference between the oxidation states of the catalyst in the reaction and regeneration zones. On the other hand, it also increases the amount of gas in the bubble phase, which retards the incorporation of oxygen into the emulsion phase, and may give rise to oxygen bypass into the reaction zone.

Figure 8 shows that, as expected, the increase in u_r decreases the butane conversion at the three feed compositions investigated. However, it is noticeable that the selectivity was maintained despite the increase in u_r. This means that the same separation of oxidation and reduction zones at a given feed composition was essentially maintained in the range of u_r investigated, which shows that the two-zone fluidized-bed reactor has enough flexibility to handle significant variations in the gas feed rate.

In fact, the concentration of reactants turned out to be a much more influential variable. Figure 8 shows that the conversion obtained decreased substantially as the concentrations of butane (P_h) and oxygen in the total reactor feed were increased. This shows that the catalyst mass in the upper part (reaction zone) of the reactor is insufficient to cope with an increase in the butane input, in contrast with the data obtained in the conventional fluidized-bed reactor (not shown), where all of the catalyst mass was available for reaction: in this case, the butane conversion increased with the reactant concentration. More important is the variation of selectivity observed in the two-zone fluidized-bed reactor
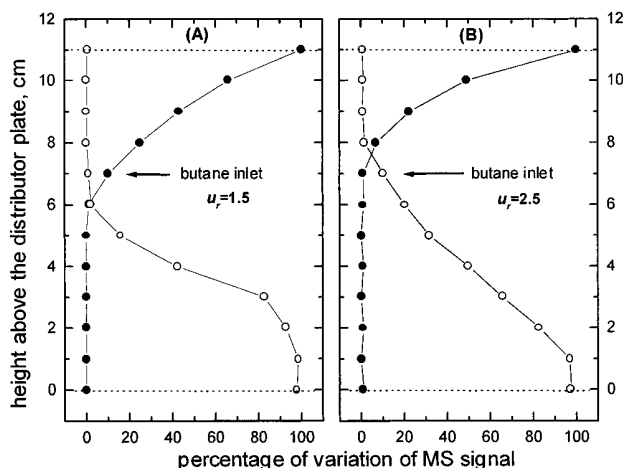
Figure 9. Variation of butane and oxygen concentrations with reactor height for two different values of u_r (indicated in the figure). The $C_4H_{10}/O_2/He$ molar ratio was 7/14/79. Other variables are at their reference values.

Figure 10. Variation of butane and oxygen concentrations with reactor height at 600 °C. Other conditions are as in Figure 9.

Figure 11. Butadiene yield (A) and CO_x yield (B) as a function of u_r for the conventional and two-zone fluidized-bed reactors, at two temperatures: 550 and 600 °C. Other variables are at their reference values.

(Figure 8): an increase in the concentrations of both reactants leads to a significant decrease of the butadiene selectivity (the selectivity to total C_4 products follows a very similar pattern). This clearly points out the overlapping of reaction and regeneration zones: an increase in the oxygen input to the reactor beyond a certain limit causes oxygen to bypass the regeneration zone and enter the reaction zone. This was confirmed by measuring the butane and oxygen concentration profiles. Figure 9 shows the results for a $C_4H_{10}/O_2/He$ ratio of 7/14/79, at two different values of u_r. It can be seen that at this concentration there is already incipient overlapping at $u_r = 1.5$ (Figure 9A), and this is not substantially changed by increasing u_r to 2.5 (Figure 9B), which is in agreement with the relatively constant selectivity obtained when varying u_r within the range studied. However, both parts A and B of Figure 9 show a much greater overlapping of the oxidation and reduction zones than Figure 3C, obtained at the same R_{oh} but with a lower reactant concentration. As can be seen in Figure 8, this resulted in a considerably higher selectivity.

Effect of Temperature. The exponential dependence of the reaction kinetics on the operating temperature means that a moderate increase of temperature is likely to increase considerably the reaction rate and, therefore, the usage of lattice oxygen in the upper part (reaction zone) of the reactor. In the same way, the mobility of lattice oxygen and the rate of catalyst reoxidation in the bottom part (regeneration zone) of the reactor will increase considerably.

Under a certain set of operating conditions, there is a limited amount of lattice oxygen that can be transferred to/from the catalyst during its residence time in the regeneration/reaction zones of the reactor; if the demand of oxygen transfer increases because of higher reactant concentrations, as we have shown overlapping of oxidation and reduction zones is likely. However, an increase in temperature may be able to accelerate the process to compensate the effects of increased reactant concentrations. This is shown in Figure 10, where the butane and oxygen profiles have been measured under the same conditions used in Figure 9, except that the temperature was 50 °C higher. This results in a neat separation of the oxidation and reduction zones, which were previously overlapping (compare to parts A and B
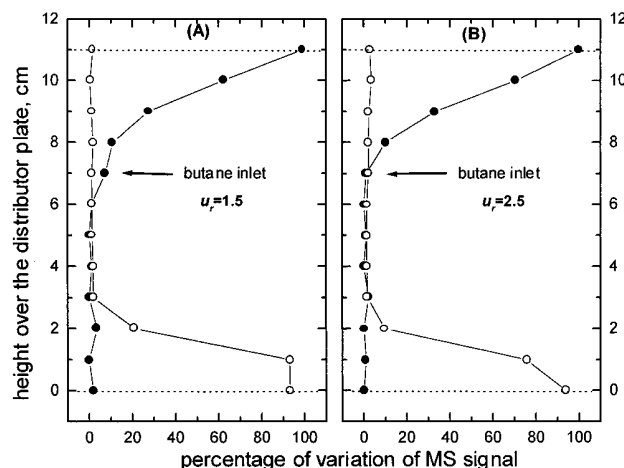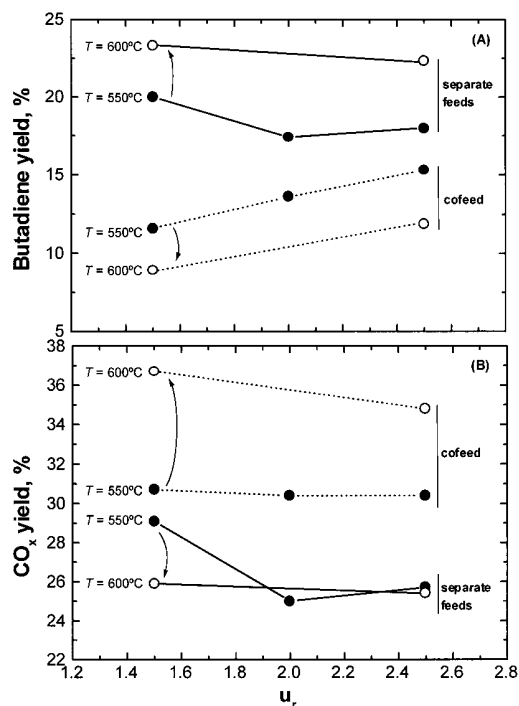
of Figure 9). The effect on reactor performance is clear: Figure 11 shows the butadiene and CO_x yields as a function of u_r at two different temperatures. Again, a small detrimental effect is observed for the two-zone (separate feed) reactor as the relative velocity u_r increases, but this is amply compensated by the increase in temperature. The opposite is true for the conventional fluidized-bed reactor, where the yield to butadiene decreases with temperature while the yield to carbon oxides increases.

Conclusions

The results presented in this work clearly show the potential of the two-zone fluidized-bed reactor to carry out selective oxidations that take place following a

Mars−van Krevelen type of mechanism; i.e., the reaction uses oxygen from the catalyst lattice, which is then regenerated by oxygen from the gas phase. In the reactor studied in this work, the oxidation and reduction zones were created in the same vessel by separating the oxygen and hydrocarbon feeds. Stable operation was obtained when the rates of oxygen transfer to (regeneration zone) and from (reaction zone) the catalyst were equal in the two zones.

Operation in the absence of gas-phase oxygen was effective to increase the selectivity. Thus, the two-zone reactor outperformed the conventional fluidized-bed reactor in terms of the yield to the desired products, especially butadiene, where yield increases of 200% over that of the conventional fluidized-bed reactor were reached. The key to the two-zone reactor performance lies in the complete separation of the oxidation and reduction zones. This can be achieved by acting upon a number of parameters such as the volumes of both zones, relative velocity, oxygen-to-hydrocarbon ratio, reactant concentration, and temperature.

The two-zone reactor is also useful to achieve a safer operation: Through segregation of the catalyst oxidation and reduction zones in the reactor, the formation of explosive mixtures in the gas phase can be avoided. Safeguards can be easily implemented to address a hypothetical situation in which zone segregation is not achieved: An oxygen probe below the hydrocarbon inlet could be used to detect any bypassing oxygen, and the signal from this probe would be interlocked to a hydrocarbon feed shutoff valve.

The applicability of the two-zone fluidized-bed reactor concept to a wider range of oxidation processes remains to be established. It will require catalysts which are reducible, fluidizable, and attrition-resistant as well as selective under anaerobic conditions and capable of sufficiently large rates of oxygen transfer. However, the potential advantages of two-zone fluidized beds are sufficiently important to justify further study of their application to other catalytic systems.

Literature Cited

(1) Vrieland, G. E.; Murchison, C. B. Anaerobic Oxidation of Butane to Butadiene over Magnesium Molybdate Catalysts. I. Magnesia Supported Catalysts. *Appl. Catal. A* **1996**, *134*, 101.

(2) Blasco, T.; López Nieto, J. M.; Dejoz, A.; Vázquez, M. I. Influence of the Acid−Base Character of Supported Vanadium Catalysts on their Catalytic Properties for the Oxidative Dehydrogenation of *n*-Butane. *J. Catal.* **1995**, *157*, 271.

(3) Callahan, J. L.; Grasselli, R. K.; Milberger, E. C.; Strecker, H. A. Oxidation and Ammoxidation of Propylene over Bismuth Molybdate Catalyst. *Ind. Eng. Chem. Prod. Res. Dev.* **1970**, *9* (2), 134.

(4) Jones, C. A.; Leonard, J. J.; Sofranko, J. A. Fuels for the Future: Remote Gas Conversion. *Energy Fuels* **1987**, *1*, 12.

(5) Contractor, R. M.; Garnett, D. I.; Horowitz, H. S.; Bergna, H. E.; Patience, G. S.; Schwartz, J. T.; Sisler, G. M. A New Commercial Scale Process for *n*-Butane Oxidation to Maleic Anhydride using a Circulating Fluidized Bed Reactor. *Stud. Surf. Sci. Catal.* **1994**, *82*, 233.

(6) Keller, G. E.; Bhasin, M. M. Synthesis of Ethylene via Oxidative Coupling of Methane. I. Determination of Active Catalysts. *J. Catal.* **1982**, *73*, 9.

(7) Coronas, J.; Menéndez, M.; Santamaría, J. Methane Oxidative Coupling Using Porous Ceramic Membrane Reactors−II. Reaction Studies. *Chem. Eng. Sci.* **1994**, *49*, 2015.

(8) Coronas, J.; Menéndez, M.; Santamaría, J. Development of Ceramic Membrane Reactors with a Non-Uniform Permeation Pattern. Aplication to Methane Oxidative Coupling. *Chem. Eng. Sci.* **1994**, *49*, 4749.

(9) Téllez, C.; Menéndez, M.; Santamaría, J. Oxidative Dehydrogenation of Butane Using Membrane Reactors. *AIChE J.* **1997**, *43*, 777.

(10) Montgomery, P. D.; Moore, R. N.; Knox, W. R. Production of Stilbene and Styrene. U.S. Patent 3,965,206, June 1976.

(11) Hupp, S. S.; Swift, H. E. Oxidative Coupling of Toluene to Stilbene. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18* (2), 117.

(12) Ramos, R.; Herguido, J.; Menéndez, M.; Santamaría, J. Oxidation of Hydrocarbons in an in situ Redox Fluidized Bed Reactor. *J. Catal.* **1996**, *163*, 218.

(13) Soler, J.; López Nieto, J. M.; Herguido, J.; Menéndez, M.; Santamaría, J. Oxidative Dehydrogenation of *n*-Butane on V/MgO Catalysts. Influence of the Type of Contactor. *Catal. Lett.* **1998**, *50*, 25.

(14) Chaar, M.; Patel, D.; Kung, M.; Kung, H. H. Selective Oxidative Dehydrogenation of Butane over V−Mg−O Catalyst. *J. Catal.* **1987**, *105*, 483.

(15) Corma, A.; López Nieto, J. M.; Paredes, N. Oxidative Dehydrogenation of Propane on Vanadium Supported on Magnesium Silicates. *Appl. Catal. A* **1993**, *97*, 159.