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Oxidative dehydrogenation of *n*-butane on V / MgO catalysts. Influence of the type of contactor

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A comparative study of the catalytic performance of a selective V–Mg–O catalyst in the oxidative dehydrogenation of *n*-butane is presented using three different types of reactor: (i) an adiabatic fixed-bed reactor; (ii) a fluidized-bed reactor; and (iii) an in situ redox fluidized-bed reactor. The results obtained indicate that the in situ redox fluidized-bed reactor outperforms the conventional fixed- and fluidized-bed reactors, especially at high *n*-butane conversions. Thus, a selectivity to C_4 olefins of 54% at *n*-butane conversions of 60% was achieved at 550°C using an in situ redox fluidized-bed reactor while selectivities to C_4-olefins lower than 43% were obtained on the other reactor types under the same reaction conditions (isoconversion and reaction temperature).

Keywords: oxidative dehydrogenation of *n*-butane, reactor selection, redox fluidized-bed reactor, vanadium magnesium mixed oxide catalyst

1. Introduction

The oxidative dehydrogenation of alkanes is an attractive route of utilizing short-chain paraffins and it can be considered as an alternative to catalytic dehydrogenation because 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 [1–6]. In order to make the process commercially feasible, the main objective is to maximize the selectivity to olefins, a significant issue since the deep oxidation of paraffins (reactant) and olefins (reaction products) is thermodynamically favoured. Although the presence of a selective catalyst, i.e. V–Mg–O based catalysts [2,7,8], can kinetically modify the selectivity to partial oxidation products, the yield achieved to date in oxidative dehydrogenation (OXDH) reactions is still low. This is mainly a consequence of the appearance of consecutive reactions (deep oxidation of olefins) of which the importance increases with the conversion of the reactant alkane [9].

In oxidative dehydrogenation processes, as occurs in partial oxidation reactions [5], the use of alternative reactors could help to obtain a higher selectivity. In this way, and although the bulk of the catalytic results on the OXDH of alkanes have been obtained using fixed-bed reactors, other reactor types, i.e. monolith-like reactors [10,11] and catalytic membranes [11–13], have been also proposed as alternative contactors. It seems clear that one of the possible procedures to increase the selectivity to oxydehydrogenation products could be to operate with little or no oxygen in the gas phase, in order to decrease the extension of deep oxidation. In fact, the above mentioned porous catalytic membranes [11–13] have been successfully used to operate with a decreased oxygen concentration in the gas phase. However, in order to avoid gas-phase oxygen completely, other types of reactor are required. One alternative would be to use redox reactors in cyclic operation. In this way, recirculation of reducible catalysts between a riser reactor and a fluidized-bed regenerator has been used for the selective oxidation of *n*-butane to maleic anhydride [14]. Recently, the use of an in situ redox fluidized-bed reactor for methane oxidative coupling has been reported [15], showing the feasibility of the in situ redox operation, i.e., avoiding external solid recirculation. In the present paper we compare the catalytic results obtained during the OXDH of *n*-butane on a V–Mg–O catalyst, using fluidized- or fixed-bed reactors. It will be demonstrated that the use of an in situ redox fluidized-bed reactor strongly increases both the selectivity and yield of C_4-olefins, especially to butadiene at high butane conversions.

2. Experimental

2.1. Catalyst preparation

MgO-supported vanadium oxide catalyst was prepared by impregnation of MgO (prepared by the calcination of magnesium oxalate at 923 K for 3 h) with an aqueous ammonium metavanadate solution, according to the previously reported procedure [8]. 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

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4 h. Chemical analysis of V and Mg by atomic absorption showed a vanadium content of 20 wt% of V_2O_5. A BET surface area of 99.0 $m^2\ g^{-1}$ was obtained in the calcined sample.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were collected in a Philips 1060 diffractometer, equipped with graphite monochromator, operating at 40 kV and 40 mA and using nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm).

The infrared spectra were recorded at room temperature on a Nicolet 710 FTIR spectrometer equipped with a Data Station. 20 mg of dried samples were mixed with 100 mg of dry KBr and pressed into a disk (600 kg cm^{-2}).

Diffuse reflectance (DR) spectra in the UV-Visible region were collected with a Shimadzu UV-2100 PC spectrophotometer equipped with a reflectance attachment.

Temperature-programmed reduction (TPR) results were obtained in a Micromeritics apparatus. Samples of 10 mg were first treated in argon at room temperature during 1 h. The samples were subsequently contacted with an H_2/Ar mixture (H_2/Ar molar ratio of 0.15 and a total flow of 50 ml min^{-1}) and heated, at a rate of 10 K min^{-1}, to a final temperature of 1173 K.

Catalyst reoxidation kinetic tests were carried out in a fixed-bed differential reactor (75 mg of catalyst), using samples previously reduced at 823 K under 50 Nml min^{-1} of a H_2/N_2 mixture, containing 10% H_2. Reoxidation was then carried out by shifting the feed to an O_2/N_2 gas stream with the same flowrate using a four-way valve. Different oxygen concentrations were used, and the oxygen signal at the reactor exit was continuously monitored using an on-line quadrupole mass spectrometer (HIDEN HAL 2/201) until a constant oxygen concentration was reached.

Catalyst reduction kinetic tests were carried out using a thermobalance (CI Electronics), on 150 mg samples. The procedure was analogous: The sample was oxidized for 15 min using a gas stream (11.7 Nml s^{-1}) containing 15% O_2 in N_2, followed by reduction under a H_2/N_2 stream with different partial pressures of hydrogen.

2.3. Catalytic tests

The catalytic tests were conducted at atmospheric pressure in the 773 to 823 K temperature interval. The feed consisted of *n*-butane, oxygen and helium in several molar ratios. Three different reactor types were used:

2.3.1. Conventional fixed-bed reactor

A continuous flow, stainless steel tubular reactor (i.d. 20 mm; length 520 mm) with a movable axial thermocouple, which was used for temperature profiling was loaded with 0.2 to 0.5 g of catalyst (particle size 0.3–0.5 mm), diluted with 8 g of Norton Silicon Carbide (particle size 0.5–0.75 mm) to obtain a constant volume in the catalyst bed. The flow rate of the reactants (100–600 ml min^{-1}) and the catalyst load were varied in order to achieve different contact times ($W/F = 2$–40 $g_{cat}\ h\ mol_{C_4}^{-1}$) and different *n*-butane conversion levels. However, in order to obtain catalytic results at high *n*-butane conversions a higher *n*-butane/O_2 ratio was used (*n*-butane, oxygen and helium in a molar ratio of 5/20/75).

2.3.2. Conventional fluidized-bed reactor

The reaction experiments were carried out in a 30 mm i.d., 25 cm long quartz fluidized-bed reactor equipped with a quartz distributor plate. The gases (*n*-butane, O_2 and helium) were cofed on the bottom of the reactor, in variable proportions. Approximately 25 g of catalyst were used, with a particle size between 100 and 250 μm giving a total bed height of 11 cm at minimum fluidization conditions (minimum fluidization velocity u_{mf} equal to 1.2 cm s^{-1}, measured in He at 823 K). The total gas flow rate was varied between 195 and 300 ml min^{-1} ($W/F = 840$–1350 $g_{cat}\ h\ mol_{C_4}^{-1}$).

2.3.3. In situ redox fluidized reactor

The reaction experiments were carried out in the same fluidized-bed reactor described above, using a different feed system. The reactor scheme is shown in figure 1.

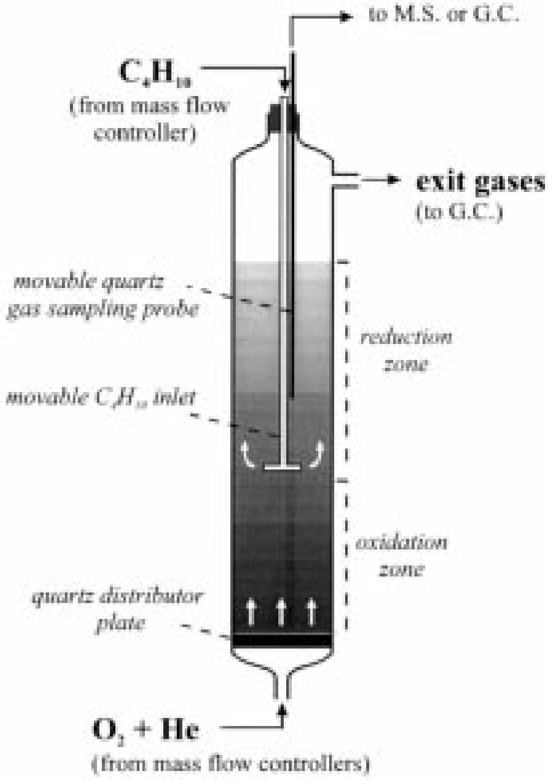


Figure 1. Schematic diagram of the in situ redox fluidized-bed reactor used.

Two axial quartz probes were used respectively to introduce the hydrocarbon feed and to take gas samples at different reactor heights. A He/O_2 mixture was fed through the quartz distributor, while n-butane entered through the two-outlet quartz probe at a specified height (7 cm for the experiments reported in this work). Both streams were mass flow controlled, and the conditions used regarding catalyst load, bed height and total flow rates were the same as in the conventional fluidized-bed reactor.

While the analysis of reactant and product streams in the fixed-bed reactor was carried out by gas chromatography [8], for both fluidized-bed reactors the analysis of reactants and products was conducted by on-line mass spectrometry (HIDEN HAL 2/201). On-line gas chromatography was sometimes used to check the concentration profiles of the different species obtained by mass spectrometry and total carbon balances in the reactor [15].

3. Results and discussion

The XRD pattern of the catalyst shows the presence of MgO ($2\theta = 42.97$ and 62.48; JCPDS 4-829), together with poorly crystalline Mg-orthovanadate, $Mg_3V_2O_8$, ($2\theta = 35.0$; JCPDS 19-779). These results are also confirmed by FTIR (presence of bands at 916, 860 and 690 cm^{-1}) and solid state ^{51}V NMR spectroscopy (with a main line at around -555 ppm) [8].

Diffuse reflectance spectra showed a strong band at 270 nm which is attributed to isolated VO_4 tetrahedron. In the case of tested samples, new bands in the 550–800 nm interval were observed the intensities of which depended on the n-butane conversions achieved as well as on the location of the sampling point in the reactor and the type of reactor used. These bands indicate the presence of V^{4+} species [9], which are formed during the reaction, and of which the amount depends on the oxygen concentration in the reactor, and therefore varies with location.

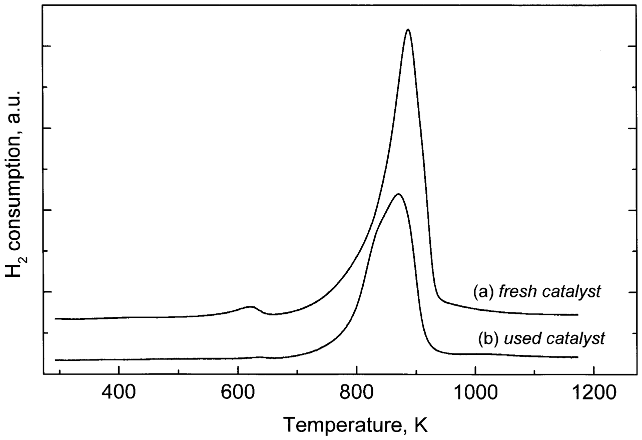


Figure 2. TPR patterns of the catalyst before (a) and after (b) the catalytic test.

TPR results of samples before and after the catalytic test are shown in figure 2. In the case of the fresh sample, the TPR pattern showed the presence of a small peak at 643 K and a second peak at 873 K. The H_2-consumption in both cases has been compared. In this way, H_2-consumption with the used sample was only 74.7% of that obtained with the fresh sample. Thus, it can be concluded that under the reaction conditions, the catalyst is partially reduced. However, vanadium species with an oxidation state lower than 4+ were not observed in the reduced catalyst.

On the other hand, figure 3 shows the evolution of

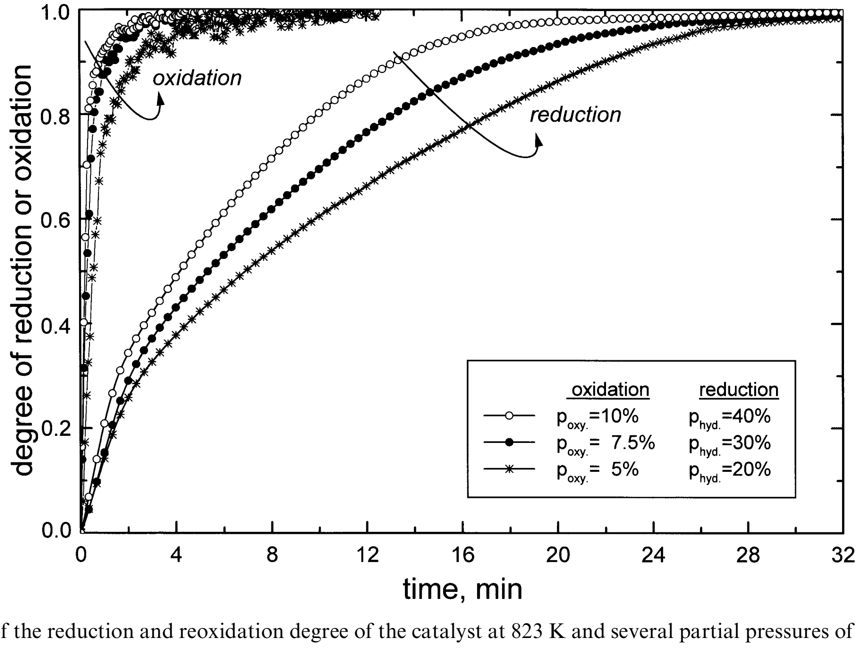


Figure 3. Variation of the reduction and reoxidation degree of the catalyst at 823 K and several partial pressures of hydrogen or oxygen, respectively.

the degree of reduction (or reoxidation) of the catalyst with time on stream at 823 K and several partial pressures of hydrogen or oxygen in the reduction and reoxidation experiments respectively. It can be seen that, even though the concentration of the reducing agent (hydrogen) was considerably higher than that of oxygen during the reoxidation runs, catalyst reoxidation was considerably faster than catalyst reduction for the range of conditions investigated. The differences are likely to be enhanced during the reaction experiments in the redox fluidized-bed reactor, where the catalyst is reduced under a butane-containing atmosphere, at butane concentrations of 4% or lower.

The catalytic properties of V–Mg–O catalyst during the OXDH of *n*-butane on the three types of reactors are compared in table 1. In all cases, C_4-olefins, CO and CO_2 were obtained. In addition to these, C_2 and C_3 hydrocarbons were observed at high conversions, during the oxidative dehydrogenation in the fixed-bed reactor while coke formation was noticed in the fluidized-bed reactor. However, coke formation and gasification processes (in oxygen-lean and oxygen-rich zones respectively) seem to reach an equilibrium, and the analysis of the catalyst after 4 h on stream shows a carbon content lower than 0.3 wt%.

Since the reaction conditions (especially the flow of reactant and the amount of catalyst) are very different, it is difficult to compare the catalytic activity of the catalyst on the three reactor types. However, it is interesting to compare the catalytic performance of the same catalyst on these reactors. Figure 4 shows the variation of the selectivity to oxydehydrogenation products (butenes and butadiene) with the conversion of *n*-butane for the three types of reactors studied. It can be seen that, as could be expected, the selectivity to OXDH products decreases with the conversion of *n*-butane for the three reactors although the decrease is more marked in both the conventional fluidized-bed and fixed-bed reactors. A considerably higher selectivity to OXDH products was obtained with the in situ redox fluidized-bed reactor throughout the conversion range investigated. Thus, in this case, a selectivity to OXDH products above 55% at an *n*-butane conversion of 60% was obtained. When comparing with previously reported catalysts (see for instance the results reviewed in refs. [1–6]), it can be seen that the catalytic results obtained with the in situ redox fluidized-bed reactor are certainly among the best obtained at high *n*-butane conversions.

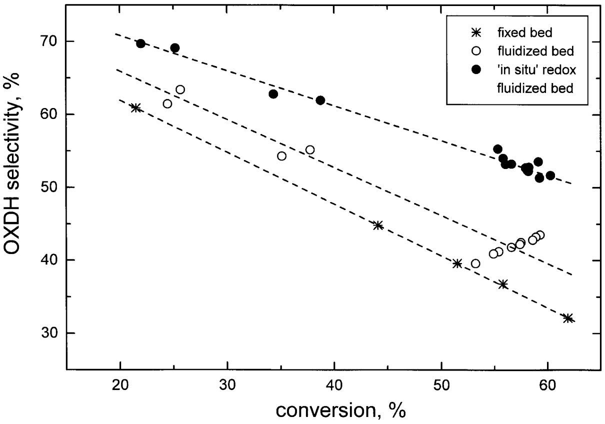
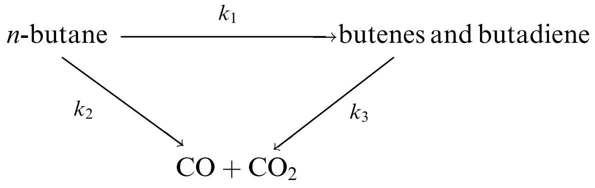


Figure 4. Variation of the selectivity to oxydehydrogenation products with *n*-butane conversion on the three reactor types studied at 823 K. Experimental conditions in text.

It is generally accepted that the OXDH of *n*-butane can be described by the following series-parallel network:



The catalytic results at high *n*-butane conversions in both fixed-bed and conventional fluidized-bed reactors can be explained by the consecutive reactions (deep oxidation of olefins and diolefins) which are favoured by the presence of molecular oxygen. However, a rather different 1-butene/2-butene/butadiene ratio was observed: 5.53/3.39/23.19 (fixed bed) and 8.83/19.74/14.65 (fluidized bed) (table 1).

In the case of the tests carried out in an in situ redox fluidized-bed reactor, a higher selectivity to oxydehydrogenation products at high *n*-butane conversions, is observed, with a high formation rate of butadiene (table 1). These results could be explained by a successful

Table 1
Conversion and selectivity to the main reaction products on the three reactor types

Reactor	Weight (g)	Total flow (ml s^{-1})	Conversion (%)	Selectivity (%)				
				1-butene	2-butene	butadiene	CO	CO_2
redox fluidized bed [a]	25.26	3.71	58.11	3.83	4.21	44.29	10.46	35.07
fluidized bed [a]	25.26	3.71	58.89	8.83	19.74	14.65	8.60	43.74
fixed bed [b]	0.40	3.33	61.92	5.53	3.39	23.19	16.99	49.91

[a] Molar ratio *n*-butane/oxygen/helium of 4/8/88; temperature of 823 K.
[b] Molar ratio *n*-butane/oxygen/helium of 5/20/75; temperature of 823 K.

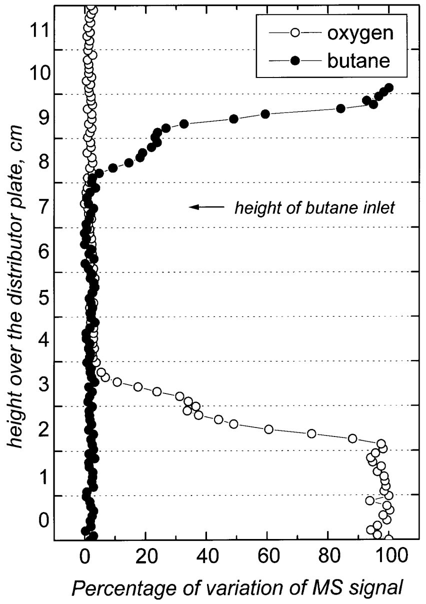


Figure 5. Variation of the relative concentrations of n-butane and oxygen along the bed in an in situ redox fluidized-bed reactor. Experimental conditions: $T = 823$ K, n-butane/oxygen/helium ratio $= 4/8/88$, total gas flow $= 3.71$ ml s^{-1} ($u = 1.5\ u_{\mathrm{mf}}$).

separation of the oxidation and reduction zones in the redox fluidized-bed reactor, which would avoid the simultaneous presence of gas phase oxygen and hydrocarbons in contact with the catalyst, thereby favouring the selective oxidation.

Figure 5 shows the concentration profiles of oxygen and butane along the redox fluidized-bed reactor. It can be seen that, under the reaction conditions indicated, the oxygen feed to the bottom of the fluidized-bed reactor is consumed before the height at which n-butane is introduced. This means that separation between molecular oxygen and hydrocarbons (n-butane and C_4-olefins) has been achieved, and therefore the consecutive reactions (step 3 in the reaction network) are minimized. However, the selectivity to butadiene was found to depend strongly on the O_2/n-butane ratio (figure 6). The best selectivity to butadiene was achieved with a n-butane/O_2 ratio of around 0.5 (figure 6).

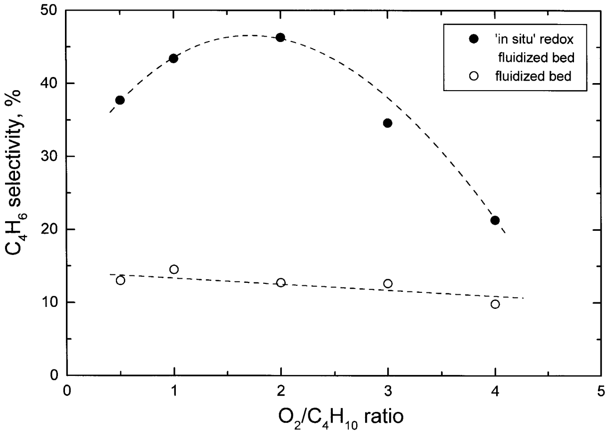


Figure 6. Variation of the selectivity to butadiene in conventional and redox fluidized-bed reactors with the n-butane/oxygen ratio at 823 K. Experimental conditions: n-butane partial pressure (overall) 4%, total gas flow $= 3.71$ ml s^{-1} ($u = 1.5\ u_{\mathrm{mf}}$), height of n-butane inlet = 7 cm.

Although from the results shown in figure 5 it can be concluded that a good separation between oxidation and reduction zones was achieved in the experimental conditions used, it is clear that the separation between oxidation and reduction zones depend on the reactions conditions, especially reaction temperature, gas velocity and n-butane/oxygen ratio [16]. This means that optimization of the reactor behaviour is possible, regarding not only the operating conditions, but also the geometry of the reactor, i.e. the ratio between the volumes of the reduction and reoxidation zones.

On the other hand, the results presented in figure 5 suggest that lattice oxygen of the catalyst must be mainly involved in the selective formation of olefins while molecular oxygen is involved in the reoxidation step. Thus, it can be concluded that lattice oxygen is the selective oxygen species in the ODH of n-butane in our reactions conditions in agreement with previous results in the literature [1–6]. The good performance of the redox fluidized-bed reactor stems from the physical separation of both processes, which for a given catalyst particle take place at a different time and location in the reactor. It has been suggested that the catalyst reoxidation process is very fast at temperatures over 723 K [18], which is in agreement with the results shown in figure 3, which confirm that the catalyst reoxidation is considerably higher than the reduction rate. This would lead to a longer residence time of the catalyst in the reaction/reduction zone.

Finally, the stability of the catalyst is an important point to consider in experiments carried out at long reaction times. In this way, an important reduction of the catalyst surface area was observed after 125 h, probably as a consequence of catalyst sintering processes. This effect must be considered in order to obtain a better long-term catalytic performance.

In conclusion, this paper presents a comparative study on the importance of the reactor type in oxydehydrogenation reactions, in order to optimize the selectivity to oxydehydrogenation products. From the results presented, it can be concluded that a good separation between the oxidation and reduction zones favours the attainment of high selectivities to olefins. In this way the in situ redox fluidized-bed reactor can be proposed as an promising alternative to conventional reactors. It is clear that the extent to which oxidation and reduction zones are separated is strongly affected by operating conditions [16,17]. Further kinetic and reactor engineering studies will be useful to optimize the catalytic performance shown in this work.

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