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Catalysis Today 100 (2005) 181–189
CATALYSIS TODAY
www.elsevier.com/locate/cattod

On the use of fluidized bed catalytic reactors where reduction and oxidation zones are present simultaneously

J. Herguido, M. Menéndez, J. Santamaría*

Department of Chemical Engineering, University of Zaragoza, Spain

Abstract

Fluidized bed reactors where separate oxidation and reduction zones are present in the same vessel have been developed in our laboratory and applied to different processes during the last decade. This type of reactors constitutes an alternative to the use of two different reactors or of a single reactor with periodic operation. The advantages of the dual-zone fluidized bed reactor have been proven in processes such as oxidative coupling of methane, oxidative dehydrogenation of hydrocarbons, butane oxidation to maleic anhydride or dehydrogenation of hydrocarbons with simultaneous catalyst regeneration in the same vessel. In this manuscript the advantages and limitations of this type of reactor are discussed.

Keywords: Fluidized bed; Oxidation; Hydrocarbons

1. Introduction

The usual procedure to carry out gas phase catalytic oxidations involves mixing a reactant with oxygen and perhaps other compounds such as inert diluents, and feeding the mixture to a fixed bed or fluidized bed catalytic reactor. However, other operating modes may be more advantageous in some cases, both regarding the conversion, and especially the selectivity that can be achieved. Among these operating modes are those in which the catalytic solid also acts as the vehicle for oxygen storage and supply. In this case, in a first step the solid reacts with the gaseous reactant, being reduced in the process, and is oxidized (regenerated) with an oxygen-containing gas mixture in a subsequent step. In a conventional reactor system, both steps may be carried sequentially in a single vessel, or simultaneously if two reactors are used and the solid catalyst is continuously transferred between them. Such is the case of the Dupont process for the oxidation of butane to maleic anhydride in a circulating fluidized bed reactor [1,2]. This is the only example of a process implemented at an industrial scale with circulation of the catalyst as an oxygen carrier, although the circulating fluidized bed reactor (CFBR) was also employed in a pilot plant developed by ARCO for oxidative coupling of methane. The separation of the oxidation and reduction processes was also proposed by Vrieland and Murchison [3] for the oxidative dehydrogenation of butane. These authors carried out laboratory-scale experiments of butane oxidation in the absence of gas phase oxygen by supplying oxygen from the catalyst lattice, which was reduced and had to be regenerated in a second stage. This separation in time of the reaction and the reoxidation of the catalyst was also employed in the seminal work of Keller and Bhasin on oxidative coupling of methane [4].

In a certain way, having the reaction (along with reduction and/or deactivation) and the catalyst regeneration in two separated steps is relatively well established. Thus, a fixed bed of catalyst deactivated by coke, is regenerated by combustion of the coke deposits in a second step, as it is done in the classical Houdry process for hydrocarbon dehydrogenation [5]. The continuous system, employing two fluidized bed reactors in a reactor–regenerator assembly, is the basis of the FCC (fluid bed catalytic cracking) units currently in operation, or of the Snamprogetti process for dehydrogenation of light alkanes [6].

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* Corresponding author.
E-mail address: iqcatal@posta.unizar.es (J. Santamaría).

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doi:10.1016/j.cattod.2004.11.004

The separation of the oxidation and reduction steps has several advantages:

(a) Improves the safety of the process, since the hydrocarbon is not mixed with gas phase oxygen, thereby avoiding the risk of explosion. This allows the feeding of hydrocarbons at higher concentrations, leading to improvements in the recovery of products (e.g. in butane oxidation with a CFBR the butane concentration may be higher than in a fixed bed, where butane concentrations above 2% will result in the formation of explosive mixtures).
(b) Often improves the selectivity, since non-selective reactions (both homogeneous and heterogeneous) related to gas phase oxygen are avoided.
(c) Allows a better control of the degree of oxidation of the catalyst, which often plays a critical role in the selectivity of partial oxidations (e.g. [7]).

The above-mentioned advantages are not exempt from some serious drawbacks. Thus, unsteady-state operation is generally considered not suitable for large-scale operation and thus, periodic redox operation of a single fixed bed reactor is avoided, in spite of its simplicity. In addition, the use of several fixed bed catalytic reactors would be required, in such way that one or more of them would be in operation, while others are being regenerated, or purged with an inert gas. On the other hand, while allowing steady-state operation, the circulation of large amounts of catalyst in the CFBR presents problems of its own, related to various aspects of solid flow. It is still a cumbersome process, in spite of the considerable expertise accumulated in control of the flow of solid catalysts with FCC units.

During the last decade, our group has been researching process alternatives to both, the CFBR and the unsteady-state operation of fixed bed reactors. The objective was to maintain the advantages of these systems, while employing a single vessel that could be continuously operated. To this end, we have developed two types of fluidized bed reactors that use separated oxygen and hydrocarbon feeds, namely the two zone fluidized bed reactor (TZFBR) and the internal circulating fluidized bed reactor (ICFBR). In this manuscript we review the characteristics and performance of these reactors in different applications, and discuss the advantages and prospects for future developments.

2. Description of the TZFBR and ICFBR

The scheme of the TZFBR is shown in Fig. 1. It consists of a fluidized bed where oxygen is fed to the lower part of the reactor, mixed with an inert gas, and the hydrocarbon (or in general the compound that should be oxidized) is fed in an intermediate point of the bed. In this way two zones are created in the reactor: in the lower zone the catalyst is re-oxidized by gas phase oxygen, a process that causes the gas stream to become depleted in oxygen. The oxygen concentration should be close to zero by the time the gas flow reaches the hydrocarbon entry point, so that hydrocarbon oxidation can take place in the absence of gas phase oxygen. In the upper zone, the hydrocarbon is oxidized using lattice oxygen from the catalyst, which becomes reduced. Reaction products, unconverted reactant and inert diluent leave together at the top of the bed. The good circulation of the solid, characteristic of the fluidized beds, provides transport of solid between both zones. This system is easy to build at laboratory scale, and has been employed for a variety of reactions, as will be described later.

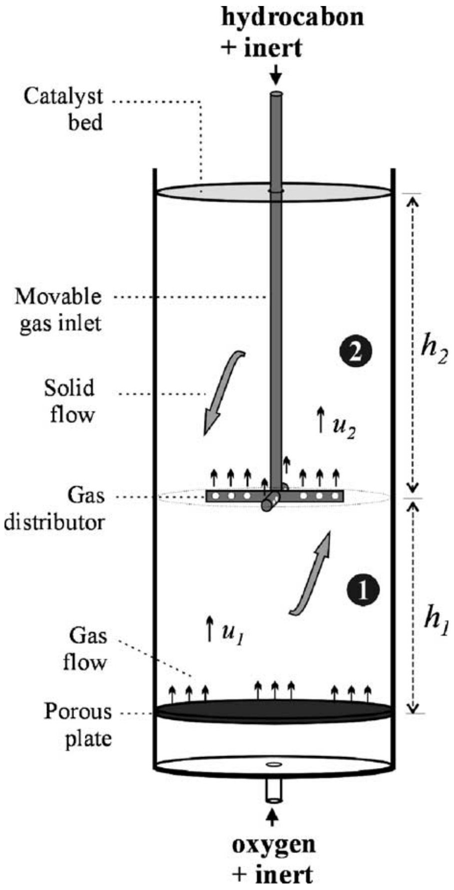

Fig. 1. Scheme of a two zone fluidized bed reactor (TZFBR). u_1 and u_2 denote the different gas velocities in different parts of the bed.

On the other hand, in reactions where the problem is the fast deactivation of the catalyst by coking, the TZFBR may be employed to implement continuous catalyst regeneration in the reactor. In this case the catalyst is not used as an oxygen carrier between oxidizing and reducing zones, but to transport the coke deposited in the reducing (hydrocarbon-rich) zone to the oxygen-rich zone, where coke is burnt. In this way a dynamic equilibrium between coke deposition and coke removal can be reached, and the decrease in conversion with time due to catalyst deactivation is avoided.

There are two critical issues regarding the operation of a TZFBR. On the one hand, the gas phase oxygen must be consumed in the lower part of the reactor (although in some cases it may be desirable to maintain a small oxygen concentration in the hydrocarbon-rich zone); on the other, the backmixing of gases must be avoided, especially of the hydrocarbon. In a fluidized bed backmixing of the gas takes place through a mechanism that is related with the mixing of solids. Thus, solid material forming the bubble wake is transported upwards with the bubbles; the same solid flow, but in the downward direction, exists in the emulsion phase that surrounds the bubbles. If the velocity of the solid moving downwards is larger than the minimum fluidization velocity (which is roughly the gas–solid velocity in the emulsion phase), then the solid in the emulsion phase draws gas downwards, and the undesired gas backmixing is produced.

This problem, that arises in certain operating regimes, prompted the development of an alternative system, aimed to obtain a better control of the solid flow and to avoid gas backmixing: the internal circulating fluidized bed reactor (ICFBR). In this system the solid flow is governed by a mechanism similar to that existing in the well-known airlift reactor employed in microbial fermentations. The reactor scheme is shown in Fig. 2. The reactor is divided in two zones by a vertical wall that allows transfer of solids between both zones through connections in the lower and upper parts of the bed. Because of the different gas velocity in each zone, a pressure gradient appears, causing solid flow between both parts of the bed. By changing the size of the connecting orifice, or the gas flow conditions in each reactor zone, the solid flow can be adjusted. In this way, the ICFBR allows the creation of two zones where a different atmosphere can be maintained, and provides catalyst transfer between them. The flow of solid in several versions of ICFBR has been studied in previous works [8–10]. This kind of reactor is widely employed for energy-related applications [11] and has been also proposed for continuous adsorption/desorption processes [12], however, its application in catalytic reactors with two zones has been described only recently [13].

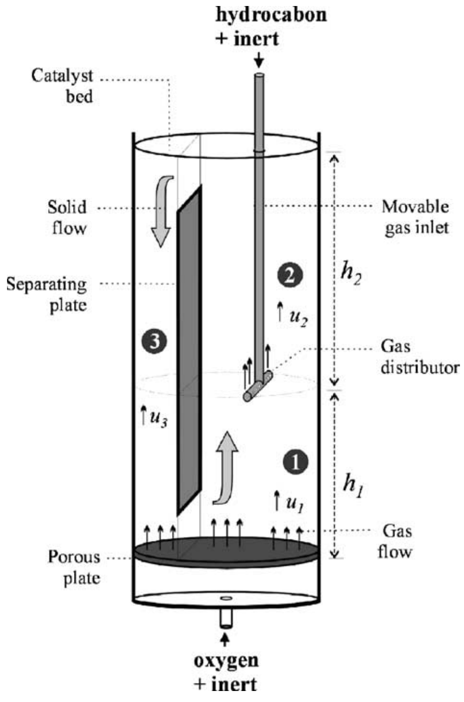

Fig. 2. Scheme of an internal circulating fluidized bed reactor (ICFBR). u_1, u_2 and u_3 denote the different gas velocities in different parts of the bed.

2.1. Safety aspects

In addition to the selectivity gains that may be obtained by running oxidations in the absence of gas phase oxygen, both the TZFBR and the ICFBR also offer the possibility of using higher hydrocarbon concentrations compared to a conventional reactor. Since the butane and oxygen feeds are segregated, it is possible to select the operating conditions to maintain the oxygen concentration in the reaction zone below the minimum value for explosion. In this way, the formation of explosive mixtures inside the reactor may be avoided, irrespective of the concentration of the hydrocarbon.

Nevertheless, there are failure modes that would cause safety problems if reactors were operated with higher hydrocarbon concentrations. Thus, a mismatch between oxygen supply in the reactor feed and consumption in zone 2 could cause oxygen breakthrough into the reaction zone, with the formation of explosive mixtures if concentrations above the safety level were reached. Such a situation could also arise if solid downflow in the ICFBR is plugged or if it does not flow as designed. It is clear that implementing any of the two reactors (TZFBR or ICFBR) industrially would require additional safety precautions (e.g. a continuous measurement of oxygen levels in the reaction zone interlocked to a hydrocarbon feed shutoff if dangerous levels are approached). However, it should be noticed that safeguards against a catastrophic failure of this kind must also be implemented in any conventional catalytic reactor dealing with gas phase oxidations at steady state. These reactors face similar problems (e.g. failure of the control loop regulating the hydrocarbon/air ratio), and therefore safety interlocks and explosion protection design are commonplace in industrial reactors. In this respect the ICFBR could offer an additional safety advantage compared to the TZFBR: in the ICFBR oxygen could be introduced independently using a separate inlet in zone 3, as done for the hydrocarbon in zone 2, while inert would still be fed at the bottom to maintain fluidization. This was not done in the laboratory reactor due to the obvious difficulties in introducing a supplementary inlet in a small diameter reactor, but should be readily implementable in a larger-scale vessel.

3. Applications of the TZFBR and the ICFBR

Both the TZFBR and the ICFBR have been applied in our laboratory to a variety of reactions belonging to two different groups: catalytic oxidations where the catalyst acts as an oxygen carrier, and dehydrogenation processes, where the catalyst becomes deactivated by coke in the reaction zone and is regenerated at the oxidizing zone. The main results in each of the processes studied are described next.

3.1. Oxidative coupling of methane

During the decade of 1980s and part of 1990s a large number of researchers were involved in the study of the catalytic oxidation of methane to obtain ethane and ethylene. The interest was high because any process capable of running this reaction with high selectivity at a reasonable cost would be enormously advantageous in the exploitation of large resources of natural gas which are available in remote locations. The selectivity problem in oxidative coupling of methane is severe because the products of the reaction (ethane, ethylene and higher hydrocarbons) are more reactive towards oxygen than the methane reactant. As a result, even with the best catalysts studied, a rapid drop of selectivity was observed with increasing conversion. This led to the use of alternative modes of contact, among these membrane reactors (e.g. [14]), polytropic reactors [15], and unconventional fluidized beds [16]. In this context, the use of a TZFBR was tested for the first time in oxidative coupling of methane [17]. The experiments were done using a quartz reactor with a diameter of 3 cm, where a helium–oxygen mixture was employed as fluidizing medium, and methane was injected in an intermediate point of the fluidized bed by means of a vertical tube. After some preliminary screening a Mn/P/Si catalyst was selected in view of its redox capability and fluidization properties. However, the catalytic properties of the Mn/P/Si catalyst were not suitable, and the selectivity was not significantly improved with the TZFBR compared with the conventional fluidized bed reactor. In spite of this, the experiments proved that the TZFBR concept was suitable to achieve stable operation with a low oxygen concentration in the reaction zone, using the oxygen transport capabilities of the catalyst. Fig. 3 shows the axial oxygen concentration profiles obtained in the reactor at different relative gas velocities ($u_r = u/u_{mf}$) and O_2/CH_4 ratios (R_{OH}). It may be seen that, when working at small values of u_r and R_{OH}, the oxygen fed at the bottom of the reactor can be consumed below the methane entry point (marked by a dashed line), thereby avoiding the simultaneous presence of oxygen and hydrocarbons in the gas phase.

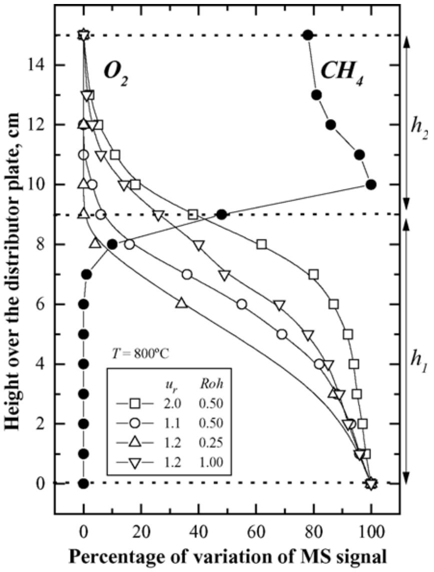

Fig. 3. Example of the axial concentration profiles obtained in the oxidative coupling of methane in a TZFBR.

3.2. Oxydative dehydrogenation of butane and propane

Once the feasibility of the TZFBR to carry out oxidations in the absence of gas phase oxygen had been established, it was applied to other processes and catalytic systems that could better benefit from the advantages of the TZFBR concept. The oxidative dehydrogenation of alkanes was an obvious target as an alternative route to olefins that avoided the main problems of conventional dehydrogenation processes, namely, the need of supplying heat at high temperature, the presence of catalyst deactivation by coking and the limitations on conversion imposed by thermodynamic equilibrium. The use of a catalyst as oxygen carrier for this reaction was suggested by Creaser et al. [18], although again their experiments were performed in a fixed bed reactor operating under oxidation–reduction cycles. In contrast, the TZFBR provided steady-state operation in oxidative dehydrogenation of butane using a conventional V/MgO catalyst prepared by impregnation. The results obtained were remarkable, with an overall increase of the selectivity to olefins and a substantial increase in the selectivity to butadiene (the most valuable product) whose yield was multiplied by a factor of up to 3 with respect to the fixed bed reactor (FBR) [19]. Some of the results obtained are given in Fig. 4, where the total selectivity to dehydrogenation products (including all the butene isomers and butadiene) is plotted as a function of butane conversion for a TZFBR and a conventional FBR. An increase in the yield to butadiene is very interesting from the process economics point of view, since butene is usually recirculated to the reactor to obtain butadiene, which is the preferred product. Thus, a large-scale process for styrene production, such as that envisaged by Creaser et al. [18], would require a previous step of butane dehydrogenation to butadiene; in this case, a substantial increase in the yield to butadiene per pass would result in extensive cost reductions.

The improvements just discussed were obtained in a small-scale laboratory reactor with an internal diameter of 3 cm. This raised some doubts on the extrapolation of the results to larger reactor sizes, since in the 3 cm reactor the gas flux could occur as slugs, giving a very different flow pattern compared to that existing in a conventional fluidized bed, with bubbles considerably smaller than the reactor

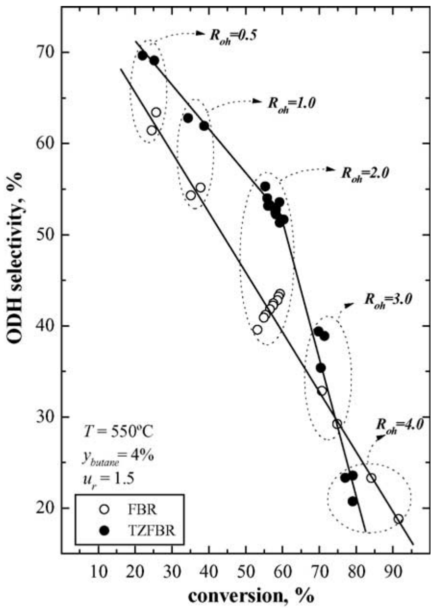

Fig. 4. Comparison of the selectivity–conversion plots for the oxidative dehydrogenation of butane carried out in a conventional FBR and in a TZFBR.

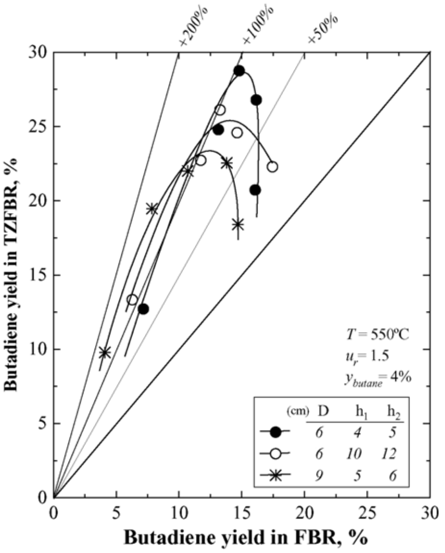

Fig. 5. Butadiene yield in the TZFBR (various reactor sizes) vs. that in a conventional FBR under comparable conditions. Data gathered at different R_{ob} ratios. For geometrical parameters h_1 and h_2 refer to Fig. 1.

diameter. Therefore, the experiments were repeated using larger fluidized bed reactors with internal diameters of 6 and 9 cm, respectively [20]. A substantial improvement in the yield to butadiene was again observed (see Fig. 5), thus confirming that the results in the 3 cm diameter reactor were not due to the existence of slugs.

It must be stressed that these improvements obtained in the TZBBR are not a universal feature; instead, they depend on the catalyst and the reacting system used. In particular, the catalyst must be stable under oxidation/reduction cycles, have a sufficient oxygen exchange capability, and perform selectively in the absence of gas phase oxygen. Thus, while the Mn/P/Si catalyst used for methane oxidative coupling presented a substantial oxygen exchange capability and was stable, its selectivity was low to moderate under reaction conditions, leading to modest hydrocarbon yields. Another example of an unsuitable system was the use of a Mo/MgO catalyst to carry out the oxidative dehydrogenation of butane in a TZFBR. In this case, a fast deactivation was observed, probably due to changes in the crystallinity with the successive reduction/oxidation steps [21]. On the other hand, when a V/MgO catalyst was used in the same process such deactivation was not observed, and the conversion was maintained for hundreds of hours of operation.

The TZFBR takes advantage of the fast mixing of solids that is an essential characteristic of fluidized beds: the solid rises in the wake of the bubbles and falls in the emulsion phase, providing a mechanism of transport of solid throughout the bed. However, there is an upper limit on the falling velocity of the solid in the emulsion phase. If the operating conditions are such that the solid falling velocity in the emulsion phase becomes larger than the minimum fluidization velocity, the gas surrounding the particles in the emulsion phase will be dragged down with them. In this case, hydrocarbons from the reaction (catalyst reduction) zone are drawn to the oxygen-rich zone and the improvements in selectivity and safety may be lost. To avoid this limitation, it would be useful to introduce further controls on the solid transport rate, something difficult to achieve in the TZFBR. Such control is possible with the internal circulating fluidized bed reactor (ICFBR). As shown in the scheme of Fig. 2, in the ICFBR a net upwards solid transport can be implemented in the reaction side, thereby avoiding the problem of hydrocarbon drag with falling solid. In addition, cold model experiments [13], indicated that much larger rates of solid circulation could be achieved in the ICFBR compared to the TZFBR, a very useful property in reactor scale up. Finally, as shown in Fig. 6 for oxidative dehydrogenation of butane, the selectivity–conversion pattern is similar for both, the TZFBR and the ICFBR for most of the conversion range explored, indicating that the ICFBR is capable of maintaining the good properties demonstrated by the TZFBR in relation to the separation of reaction and catalyst reoxidation zones.

3.3. Butane oxidation to maleic anhydride

The results obtained to date with different catalysts and technologies have not been able to produce the commercial implementation of oxidative dehydrogenation of alkanes. In contrast, the oxidation of butane to maleic anhydride is a successful selective oxidation process. It is therefore interesting to evaluate the performance of a TZFBR in the synthesis of maleic anhydride, because in this case rather than trying to exceed a hypothetical selectivity limit that would make the process viable, the results can be compared against those of a well established industrial operation.

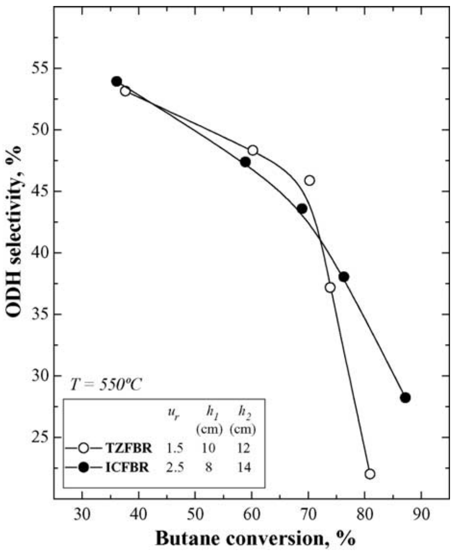

Fig. 6. Comparison of the selectivity–conversion plots for the oxidative dehydrogenation of butane carried out in a TZFBR and ICFBR.

It is worth noting that in the typical fixed bed reactor the maximum concentration of butane in the feed is around 1.5% in air, in order to avoid the formation of explosive mixtures. This concentration can be increased somewhat in a conventional fluidized bed reactor, and even more if a circulating fluidized bed is employed, as with the technology developed by Dupont [1,2]. In this case the solid (a vanadyl pyrophosphate catalyst) is employed to transport oxygen from the reactor where butane oxidation takes place using lattice oxygen (in a riser reactor), to the regenerator, where the reduced catalyst is regenerated with air.

In the TZFBR the separation of zones made it possible to use butane concentrations higher than those employed in fixed bed reactors [22], giving rise to a more concentrated product stream. On the other hand, higher oxygen concentrations could also be employed to increase butane conversion. Because of the particular characteristics of the catalyst used, the presence of some gas phase oxygen in the reaction zone of the bed was necessary to maintain the catalyst in a selective state. Otherwise, under a reducing atmosphere the VPO catalyst presents a poor selectivity to maleic anhydride [23,24]. This may impose some limitations for the use of the TZFBR, since the rate of catalyst circulation may not be enough to maintain a high average degree of oxidation of the catalyst in the reaction zone. In addition, the oxygen concentration in the reaction zone for the experiments in the TZFBR was kept below 15%, to avoid the formation of explosive mixtures. Fig. 7 compares the results obtained in the TZFBR with those previously reported in the literature for a variety of reactors, including fixed bed reactors operating under a high butane concentration, and reactors where the catalyst is being employed as oxygen storage media (pulse reactors and circulating

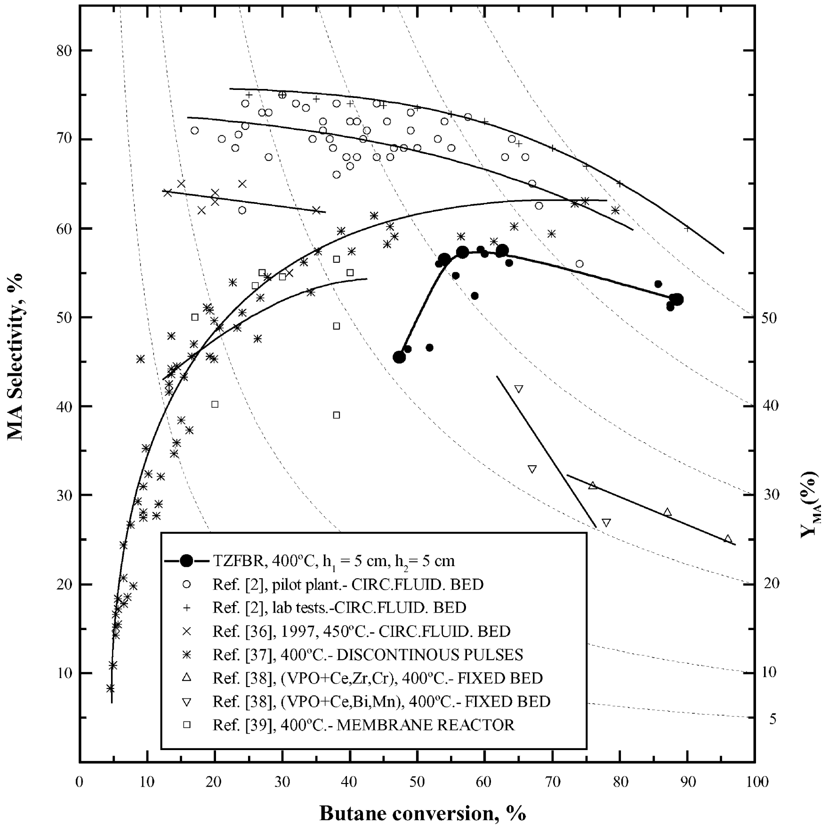

Fig. 7. Selectivity–conversion plots for the oxidation of butane to maleic anhydride in a TZFBR and in other reactors (fixed bed, pulse reactor and circulating fluidized bed). *Sources*: [2, 36–39].

fluidized bed reactors). Fig. 7 shows that the TZFBR outperforms the fixed bed reactor and the membrane reactor, and presents a selectivity–conversion behaviour approaching that of the pulse reactor. This is an interesting result, since the TZFBR allows continuous operation (not possible with the pulse reactor, that may be considered as a laboratory device) and otherwise avoids the need of using transfer lines between the reactor and regenerator, as in circulating fluidized bed systems.

3.4. Dehydrogenation of alkanes

Alkane dehydrogenations are carried out in industry using either fixed bed or circulating fluidized bed reactors. Even though the conversion is limited by thermodynamic equilibrium, this reaction is preferred over oxidative dehydrogenation processes because of the formation of carbon oxides in the latter. In any reactor, non-oxidative dehydrogenation processes have to face catalyst deactivation by coke. In the fixed bed reactor, operation is stopped when a given degree of deactivation is reached, and the catalyst is regenerated while other beds are kept in operation. In circulating fluidized bed systems the catalyst is being continuously circulated between the reactor and the regenerator. Again, a system that provides separate reduction and regeneration zones in the same vessel and continuous circulation of catalyst between them, may present attractive advantages over the existing technologies. The TZFBR has been tested in the dehydrogenation of propane and butane, using conventional Cr_2O_3/Al_2O_3 catalyst [25,26]. In both cases a stable operation was achieved, with a good separation of the oxidation and reduction zones (Fig. 8), and an oxygen concentration close to zero at the hydrocarbon feed point. For this reaction the ICFBR can also be employed, with a selectivity–conversion behaviour that is similar to that of the TZFBR, as can be seen in Fig. 9. It is worth noting that the secondary products were mainly methane and ethylene, and only a small percentage of propane was converted to carbon oxides.

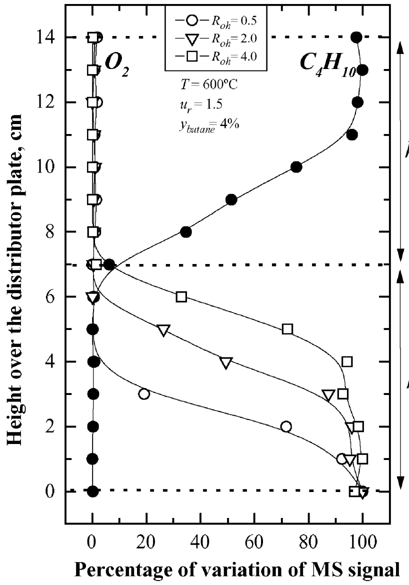

Fig. 8. Oxygen concentration profiles in a TZFBR with butane dehydrogenation in the upper zone and continuous regeneration by coke combustion in the lower zone.

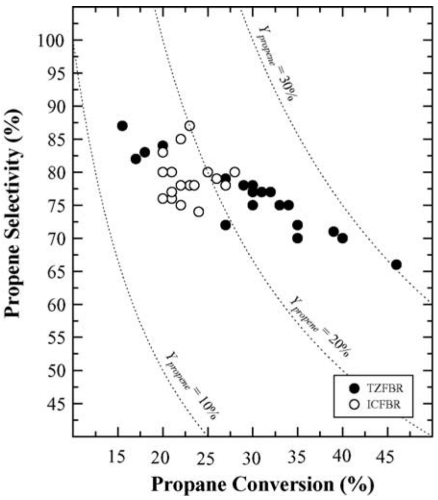

Fig. 9. Selectivity as a function of conversion for the dehydrogenation of propane in the TZFBR and ICFBR.

The production of propene from propane is an interesting challenge. Today, most of the propene is being obtained jointly with ethene by thermal cracking. However, the propene demand is raising faster than that of ethene, and the unbalance is being adjusted by building new plants for propane dehydrogenation [27]. As we have shown, a TZFBR can be used to obtain propene by oxidative dehydrogenation of propane, using oxygen from the catalyst lattice, or by non-oxidative dehydrogenation. The main difference lies in the fact that in the latter case lattice oxygen is not involved, and a high oxygen exchange capability is not needed. Since oxygen is not a reactant in the dehydrogenation process, but is only being employed to regenerate the catalyst by combustion of the coke formed in the upper part of the bed, only a modest supply of oxygen is needed. The results obtained showed that around 2% of oxygen in the reactor feed was sufficient to maintain a stable catalytic activity, by balancing coke formation in the reaction zone and coke combustion in the regeneration zone. In some cases (a very active catalyst or a high temperature) the rate of coke production increases, and a higher rate of oxygen supply may be needed. However, if too much oxygen is fed, some of it will break through into the upper part of the bed, where it will react with hydrocarbons (the Cr_2O_3/Al_2O_3 catalyst is also a good combustion catalyst), decreasing the selectivity.

4. Mathematical model of the reactor

The TZFBR is a complex system, where the interplay between reaction processes and fluid dynamics complicates the understanding of the effect of operating conditions on reactor performance. While the analysis of the axial concentration profiles of reactants and products provides useful insight on the mechanisms acting in the reactor, a mathematical model that takes into account the reaction kinetics and the gas and solid flows is needed for a fuller understanding of reactor behaviour. A reliable model is also needed for any serious attempt addressed to reactor optimization or scale up.

Since a given particle of catalyst is not under a fixed reaction environment and some of its properties are changing with time (e.g. the oxidation degree or the coke content), the usual kinetic models are not suitable, and new models capable of describing catalyst behaviour under transient conditions are needed. This is a common need of many advanced reactor systems, such as flow-reversal reactors or circulating fluidized bed reactors, and some of those kinetic models have been presented in the literature (e.g. [28]). Kinetic models must be obtained on an ad hoc basis, taking into account the particular characteristics of the system involved. Thus, we have developed kinetic models for the oxidative dehydrogenation of butane over V/MgO that incorporate the effect of changes in the degree of oxidation of the catalyst on the selectivity [29], or the influence of doping with other metals [30]. A kinetic model of propane dehydrogenation on Cr_2O_3/Al_2O_3 that takes into account the changes in the catalyst activity with time and the formation of coke has also been described [31].

In addition to catalytic kinetics, the reactor model must account for the gas and solid flows taking place in the system. Most conventional reactor models only need to consider the gas flow, since each catalyst particle is under a constant reaction environment. However, in the TZFBR the solid flow matters, as it determines the oxidation state of the catalyst. The reaction kinetics depends on the oxidation state of the catalyst, which in turn depends on the flow of the solid between the oxidizing and reducing zones. A first version of the model for a TZFBR [32] was presented for the oxidative dehydrogenation of butane, and was later adapted for application in the ICFBR [13], including transport of solid between both zones and improvements in the mathematical method of solution, among other changes. A detailed description of the model is beyond the scope of this work, and only a brief description will be given here. The model of the TZFBR takes into account the classical assumptions of the Kunii–Levenspiel model for the gas flow pattern [33]. It consider two phases, namely the emulsion and the bubble phase, in such a way that the gas rising in the bubbles passes through the bed with only a limited interaction (exchange) with the emulsion phase. The calculation of the gas exchange coefficients between the emulsion and the bubble phase has been described in the literature [34]. The second factor that must be considered is the solid flow in the bed. The solids rise in the bubble wake, and some exchange with the surrounding solids in the emulsion phase is allowed [35]. The mathematical model based in the above description of the gas and solid flows, coupled with the appropriate kinetics for reaction and catalyst reoxidation was able to predict satisfactorily the performance of the TZFBR. For the ICFBR the model must also include the flow of solid between the oxidizing and reducing regions of the bed, caused by the pressure gradient existing at the bottom of the reactor (see Fig. 2), which in turn is related to the different pressure drop of the gas rising in the two parts of the bed [13].

5. Conclusions

The TZFBR, with separate oxidation and reduction zones in the same vessel, is useful to carry out catalytic oxidations when these take place selectively using oxygen from the catalyst lattice. The main advantage of this kind of reactor is the possibility of operating continuously in the absence of gas phase oxygen in the zone where the hydrocarbon is reacting. This may generate selectivity increases in many reacting systems and can be a useful way to improve safety by avoiding the premixing of hydrocarbons and oxygen. The ICFBR constitutes a modified version of the TZFBR where the solid flow between the two zones is controlled by the difference of porosity (and thus pressure drop) between them. This allows a better tuning of the oxidation degree of the catalyst and provides higher solid circulation rates. Also, in the ICFBR the introduction of additional gas streams can be contemplated, with the aim of regulating the solid flow or of modifying the local atmosphere. This aspect remains to be explored in future work.

In summary, the TZFBR and the ICFBR provide the reaction engineer and the catalyst scientist with new opportunities in reactor design. Given the good results obtained in demanding applications (such as the selective oxidations and the simultaneous dehydrogenation/regeneration processes discussed in this work), it may be expected that the two-zone concept will also be applied to other reaction systems.

Acknowledgement

Financial support from MEC, Spain is gratefully acknowledged.

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