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

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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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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

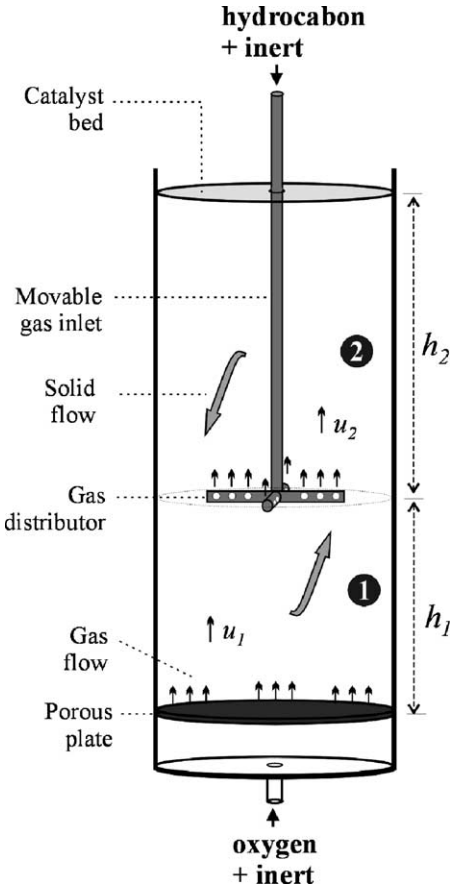

Fig. 1. Scheme of a two zone fluidized bed reactor (TZFBR). u_1 and u_2 denote the different gas velocities in different parts of the bed.

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.

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