

# Oxidative Dehydrogenation of n-butane and butenes to 1,3-butadiene over Mo-V and Mo-Bi based catalysts in a Two-Zone Fluidized Bed Reactor

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## Abstract

The oxidative dehydrogenation of n-butane and butenes has been studied in a two-zone fluidized bed reactor using Mo-V-MgO and Bi-Mo-MgO catalysts. All catalysts have been prepared by incipient wetness impregnation. The operating conditions temperature, flow velocity, hydrocarbon inlet height and oxygen/hydrocarbon molar ratio were varied to maximize 1,3-butadiene yield. At suitable conditions, the two-zone fluidized bed reactor can be operated at steady state performing chemical conversion and catalyst regeneration in a single vessel. Axial concentration profiles in the fluidized bed prove that the regeneration zone at the bottom of the fluidized bed was used to burn coke depositions as well as to fill up lattice oxygen of the catalyst. The efficient usage of the oxygen leads to high 1,3-butadiene selectivity.

## Keywords

Oxidative Dehydrogenation, 1,3-butadiene, n-butane, Two-Zone Fluidized Bed Reactor

## Introduction

Butenes and 1,3-butadiene are important building-block chemicals. 1,3-butadiene is for instance a necessary monomer for the synthetic rubber production. At the moment, steam crackers are the main production facilities for 1,3-butadiene. Naphtha as feedstock needs to be used to produce sufficient amounts of 1,3-butadiene. Due to the high supply of natural gas, especially in the United States, many steam crackers were reconstructed in order to use light olefins as feedstock. On the one hand, ethylene production increases but on the other hand 1,3-butadiene production decreases significantly. However, the global consumption of 1,3-butadiene is predicted to increase over the next years. A combination of all these factors may lead both to higher 1,3-butadiene prices and to 1,3-butadiene shortages. Thus

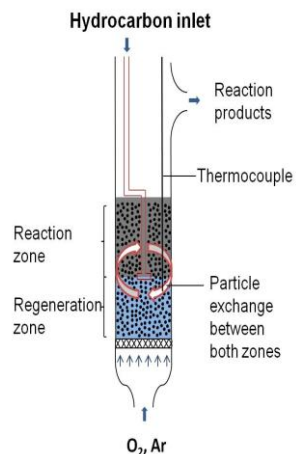


Figure 1. Sketch of a TZFBR.

alternative capabilities to produce 1,3-butadiene become more and more attractive. There are two different paths from n-butane and butenes towards 1,3-butadiene. The first one is the dehydrogenation (DH) and the second one is the oxidative dehydrogenation (ODH). A promising reactor setup for ODH as well as DH is the two-zone fluidized bed reactor (TZFBR, Fig.1), in which catalyst regeneration and reaction take place in one vessel due to two different zones in the fluidized bed [1,2]. In case of the ODH of n-butane, lattice oxygen is filled up in the regeneration zone and used in the reaction zone leading to an efficient usage of the oxygen.

## Experimental

MgO with 5 wt% graphite was pressed into pellets and crushed and sieved to a particle size of 160-250  $\mu\text{m}$ . Afterwards the particles were impregnated with a solution containing V and Mo ions, dried, and sieved again. Furthermore, different Bi-Mo catalysts were synthesised by co-precipitation. These catalysts were tested in a TZFBR consisting of a quartz glass tube with a frit to hold back the particles (Fig 1). The reaction gases were cooled and analyzed with an online GC. All experiments were performed at  $p = 1$  bar and with a fluidized bed height of

around 9 cm. The ODH of n-butane, of a mixture of trans-butene and 1-butene (50 vol% of both) and of a mixture representing a C4R2 cut of a steam cracker (25 vol% n-butane, 30 vol% trans- and cis-butene and 15 vol% 1-butene) were carried out in the TZFBR. Various reaction parameters such as hydrocarbon inlet height (0 cm to complete fluidized bed height), temperature (350-600 °C), flow velocity (0.5-1 cm/s, for total flow of 200-400 Nml/min), and oxygen/hydrocarbon molar ratio (1:1-3:1) were varied and their impact on the product distribution investigated.

## Results and discussion

Concentration profiles along the axial direction of the fluidized bed were collected with a vertically movable probe. The heights of reaction and regeneration zone were adjusted by varying the n-butane inlet height (Fig. 2). Selectivity towards 1,3-butadiene is very sensitive in relation to this parameter. Depending on the operating conditions, the V-Mo catalyst may be deactivated due to coke deposition and due to catalyst reduction.

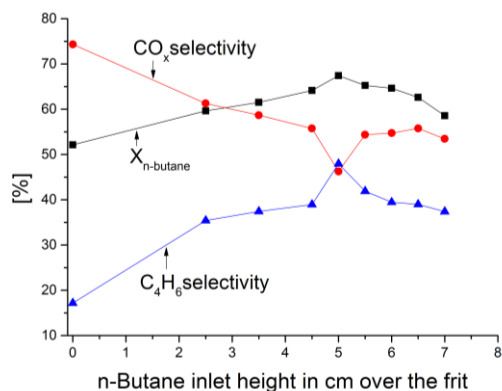


Figure 2. n-butane conversion and selectivity to CO<sub>x</sub> and 1,3-butadiene as function of the n-butane inlet height.

Both problems can be avoided under optimized conditions and 1,3-butadiene can be produced out of n-butane with a selectivity of over 50 % at a yield of over 32.5 % at steady state [1]. Concentration profiles along the axial direction show that oxygen is consumed in the regeneration zone for the chosen parameters. Besides, carbon oxides were detected in the regeneration zone, which likely were produced by burning coke deposited on the catalyst. However, the oxygen consumption was too high for being explained by the small carbon oxide amounts. Thus, oxidation of coke as well as filling up of the lattice oxygen was taking place in the regeneration zone (Fig. 3). 1,3-butadiene was produced in the reaction zone in the absence of gas-phase oxygen, which points to lattice oxygen as

reactive species for the ODH of n-butane.

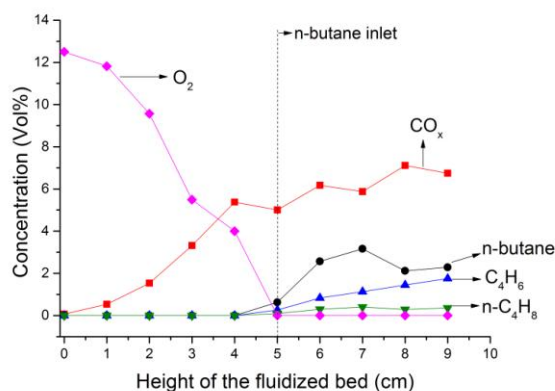


Figure 3. Axial concentration profile in the fluidized bed. (Mo-V-MgO catalyst).

Comparable axial concentration profiles were observed using the 1-butene/trans-butene mixture and the mixture representing the C4R2 cut of a steam cracker. However, different optimized conditions were found for these mixtures compared to n-butane. Especially the necessary contact time for the oxidative dehydrogenation of butenes is significantly lower compared to the one for ODH of n-butane. For this reason, the optimized inlet height for butenes is higher than for n-butane.

## Conclusion

The used Mo-V-MgO based catalyst is suitable for the oxidative dehydrogenation (ODH) of n-butane, butenes, and mixtures containing n-butane and butenes in a two-zone fluidized bed reactor (TZFBR) with a regeneration and a reaction zone, efficiently using the oxygen. Thorough variation of the operating conditions led to optimized conditions for a maximized 1,3-butadiene yield and selectivity. The oxygen coming from the bottom is used in the regeneration zone for filling up lattice oxygen as well as burning coke depositions. The TZFB technology in combination with the highly active catalyst may offer an interesting alternative route for the production of 1,3-butadiene from n-butane or butane/butene mixtures.

## Acknowledgment

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## References

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