

NEW DATA ABOUT A WELL KNOWN HOUDRY® PROCESS PARAFFIN DEHYDROGENATION

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Introduction

The Houdry® process of paraffin dehydrogenation has had commercial application for more than 60 years [1]. During this time a tremendous number of studies were devoted to the different aspects of the catalyst, process, kinetics and mechanism of the main dehydrogenation reaction. However, to the best of our knowledge, there have been no studies that were aimed to elucidate the mechanism or even pathway of formation of light gas. At the same time it is obvious that knowledge of the mechanism of light gas formation might help in improving the catalyst selectivity and understanding the temperature profile in the commercial reactor

Results and Discussion

This study was conducted on SCI Cr₂O₃/Al₂O₃ CATOFIN® catalysts, which are used in commercial propane and isobutane dehydrogenation processes. Tests with the following feed stocks were conducted: 1) propane, 2) isobutane, 3) propane-propylene- hydrogen mixture with 30 mol % H₂, 4) propane -propylene - hydrogen mixture with 60 mol % H₂ 5) isobutane - isobutylene - hydrogen mixture with 30 mol % H₂, 6) isobutane - isobutylene - hydrogen mixture with 60 mol % H₂. Before kinetic study the catalyst was operated for about 100 hours to achieve its stable activity. The catalysts were tested at LHSV from 1 to 8h⁻¹ and temperature from 537°C to 593°C and total pressure 0.5 atm. Obtained results of the experiments were presented as a ratio between yields of light gas products vs. retention time. Moreover, a comparison of the light gas yield produced by conversion of the paraffin vs. olefin / hydrogen mixture provided additional information about the main source of the light gas.

Obtained dependences between ratios of the light gases such as: propane to propylene and propylene to propane or ethane to ethylene and ethylene to ethane as a function of the reaction time indicated that olefin is formed first and only then paraffin with the same carbon number is formed from olefin (see example in Figure 1).

The results of the tests also indicate that independently of the temperature, the yield of light gas about 5 times higher in the case of conversion of olefin-hydrogen containing feedstock than in the case of the paraffin-hydrogen containing feedstock. The combined kinetic data suggests that during dehydrogenation paraffin is converted into olefin at a high rate and the majority of light gas is formed from the olefin by following reaction sequence (I):



As follows from the sequence (I), in the case of isobutane dehydrogenation, just formed by dehydrogenation reaction isobutylene is converted into propylene and methane by the hydrocracking reaction of (reaction 2). The appearance of propylene in the gas mixture where there is no propane leads to an equilibrium imbalance. In order to satisfy the thermodynamic of the system a part of propane should be hydrogenated by reaction 3. The remaining part of propylene is converted by the hydrocracking reaction 4 into ethylene and methane. The appearance of ethylene in the system without ethane again creates thermodynamic imbalance that causes fast reaction of ethylene hydrogenation into ethane (reaction 5).

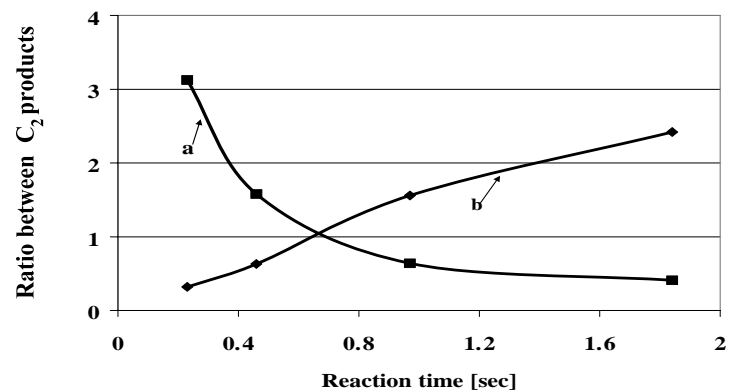


Figure 1 Ration between ethylene to ethane (a), and ethane to ethylene (b) during dehydrogenation as function of the reaction time at 599°C on Al-Cr CATOFIN ® catalyst.

It is well known from organic and catalysis chemistry that hydrocracking reaction mostly carries out by carbonium ion mechanism and olefins tends to form carbonium ion much easier than paraffins. Moreover, it is well known that usually the adsorption strength of olefins is higher than paraffins. Both of these factors make olefin conversion into light gas much more favorable than paraffin.

Obtained results were applied by SCI for the development of high selectivity propane and isobutane dehydrogenation CATOFIN® processes [2, 3].

References

1. Houdry E. *US Patent 2,419,997 (1947)*
2. V. Fridman, M. Urbancic, A. Rokicki, patent pending
3. V. Fridman, M. Urbancic patent pending

