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Highly selective propylene production via membrane assisted propane dehydrogenation

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Highlights

- Process intensification of propylene production via membrane assisted process
- Lower temperature assured increasing in catalyst lifetime and process selectivity
- High membrane stability in propane/propylene rich stream process
- Propylene production 25% higher than thermodynamic prediction with membrane integration

1. Introduction

Olefinic compounds are widely used in a number of chemical industries. Among them, propylene is the world’s second largest petrochemical commodity, being the precursor of polypropylene. Light olefins are commonly obtained by steam cracking and fluid catalytic cracking of light oil fractions, with propylene obtained as co-product of ethylene production. Only a small fraction of propylene (<10%) is produced by alternative on purpose technologies, such as propane dehydrogenation. This reaction is typically carried out in the presence of a catalyst in order to increase the overall selectivity to the desired olefin. Chromium oxide supported on alumina and Pt based catalysts supported on alkaline alumina are commonly employed [1].

However, because of cracking losses under thermal dehydrogenation conditions, the formation of coke deposits is significant. Due to that, the commercialized processes always consider a periodic catalyst regeneration step, performed under air flow and thermal oxidation of the carbonaceous deposits [2], resulting in higher plant complexity and cost as well as frequent substitution of the catalyst due to irreversible loss of activity. Despite the reduction of the reaction temperature could reduce coke formation and in turn increase catalyst lifetime, such approach suffers for a reduced propylene yield due to thermodynamic equilibrium limitations. In order to overcome the thermodynamic limitations, and accordingly increase the selectivity to propylene in combination with a slow catalyst deactivation, the use of membrane reactors could be a viable option. The aim of this work is to show some preliminary results obtained with such process concept, evaluating the effect of the use of a membrane for the hydrogen separation in a propane dehydrogenation reaction system. Particular attention is paid to the assessment of the concept feasibility and to the improvement in catalyst stability.

2. Methods

The experimental apparatus, proposed in the Fig. 1-a, and based on a proprietary concept [3] consists in two identical catalytic reactors and a hydrogen separation unit between them (Pd-based membrane, with a perm-selective surface of 1.0×10^{-2} m^2): the process stream containing hydrogen and propylene leaving the first reactor is routed to the separation unit, in which a part of the hydrogen is removed, then the residual stream is further processed in the second reactor. Catalytic tests are carried out by fixing reactors temperature to 500°C or 540°C, while membrane module is held to 370°C, nitrogen is used as sweep gas; operating pressure on process side is fixed to 5 barg. Catalytic reactors were loaded with 3 mm pellet commercial catalyst; the system was fed with propane (0.25 kg/h) and steam ($H_2O/C_3H_8 = 0.25$), assuring a WHSV = 8 h^{-1}.

3. Results and discussion

Stability tests were carried out on the first reactor, by holding operating conditions for up to 40 hours. Preliminary results showed that by decreasing the operating temperature, a significant reduction of coke production (from 3.65 to 0.45 mg / h·g_{CAT}) was observed, that in turn increased selectivity to propylene from around 95% to around 99%, moreover, a significant reduction in system deactivation was observed. In particular, by reducing operating temperature from 540°C to 500°C the estimated catalyst lifetime increased of around 1 order of magnitude.

In Fig. 1-b, catalytic performances in the integrated system were summarized. As reported, the reactors before and after the membrane showed a similar propane conversion value, however in the case of the first reactor, a discordance with thermodynamic prediction was observed, maybe because the catalyst in the R1 unit was aged for about 40 hours. The reactor R2 was fed with the retentate stream from the membrane unit, that contained an amount of propylene and hydrogen, so resulting in a lower expected propane conversion. It is anyway worth noting that the membrane was able to remove more than 50% of the hydrogen produced in the first reactor, allowing the integrated system (reactor + membrane + reactor) to be able to assure a propane conversion higher than 25%, so overcoming thermodynamic limitation. The presence of the membrane allows to increase of about 85% the conversion obtained with just one reactor.

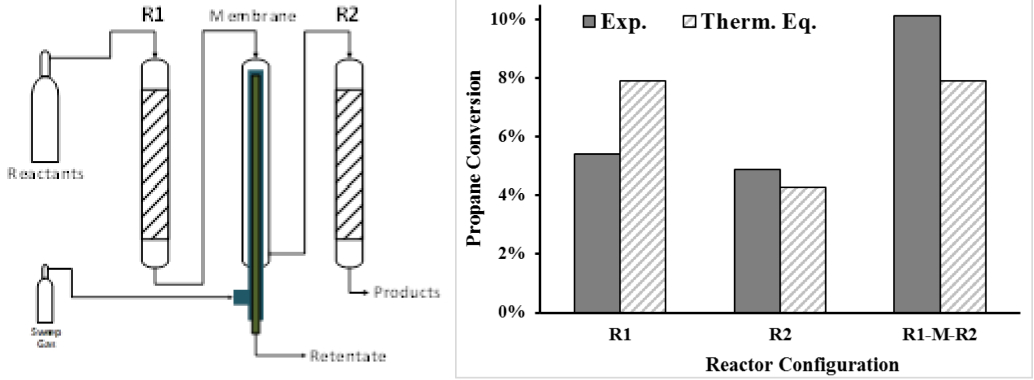

Figure 1. (a) Experimental apparatus scheme; (b) propane conversion in the experimental apparatus ($T_{R1} = T_{R2} = 500°C$)

4. Conclusions

Membrane assisted catalytic propane dehydrogenation was considered for the selective production of propylene. Experimental results demonstrated that beside the high operating pressure, the catalytic system evidenced a deactivation comparable with industrial operating conditions, while an impressive propylene selectivity could be observed along the entire stability tests. It was moreover demonstrated that the addition of a membrane (for the hydrogen removal) between two catalytic units was able to assure the overcoming of thermodynamic prediction just after the second reaction unit. The reported achievement candidates the membrane assisted propane dehydrogenation as a viable solution for the highly selective propylene production.

References

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Keywords
Propane dehydrogenation, membrane-assisted process, process intensification