MODELLING LAYERED FIXED-BED CATALYTIC REACTORS FOR THE OXIDATIVE COUPLING OF METHANE Laura Pirro¹, Pedro S. F. Mendes¹, Joris De Keulenaer¹. Bart D. Vandegehuchte², Guy B. Marin¹ and Joris W. Thybaut¹

¹Laboratory for Chemical Technology, Ghent University (Belgium) ²Total Research and Technology Feluy (Belgium)

Introduction

Direct natural gas conversion to ethylene via Oxidative Coupling of Methane (OCM) has presented for decades an open challenge in catalytic reaction engineering [1]. However, the screening of numerous catalysts and reactor configurations has still not led to a real breakthrough in addressing the issues of low yields and high exothermicity. Among the possibilities for OCM performance enhancement, the layering of different catalytic materials in fixed-bed reactors has been proposed [2, 3]. Nevertheless, a dedicated study concerning the optimal catalyst layering is still missing and is, hence, addressed via detailed kinetic modelling in the present work.

Methodology

The OCM kinetics are described via a previously developed microkinetic model [4], accounting for both gas-phase and surface reactions. The model catalysts considered are Sr/La₂O₃ (high activity and low selectivity) and NaMnW/SiO₂ (lower activity and higher selectivity). The layered reactor is simulated via an in-house heterogeneous

fixed-bed reactor model which has been modified to explicitly take into account the transfer of reactive intermediates at the boundary between consecutive catalyst layers. This transfer was indeed found to influence the outlet composition, being thus important to distinguish between modelling a layered fixed-bed reactor and modelling reactors in series, see Figure 1.



Results and discussion



In Figure 2, the performances of an optimized layered reactor are compared to the performances of the single catalysts, in both isothermal (A) and adiabatic (B) operation. The comparison is based on the C_{2+} yield, defined as CH_4 conversion times C_{2+} selectivity, and the C_{2+} space-time-yield (STY), defined as molc₂₊ produced per s kg_{cat}. Both performance indicators are evaluated at complete oxygen conversion. For the isothermal case, the optimal configuration, consisting of a long layer of selective NaMnW/SiO₂ catalyst followed by a thin layer of the active Sr/La₂O₃ catalyst, results in doubling the C₂₊ STY compared to the single NaMnW/SiO₂ and in a 80% increase in the C₂₊ yield compared to the single Sr/La₂O₃. The Rate of Production Analysis pointed to the most selective catalyst NaMnW/SiO₂ being more beneficial in the upper part of the reactor, i.e., where methane concentration is higher. For the adiabatic case, the optimal layered configuration is reversed and, despite a slight decrease (5.2%) in the C₂₊ yield compared to the single NaMnW/SiO₂, the resulting STY is four times higher, even at a lower inlet temperature. The higher activity of Sr/La₂O₃ was found to be key in developing a temperature profile along the reactor, which would then lead to the activation of the subsequent NaMnW/SiO₂ catalyst.



Figure 2. Comparison of an optimally layered configuration vs single-catalyst reactors, for isothermal (A) and adiabatic (B) operation of an OCM fixed-bed reactor. STY: space-time-yield; X₀₂= oxygen conversion.

Conclusions

Intensified ethylene production from natural gas can be achieved by exploiting synergies in sub-optimal OCM catalysts in layered fixed-bed reactors. For isothermal operation, adequate choice of the layering order can address selectivity limitations of individual catalysts. In adiabatic operation, lighting off the reaction with a 'pre-heating' catalyst layer [3] was confirmed to be crucial to maximize the space-time-yield without jeopardizing the C_{2+} selectivity.

References

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