Assessing adiabatic operation of OCM fixed-bed reactor via a microkinetic analysis of light-off behavior

Laura Pirro[1], Ana Obradović[1], Bart Vandegehuchte[2], Guy B. Marin[1], Joris W. Thybaut[1*]

1 Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052 Ghent, Belgium;
2 Total Research & Technology Feluy, Zone Industrielle Feluy C B-7181, Seneffe, Belgium

**Corresponding author: Joris.Thybaut@UGent.be*

Highlights

- Microkinetic network for OCM is implemented in an adiabatic fixed-bed reactor model.
- Performance of different catalysts is assessed over a wide range of operating conditions.
- Light-off curves and corresponding C_2 yields at the reactor outlet are evaluated.
- Adiabatic operation can increase C_2 yield but requires special attention for safety.

1. Introduction

In spite of decades of research not yet leading to widespread commercial-scale application, production of C_2 hydrocarbons via Oxidative Coupling of Methane (OCM) remains an attractive and challenging topic both for academia and the chemical industry [1]. The main challenges lie in the competing partial and total oxidation reactions, which provoke a difficult temperature control, and in the inverse relationship between conversion and selectivity. The design of active, selective and stable catalysts for OCM should be complemented by an adequate reactor configuration embedded in a corresponding process scheme. Simulation of the performances of adiabatic fixed-bed reactors for different catalysts is therefore crucial to the overall optimization framework [2].

2. Methods

A detailed microkinetic model [3], which takes into account the complex chemistry of the OCM reactions both in the gas phase and on the catalyst surface, is implemented in an adiabatic fixed-bed reactor model. The model is 1-D on the reactor scale and heterogeneous: on the pellet scale two different phases have been considered, i.e. the porous catalyst particles and the gas flowing around the particles. In order to solve the system of PDEs which arises from this steady-state multiscale modelling, orthogonal collocation is applied on the pellet scale. The resulting set of DAEs is integrated along the axial reactor coordinate using a variable-step BDF integration method. The catalyst descriptors for the catalysts considered in the present study have been reported before [4]. Together with the yield to desired C_2 products, the reaction light-off curves [5] have been considered as suitable model outputs in the evaluation of the different catalysts and at different operating conditions (i.e. inlet temperature T_0, reactant partial pressure p_r, reactants inlet ratio $CH_4/O_2|_{z=0}$, space time W/F_0, gas phase dilution).

3. Results and discussion

Due to the exothermicity of the involved reactions and corresponding temperature increase along the axial reactor coordinate, a boost in the C_2 yield could be observed. As an example, in Fig. 1 the temperature profiles along a bed of 1wt%Sr/La_2O_3 catalyst are reported both for isothermal and adiabatic simulations for three values of the space time W/F_0 (F_0= mol_{CH4}+$mol_{O2}|_{z=0}$), together with the corresponding C_2 yields. It can be observed that once light-off - defined as the operating point for which the outlet conversion of the limiting reagent (O_2) is above 50% - is achieved (curve C), the yield at the reactor outlet is higher compared to the isothermal case, even for a 100K lower inlet temperature. At the same operating conditions reported in the caption of Fig. 1, an adiabatic bed of a less active catalyst such as 1wt%Na-3%W-2%Mn/SiO_2, shows an approximately constant temperature profile and

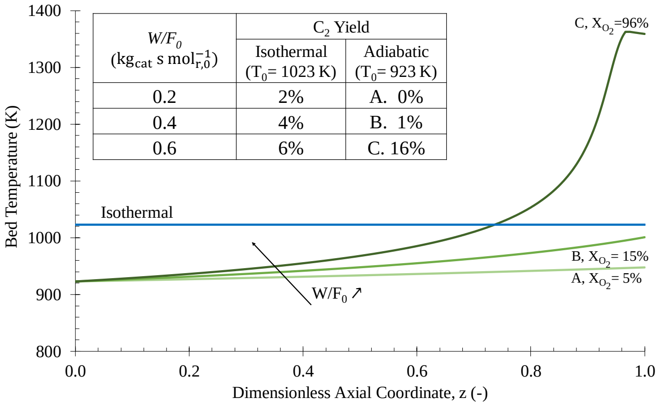

Figure 1. Adiabatic axial temperature profiles of a bed of Sr/La_2O_3 catalyst as a function of W/F_0: T_0= 923K, p_r= 190 kPa, $CH_4/O_2|_{z=0}$= 6, gas-phase dilution by N_2: 50%. The isothermal reference case is at T_0 = 1023 K. The table in the figure reports the yield of the desired C_2 products for both isothermal and adiabatic operation.

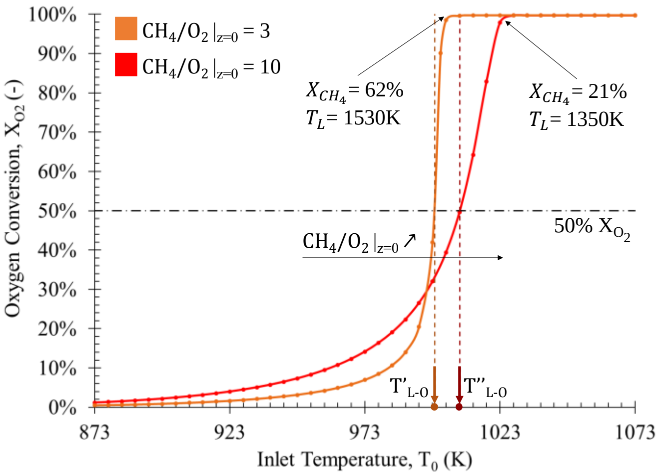

Figure 2. Oxygen conversion X_{O2} as a function of T_0 (i.e. light-off curve) of a Sn-Li/MgO catalytic bed: p_r= 190 kPa, W/F_0= 0.8 kg_{cat} $s/mol_{r,0}$, no inert gas in the feed, $CH_4/O_2|_{z=0}$= 3 (orange curve) and $CH_4/O_2|_{z=0}$= 10 (red curve). Methane conversion X_{CH4} and temperature at the reactor outlet T_L are reported for X_{O2}=100%. $T'_{L\text{-}O}$ and $T''_{L\text{-}O}$ are the light-off temperatures.

consequently low yields, i.e. higher inlet temperatures (T_0> 1200K) or higher space times (W/F_0> 10 kg_{cat} $s/mol_{r,0}$) are necessary to light-off the reaction.

After several operating conditions have been investigated, a general conclusion can be drawn: the operating configurations which result in higher C_2 yields at lower inlet temperatures (high pressure, no gas phase dilution, high oxygen content in the feed) are also those determining potential safety concerns due to lack of thermal control of the reaction. As an example, the effect of the reactants inlet ratio $CH_4/O_2|_{z=0}$ on the light-off curve of a Sn-Li/MgO catalytic bed is reported in Fig. 2. At higher reactants inlet ratio methane conversion is strongly penalized in favor of a significant decrease in the steepness of the curve and in the outlet temperature, thus enabling feasible and safe reactor operation.

4. Conclusions

An accurate tuning of the operating conditions enables the light-off of the OCM reaction in an adiabatic fixed-bed reactor, which can lead to higher C_2 yields at lower inlet temperatures, compared to isothermal operation. This characteristic is more pronounced for highly active catalysts, such as alkaline earth-promoted La_2O_3 catalysts. The quest for the optimal operating conditions required to achieve an industrially interesting yield has to take into account potential safety concerns caused by the highly exothermic and fast reactions and, hence, depends on the selected catalyst.

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Keywords
Oxidative coupling; methane; adiabatic reactor; light-off curve.