

# Towards an Optimal Ethylene Oligomerization Catalyst based on Single-Event MicroKinetic Modelling

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## Introduction

As the world's crude oil reserves are declining, the global energy demand is rising and the environmental legislation is becoming more and more strict, the search for low-emission fuels and chemicals is evermore a hot topic. Alternative routes are being explored to valorize methane, e.g., via ethylene formation by oxidative coupling. At present, ethylene oligomerization using homogeneous catalysis is an established industrial process, resulting selectively in even carbon atom numbered alpha alkenes. Heterogeneous catalysis is preferred over homogeneous catalysis, among others, because of environmental reasons. Moreover, heterogeneous catalysis offers more opportunities to tune the product yields to the market demands, i.e., linear  $\alpha$ -alkenes or a complex mixture to be used as high octane fuel blend [1]. The aim of this work is to contribute to the development of an active, stable and selective catalyst for ethylene oligomerization. This challenge is addressed via fundamental modeling using Single-Event MicroKinetics (SEMK) [2]. An intrinsic kinetic data set is being acquired on a bench mark catalyst and will be used for regression purposes, i.e., to determine the model parameters, which can be classified as kinetic and catalyst descriptors. In particular the latter descriptors can be varied through simulation, in order to identify the optimal catalyst behavior.

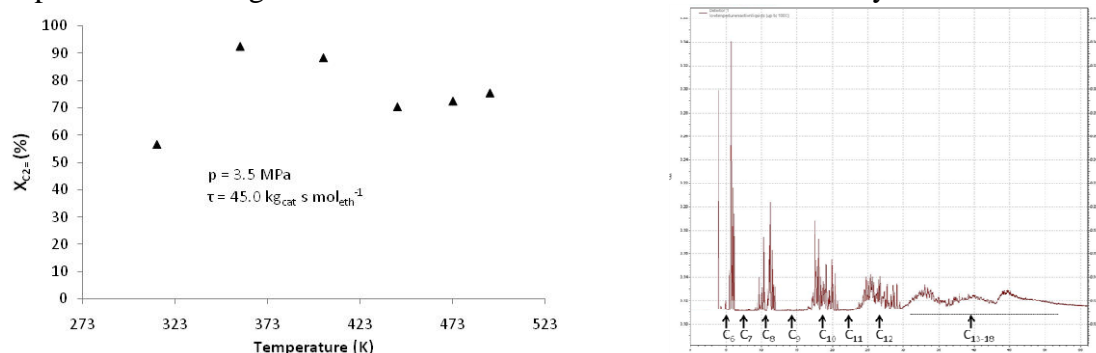
## Procedures

Experiments are performed in a fixed bed plug-flow reactor on a bench-mark silica-alumina catalyst impregnated with 1.8 wt% Ni. The temperature was varied from 443 K to 503 K, i.e., the range in which acid catalyzed reactions are reflected in the product yields [1]. Total pressures between 1.0 and 3.5 MPa are used with a molar ethylene content in the feed of 60%. The space time was varied from 3.0 to 45.0 kg<sub>cat</sub> s mol<sub>eth</sub><sup>-1</sup>. Care is taken to avoid heat and mass transfer limitations.

A microkinetic model was constructed describing the intrinsic ethylene oligomerization kinetics according to the SEMK methodology [2]. The reaction network was limited to molecules with a maximum carbon number of 12 and consisted of over 3000 species and over 10000 elementary steps. Physical adsorption of the components inside the catalyst pores, prior to any chemical elementary step was included via a Langmuir isotherm.

## Results and discussion

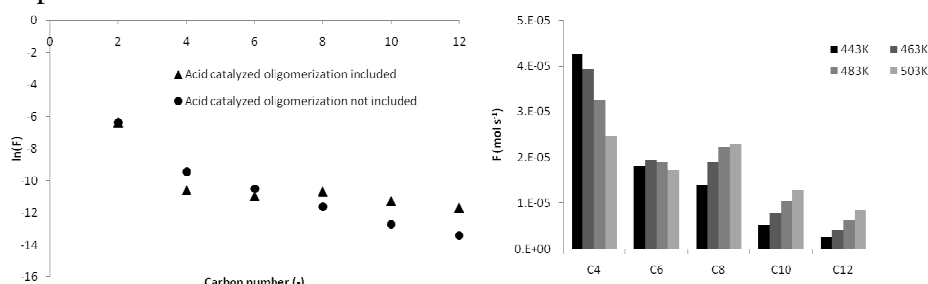
As reported in the literature [1, 3], the catalyst exhibited two regions of activity as function of the temperature, see Figure 1 (left). At low temperatures mainly linear  $\alpha$ -alkenes are obtained as products resulting from a coordinated insertion mechanism of ethylene on an



**Figure 1: Left: experimental conversion of ethylene as function of temperature at 3.5 MPa and 45.0 kg<sub>cat</sub> s mol<sub>eth</sub><sup>-1</sup>; Right: chromatogram of the collected liquid phase (C<sub>6</sub> to C<sub>18</sub>) mixed for several experiments at different conditions.**

active nickel cation site. Between 373 and 403 K, in the presence of ethylene, an irreversible transformation of Ni occurs leading to an activity loss of the catalyst below this temperature [1]. At higher temperatures, i.e., above 423 K, stable catalyst behavior was obtained for a time-on-stream up to 6 hours. The absence of odd carbon numbered alkenes in the product spectrum shows that no cracking occurred, see Figure 1 (right).

Because higher operating temperatures offer a wider range of possibilities for tuning the product yields, the corresponding data are assessed first using the microkinetic model. At present simulations have been performed using initial parameter values based on literature data [1] and have not been further optimized yet by regression. The metal-ion function is critical for ethylene dimerization to butene. In contrast to ethylene, which can only form primary carbenium ions, butenes can lead to more stable secondary carbenium ions that participate in acid catalyzed oligomerization reactions. While the C<sub>4</sub> fraction is entirely built up out of linear alkenes, C<sub>6</sub> and heavier fractions also contain branched isomers. Pure metal-ion catalyzed oligomerization results in an Anderson Schulz Flory distribution. The acid catalyzed oligomerization disturbs this ASF distribution, however, see Figure 2, left. This is more pronounced with increasing temperatures, see Figure 2 right. The decrease with the temperature of the linear alkene content in the C<sub>8</sub> fraction from 43.2 % at 443 K to 25.2 % at 503 K, also illustrates the increase of the relative importance of acid catalyzed reactions at higher temperatures.



**Figure 2: Left: natural logarithm of the molar outlet flow rates as function of the carbon number; Right: product distribution as function of temperature, acid catalyzed oligomerization included at 3.5 MPa and 6.7 kg<sub>cat</sub> s mol<sub>eth</sub><sup>-1</sup>.**

## Conclusions

A microkinetic model for ethylene oligomerization at higher temperatures is constructed and is able to qualitatively reproduce the experimental trends. The C<sub>4</sub> species formed all have a linear character because ethylene dimerization occurs on the metal-ion sites, while the C<sub>6</sub> to C<sub>12</sub> species are mainly branched, due to the acid catalyzed reactions. Because of the acid catalyzed reactions, deviations from the Anderson Schulz Flory product distribution are obtained. No odd carbon numbered alkenes are present, indicating the absence of cracking. The kinetic and the catalyst descriptors in the Single-Event MicroKinetic model will be quantitatively determined by regression and optimal catalyst descriptor values will be identified.

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## References

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