

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

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Introduction

Homogeneously catalyzed ethylene oligomerization is an established industrial process, mainly resulting in even carbon atom numbered α alkenes. Heterogeneous catalysis is preferred, however, e.g. because of environmental reasons and for avoiding a catalyst separation step from the product. Moreover, heterogeneous catalysis offers more opportunities to tune the product distribution and corresponding yields to the market demands, i.e. even-numbered, linear α -alkenes versus a high octane fuel blend hydrocarbon mixture [1].

The present work aims at developing an active, stable and selective catalyst for ethylene oligomerization. This challenge is addressed via fundamental modeling using Single-Event MicroKinetics (SEMK) [2]. Model parameters are determined which can be classified as kinetic and catalyst descriptors. The first type of parameters is specific to the reaction family considered and independent from the catalyst, while the latter specifically accounts for the effect of catalyst properties, such as Si/Al ratio, metal ion site concentration... on the kinetics, e.g. via chemisorption enthalpies, sterical constraint factors,... Through simulation, the catalyst descriptors can be varied in order to identify optimal catalyst behavior defined in terms of product selectivity or yield.

When brought into contact with an acid catalyst, ethylene is relatively stable at mild conditions because it can only form primary carbenium ions [3]. Therefore, typically a metal ion function is introduced to activate ethylene and dimerize it to butylene. Consecutive ethylene insertions are possible on metal ion sites but also on the acid sites, because of the involvement of more stable secondary carbenium ions. In the present work, for kinetic modeling purposes, the kinetics occurring on the metal ion sites are aimed at, i.e. in the absence of acid catalyzed oligomerization.

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 423 K to 503 K, i.e., the range in which acid catalyzed reactions, if any, are reflected in the product yields [1]. Total pressures between 1.5 and 3.5 MPa are used with a molar ethylene content in the feed of 10% to 60%. The space time was varied from 4.8 to 45.0 $\text{kg}_{\text{cat}} \text{s mol}_{\text{eth}}^{-1}$. Care is taken to avoid heat and mass transfer limitations.

Kinetic modelling

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 8 and consisted of over 140 species and over 400 elementary steps. Physical adsorption of the components inside the catalyst pores, prior to any chemical elementary step was included via a Langmuir isotherm.

The kinetics for metal ion oligomerization are expressed in terms of 4 elementary steps, see Figure 1, based upon similarity with homogeneous catalysis [4]: initiation of the metal ion by an ethylene molecule, chemisorption of ethylene on the active site, insertion of ethylene into the growing

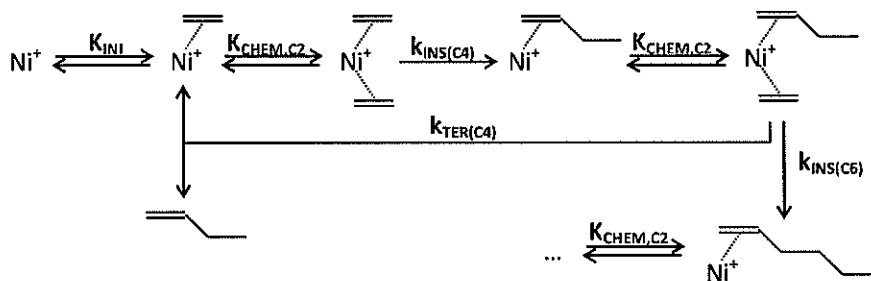


Figure 1: Proposed reaction mechanism for metal ion oligomerisation.

chain and termination, i.e. desorption of the product after ethylene insertion. The initiation is assumed to be in quasi-equilibrium and insertion and termination are assumed irreversible. (de-)Protonation ensures double bond isomerization and is assumed to be in quasi-equilibrium too.

Due to the experimental absence of acid catalyzed oligomerization, carbon skeleton rearrangement and cracking on the catalyst studied, the model parameters to be determined are two equilibrium coefficients, K_{INI} , $K_{CHEM,C2}$, two rate coefficients k_{INS} , k_{TER} and the components' physisorption coefficients. The latter are calculated using literature data [5]. Applying the SEMK concept, only 4 pre-exponential factors and reaction enthalpies/activation energies are to be determined. The pre-exponential factors are calculated based on statistical thermodynamics, i.e. assuming a certain degree of entropy loss/gain during transition state formation. The remaining four reaction enthalpies/activation energies for, respectively, initiation (ΔH_{INI}), chemisorption ($\Delta H_{CHEM,C2}$), insertion ($E_{a,INS}$) and termination ($E_{a,TER}$) are estimated by regression to the experimental data. From regression it was clear that ΔH_{INI} was a parameter with a high absolute value. The corresponding heat release was observed experimentally during the first few minutes on stream of a freshly loaded catalyst sample. Kinetic data samples were only taken after a period of ca. 20 minutes when the operating conditions were stabilized. Correspondingly, it was assumed in the model that all available nickel is instantaneously initiated. The remaining parameter estimates that were obtained are reported in Table 1, which are equal to the parameter values obtained after regression with ΔH_{INI} included in the model, confirming the . The regression was globally significant while the kinetic model is adequate. The calculated molar outlet flow rates of ethylene, butenes and hexenes are in very good correspondence with the experimentally observed molar outlet flow rates, see Figures 2 to 4. The residuals for these responses are not dependent from reaction conditions (not shown).

Table 1: Estimated parameters and statistical test for the SEMK model for ethylene oligomerization

Estimated parameters	Values (kJ mol^{-1})
$\Delta H_{CHEM,C2}$	-73.0 ± 1.0
$E_{a,INS}$	119.5 ± 1.0
$E_{a,TER}$	116.5 ± 1.1
F-value (regression significance): 12001 (F_{tab} : 3.59)	
F-value (model adequacy): 2.01 (F_{tab} : 2.55)	

Conclusions

Using the SEMK methodology, a microkinetic model was constructed and the corresponding kinetic parameters for metal ion oligomerization were determined. The model involved initiation of the Ni sites for oligomerization, ethylene chemisorption on an initiated site, ethylene insertion into a

growing chain and termination by desorption. Ni site initiation was assumed to occur instantaneously and ethylene chemisorption was assumed to be quasi equilibrated. Finite rates were used for the insertion and termination elementary steps. The kinetic model was able to adequately describe the experimental observations. The preexponential factors were calculated from first principles while the activation energies and reaction enthalpies were estimated significantly with a clear physical meaning. In future work the acid catalyzed oligomerization will also be assessed experimentally and corresponding SEMK model parameters will be determined.

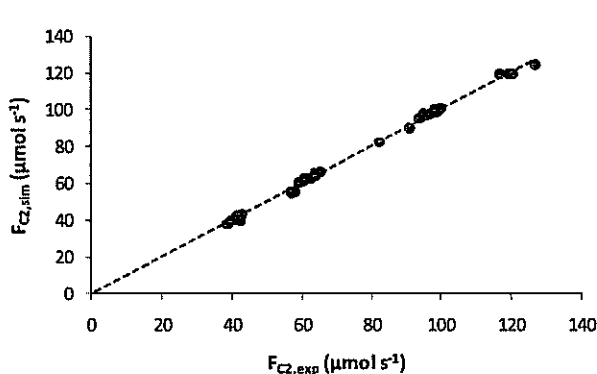


Figure 2: Parity diagram of the molar outlet flow rate of ethylene.

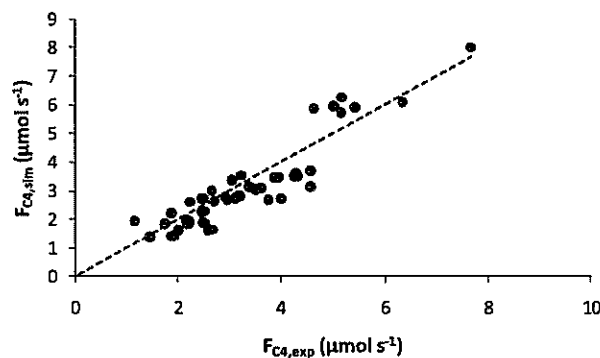


Figure 3: Parity diagram of the molar outlet flow rate of butenes.

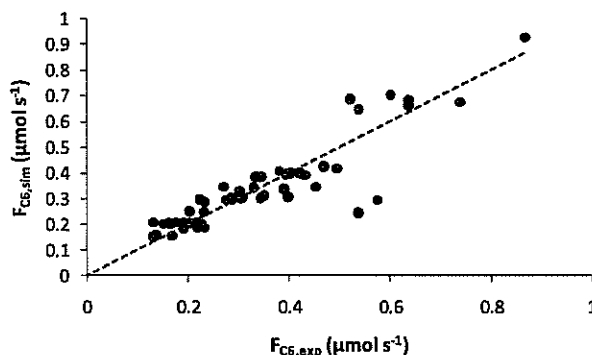


Figure 4: Parity diagram of the molar outlet flow rate of hexenes.

Acknowledgements

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