ETHYLENE OLIGOMERIZATION CATALYST OPTIMIZATION USING FUNDAMENTAL KINETIC MODELING

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Introduction

Homogeneously catalyzed ethylene oligomerization is an established industrial process, mainly resulting in even carbon atom numbered alpha 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.

Experimental Investigation of Ethylene Oligomerization

Experimental ethylene oligomerization data have been gathered on three different catalysts, i.e. 1.8wt% $Ni-SiO_2-Al_2O_3$, 2.7wt% Ni-Beta and 1.7wt% Ni-USY. At 393 K, a total pressure of 3.5 MPa and a space time equal to 48 kg_{cat} s mol_{eth}^{-1}, see Figure 1, stable behavior up to 9h time on stream was exhibited by $Ni-SiO_2-Al_2O_3$ and Ni-Beta, whereas Ni-USY suffered a significant activity loss. $Ni-SiO_2-Al_2O_3$ was more active than Ni-Beta and the product distributions obtained indicated that on the Ni-Beta acid catalyzed oligomerization was responsible for the formation of mainly C_8 and C_{10} components, while this did not occur on the $Ni-SiO_2-Al_2O_3$. Hence, the 1.8wt% $Ni-SiO_2-Al_2O_3$ was selected as the benchmark catalyst for modeling purposes in this work. As observed in Figure 2, the obtained reaction products mainly comprised even-numbered alkenes in the C_4-C_{12} range. Only traces of odd-numbered alkenes were found at the reaction conditions studied. A different product distribution was observed over the silica-alumina-based and microporous Beta-based catalysts. While a typical Schulz Flory distribution was obtained with the $Ni-SiO_2-Al_2O_3$ catalyst, indicative of a single

growth and termination mechanism, the product distribution on the Ni-Beta catalyst exhibited a minimum at C_6. The $C_{10}+$ fraction (diesel products) was significantly higher on the Ni-Beta compared to the Ni-SiO$_2$-Al$_2$O$_3$ catalyst, i.e. 38 wt% versus 17 wt %. The acid catalyzed ethylene insertion in heavier alkenes and dimerization of butene on the Ni-Beta catalyst may explain these observations.
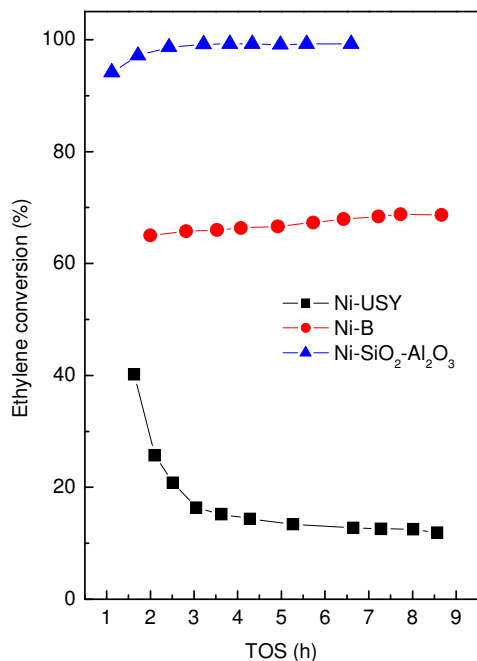

Figure 1: Ethylene conversion on 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$, 2.7% Ni-Beta and 1.7 wt%Ni-USY as function of time on stream at 393 K, 3.5MPa and 48.0 kg$_{cat}$ s mol$_{eth}^{-1}$
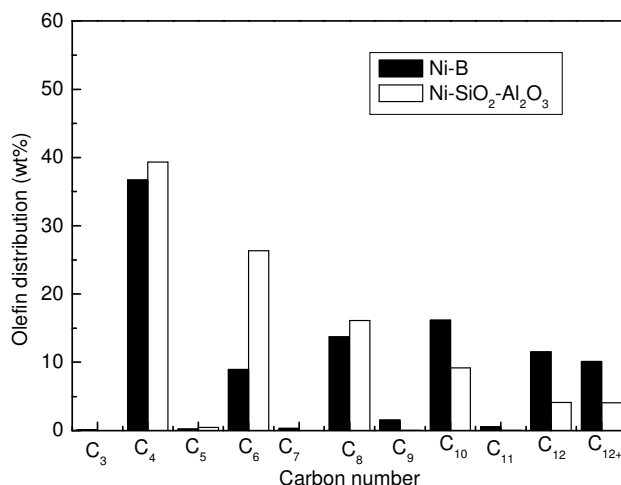

Figure 2: Olefin distribution obtained on 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$ and 2.7% Ni-Beta at 393 K, 3.5MPa and 48.0 kg$_{cat}$ s mol$_{eth}^{-1}$

A more elaborate experimental study has been performed on the 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$ within a temperature range from 323 K to 503 K, pressure range from 1.5 to 3.5 MPa, with a molar ethylene content in the feed of 10% to 60% and a space time ranging from 4.8 to 45.0 kg$_{cat}$ s mol$_{eth}^{-1}$. As previously reported in the literature [1,4], two distinct activity regions were observed as a function of the temperature, see Figure 3. At low temperatures mainly linear α-alkenes are obtained through a coordinated ethylene insertion mechanism on an active Ni cation site. Between 373 and 403 K, in the presence of ethylene, an irreversible transformation of Ni occurs which leads to a significantly lower activity of these Ni sites [1]. At higher temperatures, i.e., above 423 K, the Ni cation sites becomes more active again, resulting in an increase of the ethylene conversion. The absence of odd carbon numbered alkenes in the product spectrum shows that no cracking occurred, see Figure 2.
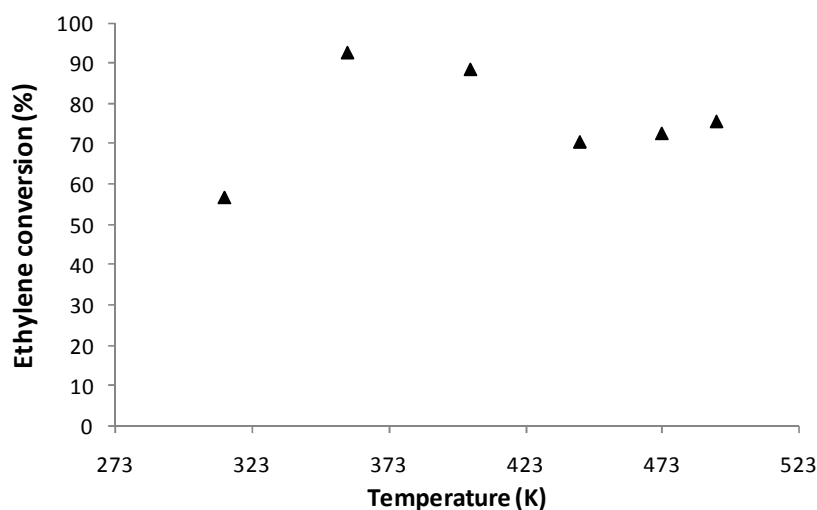
Figure 3: Ethylene conversion on 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$, as function of temperature at 3.5MPa, molar ethylene content in the feed of 60% and 45.0 kg$_{cat}$ s mol$_{eth}$$^{-1}$

In the experimental dataset, it was aimed at obtaining a kinetic dataset for which intrinsic kinetics were measured, i.e. in the absence of any transport limitations. Also, a large number of experiments were done at the higher end of the temperature range, i.e. from 443 to 503 K, since higher operating temperatures offer more possibilities for tuning the product distribution. In total, 51 experimental points were included in this range of which 10 are repeat experiments. The kinetic behavior was as expected, i.e. increasing temperature, (partial) pressure and space time all lead to an increase of ethylene conversion, see Figure 4 and Figure 5.
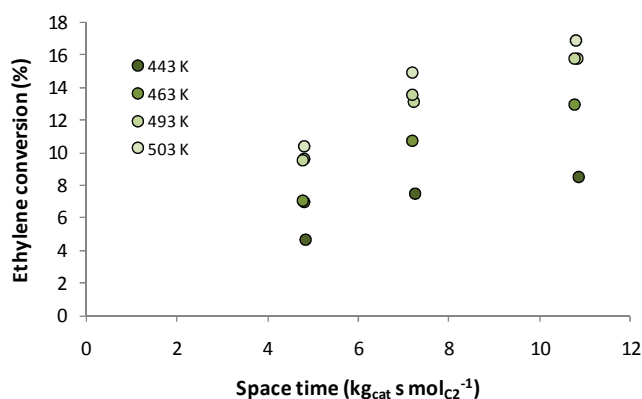

Figure 4: Ethylene conversion on 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$, as function of space time at 3.5MPa, molar ethylene content in the feed of 10% and different temperatures
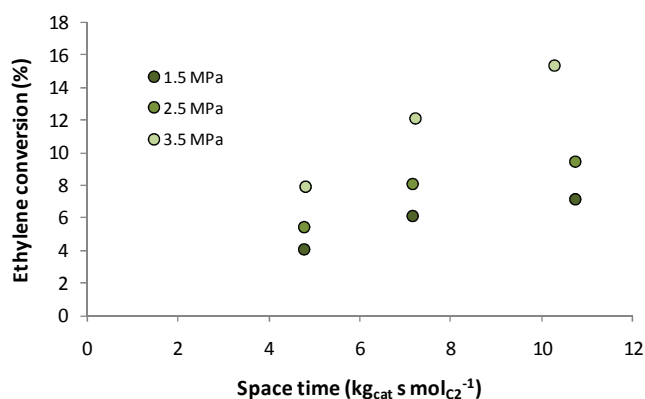

Figure 5: Ethylene conversion on 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$, as function of space time at 473K, molar ethylene content in the feed of 10% and different pressures

The product yields are varying linearly with the ethylene conversion, see Figure 6, indicating that product selectivities are independent from reaction conditions. Generally, the product stream consisted out of (mol%) ±85% butene, ±12% hexene and ±3% octene. No odd carbon numbered products were detected, in correspondence with the first set of experiments. However, no components heavier than octene were present in the reactor outlet, mainly due to the low molar fraction of ethylene

in the reactor feed. Also, the temperature at which high molar mass components were detected was within the low-temperature range, i.e. up to 393K, which exhibits higher activity than the high temperature range, see Figure 3. Additional experiments at more severe conditions, i.e. 543K and 43.9 kg_{cat} s mol_{eth}^{-1} confirmed these observations. NH_3-TPD measurements revealed only weak acid sites on the catalyst with NH_3 desorption occurring between 473 – 523 K. All these observations indicated that acid catalyzed oligomerization does not occur on the 1.8wt% Ni-SiO_2-Al_2O_3.
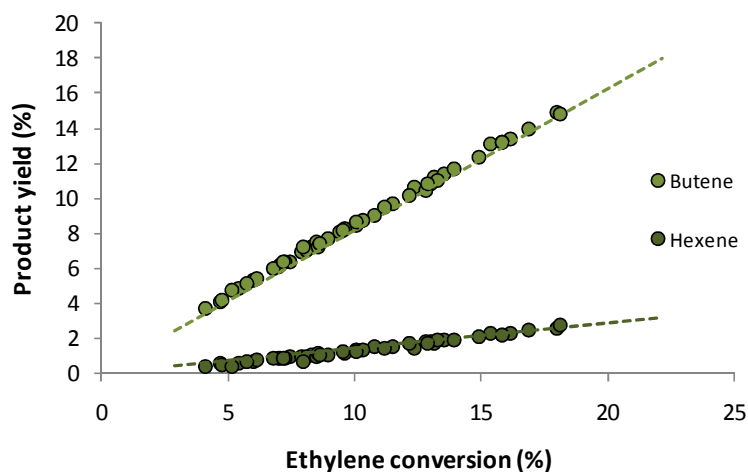

Figure 6: Product yield of butenes and hexenes (octenes not shown) on 1.8wt% Ni-SiO_2-Al_2O_3 as function of ethylene conversion with reaction conditions ranging from 443 to 503 K, 1.5 to 3.5 MPa, a molar ethylene content in the feed from 10 to 30% and a space time between 4.8 and 14.4 kg_{cat} s mol_{eth}^{-1}.

Kinetic Modeling

The reaction network considered in the SEMK model was limited to molecules with a maximum carbon number equal to 8 since no heavier components were observed experimentally. The modeling tools are developed as such that the use of larger networks involving heavier components is straightforward. The considered network consists of 82 alkenes and 60 carbenium ions. Although not evident from the data that are currently assessed, acid catalyzed reactions, e.g. protonation, acid catalyzed oligomerization and isomerization, are already included in the network for future purposes. In total, 403 elementary steps are considered interconverting the considered species. Physical adsorption of the components on the catalyst surface, prior to any chemical reaction was also accounted for using the Langmuir hypothesis. With increasing maximum carbon number of the molecules considered, the reaction network grows exponentially. For a maximum carbon number of 12 over 3000 species and over 10000 elementary steps are involved.

The kinetics for metal ion oligomerization are expressed in terms of 4 elementary steps, see Figure 7, based upon similarity with homogeneous catalysis [5]: initiation of the metal ion by an ethylene molecule, chemisorption of ethylene on the active site, insertion of ethylene into the growing 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 bound isomerization and is assumed to be in quasi-equilibrium too.
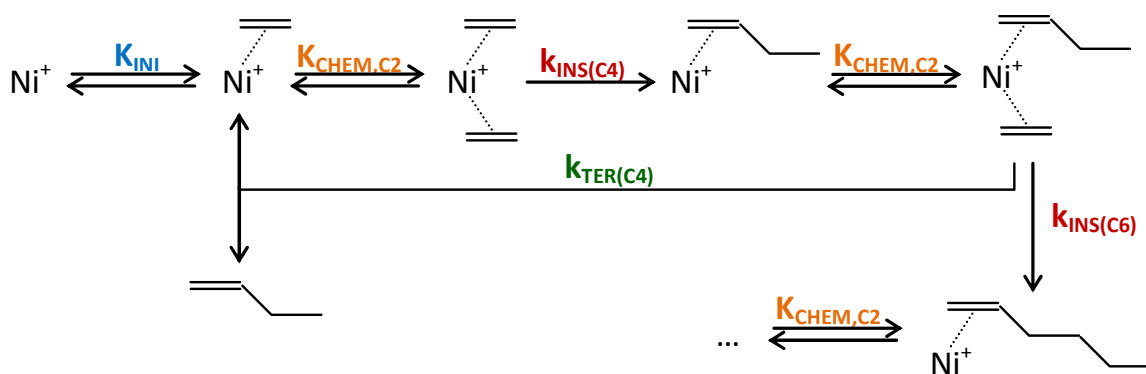
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Figure 7: Proposed reaction mechanism for metal ion oligomerisation.

Due to the 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}, two rate coefficients k_{INS}, k_{TER} and the components' physisorption coefficients. The latter are calculated using literature data [6]. 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. An equal loss of degree of freedom during transition state formation for initiation and chemisorption is assumed due to the similar nature of the elementary steps and was equal to a net loss of chemisorption entropy of ethylene. For insertion, no change in entropy is expected because prior to ethylene insertion, the two chemisorbed components already have lost their translation entropy via physisorption and chemisorption, and only by rotational movement, the transition state is formed [5]. For termination, one might expect an increase of entropy equal to the chemisorption entropy of the component released. However, based upon quantum mechanical calculations, the formation of the transition state itself does not contain any difference in entropy [5], and, thus this entropy change is set equal to zero too. 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. The results are given in Table 1. The global regression was globally significant while the kinetic model is adequate. All parameters have a clear physical meaning. The activation energies of ethylene insertion and termination being close to each other is in line with the quasi-independency of the product distribution on the reaction conditions and the temperature in particular. 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 8 to 10. 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

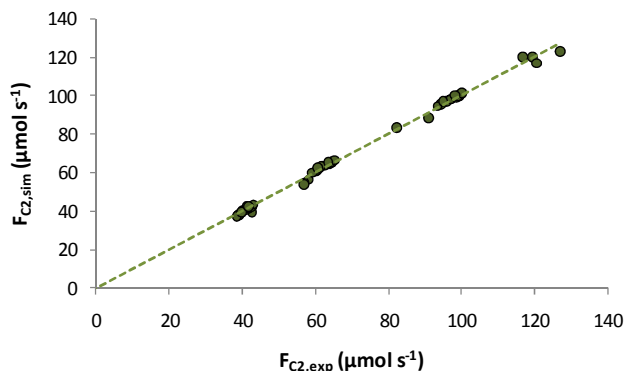| Estimated parameters	Values (kJ mol^{-1})
ΔH_{INI}	-103.1
$\Delta H_{CHEM,C2}$	-26.4
$E_{a,INS}$	89.8 ± 0.2
$E_{a,TER}$	87.0 ± 0.7
F-value (regression significancy): 8585 (F_{tab}: 3.59)	
F-value (model adequacy): 1.93 (F_{tab}: 2.55)	

5

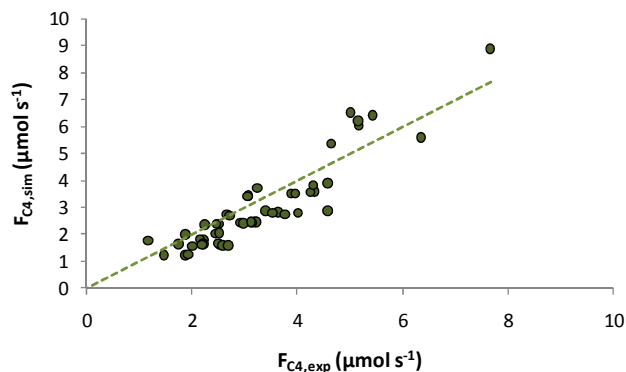**Figure 8: Parity diagram of the molar outlet flow rate of ethylene.**

Figure 9: Parity diagram of the molar outlet flow rate of butenes.
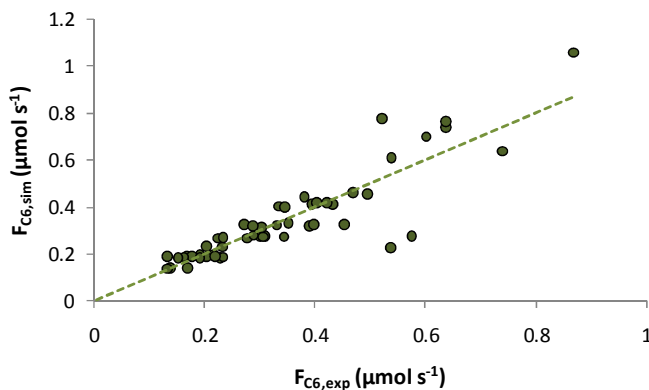

Figure 10: Parity diagram of the molar outlet flow rate of hexenes.

While acid catalyzed oligomerization parameters are not determined with this experimental dataset, the kinetic model is capable of describing these effects using literature reported values for a catalyst containing stronger acid sites [7]. The following simulations are done with a reaction network with molecules having a maximum carbon number of 12. Metal ion catalyzed oligomerization leads to an Anderson Schulz Flory-like product distribution, while the acid catalyzed oligomerization reactions disturb this ASF-like distribution, see Figure 11, left. This is more pronounced with increasing temperatures, see Figure 11 right. Even when acid catalyzed oligomerization occurs, the C_4 fraction obtained is entirely built up out of linear alkenes. C_6 and heavier fractions also contain branched isomers. The decrease with the temperature of the linear alkene content in the C_8 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.
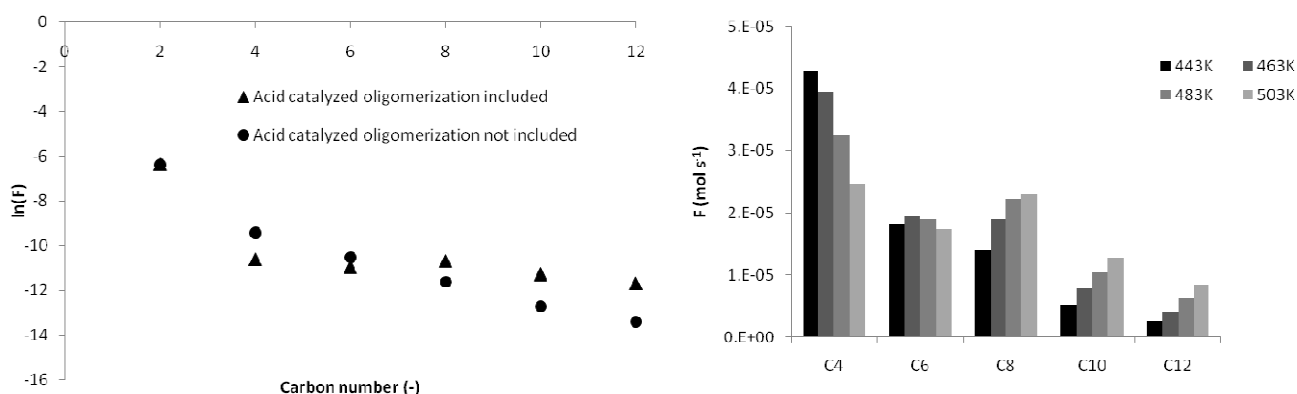
Figure 11: Left: natural logarithm of the molar outlet flow rates as function of the carbon number; Right: product distribution as a function of temperature, acid catalyzed oligomerization included at 3.5 MPa and 6.7 kg$_{cat}$ s mol$_{eth}^{-1}$.

Conclusions

In the present work, three catalyst candidates were screened for activity and stability in ethylene conversion to oligomers. 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$ and 2.7wt% Ni-Beta showed stable behavior, while 1.7% Ni-USY exhibited a fast initial deactivation. 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$ was the most active catalyst and did not exhibit any acid catalyzed oligomerization. A more extended data set was acquired on this catalyst in order to accurately determine the oligomerization kinetics on Ni ion sites.

Using the SEMK concept, a microkinetic model was constructed and the corresponding kinetic parameters for metal ion oligomerization were estimated. The kinetic model was able to adequately describe the experimental observations. The parameters were estimated significantly with a clear physical meaning. The effect of acid catalyzed oligomerization was investigated by model simulations. It was found to disturb the Anderson Schulz Flory distribution and lead to alkene isomerization while the extent of cracking was still negligible. These simulations illustrate how the SEMK model can be used in catalyst design. In future work the acid catalyzed oligomerization will also be assessed experimentally and corresponding SEMK model parameters will be determined.

Acknowledgements

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