# Single-Event Kinetic Model for Cracking and Isomerization of 1-Hexene on ZSM-5

*T. von Aretin and O. Hinrichsen, Technische Universität München, Catalysis Research Center and Chemistry Department, D-85748 Garching b. München, Germany*

Both ethene and propene offer a wide range of applications for the production of synthetic materials. They are mainly produced by steam cracking of naphtha or catalytic cracking of crude oil into petroleum fractions. Since the demand for propene is growing faster than for ethene, the production of low olefins on demand offers economic advantages. In this context the catalytic cracking of higher olefins on acid zeolites allows a process design with high propene yield. To obtain further mechanistic insights into the reaction pathways occurring during catalytic cracking of olefins, a kinetic model of the reaction is developed. Due to the large number of reaction pathways leading to an experimentally observed product distribution, the single event kinetic (SEK) modeling approach is applied [1].

**Model Development:**

The reactivity on the acid sites of the zeolite follows the well known carbenium ion chemistry [2]. Thus, the observed elementary reactions are (de)-protonations, alkyl shifts, hydride shifts, PCP-branchings, which proceed through a protonated cyclopropane (PCP) ring as the transition state, cracking reactions *via* beta scission as well as dimerization as the reverse reaction of cracking.

To incorporate this reactivity of olefins into a kinetic model, a reaction network including all possible elementary reactions on the acid catalyst is generated. In the reaction network every product has also been considered as a reactant, thus ensuring that all reaction possibilities are taken into account. A matrix notation, which ascribes a unique Boolean relation matrix to every olefin and carbenium ion, allows the computer aided generation of elementary reactions on the zeolite independent of the considered olefin. Using the concept of rate determining steps, these elementary reactions are combined to reaction pathways. Thereby, a reaction pathway comprises several elementary reactions leading from gas-phase educts *via* a rate determining step on an acid site to gas-phase product olefins.

To handle the large number of parameters necessary for the kinetic description of this reaction network, the SEK model is applied [3]. Using the single event approach the rate constant for every elementary reaction is divided into two parts. The first is an enthalpic part accounting for the different types of carbenium ions involved, e.g. secondary or tertiary ions. This procedure subdivides the elementary reactions into different reaction families, which are described by only one rate constant depending on the reactant and product carbenium ion. The second part of the rate constant accounts for the structure of the molecules and considers the entropy difference between reactant and transition state. Thus, multiple elementary reactions are comprehended by a limited amount of kinetic parameters.

**Reaction pathways:**

A test case with experimental data from literature [4] is used to show the suitability of the SEK model for the description of the complex reactivity observed in olefins cracking. The catalytic cracking of 1-hexene on ZSM-5 is considered, because a detailed product spectrum depending on conversion in the absence of deactivation is given [4]. In the literature, experimentally observed reactions include cracking and isomerization of hexenes as well as dimerization reactions forming dodecenes [4]. These dodecenes can undergo numerous isomerization and subsequent cracking reactions, leading to the observed product spectrum.

A reaction network for cracking and isomerization of 1-hexene describing these reaction pathways is generated with dodecenes being the largest considered olefins [4]. The influence of the catalyst on the reactivity is included into the model *via* steric constraints. Thus, compared to the free gas-phase chemistry reaction pathways are excluded from the reaction network. According to experimental observations [4] olefins with a high degree of branching or containing quaternary carbon are not observed due to pore size restrictions. Thus, the corresponding reaction pathways are excluded and not considered for calculating the reaction rates.

The rate constants for cracking and dimerization are not independent from each other since these two pathways are forward and reverse reactions. Thus, the single event rate constants for dimerization are expressed *via* the corresponding single event rate constants for cracking and an equilibrium condition to ensure microscopic reversibility of the reaction pathways.

**Results:**

Rate equations for every pathway and, based on these, the rates of formation for all olefins are set up according to the SEK model [1]. Since physisorption and protonation are regarded to be in quasi-equilibrium, the rate determining steps are methyl shift, PCP-branching, cracking and dimerization. Hereby, dimerization pathways *via* secondary educt and tertiary product carbenium ions are found to be excluded from the reaction network due to steric constraints in the pores of ZSM-5.

In total the kinetic model is based on 144 methyl shift, 784 PCP-branching, 141 cracking and 119 dimerization reactions with 593 different olefins being considered. Ratios of single event rate constants allowing to reproduce the experimental product distribution depending on conversion are estimated with a Levenberg-Marquardt algorithm [4].

The model predictions of 20 product olefins and the combined $C_7^=$ - $C_{12}^=$ olefins are in good agreement with the corresponding experimental mass fractions. Thus, the SEK modeling approach is capable of describing the complexity of the reaction pathways occurring during cracking and isomerization of 1-hexene on ZSM-5.

The advantage of applying the SEK modeling approach is the small number of parameters necessary to describe this complex reactivity. With quaternary carbon atoms being excluded from the reaction network, cracking reactions with tertiary product carbenium ions become impossible. The same holds for methyl shift reactions involving tertiary carbenium ions as well as for PCP-branching reactions between tertiary educt and product carbenium ions. Thus, the number of single event rate constants to be determined from the experimental data is reduced to six.

Insight into the ratios of reaction rates for different reaction pathways leading to the detailed experimental product distribution on ZSM-5 is obtained from the estimated single event rate constants. To describe the reaction rates of olefins on the zeolite, the concept of rate determining steps and quasi-equilibrated elementary reactions in the different reaction pathways can be used. Hereby, the complex product spectrum on ZSM-5 with experimental data points for 21 different species is reproduced by kinetic modeling based on the proposed reaction pathways. The agreement between model and experiment is exemplarily shown for two different olefins in figure 1.

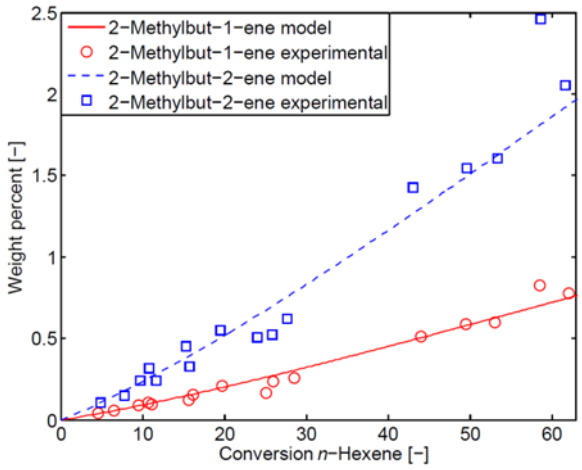



Figure 1: Comparison between experimental product distribution [4] and model predictions for 2-methylbutenes

**Outlook:**

The aim of further work on olefins cracking is to link catalyst design and product distribution. Therefore, catalyst descriptors like the acid strength of the zeolite shall be included into the kinetic model. In order to enhance the rate of reaction pathways leading to an increased propene yield, the effect of acid strength on the product distribution shall be investigated. By accounting for the temperature dependency of the reaction rate, the influence of experimental conditions on reaction pathways forming ethene or propene shall be studied. Thereby, the reactor model will be used for optimization purposes to increase the yield of lower olefins in the catalytic cracking on ZSM-5.

[1] Thybaut, J.W., Marin, G. B., Baron, G. V., Jacobs, P. A. and Martens, J. A., J. Catal. 202:324-339, 2001

[2] Brouwer, D.M., *Reactions of Alkylcarbeniumions in Relation to Isomerization and Cracking of Hydrocarbons,* Prins, R. and Schuit, G.C., Eds., *Sijthoff & Noordhoff, 1980, pp 137-160*

[3] Vynckier, E. and Froment, G.F., *Kinetic and Thermodynamic Lumping of Multicomponent Mixtures,* Astarita, G. and Sandler, S.I., Eds., *Elsevier, 1991, pp 131-161*

[4] Abbot, J. and Wojciechowski, B.W., Can. J. Chem. Eng. 63:451-461, 1985