# Optimization of the product spectrum for 1-pentene cracking on ZSM-5 using single-event methodology. Part 2: Recycle reactor

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HIGHLIGHTS

- Single-event kinetic model applied for reactor design.
- High accordance between simulated and experimental results from literature for different feed olefins.
- Implementation of a recycle reactor for high propene yields.
- Optimization of recycle reactor, compromise between propene yields and process costs.
- Assessment of effect of catalyst deactivation with kinetic model.

GRAPHICAL ABSTRACT
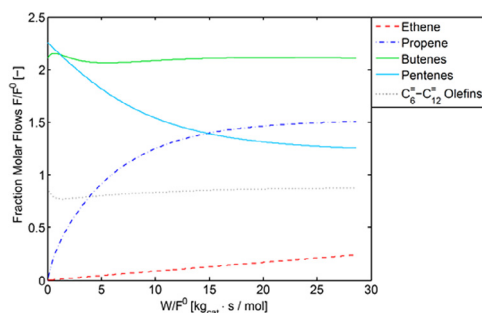
ABSTRACT

This study is the second part of a mechanistic approach to incorporate kinetics into a reactor model. The single-event kinetic modeling concept is used to optimize a recycle reactor for 1-pentene cracking on ZSM-5. A flow scheme for this kind of reactor is presented in which the reactor outlet stream is separated into $C_4^=$–$C_{12}^=$ olefins for recycle and into the product stream consisting of propene and ethene. Since the latter only contains propene and ethene in this idealized reactor configuration, the 1-pentene feed can be selectively converted to these lower olefins. The validity of the applied single-event kinetic model to different feed olefins is shown by comparing simulated product distributions obtained for 1-hexene, 1-pentene and 1-butene as feed to own experiments and literature results. The implemented recycle reactor model is used to optimize the reaction conditions with the aim of maximizing propene yield and minimizing ethene yield from a 1-pentene feed by varying reaction temperature as well as residence time.

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1. Introduction

The ever increasing importance of industrial polymer production leads to a growing demand for lower olefins like ethene and propene which offer a wide range of applications. Their synthesis routes via steam cracking of naphtha or catalytic cracking of crude oil [1] lack the possibility of producing olefins on demand. This concept has significant economic advantages since the demand for propene is more and more decoupled from the demand for ethene and, thus, is growing faster [2]. As a consequence, the aim of catalytic cracking of higher olefins on acid zeolites is to obtain high propene yields. Because the network of such an olefin interconversion is very complex, kinetic modeling could give insight into the reactivity to support the transfer to large-scale reactors.

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Nomenclature

C_{O_i}	concentration of physisorbed olefin O_i on the zeolite surface (mol kg_{cat}^{-1})
$C_{R_i^+}$	concentration of carbenium ion R_i^+ on the zeolite surface (mol kg_{cat}^{-1})
C_t	total concentration of acid sites on the zeolite (mol kg_{cat}^{-1})
F	molar flow rate in the reactor (mol s^{-1})
$F_{O_{CN}}$	molar flow rate of all olefin isomers O_{CN} with carbon number CN in the reactor (mol s^{-1})
F^0	molar flow rate of 1-pentene at the reactor inlet (mol s^{-1})
$K_{phys}(O_i)$	equilibrium constant for physisorption of olefin O_i (bar^{-1})
k	regular rate coefficient (s^{-1}) or (bar^{-1} s^{-1})
$k_{Cr}(m;n)$	regular rate coefficient for cracking reaction between reactant carbenium ion of type m to product carbenium ion of type n (s^{-1})
$k_{Dim}(m;n)$	regular rate coefficient for dimerization reaction between reactant carbenium ion of type m to product carbenium ion of type n (bar^{-1} s^{-1})
$\widetilde{K}_{isom}(O_i;O_{ref})$	single-event equilibrium constant for isomerization of olefin O_i to reference olefin O_{ref} (–)
$\widetilde{K}_{prot}(O_{ref};m)$	single-event equilibrium constant for protonation of reference olefin O_{ref} to carbenium ion of type m (–)
$\tilde{k}$	single-event rate coefficient (s^{-1}) or ($bar^{-1}s^{-1}$)
$\tilde{k}_{Cr}(m;n)$	single-event rate coefficient for cracking reaction between reactant carbenium ion of type m to product carbenium ion of type n (s^{-1})
$\tilde{k}_{Dim}(m;n)$	single-event rate coefficient for dimerization reaction between reactant carbenium ion of type m to product carbenium ion of type n (bar^{-1} s^{-1})
m	type of carbenium ion: tertiary, secondary or primary (–)
n	type of carbenium ion: tertiary, secondary or primary (–)
n_e	number of single events (–)
p_{O_i}	partial pressure of olefin O_i (bar)
p_{O_v}	partial pressure of olefin O_v (bar)
$R_{O_{CN}}$	net rate of production of all olefin isomers with the carbon number CN (mol kg_{cat}^{-1} s^{-1})
$r_{Cr}(m;n)$	reaction rate for cracking as rate-determining step from reactant carbenium ion of type m to product carbenium ion of type n (mol kg_{cat}^{-1} s^{-1})
$r_{Dim}(m;n)$	reaction rate for dimerization as rate-determining step from reactant carbenium ion of type m to product carbenium ion of type n (mol kg_{cat}^{-1} s^{-1})
W	catalyst mass (kg_{cat})
σ_{O_i}	symmetry number of olefin O_i (–)
$\sigma_{O_i}^{\neq}$	symmetry number of transition state with olefin O_i as reactant (–)
$\sigma_{R_i^+}$	symmetry number of carbenium ion R_i^+ (–)

In literature, there are many experimental studies for catalytic cracking of olefins on ZSM-5 [3–14]. Most of them address 1-butene cracking [3–5,7–9,11–13], whereas only a few investigate pentene cracking [10] or different feeds ranging from C_2 to C_3 [6] or from C_3 to C_7 [14]. Despite this variety of experimental data, only a few publications concern the kinetic modeling of these processes. Epelde et al. [15] report a kinetic model for 1-butene cracking on ZSM-5 which contains eight lumps: ethene, propene, butenes, C_5 or higher aliphatics, BTX aromatics, C_2–C_3 paraffins, C_4 paraffins and methane. Kinetic parameters are fitted to experimental data on a potassium modified catalyst (1 wt%) with a Si/Al ratio of 280 at zero time on stream (TOS). In their reaction network, ethene, all paraffins and all aromatics are considered to be final products. After expressing the different reaction steps with rate equations, they estimate activation energies for each of the ten proposed rate coefficients. The individual steps are assumed to be elementary; an inclusion of adsorption terms via LHHW kinetic expressions brings no significant improvement. The estimated parameters lead to high parity between measured and modeled results. In a final step, the authors show that a reaction network with only five lumps (ethene, propene, butenes, C_5 or higher aliphatics plus BTX aromatics and paraffins) is also sufficient. Huang et al. [14] perform their kinetic measurements with C_3 to C_7 feeds on ZSM-5 with a Si/Al ratio of 200. Opposed to Epelde et al. [15], they neglect hydrogen transfer products, i.e. paraffins and aromatics, because of short contact times and low conversions. A reaction network is established including both alkylation with subsequent cracking and monomolecular cracking when possible. Parameter estimation is performed which leads to activation energies for each step of the network. Their kinetic model explicitly includes adsorption terms (LHHW-type) for olefins and also for water since they feed C_3 to C_7 alcohols instead of directly using the corresponding olefins. The adsorption constant is assumed to be the same for all olefins. With these assumptions, reproduction of measured values is successfully performed. Furthermore, the model is able to describe a mixture of different olefins as feed. Chen et al. [16] establish a kinetic model where they consider β-scission of different feeds, ranging from C_4 to C_6 olefins, on ZSM-5 with a Si/Al ratio of 42.6. Since the experimental data is collected only for low conversion (less than 15%), the exclusion of alkylation and hydrogen transfer is possible. Their calculations include an adsorption constant for every olefin assuming surface alkoxides which allows the differentiation between secondary and tertiary intermediates. Thus, they are able to calculate intrinsic activation barriers for different cracking modes. Their fitted results confirm the values from Mazar et al. [17] who also investigate different β-scission modes of C_6 and C_8 olefins. In contrast to Chen et al. [16], their results are completely based on theoretical calculations using dispersion-corrected DFT. Borges et al. [18] present a kinetic model for light olefin conversion on ZSM-5. For the kinetic measurements, either ethene, propene or 1-butene are led over catalysts with Si/Al ratio of 30 and varying numbers of acid sites. They account for adsorption using a Langmuir approach and assume that all olefins have the same adsorption constant. This hypothesis is confirmed with DFT calculations. In the next step, they compare the theoretically obtained catalytic activity with their experimental results which shows high parity. A subsequent study by Oliveira et al. [19] focusses on the influence of acidity on the transformation of ethene, propene and 1-butene on ZSM-5. For that, they measure the activation energy of ammonia desorption and include it into both adsorption enthalpy and activation energy via a linear Polanyi-term. The influence of the olefinic chain length was implemented with empirical equations. This model also accounts for hydrogen transfer products. In a very recent study, Ying et al. [20] show a kinetic model of the interconversion of different olefins ranging from C_2 to C_7. A commercial ZSM-5 catalyst with a Si/Al ratio of 103 was used for the measurements. In their reaction network, seven lumps are used: ethene, propene, butenes, pentenes, hexenes, heptenes plus octenes and hydrogen transfer products (paraffins and aromatics). From the experimental results