

MICROKINETIC MODELING OF LIGHT ALKENE OLIGOMERIZATION ON ACIDIC ZEOLITES

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Abstract

A microkinetic model has been developed to simulate the oligomerization process of light olefins over acidic zeolites. The kinetic parameters governing the process were estimated according to thermodynamic considerations. The chemistry of the process was organized into reaction families, each of them associated to a unique reaction operator. A kinetic network was automatically generated by applying the reaction operators to the reactive species and their progeny. The model predictions were successfully validated using the results of experimental data collected under different temperatures, reactant pressures, and space velocities.

Keywords

Oligomerization, H-ZSM-5, Modeling, Catalysis, Zeolites.

Introduction

Light alkanes with relatively low fuel value are abundant components of shale gas, and by-products from refinery units and petrochemical plants. Dehydrogenation of these hydrocarbons is a common process leading to light olefins that can be oligomerized to produce liquid fuels and chemicals (Labinger et al., 2015). Significant research efforts are directed toward the kinetic modeling of complex reaction networks involved in olefin oligomerization processes, which significantly aid in improving the design of industrial reactors and novel catalysts.

This paper originates from the Mobil-olefin-to-gasoline and distillate (MOGD) process, based on the use of the proton-exchanged zeolite H-ZSM-5. The pore geometry of this catalyst imposes restrictions on the degree of branching of the products, influencing the product distributions of low temperature (250-300 °C) olefin oligomerization (Sarazen and Iglesia, 2018). The typical approach applied to study these reacting systems is “pathways-level modeling”, consisting of the lumping of several reactions in a single one describing the conversion

of a reagent into a product and disregarding any reaction intermediate(s). However, due to the rough lumping by carbon number, these models are not detailed enough to predict the product distribution and the process selectivity. Furthermore, molecular information is obscured by the multicomponent nature of each lump. This affects the “predictive power” of the model which can be applied beyond the range of conditions for which it was specifically developed with little confidence.

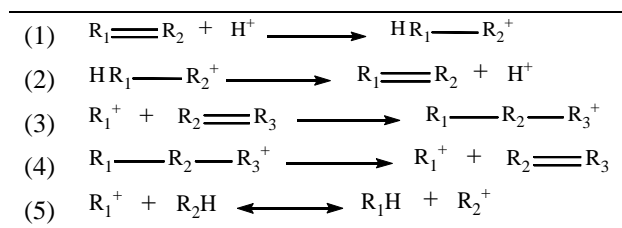
The alternative proposed in this paper is based on the development of microkinetic models. A microkinetic model is composed of elementary steps obeying the law of microscopic reversibility. The reaction rate of each step can be expressed by an elementary rate law containing specific kinetic coefficients. To date, detailed mechanistic models of acid-based olefin oligomerization have not been proposed in the literature due to the enormous complexity of these systems and the difficulties in assembling its mechanism by hand.

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Methods

The oligomerization of ethylene and propylene is characterized by an extremely complex product distribution due to the large amount of ionic species formed during the process. For this reason, computational methods are essential to develop a reaction mechanism and solve the corresponding reactor models. The reaction network contains thousands of species and even more distinct reactions. The large network can be condensed into reactions that occur with similar chemistry. For this reason, the chemistry of the system was organized into reaction families (Table 1), and a unique mathematical operator was specified for each reaction family (Broadbelt et al., 1994).

Table 1. List of reaction families: (1) protonation, (2) deprotonation, (3) oligomerization, (4) β -scission, (5) hydride transfer. Isomerization steps are not included in the table.



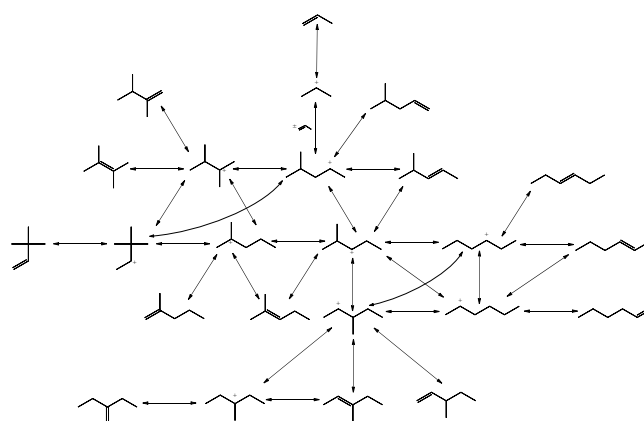
The species present in the reacting system were represented using bond and electron (BE) matrices based on graph theory. The reaction mechanism was then created automatically by applying the operators to all the different reactants and their progeny. Rate coefficients for all the elementary steps were expressed in Arrhenius form. The Evans-Polanyi relationship was used to relate the activation energy to the heats of reaction of each reaction step. The heats of reactions were calculated based on the heats of formation of the reacting species. The frequency factors were estimated directly from transition state theory knowing the entropy change between the reactants and the corresponding transition states.

Results

The reaction network is initiated via formation of an ionic species by protonation of the double bond of the reacting olefin. The kinetic parameters governing the stability of the resulting ionic species are derived from literature that characterizes them as alkoxide species or carbenium ions. The reverse reaction, deprotonation, is a termination step that desorbs the alkenes from the surface of the catalyst returning a proton to the acid site. Oligomerization proceeds through addition of an alkene to an ionic species and consequent formation of a new sigma bond. β -scission breaks the bond between the carbon atom in the β -position with respect to the charged carbon atom, representing the reverse step of oligomerization.

Cyclization reactions for molecules with carbon atoms higher than 4 were also included in the network together with several isomerization steps. The application of these reaction families was restricted to a limited number of reactants to generate molecular species with relatively low carbon number (≤ 12) to control the growth of the oligomerization mechanism (Susnow et al., 1997). Figure 1 shows a section of the oligomerization network involving C6 ionic and molecular species.

Figure 1. Extract of the oligomerization network showing C6 ionic and molecular species.



The developed reaction network and the estimated kinetic coefficients were coupled with the design equations of a PFR to build a continuum kinetic model. The resulting system of differential equations was then integrated using a numerical solver to simulate reaction kinetics, product yields and selectivity. The proposed mathematical model was validated to confirm its reliability using the results of experimental runs conducted under varying operating conditions.

Conclusions

The microkinetic analysis presented in this paper unravels mechanistic details of acid-catalyzed oligomerization chemistry of light olefins with high industrial relevance. The developed mathematical model represents a powerful tool to reproduce and predict the product distribution obtained from experimental activities.

References

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