Kinetic modeling of the Brønsted acid-based ethylene oligomerization on zeolites

Sergio Vernuccio, Linda J Broadbelt*

Department of Chemical and Biological Engineering, Northwestern University, Evanston IL, USA

**Corresponding author: broadbelt@northwestern.edu*

Highlights

- A detailed mechanism is proposed for the acid-based oligomerization of ethylene.
- Kinetic parameters are estimated to describe the behavior of the system.
- The resulting mathematical model is validated using experimental results.

1. Introduction

Light hydrocarbons with relatively low fuel value are abundant by-products from refinery units and petrochemical plants. The oligomerization of light olefins, particularly ethylene and propylene, is an attractive route to produce liquid fuels that can be condensed, easily transported and processed [1]. Significant research efforts are directed toward the kinetic modeling of these processes, which is a pre-requisite for designing and operating efficient industrial reactors. 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 [2]. 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. Detailed mechanistic models of acid-based ethylene oligomerization have not been proposed in the literature to date due to the enormous complexity of this system and the difficulties in assembling its mechanism by hand.

2. Methods

The oligomerization of ethylene is characterized by an extremely complex product distribution. 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. However, despite the large dimension of the network, the number of reactions that occur with similar chemistry can be small. For this reason, the chemistry of the system was organized into reaction families (e.g., hydride transfer, oligomerization, β-scission), and a mathematical operator was specified for each family [3][4]. 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. In order to develop a mechanistic model that is of reasonable size, certain reaction rules were introduced for the system. Rate coefficients for all the elementary steps were expressed in Arrhenius form. The Evans-Polanyí 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 either directly from transition state theory or indirectly from thermodynamic properties derived from quantum chemical calculations.

3. Results and discussion

Figure 1 shows a section of the reaction network of ethylene oligomerization. Only products with carbon number up to 4 are depicted. The reaction network is initiated via formation of carbenium ions by protonation of a double bond. The reverse reaction, deprotonation, is a termination step that desorbs the alkene from the surface of the catalyst returning a proton to the acid site. Oligomerization proceeds through addition of an alkene to a carbenium ion 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. One of the most prolific elementary steps is hydride transfer that occurs with greater diversity due to possible binary combinations more than any other step. Hydride and methyl shifts are responsible for changes in the position of the carbenium ion, resulting in different locations of branch positions. Cyclization reactions for molecules with carbon atoms higher than 4 were also included in the network. The application of these reaction families was restricted to a limited number of reactants (carbon number ≤ 20) to control the growth of the oligomerization mechanism.

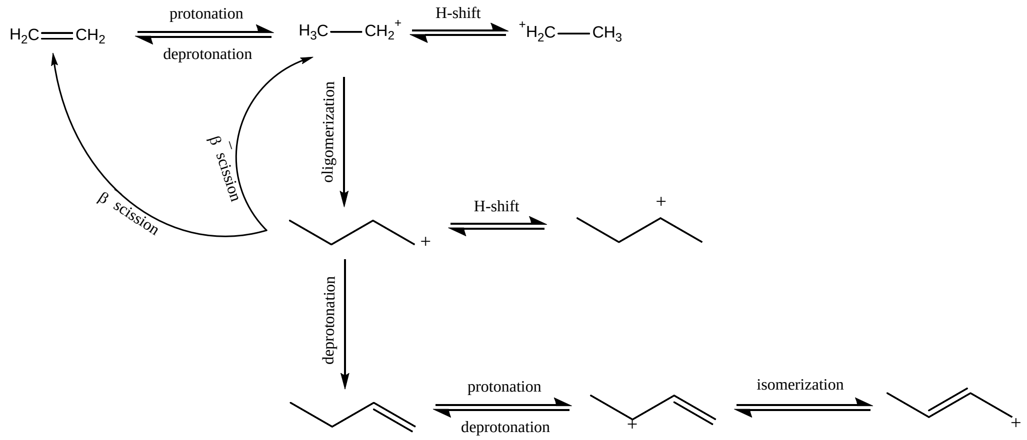

Figure 1. Simplified reaction network of ethylene oligomerization. Only species with $C \leq 4$ are shown. All the elementary steps are considered to be reversible.

The developed reaction network and the estimated kinetic coefficients were coupled with the design equations of a batch reactor to build a continuum kinetic model. The resulting system of differential equations was then integrated using a numerical solver to simulate reaction kinetics and product yields. The proposed mathematical model was finally validated – to confirm its reliability – using the results of experimental runs conducted over a wide range of operating conditions.

4. Conclusions

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

References

[1] J. A. Labinger, D. C. Leitch, J. E. Bercawl, M. A. Deimund, M. E. Davis, Top. Catal. 58 (2015) 494–501.
[2] M. Bernauer, E. Tabor, V. Pashkova, D. Kaucky, Z. Sobalík, B. Wichterlová, J. Dedecek, J. Catal. 344 (2016) 157–172.
[3] L. J. Broadbelt, S. M. Stark, M. T. Klein, Chem. Eng. Sci. 33 (1994) 790–799.
[4] R. G. Susnow, A. M. Dean, W. H. Green, P. Peczak, L. Broadbelt, J. Phys. Chem. A 101 (1997) 3731–3740.

Keywords
Oligomerization; Ethylene; Kinetic Model; Zeolite