Rational design of optimal catalysts to produce sustainable fuels from olefin oligomerization

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Highlights

- A detailed microkinetic model is proposed for the oligomerization of olefins on acidic zeolites.
- An automated network generator constructs the network from elementary reaction families.
- The model is used to optimize the process through identification of catalyst descriptors.

1. Introduction

The utilization of light olefin oligomerization for fuel production offers a sustainable route to produce clean, sulfur-free fuel. This is particularly significant given the growing demand for such fuel, driven by the potential renewable source of light olefins. Bioethanol, derived from biomass, can be efficiently converted into ethylene and other short-chain olefins through dehydration reactions[1]. Subsequently, these light olefins can be converted into longer-chain chemicals through heterogeneous zeolite-catalyzed oligomerization. Acidic zeolites in particular, attracts increasing attention because of their three-dimensional large-pore channel system and large available micropore volume. Significant efforts are also directed toward zeolite framework design and optimization that represents a continuously ongoing research challenge. One of the most interesting approaches in the development and optimization of new catalytic materials is microkinetic modelling that relies on the mechanistic understanding of the complexity of the process. Microkinetic models are currently one of the most powerful tools to analyze catalytic reaction mechanisms, identify surface intermediates and specific reaction pathways that dominate the formation of desired products. These models provide practical tools to directly optimize process conditions and to guide the design of improved catalysts. This work presents the construction of a microkinetic model to describe the intrinsic kinetics of olefin oligomerization. A library of virtual catalysts was generated by tuning some of the characteristic descriptors that account for the influence of the catalyst framework on the kinetics of the process. The developed model was used to test these virtual catalysts in the olefin oligomerization process with the aim of identifying the descriptors to assist in optimizing performance.

2. Methods

In this work, a reaction family approach was utilized to automatically generate the reaction network under the assumption that reactions with similar chemistry can be grouped together into a single type of reaction. A reaction network consisting of 3705 surface reactions and 538 physisorption/desorption steps and involving 909 molecular and ionic species was automatically constructed by using a reaction network generator [2]. The frequency factors were computed in the framework of transition state theory based on the entropy changes between reactants and transition states that were obtained from the results of DFT calculations. The activation energies were expressed as linear functions of the heats of reaction in the physisorbed state, which were calculated from group additivity methods and thermodynamic considerations [3].

3. Results and discussion

The microkinetic model was incorporated into the design equation of a plug flow reactor and successfully validated using experimental data collected under a wide range of operating conditions, including temperature, pressure, catalyst loading, and flowrate. Several simulations were conducted by

changing the operating pressure and adjusting the space velocity in the reactor to maintain constant conversion. This analysis demonstrated that increasing the operating pressure decreases the prevalence of cracking phenomena and confirmed that, at low conversion, the oligomerization of propylene on acidic zeolites is driven by the addition of C6 neutral species to propoxides that are most abundant surface intermediates on the zeolite [3]. In the "catalyst optimization phase", the developed model was used to simulate the process selectivity by varying the stabilization enthalpies of the ionic intermediates. The stabilization enthalpy can be translated to a material property because of its direct relation to the zeolite acid strength. The model demonstrated that increasing the stabilization enthalpy of the ionic intermediates drives the selectivity of the process toward the production of C9 species. This would result into a more efficient oligomerization process whose target is the production of gasoline blend with high concentration of heavy and highly branched olefins and, as a consequence, with high octane number [4].

4. Conclusions

This study revealed mechanistic details of acid-catalyzed oligomerization chemistry of light olefins. The developed microkinetic model represents a powerful tool to predict the product distribution, optimize the conditions of the process and design more efficient catalysts for sustainable applications.

References

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