

Kinetic Modeling of Plastic Waste Catalytic Cracking over Phosphorous-Modified Mesoporous ZSM-5: an Isooctane Model Compounds Study

Yannick Ureel, Anas Jamil Abdulrahman, Oğuzhan Akin, Maarten K. Sabbe,
Kevin M. Van Geem*

Laboratory for Chemical Technology, Department of Materials, Textiles and Chemical Engineering, Ghent University, Ghent, Belgium

**Corresponding author: Kevin.VanGeem@UGent.be*

Highlights

- Demonstration of a novel heterogeneous reaction network generator.
- Development of elementary kinetic model for iso-octane cracking.
- Reaction pathways found for the ex-situ catalytic pyrolysis of plastic waste.

1. Introduction

The recycling of plastic waste will be an essential asset in the transition to a sustainable and climate neutral industry. At present, heterogeneous polyolefin waste corresponding to 60% of plastic waste is challenging to recycle via solely mechanical processes because of polymer immiscibility and thermo-mechanical degradation. Therefore, chemical recycling of polyolefin waste to its monomers (ethylene and propylene) is a promising pathway. One of the most carbon efficient processes is the ex-situ catalytic pyrolysis of polyolefin waste. Here, the plastic waste is thermally pyrolyzed after which the volatiles are converted further with a highly acidic zeolite into valuable light olefins. The zeolite composition has a major influence in catalytic pyrolysis on the selectivity towards ethylene and propylene [1]. Hence, the design of the zeolite is an essential step in improving the carbon efficiency of chemical recycling via ex-situ catalytic pyrolysis. A phosphorus-modified mesoporous ZSM-5 zeolite has shown to yield a record-breaking 83% of light (C_2 - C_4 olefins) from plastic waste [2]. To further improve upon this catalyst, fundamental knowledge is required on the reaction mechanism and the influence of the zeolite on the reaction pathways.

In this work, iso-octane as model compound was catalytically cracked over the high-performance phosphorus-modified mesoporous ZSM-5 zeolite. The obtained experimental yields were modelled via an automatically generated microkinetic model. A complex elementary reaction network was generated via an in-house developed heterogeneous catalytic network generator. The kinetic parameters were determined via a combination of Bayesian optimization and gradientless local optimization. In this way, accurate reaction parameters could be obtained and the reaction pathways for the catalytic cracking within the phosphorus-modified mesoporous ZSM-5 zeolite were found. This allows to elucidate the relevant reaction paths and provide further insight into how this high-performance zeolite can be improved further to facilitate the chemical recycling of polyolefin waste.

2. Methods

The experiments were conducted in a fixed bed plug flow reactor where the iso-octane was diluted with nitrogen in a respectively 20:80-molar ratio. One gram of phosphorus-modified mesoporous ZSM-5 zeolite was pelletized and grinded to particles of 100 μm and diluted with 25 grams of $\alpha\text{-Al}_2\text{O}_3$. The flowrate of iso-octane varied between 24.6 g/h and 98.5 g/h while the temperature varied between 698-748 K. It was explicitly verified that intrinsic kinetics were obtained for all performed experiments.

The Genesys automatic reaction network generator [3] has been extended to facilitate the generation of reactions for heterogeneous catalytic models. This enhanced version of Genesys enables the simultaneous development of both gas-phase and surface-phase reactions. It now includes the capability to account for charged carbenium-ions, a crucial aspect given that catalytic cracking of hydrocarbons leads to the creation of these carbenium-ion intermediates. Additionally, the extended Genesys incorporates two distinct adsorption modes: chemisorption and physisorption. In chemisorption, a localized bond forms between the zeolite and the hydrocarbon, while physisorption involves a

delocalized interaction between the hydrocarbon and the catalyst surface. This differentiation between the two adsorption modes is fundamental for the automatic generation of heterogeneous catalytic networks.

The kinetic properties of the microkinetic model are determined by combining Bayesian optimization and local optimization techniques to obtain a global optimum. For every type of reaction family, the pre-exponential factor is optimized resulting in an 8-dimensional optimization. The Bayesian optimization was implemented via Python and the scikit-learn package, where a rational quadratic kernel was employed for the Gaussian Process [4].

3. Results and discussion

A reaction network based on 23 reaction families was generated consisting of physisorption, protolytic scission, protonation, β -scission, intramolecular hydrogen transfer, PCP-branching, methyl-shifts, and intermolecular hydrogen abstraction. For every reaction family different modes are considered depending on the order of the formed or reacting carbenium ions (secondary or tertiary). No primary carbenium ions were considered besides the intermediates required to produce ethylene. The reaction network comprises of 216 adsorbed or gaseous species and 881 elementary reactions.

A machine learning model and quantum chemical calculations have been utilized to determine the thermodynamic properties of gas-phase molecules, covering both charged and uncharged hydrocarbons [5]. Corrections to the adsorption enthalpy and entropy are applied based on the zeolite topology, as outlined in the literature [6, 7]. The activation energies of the reaction families were obtained from molecular dynamic calculations from literature and slightly modified via Bayesian optimization to match the experimental results.

4. Conclusions

A new heterogeneous catalytic reaction network generator was developed and employed to create an elementary model of the catalytic cracking of iso-octane over phosphorus-modified mesoporous ZSM-5. The combination of thermodynamic properties from quantum chemical calculations and the estimation of kinetic properties allows an accurate description of the reaction pathways. Future work aims to correlate kinetic properties with zeolite structures, extending to diverse zeolites. Similar kinetic models for varied frameworks will determine their kinetic properties. Quantum chemical analyses will explore how zeolite structure influences kinetics, enhancing activation energies and pre-exponential factors. In this way, zeolites with improved selectivities and activities can be designed for the ex-situ catalytic pyrolysis of plastic waste.

References

- [1] Ureel Y, Dobbelaere MR, Akin O, Varghese RJ, Pernalet CG, Thybaut JW, Van Geem KM. Active learning-based exploration of the catalytic pyrolysis of plastic waste. *Fuel* 2022;328:125340.
- [2] Eschenbacher A, Varghese RJ, Delikonstantis E, Mynko O, Goodarzi F, Enemark-Rasmussen K, et al. Highly selective conversion of mixed polyolefins to valuable base chemicals using phosphorus-modified and steam-treated mesoporous HZSM-5 zeolite with minimal carbon footprint. *Applied Catalysis B: Environmental* 2022:121251.
- [3] Vandewiele NM, Van Geem KM, Reyniers M-F, Marin GB. Genesys: Kinetic model construction using chemo-informatics. *Chemical Engineering Journal* 2012;207:526-38.
- [4] Pedregosa F, Michel V, Grisel O, Blondel M, Prettenhofer P, Weiss R, et al. Scikit-learn: Machine Learning in Python. *Journal of Machine Learning Research*. 12. 2011:2825-30.
- [5] Ureel Y, Vermeire FH, Sabbe MK, Van Geem KM. Beyond group additivity: Transfer learning for molecular thermochemistry prediction. *Chemical Engineering Journal* 2023;472:144874.
- [6] Nguyen CM, De Moor BA, Reyniers M-F, Marin GB. Physisorption and chemisorption of linear alkenes in zeolites: a combined QM-Pot (MP2//B3LYP: GULP)–statistical thermodynamics study. *The Journal of Physical Chemistry C* 2011;115(48):23831-47.
- [7] De Moor BA, Reyniers M-Fo, Gobin OC, Lercher JA, Marin GB. Adsorption of C₂– C₈ n-Alkanes in Zeolites. *The Journal of Physical Chemistry C* 2011;115(4):1204-19.

Keywords

Catalytic Pyrolysis; Chemical Recycling; Plastic Waste; Microkinetic Model