

MOLECULAR SINGLE-EVENT MICROKINETICS OF N-HEXADECANE HYDROCRACKING ON Pt/H-BETA

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Summary

The Single-Event MicroKinetic (SEMK) methodology for hydroisomerisation and –cracking has been extended from Pt/USY and Pt/ZSM-22 zeolites to a Pt/BETA zeolite. For the first time, the hydrocracking behavior of a hydrocarbon as heavy as n-hexadecane has been assessed using the molecular rather than the lumped version of the SEMK methodology. Compared to USY, the BETA zeolite was found to have stronger acid sites by 6 kJ mol⁻¹, and to exhibit more pronounced cracking. The latter effect could only be accounted for by allowing to decrease the related kinetic descriptors by about 10 kJ mol⁻¹.

Keywords

Reaction Path Analysis, Sustainability.

I. Introduction

Current trends in world energy consumption predict that crude oil will be the first fossil fuel source to be depleted. The exploitation of alternative sources such as natural gas, coal or biomass is becoming more and more attractive. A potential route goes through synthesis gas formation and Fischer-Tropsch (FT) synthesis. FT synthesis yields mainly linear alkanes with a boiling point beyond the desired range. Hence, FT synthesis is typically followed by a hydroisomerization and –cracking step in order to convert the heavy, linear alkanes into lighter components with generally a higher branching degree.

In the absence of known poisons such as sulphur or nitrogen containing components, bifunctional catalysts consisting of a noble metal supported on an acid zeolite are used in hydrocracking. In the present work, n-hexadecane as a model molecule was sent over a BETA zeolite (Si/Al = 13) in a gas phase plug flow reactor. The framework of the catalyst mainly consists of a large-pore network (about 5.7 x 6.8 Å) and, hence, the molecules are not sterically hindered while entering or exiting the catalyst micropores. The SEMK model originally constructed for hydrocracking of lighter alkanes on USY zeolites is used and extended to describe the current data set.

II. Model Development

A catalytic cycle in hydrocracking consists of alkane physisorption into the catalyst pores, alkane dehydrogenation into an alkene at a metal site, alkene

protonation at an skeletal acid site and rearrangement or cracking of the resulting carbenium ions. Skeletal rearrangements can occur through alkyl shifts or protonated cyclopropane (PCP) reactions while cracking goes via β-scission. The product carbenium ions leave the catalyst micropores through the reverse sequence as just described.

The reaction networks consists of a vast number of elementary steps. The number of rate parameters required by the model can be reduced by recognizing that these elementary steps can be classified into a limited number of reaction families, defined by the type of the reaction and the type of the carbenium ions involved. Within a reaction family variations in the rate coefficients for an elementary step may originate from symmetry differences between reactant and transition state and are accounted for by the ‘number of single events’ n_e . For each reaction family, a unique ‘single-event’ rate coefficient \tilde{k} is determined.

$$r^{AS/PCP/\beta} = k^{AS/PCP/\beta} C_{R^*} = n_e \tilde{k}^{AS/PCP/\beta} C_{R^*} \quad (1)$$

Assuming a Langmuir physisorption model and quasi-equilibrium for (de)hydrogenation and (de)protonation, the carbenium ion concentration C_{R^*} can be written as a function of the alkane partial pressure p_p :

$$C_{R^*} = \frac{C_{sat} C_i K_{prot} K_{deh} K_L \frac{p_p}{p_{H_2}}}{1 + \sum K_L p_p + \sum C_{sat} K_{prot} K_{deh} K_L \frac{p_p}{p_{H_2}}} \quad (2)$$

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The reaction rates do not solely depend on the kinetic parameters, denoted as ‘kinetic descriptors’, but also on catalyst properties such as (i) the saturation concentration C_{sat} , (ii) the total acid site concentration C_t , (iii) the Langmuir physisorption coefficient K_L and (iv) the equilibrium coefficient for protonation K_{prot} . These are commonly denoted as ‘catalyst descriptors’ and are determined from independent measurements as much as possible.

III. Results and discussion

In particular the catalyst descriptors are to be determined when extending the SEMK model from one zeolite to another. E.g. the total acid site concentration on the BETA zeolite used is obtained from NH_3 -TPD experiments while the physisorption parameters for n -hexadecane are extrapolated from values reported for lower n -alkanes on a BETA zeolite with a similar Si-Al ratio,¹ vide Table 1. The protonation enthalpies leading to secondary and tertiary carbenium ions were to be determined by regression. Because of the more pronounced cracking on the BETA compared to the original USY zeolite also the kinetic descriptors, especially those related to cracking, needed to be adjusted.

Table 1. Values for the total acid site concentration, the saturation concentration, the physisorption enthalpy and the Henry pre-exponential factor for C_{16} components.

C_t (mol kg ⁻¹)	C_{sat} (mol kg ⁻¹)	$-\Delta H_{phys}$ (kJ mol ⁻¹)	K_0 (mol kg ⁻¹ MPa ⁻¹)
0.557	0.389	162.6	8.6×10^{-9}

A comparison of calculated and experimental data is shown in Figure 1 and illustrates the adequacy of the proposed SEMK model. Even though the physisorption parameters were extrapolated over a wide range of carbon numbers, a good agreement is generally obtained between model and experimental results, particularly for monomethyl C_{16} isomers.

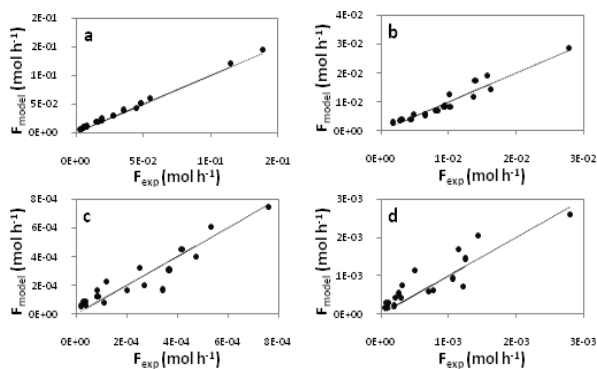


Figure 1. Parity diagrams for the outlet flow rates for some typical hydrocracking products from hexadecane on Pt/H-BETA (a) n - C_{16} , (b) monomethyl isomers of C_{16} , (c) C_3 cracking products, and (d) C_{11} cracking products.

The estimated parameter values are shown in Table 2. Values determined from n - C_8 hydroconversion data on CBV760 (USY – Si/Al=30) are selected as reference.² The acid strength of the active sites on the BETA zeolite is higher as the values for the protonation enthalpies for secondary and tertiary carbenium ion formation are about 6 kJ mol⁻¹ more negative. This leads to higher reaction rates on the BETA zeolite compared to the USY. In addition, all kinetic descriptors have decreased, especially those related to β -scissions, resulting in an even more pronounced enhancement of the reactivity of the BETA compared to the USY zeolite.

Table 2. Estimates for the adjustable parameters (kJ mol⁻¹) compared to the reference values for n - C_8 hydrocracking on a USY zeolite.

	$\Delta H_{prot}(s)$	$\Delta H_{prot}(t)$	$E_{a,AS}(s;s)^b$	$E_{a,AS}(s;t)$
USY	-64.9 (± 0.5) ^a	-95.6 (± 1.2)	77.5 (± 0.2)	74.4 (± 0.1) ^c
BETA	-70.8 (± 0.1)	-101.6 (± 0.1)	69.8 (± 0.1)	67.7 (± 2.8)
	$E_{a,AS}(t;t)$	$E_{a,PCP}(s;s)$	$E_{a,PCP}(s;t)$	$E_{a,PCP}(t;t)$
USY	104.5 (± 1.2)	108.7 (± 0.7)	98.6 (± 1.9) ^c	127.9 (± 3.3)
BETA	N/A	109.6 (± 0.1)	92.0 (± 0.1)	123.6 (± 0.1)
	$E_{a,\beta}(s;s)$	$E_{a,\beta}(s;t)$	$E_{a,\beta}(t;s)$	$E_{a,\beta}(t;t)$
USY	142.7 (± 1.0)	127.9 (± 4.9)	148.6 (± 1.0)	125.1 (± 3.8)
BETA	131.0 (± 0.1)	119.3 (± 10.0)	138.0 (± 0.5)	125.7 (± 2.2)

^a 95% confidence region, ^b type of reactant and/or product ion (secondary or tertiary), ^c $E_a(t;s) = \Delta H_{prot}(s) + E_a(s;t) - \Delta H_{prot}(t)$, ^d not significantly estimated.

Conclusions

The Single-Event MicroKinetic (SEMK) model at the molecular level has been adequately extended to heavier alkanes on a new zeolite, i.e., a BETA zeolite. It indicates the reliability of the extrapolation of the physisorption parameters in the model as well as the feedstock independence of the SEMK model. Stronger acid sites were found at the BETA zeolite leading to changes in activation energies. The latter were more pronounced for β -scission, which confirms the reputation of the BETA zeolite as an active ‘cracking’ catalyst.

Acknowledgements

The Special Research Fund (Bijzonder Onderzoeksfonds) is acknowledged for financial support. This research has been carried out in the framework of IDECAT in association with ITQ-CSIC, University of Valencia, Spain.

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