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 relumped 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 \(\beta\)-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.

\[
r^{AS/PCP/\beta}_{AS/PCP/\beta} = \tilde{k}^{AS/PCP/\beta} C_w = n_e \tilde{k}^{AS/PCP/\beta} C_w
\]

Assuming a Langmuir physisorption model and quasi-
equilibrium for (de)hydrogenation and (de)protonation, the
carbenium ion concentration \(C_w\) can be written as a
function of the alkane partial pressure \(p_r\):

\[
C_w = \frac{C_{\text{m},C} K_{\text{prot}} K_{\text{deh}} K_{\text{c}} \frac{p_r}{p_n}}{1 + \sum K_{c} p_r + \sum C_{\text{m},C} K_{\text{prot}} K_{\text{deh}} K_{\text{c}} \frac{p_r}{p_n}}
\]

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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 \( C_{\text{sat}} \), (ii) the total acid site concentration \( C_a \), (iii) the Langmuir physisorption coefficient \( K_\text{prot} \) and (iv) the equilibrium coefficient for protonation \( K_\text{prot} \). 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, vide Table 1. The protonation enthalpies leading to 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 \( \beta \)-scissions, resulting in an even more pronounced enhancement of the reactivity of the BETA compared to the USY zeolite.

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.

<table>
<thead>
<tr>
<th>( C_a ) (mol kg(^{-1}))</th>
<th>( C_{\text{sat}} ) (mol kg(^{-1}))</th>
<th>( \Delta H_\text{phys} ) (kJ mol(^{-1}))</th>
<th>( K_\text{prot} ) (mol kg(^{-1}) MPa(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.557</td>
<td>0.389</td>
<td>162.6</td>
<td>8.6 x 10(^{-7})</td>
</tr>
</tbody>
</table>

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.

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 \( \beta \)-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.

<table>
<thead>
<tr>
<th>( \Delta H_\text{prot}(t) )</th>
<th>( \Delta H_\text{prot}(s) )</th>
<th>( E_{\text{prot}(s)} )</th>
<th>( E_{\text{prot}(t)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>USY</td>
<td>-64.9 (±0.5)(^a)</td>
<td>-95.6 (±1.2)</td>
<td>77.5 (±0.2)</td>
</tr>
<tr>
<td>BETA</td>
<td>-70.8 (±0.1)</td>
<td>-101.6 (±0.1)</td>
<td>69.5 (±0.1)</td>
</tr>
</tbody>
</table>

a 95% confidence region, \( b \) type of reactant and/or product ion (secondary or tertiary), \( c \) \( E_{\text{prot}(s)} = \Delta H_\text{prot}(s) + E_{\text{prot}(s)} - \Delta H_\text{prot}(t) \), \( d \) 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 \( \beta \)-scission, which confirms the reputation of the BETA zeolite as an active ‘cracking’ catalyst.

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References