Relumped Single-Event MicroKinetic Model for Aromatics Hydrogenation on Pt Catalyst

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• fuel quality: cetane number for diesel
  smoke point for jet fuel

• environmental: carcinogenic character

• industrially: cyclohexane from benzene hydrogenation, a base chemical of nylon
(relumped) microkinetics

- fundamental understanding
  - model compounds
  - detailed analyses
- extended computation times

microkinetics vs. lumped kinetics

- real-life applications
  - global characterization
  - fast feedback loops
• introduction
• SEMK model for aromatics hydrogenation
  – single-event concept
  – benzene hydrogenation on Pt
• relumped SEMK microkinetics
  – potentially dominant reaction pathways
  – lumping coefficients
  – relumped model performance
• conclusions
Single-Event MicroKinetics (SEMK)

- large number of species and elementary steps
- limited number of reaction families defined based on (energy/enthalpy)
  - reaction type
  - types of intermediates involved
- accounting for symmetry effects (entropy)

\[ k(m,n) = \frac{\sigma_{\text{reactant}}^{\text{global}}}{\sigma_{\text{global}}^{\#}} \frac{k_b T}{h} \exp \left( \frac{\Delta S^{0,\#}}{R} \right) \exp \left( -\frac{\Delta H^{0,\#}}{RT} \right) = n_e \tilde{k}(m;n) \]
hydrogenation elementary steps

- Horiuti-Polanyi mechanism

\[
\begin{align*}
\text{H}_2(g) + 2^* & \rightleftharpoons 2 \text{H}^* & K_{\text{H}_2} \\
\text{A}(g) + ^* & \rightleftharpoons \text{A}^* & K_A \\
\text{A}H_i^* + \text{H}^* & \rightleftharpoons \text{A}H_{i+1}^* + ^* & K_{i+1} \quad (i=0,..5) \\
\text{A}H_6^* & \rightleftharpoons \text{A}H_6(g) + ^* & K_{\text{A}H_6}
\end{align*}
\]
reaction families

- branching degree
- number of unsaturated nearest neighbors

Berty-reactor:
- gas phase
- perfectly mixed
- continuous flow

\[ F_{j,\text{out}} - F_{j,\text{in}} = R_j W \]

<table>
<thead>
<tr>
<th>( p_{\text{tot}} ) (MPa)</th>
<th>( T ) (K)</th>
<th>( p_{\text{aro}} ) (kPa)</th>
<th>( p_{\text{hyd}} ) (kPa)</th>
<th>space time (kg_{\text{cat}} s mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – 3</td>
<td>423 – 498</td>
<td>10 – 60</td>
<td>100 – 600</td>
<td>20-70</td>
</tr>
</tbody>
</table>

rate equations

\[ R_j = \sum_i r_{i \rightarrow j}^{\text{hyd/deh}} - r_{j \rightarrow i}^{\text{deh/hyd}} \]

i,j: metal chemisorbed cyclic hydrocarbons

\[ R_j = \sum_i \left( n_{e,i \rightarrow j} \left[ \tilde{k}_{\text{hyd}}(m_i,n_i)C_{H^*} + \tilde{k}_{\text{deh}}(m_i,n_i)C_* \right] C_i - n_{e,j \rightarrow i} \left[ \tilde{k}_{\text{hyd}}(m_i,n_i)C_{H^*} + \tilde{k}_{\text{deh}}(m_i,n_i)C_* \right] C_j \right) \]

\( C_i, C_{H^*} \) and \( C_* \) obtained from:

- chemisorption equilibria for aromatic, hydrogen and cyclohexane
- pseudo steady state approximation for all other metal chemisorbed cyclic hydrocarbons

- site balance

set of \( n_{\text{int}}-2 \) equations

= 13 for benzene, 40 for toluene and 36 for o-xylene
### Parameter Value (kJ mol$^{-1}$)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a(0,2)$</td>
<td>57.5 ± 0.5</td>
</tr>
<tr>
<td>$E_a(1,2)$</td>
<td>65.1 ± 1.9</td>
</tr>
<tr>
<td>$E_a(2,2)$</td>
<td>57.5 ± 0.5</td>
</tr>
<tr>
<td>$\Delta H(0,2)$</td>
<td>7.9 ± 0.4</td>
</tr>
<tr>
<td>$\Delta H(1,2),*$</td>
<td>4.5</td>
</tr>
<tr>
<td>$\Delta H(2,2)$</td>
<td>1.2 ± &lt;0.5</td>
</tr>
<tr>
<td>$\Delta H_B$</td>
<td>-56.0 ± &lt;0.5</td>
</tr>
<tr>
<td>$\Delta H_{H_2}$</td>
<td>-59.4 ± &lt;0.5</td>
</tr>
<tr>
<td>$\Delta H_{CHA},*$</td>
<td>5.3</td>
</tr>
<tr>
<td>F value</td>
<td>4150</td>
</tr>
</tbody>
</table>

**Conversion (%)**

- 1 MPa
- 2 MPa
- 3 MPa

**Surface coverage (%)**

- Hydrocarbon
- Hydrogen
- Free site

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Bera et al. I&ECR, (2011)
reaction path analysis

- numbers indicate % contribution of disappearance of species
- thickness of the arrows corresponds to the order of magnitude of rates
- **hydrogenation** / **dehydrogenation**
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potentially dominant reaction pathways

- 14 ‘forward’ pathways contributing to hydrogenation
rate along a pathway

\[ R_{AH_6(g),p} = C_t k(0,2) \theta_{12} \cdot \theta_{H^*} - C_t \frac{k(0,2)}{K(0,2)} \theta_{13} \]

intermediates: \[ 0 = k(2,2) \theta_{H^*} \cdot \theta_{1} - \left[ \frac{k(2,2)}{K(2,2)} \theta_{1} + k(1,2) \theta_{H^*} \right] \theta_{2} + \frac{k(1,2)}{K(1,2)} \theta_{3} \]

chemisorption: \[ \theta_{1} = \theta \cdot K_{A} p_{A}, \quad \theta_{H^*} = \theta \cdot \sqrt{K_{H_2} p_{H_2}} \]

site balance: \[ 1 = \theta + \theta_{H^*} + \theta_{1} + \theta_{2} + \theta_{3} + \theta_{6} + \theta_{9} + \theta_{12} \]

\[ R_{AH_6(g),p} = C_t k(0,2) \frac{B^5(1,2)K(2,2)K(0,2)k(1,2)k(2,2) \sqrt{K_{H_2} p_{H_2}}K_{B}p_{B}}{K(0,2) \left[ B^5(1,2)K(2,2)k(1,2) \right] + B^4(1,2)k(2,2) + B^3(1,2)k(2,2) + B^2(1,2)k(2,2) + B(1,2)k(1,2) + K(1,2)k(1,2)} \theta^2 \]

with \[ B(1,2) = K(1,2) \frac{\theta_{H^*}}{\theta} = K(1,2) \sqrt{K_{H_2} p_{H_2}} \]
relumped reaction rate

\[ R_{\text{CHA(g)}} = (LC)_{\text{hyd}} \sum_p R_{\text{CHA(g), p}} \]

- Lumping coefficients account for
  - different nr. of hydrocarbon species in site balance (7 vs 13)
  - variations in relative surface concentrations

\[ (LC)_{\text{hyd}} = \frac{7}{13} e^{-\frac{\Delta H_{\text{correction}}}{R}} \]

\[ \Delta H_{\text{correction}} = 13 \text{ kJmol}^{-1} \]

Surface thermodynamics correction factor
## Surface Intermediates Concentrations

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Free site (%)</th>
<th>Hydrogen (%)</th>
<th>Total hydrocarbon (%)</th>
<th>Benzene (%)</th>
<th>Cyclohexyl (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rel</td>
<td>Det</td>
<td>Rel</td>
<td>Det</td>
<td>Rel</td>
</tr>
<tr>
<td>423</td>
<td>6.4</td>
<td>5.7</td>
<td>29.6</td>
<td>25.3</td>
<td>64</td>
</tr>
<tr>
<td>448</td>
<td>14.5</td>
<td>11.8</td>
<td>42.1</td>
<td>32.3</td>
<td>43.4</td>
</tr>
<tr>
<td>473</td>
<td>27</td>
<td>24.6</td>
<td>51</td>
<td>44.6</td>
<td>21.4</td>
</tr>
<tr>
<td>498</td>
<td>39.4</td>
<td>37.9</td>
<td>51.6</td>
<td>48.4</td>
<td>9</td>
</tr>
</tbody>
</table>
relumped model performance
conclusions

- relumped SEMK model for aromatic hydrogenation adequately describes benzene data on Pt
- sum of rates of potentially dominant reaction pathways
- lumping coefficients account for
  - different number of hydrocarbon surface species in pathway
  - surface thermodynamics correction
Acknowledgements

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