Pyridine hydrodenitrogenation over an industrial NiMo/γ-Al₂O₃ catalyst
Application of gas phase models to liquid phase reactions

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introduction and motivation

Environmental Issues
Government Regulations
Technical

Industrial reactors
- Three Phase reactions
- Kinetics may be disguised by hydrodynamic phenomenon

Laboratory Reactors
- G-S / G-S-L reactions
- Intrinsic kinetics
- Used for model construction and discrimination

Trickle Bed Reactor
(Ni/Co)Mo/ Al₂O₃
200 – 400 °C
10 – 40 bar

HDN

Three phase
✓ Fischer Tropsch
✓ Hydrocracking
✓ Hydroprocessing

Bridging the gap between laboratory and industrial reactors
methodology

- Extended set of gas phase experimentation
- Limited liquid phase experimentation
- Three phase industrial reactor simulation

- Operating conditions
- Reaction pathway
- Detailed kinetics
- Model construction
- Evaluation estimated parameters

- Effect of

- Liquid phase conditions on
- Formation of new compounds
- Solvent adsorption
- Assessment of liquid phase non ideality

- Validation of data available from industrial / Pilot plant studies

Berty Reactor
Robinson Mahoney Reactor
• Gas versus liquid phase experiments
  – network elucidation and difference in experimental programmes
• Liquid phase experimental results
• Thermodynamic non ideality in liquid phase
• Gas phase model and subsequent extension
• Liquid phase model
• Conclusions
gas and liquid phase experiments

- 1-pentylpiperidine observed in the liquid phase experiments only
  - observed with 2D GC - MS analysis
  - due to the varying operating conditions and higher bimolecular reactions
- Highly reactive/unstable intermediates not observed during analysis

**Challenges in extension**

- Differing denitrogenation kinetics in gas and liquid phase
- Accounting for additional response in the model
<table>
<thead>
<tr>
<th>Program</th>
<th>Gas Phase(^a)</th>
<th>Liquid Phase(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor type</td>
<td>Berty type (CSTR)</td>
<td>Robinson Mahoney (CSTR)</td>
</tr>
<tr>
<td>Temperature range (K)</td>
<td>573 – 633</td>
<td>543 – 613</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>1.5 – 4.0</td>
<td>6.0 – 8.0</td>
</tr>
<tr>
<td>(\text{H}_2/\text{pyridine (mol/mol)})</td>
<td>80 – 600</td>
<td>10 – 15</td>
</tr>
<tr>
<td>Space time (kg(_{\text{cat}}).s/mmol)</td>
<td>0.36 – 1.8</td>
<td>0.65 – 3</td>
</tr>
<tr>
<td>Solvent/pyridine (mol/mol)</td>
<td>40</td>
<td>20 - 40</td>
</tr>
<tr>
<td>Solvent</td>
<td>n-hexane</td>
<td>Halpasol(^\circ)</td>
</tr>
</tbody>
</table>

- **Catalyst**
  - NiMoP/Al\(_2\)O\(_3\)
  - Gas and liquid phase experiments
  - PROCATALYSE

- **Literature insights**
  - Temperature dependent
  - \(\text{H}_2\text{S}\) has a promoting effect on the C-N bond scission reaction

- **Halpasol\(^\circ\)**: Mixture of C9-C14 paraffins

\(^a\) R. Pille, G. Froment, Hydrotreatment and Hydrocracking of Oil Fractions 106 (1997) 403-413.
\(^b\) This work
\(\copyright\) : Haltermann products GmbH
Operating conditions: 6.0 MPa, Spacetime: 790 kg\textsubscript{cat}.s/mol H\textsubscript{2}/pyridine: 10 (mol/mol) H\textsubscript{2}S/pyridine: 0.04 (mol/mol)

- Assessment of Influence of temperature on HDN conversion

<table>
<thead>
<tr>
<th>T</th>
<th>P</th>
<th>W/Fp$^\circ$</th>
<th>H\textsubscript{2}S/P</th>
<th>X</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K)</td>
<td>(MPa)</td>
<td>(kg.s/mol)</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>573</td>
<td>6.0</td>
<td>1129</td>
<td>0.04</td>
<td>0.64</td>
<td>0.34</td>
</tr>
<tr>
<td>583</td>
<td>6.0</td>
<td>790</td>
<td>0.04</td>
<td>0.65</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Liquid Phase Experimental results

- H₂S has positive effect on the C-N bond scission
- Higher hydrocarbon yield at higher H₂S/pyridine
- Lower intermediate piperidine yield
- Substitution pathway is more pronounced at higher H₂S partial pressures

operating conditions: 6.0 MPa, spacetime: 439 kg_cat·s/mol, H₂/pyridine: 10 (mol/mol)
Thermodynamic non-ideality and effect of aggregation state

✓ Non ideality in liquid phase

\[ f_i^v = f_i^l \quad i = 1, \ldots, n \]

✓ Effect of aggregation state (gas / liquid phase)

✓ Description of kinetics, independent of phase in which reaction occurs

✓ Difference between vapour and liquid phase kinetics is situated in the chemisorption step

\[ A + * \leftrightarrow A - * \quad K_{A,\tau} = \frac{\theta_{A-^*}}{f_A \theta_*} \]

\[ f_i = \varphi_i \cdot P y_i = \varphi_k C_i V_m P \quad \varphi_i = \frac{f_{i,g}}{P y_i} \]
gas phase model

- Development of gas phase model
  - Model assumptions based on previous literature insights
- Two site model related to CUS and SA sites
- Model discrimination performed between 48 rival models
- RDS: 3rd hydrogen addition and ring opening

\[ R_{P \to PP} = k_{P,+} K_{P-PH} K_{H2} K_P C_*^2 \sqrt{\delta \mu} \left( P_{H2} P_{C_5H5N} - \frac{1}{K_{Equi}} \frac{P_{C_5H10NH}}{P_{H2}^2} \right) \]

\[ R_{PP \to PA} = k_{PP} K_{PP-PH} K_{PP} \mu P_{C_5H10NH} C_*^2 \]

\[ \delta = 1 + K_P P_{C_5H5N} + K_{PP} P_{C_5H10NH} + K_{NH3} P_{NH3} \]

\[ \mu = K_{H2} P_{H2} + K_{H2S} P_{H2S} \]

\[ C_* = C_*,tot / \left( \delta + \mu \frac{C_{S^{2-}}}{C_{S^{2-}H^+}} \right) \]


\(^b\)CUS: Coordinatively unsaturated sites, SA: Sulphur anion sites
Extension of gas phase model

- the non ideality

\[
\begin{align*}
    r_{P \rightarrow PP} &= k_p + K_{P-PH2} \ K_{H2} \ K_P \ C^2 \ \sqrt{\delta \ \mu} \left( f_{H2} f_{C5H5N} - \frac{1}{K_{Equi}} \ f_{C5H10NH} f_{H2}^2 \right) \\
    r_{PP \rightarrow PA} &= k_{PP} \ K_{PP-PH} \ K_{PP} \ \mu \ f_{C5H10NH} \ C^2 \\
    \delta &= 1 + K_P f_{C5H5N} + K_{PP} f_{C5H10NH} + K_{NH3} f_{NH3} \\
    &\quad + K_{solvent} f_{solvent} + K_{PentylPP} f_{PentylPP} \\
    \mu &= K_{H2S} f_{H2S} + K_{H2} f_{H2}
\end{align*}
\]

- site balances

✓ Accounting for additional response,
  ✓ Two possible reaction networks
  1. 2 Piperidine → 1-Pentylpiperidine
  2. Piperidine + Pentylamine → 1-Pentylpiperidine
Extension of gas phase model

1) Gas phase kinetics
2) Gas phase kinetics
3) Relative pentylamine reaction rate
4) Dealkylation of 1-pentylpiperidine

Pentyl amine denitrogenation

$$r_{PA\rightarrow C5} = k_{PA} K_{PA-PAH} K_{PA} \mu f_{C_5H_{11}NH_2} C_*^2$$

Condensation of PP and PA

$$r_{PA+PP\rightarrow PentylPP} = k_{PA+PP} K_{PP} K_{PA} \sqrt{\frac{\mu}{\delta}} f_{C_5H_{10}NH} f_{C_5H_{11}NH_2} C_*^2$$

Dealkylation of PPP

$$r_{PentylPP\rightarrow PP+C5} = k_{PentylPP} K_{PentylPP-PentylPPH} K_{PentylPP} \mu f_{PentylPP} C_*^2$$
Results: Liquid phase model

Pre exponential factors\textsuperscript{a}

\[
k = \frac{k_b T}{h} \frac{Q_{A-H}''}{Q_A Q_H} \exp - \frac{E^o}{k_b T}
\]

\begin{align*}
\kappa_{\text{surface}} &\approx 10^{10} \text{ to } 10^{16} \text{ s}^{-1} (\Delta S \approx -58 - 56 \text{ J/mol} \cdot \text{K}) \\
K_{\text{surface}} &\approx 1 \text{ to } 10^{-5} \\
K_A &\approx 10^{-10} \text{ to } 10^{-13} \text{ Pa}^{-1} \\
K_{H_2,H_2S} &\approx 10^{-8} \text{ to } 10^{-13} \text{ Pa}^{-1}
\end{align*}

\[
K_{\text{solvent}} - \Delta S \quad 98.0 \quad \text{J/mol K}
\]

\[
K_{1\text{-pentylpiperidine}} - \Delta S \quad 170 \quad \text{J/mol K}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{solvent}}$</td>
<td>$-\Delta H$ $34.5\pm0.77$ kJ/mol</td>
</tr>
<tr>
<td>$K_{1\text{-pentylpiperidine}}$</td>
<td>$-\Delta H$ $85.8\pm1.6$ kJ/mol</td>
</tr>
<tr>
<td>$k_{\text{ratio}} = \frac{k_{PA}}{k_{PA+PP}^*}$</td>
<td>$E_a$ $108\pm12$ kJ/mol</td>
</tr>
<tr>
<td>$k_{\text{PentylPP--&gt;PP+C5}}$</td>
<td>$E_a$ $83.0\pm78.0$ kJ/mol</td>
</tr>
<tr>
<td>$C^*$</td>
<td>$1.7\pm0.3$ (-)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} J.A. Dumesic et al The Microkinetics of heterogenous catalysis, 1993
Results

Pressure = 6.0 MPa, Space time = 790 kg s / mol, H₂/pyridine = 10, H₂S/pyridine = 0.04, Solvent/pyridine = 40;

Operating conditions: total pressure = 6.0MPa, space time = 439 kg s / mol, H₂/pyridine = 10, H₂S/P = 0.04, Solvent/pyridine = 40

Temperature = 573.15K, Spacetime = 564 kg.s/mol, H₂S/pyridine = 0.04; Solvent/pyridine = 40

Pressure = 6.0 MPa, Temperature = 573K, Spacetime = 564 kg.s/mol, H₂S/pyridine = 0.04, Solvent/pyridine = 40

Temperature = 573.15K, space time = 1400 kg cat · s /mol, H₂/Pyridine = 620 and H₂S/Pyridine = 15, solvent/pyridine = 40
Conclusions

- Reconciliation of data at two different reaction conditions
- Effects of aggregation states (G-S / L-S) on kinetics
- Successful extension of gas phase kinetics to liquid phase reactions
  - By taking thermodynamic non ideality in liquid phase
  - Additional compound formed at liquid phase conditions

- A robust model that performed well in three phase and gas phase conditions
Acknowledgements

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Thank you for your attention
• Also called active centre. Those sites for adsorption which are the effective sites for a particular heterogeneous, catalytic reaction.

• Aggregation State: A physically distinctive form of a substance, such as solid, liquid and gaseous state.

• Fugacity: Thermodynamic activity in a non ideal phase with the ideal gas state as the reference state.

• Heterolytic dissociation: Breaking a chemical bond to produce two oppositely charged fragments, e.g. $\text{H}_2$ into $\text{H}^+$ and $\text{H}^-$. 
model assumptions

- Two sites located at the edges of the sulphided NiMo are considered.
- Hydrogenation proceeds via successive hydrogen additions either from coordinatively unsaturated sites (CUS) or from sulphur anions (SA).
- Chemisorption of hydrocarbon/nitrogen species can only occur on the coordinatively unsaturated sites due to the electronic nature of this interaction\(^{a,b}\).
- No interconversion of active sites is considered because sulphydril on a CUS is electronically different from a hydrogen atom or proton on a SA.

Thermodynamic non-ideality in the liquid phase

✓ Non ideality in mixtures\(^b\)

✓ Chemical potential : Independent of standard state used

\[
\mu_i = \mu_{i,\text{standard}} + RT \ln a_i \\
\mu_i^v = \mu_i^l \quad i = 1, \ldots, n
\]

✓ Condition for phase equilibrium

\[
f_i^v = f_i^l \quad i = 1, \ldots, n
\]

✓ Basis of V-L relationships : Relate fugacity to compositions and intensive properties \((T, P)\)

\[
f = fn(T, P, y_i)
\]