Microkinetic modeling for exhaust gas after-treatment technologies

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Outline

• Evolution of catalytic kinetics modeling
  – Modeling approaches
• Development of microkinetic models
• Use
• Applications
  – \(2NH_3 \rightarrow 3H_2+N_2\)
  – Combustion (\(H_2, CO, CO+O_2+H_2O\), PROX: \(CO+H_2+O_2; HCs\))
  – WGS reaction (\(CO+H_2O\))
  – Reforming (steam, dry, autothermal), partial oxidation of small alkanes (syngas, alkenes, biomass)
  – Hydrogenation/dehydrogenation
  – Chemicals: ethylene, propylene, acrolein production
  – Exhaust related systems (CO oxid., CO oxid. with little \(H_2\), NO oxid., \(NH_3\) decomposition)
Surface reaction rate calculation paradigm

- Calculation of surface reaction rates has followed the hierarchy

Empirical rate-law; typically fitted to experimental data

Langmuir-Hinshelwood rate-law; developed using rate determining step (RDS) and MF theory

Microkinetic analysis; No assumptions on RDS (Dumesic, 1993)

Complexity/Reliability/Accuracy

Summary of LH rate expressions

- LH expressions are based on *a priori* assumptions and intuition
- They are usually fitted using a limited number of data
- Multiple rate expressions can describe the same data
- Multiple parameters even for the same rate expression may exist
- Even if data is well-fitted, parameters may be physically unreasonable
- LH expressions, even if correct, are limited to one regime and cannot describe changes in RDS, MARI, etc. with operating conditions
**LH rates on Rh**

- **CH₄ total oxidation** 
  (combustion)
  \[ \text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} \]

- **Steam reforming of CH₄**
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]

- **CO₂-reforming of CH₄**
  \[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \]

- **RWGS**
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

\[ r_{TO} = \frac{k_{TO} \cdot P_{\text{CH}_4}}{\left(1 + K_{H_2O}^{\text{ads}} \cdot P_{\text{H}_2O}^{\text{ads}}\right)^2} \]

\[ r_{SR} = \frac{k_{SR} \cdot P_{\text{CH}_4} \cdot (1 - \eta_{SR})}{\left(1 + K_{\text{H}_2O}^{\text{ads}} \cdot P_{\text{H}_2O}^{\text{ads}} + K_{\text{CO}_2}^{\text{ads}} \cdot P_{\text{CO}_2}^{\text{ads}}\right)^2} \]

\[ r_{\text{CO}_2,r} = \frac{k_{\text{CO}_2,r} \cdot P_{\text{CH}_4} \cdot (1 - \eta_{\text{CO}_2,r})}{\left(1 + K_{\text{H}_2}^{\text{ads}} \cdot P_{\text{H}_2}^{\text{ads}} + K_{\text{CO}_2}^{\text{ads}} \cdot P_{\text{CO}_2}^{\text{ads}}\right)^2} \]

\[ r_{\text{RWGS}} = \frac{k_{\text{RWGS}} \cdot P_{\text{CO}_2} \cdot P_{\text{H}_2} \cdot (1 - \eta_{\text{RWGS}})}{\left(1 + K_{\text{H}_2}^{\text{ads}} \cdot P_{\text{H}_2}^{\text{ads}} + K_{\text{CO}_2}^{\text{ads}} \cdot P_{\text{CO}_2}^{\text{ads}}\right)^2} \]

\[ \eta = \text{effectiveness factor} \]

**Comparison of model to data:**

**Conversion**

- Process is away from equilibrium
- Model fits data fairly well
- Reactions in series is proposed
- Combustion of syngas is important

\[ \text{dashed lines} = \text{model w/o consecutive combustion of CO and H}_2; \]
\[ \text{solid lines} = \text{model with consecutive CO and H}_2 \text{ combustion} \]
Are the parameters/model reasonable?

### Estimated parameters

<table>
<thead>
<tr>
<th>Surface adsorption</th>
<th>$K_{ad, J} \ [\text{atm}^{-J}]$</th>
<th>$\Delta H_{ad, J} \ [\text{kcal/mol}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2$</td>
<td>42.53</td>
<td>13.9</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>2.216 $\times$ 10^{-1}</td>
<td>39.5</td>
</tr>
<tr>
<td>$\text{CO}$</td>
<td>15</td>
<td>6.2</td>
</tr>
</tbody>
</table>

- **Models may fit but they most often than not include unrealistic parameters**

### Microkinetic modeling

- **All relevant elementary reactions**
  - Written by hand or computer generated
- **No simplifying assumptions**
  - e.g., on a rate determining step (RDS), partial equilibrium (PE), quasi-steady state (QSS), and a most abundant reaction intermediate (MARI)
- **Mass action kinetics**
- **Reactor + Catalyst model needed**
  - Solution via a suitable numerical method
  - Computer software, such as surface CHEMKIN or Matlab makes use trivial
- **Microkinetic models may hold over the entire parameter space**
  - More robust numerics than global rate expressions!
Microkinetic modeling

• Output
  – Coverages (concentrations), Rates, Conversion, Selectivity
  – RDS, QSS, PE, important steps

• Input
  – Reaction rate const. parameters

• **Rate constants of all elementary reactions are not necessarily available for most reactions**

Parameter estimation techniques

• Fitted to data
  - Empirical; multiple parameter sets; limited predictive power

• Semi-empirical theoretical methods
  - Fast; fairly accurate; not first principles

• Density functional theory (DFT)
  - First principles; expensive; limited to small mechanisms and ‘bimolecular’ type of reactions (combinatorial explosion)

• Independent of theoretical method, parameters are uncertain and models are semi-quantitative in most cases
  - Parameter refinement is necessary
Limitations of most microkinetic models

- Inability to predict multiple experimental sets
- Thermodynamic inconsistency
- Coverage dependence on activation energies of surface rxns
- Lack of a comprehensive set of reaction paths
- Coupling effects appear in multicomponent systems
- Mean field assumption for both catalyst and adsorbates
- Materials and pressure gaps
  - From UHV/single crystals parameters to actual conditions

Most literature mechanisms fail to describe multiple data

CH$_4$ CPOX in a fluidized bed

Ethane ign over a Pt foil
Most literature mechanisms are thermodynamically inconsistent.

WGS: \( \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \)

CO oxidation: \( \text{CO}_2 = \text{CO} + \text{O} \)

Complex feeds cannot be captured.

- \( \text{H}_2 \) even at ppm level promotes CO light off
  - Heat effect (unimportant for ppm \( \text{H}_2 \))
  - Chemical effect
- Predicted trend is opposite from the experimental one
- Complex feed composition also in PROX conditions (\( \text{H}_2 \) rich-CO lean)
Role of H₂O in CO oxidation on Pt


TPR experiments:
Annealing, i.e., CO + O + OH
Non-annealing, i.e., CO + O + H₂O

H₂O promotes CO oxidation!

ONLY CO+O

CO+O+OH

CO+O+H₂O

Expt. 1
Expt. 2
Expt. 3

Rₐ

Temperature

Temperature

Temperature

Performance of literature mechanisms

- Several mechanisms are available for H₂, CO, and CH₄ oxidation on Pt
- Oxidation pathways include
  - CO+O → CO₂
  - H+O → OH and H+OH → H₂O
  - No other oxidation paths exist
- Literature mechanisms do not capture the H₂O promotion and are thermodynamically inconsistent

**Parameter estimation techniques**

- **Fitted to data**
  - Empirical; limited predictive power
- **Semi-empirical theoretical methods**
  - Fast; fairly accurate; not first principles
- **Density functional theory (DFT)**
  - First principles; expensive; limited to small mechanisms and ‘bimolecular’ type of reactions (combinatorial explosion)
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**The multiscale simulation paradigm:**
**A bottom-up ladder**

- **Direct multiscale simulation (hybrid, coarse graining) is possible for systems of moderate complexity**
- **It is plagued by computational cost for complex systems, such as chemical reactors**
- **Are all scales and phenomena important?**

![Multiscale Simulation Diagram](image)

**Reviews:**
- Raimondeau and Vlachos, *Chem. Eng. J.* 90, 3 (2002);
- Chatterjee et al., *Chem. Eng. Sci.* ISCRE Issue (2004);
Overarching concept of hierarchical multiscale modeling

- Start with a sufficiently simple but physically relevant model at each scale
- Link all models
- Perform a sensitivity analysis
- Identify important scale and parameter(s)
- Use higher level theory for this scale and parameter(s)
- Iterate

Irrespective of how good job we do, there is always uncertainty in models: Need for data

Hierarchy enables rapid screening of chemistry, fuels, and catalysts

- Hierarchy adds a new dimension to multiscale: at each scale, more than one model can be run
**Bond-order conservation (BOC) and TST: Features**

- **Activation energies**
  - Semi-empirical technique
  - Coverage dependent binding energies
  - Coverage dependent activation energies
  - Accuracy within 2-4 kcal/mole
  - High computational efficiency
  - Thermodynamic consistency at enthalpic level

- **Pre-exponentials**
  - Severely constrained from TST and thermodynamic consistency
  - Refined with experimental data

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**NH₃ decomposition on Ru: 2NH₃ ⇌ N₂+3H₂**

- NH₃ as a storage medium
- ‘Pure’ H₂ – No COₓ
- A microkinetic model is build using BOC and TST
- Our microkinetic model captures the trend
- High N* coverages

\[
\begin{align*}
\text{NH}_3^+ & \rightleftharpoons \text{NH}_2^+ \\
\text{NH}_2^+ & \rightleftharpoons \text{NH}_2^+ + \text{H}^+ \\
\text{NH}_2^+ & \rightleftharpoons \text{NH}^+ + \text{H}^+ \\
\text{NH}^+ & \rightleftharpoons \text{N}^+ + \text{H}^+ \\
2\text{N}^+ & \rightleftharpoons \text{N}_2 + 2\text{H}^+ \\
2\text{H}^+ & \rightleftharpoons \text{H}_2 + 2\text{H}^+
\end{align*}
\]

Expts. [Ganley et al.], *AIChE J.* 2003

DFT is used to estimate lateral interactions

- DACAPO (solid-state electronic structure package by Hammer and coworkers*)
- 3-Layer slab of Ru(0001)
- $2 \times 2$ unit cell
- All layers are relaxed
- Plane wave cutoff = 350eV
- 18 k-points for surface Brillouin zone
- Generalized gradient approximation (PW-91)

\[ \text{Linear fit } Q_N (\text{at } H^* = 0) = 128.2 - 33.3N^* \]
\[ \text{Linear fit } Q_N (\text{at } N^* = 0.25) = 120.1 - 6.2H^* \]

* Hammer et al., DACAPO version 2.7 (CAMP, Technical University, Denmark)

DFT-retrained microkinetic model describes the experimental data well

- H-H and N-H interactions are small
- N-N interactions completely change the chemistry
- Extensive validation against UHV and high P data has been done

**Energetics and interactions for H₂/O₂ on Pt: Comparison with experiments**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1) $H^<em>+O^</em>\rightarrow OH^*+*H$</td>
<td>12.1</td>
<td>8.8</td>
<td>13.4</td>
<td>≤13.</td>
<td>13.8</td>
<td>2.5</td>
</tr>
<tr>
<td>2) $OH^<em>+H^</em>\rightarrow H_2O^<em>+</em>$</td>
<td>24.4</td>
<td>25.9</td>
<td>18.4</td>
<td>≤29.</td>
<td>16.0</td>
<td>5.0</td>
</tr>
<tr>
<td>3) $H^<em>+OH^</em>\rightarrow H_2O^<em>+</em>$</td>
<td>12.4</td>
<td>9.3</td>
<td>0.0</td>
<td>16 ± 2.</td>
<td>18.0</td>
<td>15.0</td>
</tr>
<tr>
<td>4) $HO^<em>+\rightarrow H_2^</em>+OH^*$</td>
<td>18.4</td>
<td>20.2</td>
<td>39.1</td>
<td>25.0</td>
<td>37.0</td>
<td></td>
</tr>
<tr>
<td>5) $2OH^<em>\rightarrow H_2O^</em>+O^*$</td>
<td>18.9</td>
<td>18.9</td>
<td>0.0</td>
<td>18 ± 3.</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>6) $H_2O^<em>+O^</em>\rightarrow 2OH^*$</td>
<td>12.6</td>
<td>12.6</td>
<td>34.1</td>
<td>10.0</td>
<td>31.0</td>
<td></td>
</tr>
</tbody>
</table>

Coverage-dependent reaction energetics necessary to capture experimental trends


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**What can we use detailed models for?**

- Reconcile apparently contradictory experimental data
- Mechanistic understanding
- Perform reactor optimization
- Model-based design of experiments to assess model
- Rational catalyst design
  - Composition
  - Size
  - Shape
What can we use detailed models for?

- Reconcile apparently contradictory experimental data
- **Mechanistic understanding**
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H₂O promotes CO oxidation at UHV conditions

Effect of Excess Hydrogen on CO Conversion: PROX conditions

- The carbon monoxide conversion increases in the presence of H₂ at low temperatures but is inhibited at high temperatures

**CO oxidation mechanisms on Pt**

\[
\begin{align*}
CO + O^* &\rightarrow CO_2 + ^* \quad 21 \text{ kcal/mol} \\
CO + OH^* &\rightarrow COOH^* + ^* \rightarrow CO_2 + H^* \\
&\quad 8-10^a, \sim 1.0^a, \sim 0.0^b
\end{align*}
\]

Direct path

Indirect path

- Semi-empirical BOC
- Periodic DFT

\[0\text{H}_2 \rightarrow \text{H}_2\text{O} \quad \text{O}_2 \rightarrow \text{OH} \quad \text{H}_2\text{O}\]

Carboxyl COOH* Formate HCOO**
Incorporating hydrogen bonding effects into a microkinetic model for CO-H₂O coupling

Heats of chemisorption are parameterized using DFT calc. of Michaelides and Hu, \textit{JACS} (2001)

\begin{align*}
Q_{H₂O} &= Q_{H₂O}^0 + 25θ_{OH} \\
Q_{OH} &= Q_{OH}^0 + 25θ_{H₂O}
\end{align*}

Coverage dependent activation energies

Our microkinetic model:
- H-bonding is important
- Coupling steps are required (no peak without coupling)

Effect of exhaust composition on light-off temperature of CO

Effect of CO fraction

Effect of H₂ fraction

Experiments by \textit{Salomons et al.}
Simulations by Wulf Hauptmann

Simulated CO light-off temperature

Effect of H₂ on CO light-off temperature

<table>
<thead>
<tr>
<th>CO oxidation</th>
<th>H₂ effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation</td>
<td>H₂ effect</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\phi_0(\text{CO}) / \text{Vol.-ppm})</th>
<th>(\phi_0(\text{H}_2) / \text{Vol.-ppm})</th>
<th>CO Light-Off Temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0</td>
<td>131</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
<td>153</td>
</tr>
<tr>
<td>1500</td>
<td>0</td>
<td>166</td>
</tr>
<tr>
<td>2000</td>
<td>0</td>
<td>171</td>
</tr>
<tr>
<td>2000</td>
<td>225</td>
<td>153</td>
</tr>
<tr>
<td>2000</td>
<td>300</td>
<td>154</td>
</tr>
<tr>
<td>2000</td>
<td>1000</td>
<td>150</td>
</tr>
<tr>
<td>1000</td>
<td>500</td>
<td>130</td>
</tr>
<tr>
<td>1000</td>
<td>2000</td>
<td>127</td>
</tr>
</tbody>
</table>
**NO oxidation to NO₂ on Pt**

Sensitivity analysis

Comparison between experimental and simulated light-off

430 vol.-ppm NO and 6 vol.-% O₂
Heating rate was 5 °C min⁻¹
GHSV was 25 000 h⁻¹.

**CO oxidation on supported Au catalyst**

- Bulk Au is a chemically inert metal

Haruta et.al., Chem. Lett. 405, (1987)
Bell, Science 299, 1688 (2003)

- Only edges, corners, steps of NPs are active¹

Haruta, Cattech 6, 102-115, (2002)

- Au clusters and NPs (3-5 nm) are chemically active²


- Reducible supports are most active for CO oxidation on Au, whereas irreducible supports are less active³
What can we use detailed models for?

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**Modern**
- Rational catalyst design
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---

Computer-aided chemistry reduction

- Sensitivity and Principal Component Analyses
  - No *a priori* assumptions
  - Identification of important reactions and species
- Small parameter asymptotics on species balances and site conservation
  - Simple algebra to derive a rate expression

**Reduced Model**
\[
\sigma_{N_2} = k_4 \theta_{N_2}^2 - k_3 P_{N_2} \theta_{N_2}^2
\]
\[
\sigma_{H_2} = 3 \sigma_{N_2}
\]
\[
\sigma_{NH_3} = 2 \sigma_{N_2}
\]

**Full Model**
\[
\frac{d}{dt} \begin{bmatrix} \theta_{N_2} \\ \theta_{N_2}^2 \\ \theta_{N_2}^2 \\ \theta_{N_2} \end{bmatrix} = \begin{bmatrix} k_4 P_{N_2} \\ -k_3 P_{N_2} \\ k_3 P_{N_2} \\ -k_1 \end{bmatrix}
\]

---

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---

Model, System and Parameters

```
Temperature
Pressure
Residence time
Cat. surf. area
Inlet mole fractions
```

```
Conversion
Outlet mole fractions
Surface coverage
```

```
Domain / Range / Input space
```

```
Output space
```

```
Parameters
```

Find optimum in X (input) to maximize info on P given Y (output)

- R1: H₂ + 2* = 2H*
- R2: N₂ + 2* = 2N*
- R3: NH²⁺ + * = N⁺ + H*
- R4: NH₂⁺ + * = NH⁺ + H*
- R5: NH₃⁺ + * = NH₂⁺ + H*
- R6: NH₄⁺ + * = NH₃⁺

---

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**Optimal Designs**

- Experiments: vary 1-2 variables (pressure, temperature), conducted at disparate conditions (UHV, atmospheric pressure)
- Model response over all variables (including industrial conditions) for synthesis and decomposition

- Other variables explored: residence time, inlet compositions, catalyst dispersion and loading

\[
\begin{align*}
\text{R4: } & \mathrm{NH}_2^* + *= \mathrm{NH}^* + \mathrm{H}^* \\
\text{R2: } & \mathrm{N}_2 + 2* = 2\mathrm{N}^* \\
\text{R5: } & \mathrm{NH}_3^* + *= \mathrm{NH}_2^* + \mathrm{H}^*
\end{align*}
\]

Temperature

Pressure

1 atm

UHV
Generating a Large Ensemble of Operating Conditions (HTM)

- Global Monte Carlo search in input space ($\tau$, P, T, composition, catalyst A/V).
- Uniformly randomly distributed operating conditions.
- Composition space spanned in unbiased manner using constraint $\sum x_i = 1$

Microkinetic model assessed via throughput-model based design of experiments

- Experiments with varying inlet composition, temperature, amount of catalyst, dilution, flow rate
- Bioinformatics tools are used for ‘clustering’, i.e., identification of regions where one should do experiments

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Mappings from atomic BEs to Es

<table>
<thead>
<tr>
<th>Reaction</th>
<th>activation energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(S) + O(S) =&gt; CO(S)</td>
<td>77.11 kJ/mol</td>
</tr>
<tr>
<td>C(S) + H(S) =&gt; CH(S)</td>
<td>78.23 kJ/mol</td>
</tr>
<tr>
<td>CH(S) + O(S) =&gt; CO(S) + H(S)</td>
<td>79.35 kJ/mol</td>
</tr>
<tr>
<td>CO(S) + PT(S) =&gt; C(S) + O(S) + PT(B)</td>
<td>80.47 kJ/mol</td>
</tr>
<tr>
<td>C(S) + H(S) + PT(B) =&gt; CH(S) + O(S) + PT(S)</td>
<td>81.59 kJ/mol</td>
</tr>
</tbody>
</table>

Coverage Dependence Through DFT-based Scaling Relationships

Adsorption Energies for AH\textsubscript{x} Species on Transition Metals


\[ Q_{AH_x} = \gamma Q_A + \xi \]
\[ \gamma = (x_{\text{max}} - x) / x_{\text{max}} \]

A = C,S,N,O
\( x_{\text{max}} \) = maximum # H on molecule
\( \xi \) = Constant

Our Coverage Dependence Extension & Application to NH\textsubscript{3} System

\[ Q_{AH_x} = \gamma Q_A (\theta_{AH_x}, \theta_A) + \xi \]
\[ \gamma = (3 - x) / 3 \]

Multiscale model-based catalyst design

- Search is done on atomic descriptors while running the full chemistry model
  - Link macro and micro scales
- Potential catalyst candidates are identified

Summary of microkinetic models

- Hierarchical multiscale modeling framework delivers reliable reaction mechanisms in an efficient manner

**Key concepts**
- Models describe multiple data for a single fuel
- Models describe coupling effects in multicomponent systems
- Thermodynamic consistency
- Coverage dependence on activation energies of surface rxns
- Different reaction paths can easily be explored

**Summary**
- Complex models can be reduced to simple ones for system optimization/scale up studies
  - Enables CFD simulation
- A framework for model-based design of experiments has been proposed
  - Model validation and mechanism understanding
- Complex models could be used for rational, model-based catalyst design